Foth & Van Dyke

REPORT

Operational Phase and Long Term Care Quality Assurance Plan

Scope ID: 93F019

Flambeau Mining Company
Ladysmith, Wisconsin

November 1993

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November 30, 1993

Mr. Gordon Reinke, Chief
Mine Reclamation Section
Bureau of Solid Waste Management
Wisconsin Department of Natural Resources
101 South Webster Street, GEF II
Madison, WI 53707

Dear Mr. Reinke:

RE: Flambeau Mining Company Project

On behalf of the Flambeau Mining Company (Flambeau), we are submitting 12 copies of the attached Operational Phase and Long Term Care Quality Assurance Plan meeting the general requirement of Part 4-8 of the conditions of the Mine Permit Approval for the Flambeau project in Rusk County, Wisconsin. As you are aware, this submittal incorporates changes to the previously submitted *Revised Quality Assurance/Quality Control Document* of August 1991.

If you have any comments or questions regarding this submittal, please contact us at 414-497-2500.

Sincerely,

Foth & Van Dyke

James B. Hutchison, P.E.
Project Engineer

Jerry W. Sevick, P.E.
Group Vice President

JBH:GWS:cac

[32-15]93F019

Distribution

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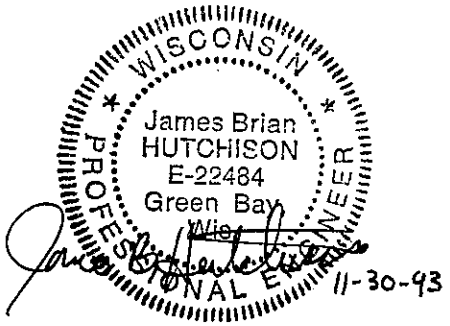
Operational Phase and Long Term Care Quality Assurance Plan

Scope I.D. 93F019



Prepared for
Flambeau Mining Company

Prepared by
Foth & Van Dyke and Associates Inc.

November 1993

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Operational Phase and Long Term Care Quality Assurance Plan

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3 Project Description

This Flambeau Project monitoring and quality assurance plan has been developed for the operation and long term care/maintenance phase in response to NR 132.06(3)(d), NR 182.08(2)(e)(8) and NR 182.09(2)(a)7 and the project's long term care and maintenance phase in response to NR 132.08, NR 182.09, NR 182.16 and NR 182.19. This monitoring will cease when site closure has been completed.

Operation and long term care/maintenance phase monitoring includes individual programs for groundwater, Type I stockpile exfiltrate, surface water, terrestrial ecology, total suspended particulate (TSP), asbestiform minerals, meteorology and pit inflows, as well as effluent discharges to surface water.

Monitoring during the long-term care and maintenance phase of the project will include groundwater monitoring of wells located in the backfilled pit and outside the pit area, water level measurements in selected wells, surface water monitoring (to include sediments, macroinvertebrates, fish as well as water quality) and monitoring of vegetation and wildlife (see Appendix B for sampling location).

Pursuant to the approved Mining Permit Conditions, Part 4, Section 8, the quality assurance documents are required to be submitted to the Wisconsin Department of Natural Resources (WDNR or the Department) at least 90 days prior to implementation of an element of the monitoring plan. A document titled *Revised Mining Permit Quality Assurance/Quality Control Document* was submitted to the Department in August of 1991 to satisfy these requirements. Due to a change of laboratories for some of the monitoring and a change in some of the duties by the responsible parties, this document was prepared for the operation and long term phases of this project. This document is intended to satisfy those requirements. Contained within are methodologies for sample collection, handling and analyses as well as monitoring data reporting and evaluation procedures. Other elements of this plan will specify equipment calibration and preventive maintenance procedures.

This quality assurance plan is structured to meet the intent of the Department's requirement for quality assurance documents and the United Stated Environmental Protection Agency's (USEPA's) guidelines and specifications for preparing quality assurance project plans.

4 Organization and Responsibility

This section of the quality assurance plan will describe the organization and responsibilities for field operations and laboratory operations.

4.1 Field Operations

Field monitoring and sample collection activities will be performed by personnel from Flambeau Mining Company or their subcontractors. Field operations will generally consist of sample procurement and ancillary activities, measurement of sample characteristics, sample filtration, sample preservation, sample documentation and recordkeeping, as well as sample shipment to the laboratory for analysis.

The field operations staff structure is shown on Figure 4-1. The key field operations positions are shown along with lines of authority. Individual members of the project team are responsible for project quality assurance activities on a day-to-day basis. A quality assurance officer is assigned to the project and is responsible to assure that:

- Appropriate project QC protocol is used.
- Project records are maintained in accordance with this plan and/or standard operation procedures.
- The intent of this quality assurance plan is carried out as described.

4.2 Laboratory Operations

Laboratory analytical activities will be performed by the Northern Lake Service Inc. (NLS) except for the following analytical activities which will be performed by Superior Testing Laboratories of Superior, Wisconsin (Superior):

- Total suspended particulate (TSP)

and the following analyses which will be performed by Wisconsin Occupational Health Laboratory (WOHL).

- Asbestiform analysis

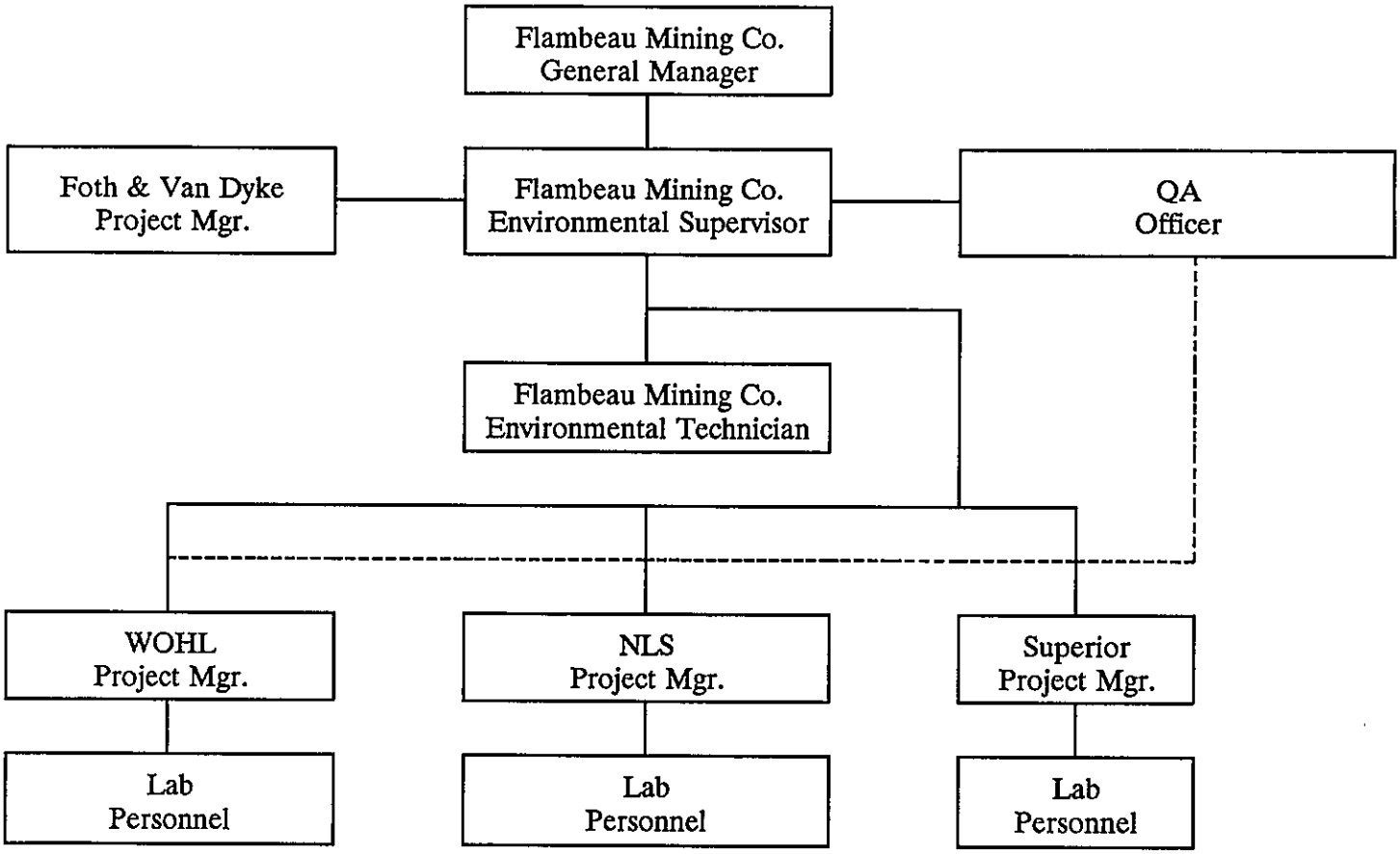
NLS is an NR 149 certified laboratory. A copy of their DNR certification is included in Appendix A. A copy of NLS's quality assurance plan is also included in Appendix A. Flambeau Mining Company will expect NLS to undertake their analytical activities in accordance with the requirements of their quality assurance plan.

For the laboratory work highlighted above, which will be performed by Superior, the quality assurance requirements are described in Appendix E.

For the laboratory work performed by WOHL, the quality assurance requirements are described in Appendix J.

Figure 4-1

Quality Assurance Plan Organization



5 Quality Assurance Targets for Precision, Accuracy and Method Detection Limits

The purpose of quality assurance objectives is to define the precision and accuracy targets as well as the method detection limits which will be used for both laboratory and field measurement data.

All measurements must be made such that results are representative of the media (air, water, biota, etc.) and conditions being measured. Unless otherwise specified, data will be calculated and reported in consistent units from one sampling event to the next. Metals results for solid samples, i.e., tissue, sediment and soil will be reported on a dry-weight basis.

Data quality objectives for accuracy and precision for each measurement parameter will be based on the measurement system employed and the requirements of this plan.

Quality assurance objectives for field measurement data are found in Table 5-1 while those for laboratory data are found in Table 5-2.

Table 5-1

Quality Assurance Objectives for Field Measurement Data

Parameter	Matrix	Analytical Method	Precision	Accuracy	Method Det. Limit	Holding Time
Groundwater Elevation	GW, SW	N/A	N/A	N/A	0.01 ft	N/A
Conductivity	GW, SW	120.1(A)	20	N/A	1 umho/cm	28 dy
pH	GW, SW	150.1(A)	20	N/A	0.1SU	1 hr
Color	GW, SW	(B)	N/A	N/A	N/A	N/A
Odor	GW, SW	(B)	N/A	N/A	N/A	N/A
Turbidity	GW, SW	(B)		N/A	N/A	N/A
Wind Direction	Air	N/A	N/A	±3°	N/A	N/A
Wind Speed	Air	N/A	N/A	±0.25 mph	N/A	N/A

N/A : Not Applicable.
(A) : Methods for Chemcial Analysis of Water and Wastes EPA 600/4-79-020 Revised March 1983
(B) : Groundwater Sampling Procedures Wisconsin Department of Natural Resources PUBL-WR-168.
Color : Note against a white background.
Odor : Wave hand over sample container and note distinct smell.
Turbidity : Comment on level of turbidity, e.g., cloudy, turbid, clear.
GW : Groundwater
SW : Surface Water

Table 5-2

Quality Assurance Objectives for Laboratory Measurement Data

Parameter	Matrix	Method	Precision	Accuracy	MDL	HOLDTIME	PRESERVE	SAMP VOL.
pH	Water	150.1(A)	20	--	N/A	24 hr	N/A	100(P)
TDS	Water	160.1(A)	20	--	2 mg/L	48 hr	4 C	200(P)
Iron	Water	6010(B)	34	111-88	0.015 mg/L	6 mo	HNO3,PH<2	1000(P)
	Sediment	6010(B)	20	120-80	1.5 mg/kg	6 mo	4 C	1000(P)
	Fish	*	30	140-60	1.5 mg/kg	6 mo	4 C	***
Manganese	Water	6010(B)	12	111-86	0.004 mg/L	6 mo	HNO3,PH<2	1000(P)
	Sediment	6010(B)	20	120-80	0.4 mg/kg	6 mo	4 C	1000(P)
	Fish	*	30	140-60	0.4 mg/kg	6 mo	4 C	***
Sulfate	Water	375.4(A)	20	120-80	2 mg/L	28 dy	4 C	200(P)
Copper	Water	6010(P)	5	115-82	0.012 mg/L	6 mo	HNO3,PH<2	1000(P)
	Sediment	6010(P)	20	120-80	1.2 mg/kg	6 mo	4 C	1000(P)
	Fish	*	30	140-60	1.2 mg/kg	6 mo	4 C	1000(P)
	Fauna	**	30	140-60		6 mo	4 C	***
Total Alka-linity	Water	310.1(A)	20	103-95	2 mg/L	14 dy	4 C	100(P)
Total Hardness	Water	130.2(A)	9	106-93	2 mg/L	6 mo	HNO3,PH<2	100(P)
Arsenic	Water	206.2(D)	20	133-74	2 ug/L	6 mo	HNO3,PH<2	1000(P)
	Sediment	206.2(D)	20	120-80	0.2 mg/kg	6 mo	4 C	1000(P)
	Fish	*	30	140-60	0.2 mg/kg	6 mo	4 C	
	Fauna	**	30	140-60		6 mo	4 C	
Barium	Water	6010(B)	8.6	115-88	0.015 mg/L	6 mo	HNO3,PH<2	1000(P)
Cadmium	Water	213.2(D)	25	130-66	0.2 ug/L	6 mo	HNO3,PH<2	1000(P)
	Sediment	213.2(D)	20	120-80	20 ug/kg	6 mo	4 C	1000(P)
	Fish	*	30	140-60	20 ug/kg	6 mo	4 C	***
	Fauna	**	30	140-60		6 mo	4 C	***
Chromium	Water	218.2(D)	17	123-78	1 ug/L	6 mo	HNO3,PH<2	1000(P)
	Sediment	218.2(D)	20	120-80	100 ug/kg	6 mo	4 C	1000(P)
	Fish	*	30	140-60	100 ug/kg	6 mo	4 C	***
	Fauna	**	30	140-60		6 mo	4 C	***
Lead	Water	239.2(D)	11	130-68	1 ug/L	6 mo	HNO3,PH<2	1000(P)
	Sediment	239.2(D)	20	120-80	100 ug/kg	6 mo	4 C	1000(P)
	Fish	*	30	140-60	100 ug/kg	6 mo	4 C	***
	Fauna	**	30	140-60		6 mo	4 C	***
Mercury	Water	245.1(D)	28	129-76	0.2 ug/L	6 mo	HNO3,PH<2	1000(P)
	Sediment	245.1(D)	20	120-80	20 ug/kg	6 mo	4 C	1000(P)
	Fish	*	30	140-60	20 ug/kg	6 mo	4 C	***
	Fauna	**	30	140-60		6 mo	4 C	***
Selenium	Water	270.2(D)	16	151-39	2 ug/L	6 mo	HNO3,PH<2	1000(P)
	Sediment	270.2(D)	20	120-80	200 ug/kg	6 mo	4 C	1000(P)
	Fish	*	30	140-60	200 ug/kg	6 mo	4 C	***
	Fauna	**	30	140-60		6 mo	4 C	***
Silver	Water	272.2(D)	20	111-71	0.5 ug/L	6 mo	HNO3,PH<2	1000(P)
	Sediment	272.2(D)	20	120-80	50 ug/kg	6 mo	4 C	1000(P)
	Fish	*	30	140-60	50 ug/kg	6 mo	4 C	***
	Fauna	**	30	140-60		6 mo	4 C	***
Nickel	Sediment	249.2(D)	20	120-80	10 ug/L	6 mo	HNO3,PH<2	1000(P)
	Fish	*	20	120-80	1 mg/kg	6 mo	4 C	***
	Fauna	**	30	140-60		6 mo	4 C	***
Zinc	Water	289.2(D)	20	120-80	0.5 ug/L	6 mo	HNO3,PH<2	1000(P)
	Sediment	289.2(D)	20	120-80	50 ug/kg	6 mo	4 C	1000(P)
	Fish	*	30	140-60	50 ug/kg	6 mo	4 C	***
	Fauna	**	30	140-60		6 mo	4 C	***
Aluminum	Sediment	6010(B)	20	120-80	0.034 mg/L	6 mo	HNO3,PH<2	1000(P)
	Fish	*	30	140-60	3.4 mg/kg	6 mo	4 C	***
	Fauna	**	30	140-60		6 mo	4 C	***
Particle Size	Sediment	D1140, D442(E)	25	N/A	1 %	N/A	N/A	500 gm

Table 5-2 *(cont.)*

% Vol. Solids	Sediment	160.2(A) 160.4(A)	20	120-80	2% DWB	7 dy	4 C	200(P)
Total Suspended Partic-ulates	Glass Fiber Filter	091(1) 11101(2)	N/A	Flow +/- 9%, Weight +/1 3.3-5 mg, Conc. +/1 1.65-2.5 mg/m3	0.0005 gm	N/A	N/A	
Asbestos	Mixed Cellulose Ester Filter	7400(3)	0.10 to 0.12	80 to 100 fibers	0.25 um	N/A	N/A	50-150 cubic feet of air
Arsenic	Glass Fiber Filter	206.2(A)	20	120-80	0.0000158 ug/m^3	N/A	None	
Chromium	Glass Fiber Filter	200.7(A)	20	120-80	0.0000158 ug/m^3	N/A	None	
Cadmium	Glass Fiber Filter	200.7(A)	20	120-80	0.00000475 ug/m^3	N/A	None	
Berrylium	Glass Fiber Filter	200.7(A)	20	120-80	0.00000316 ug/m^3	N/A	None	
Nickel	Glass Fiber Filter	200.7(A)	20	120-80	0.000158 ug/m^3	N/A	None	
Mercury	Glass Fiber Filter	200.7(A)	20	120-80	0.00000791 ug/m^3	N/A	None	

Method 620.2(C)/6010(B)
*** Method 620.1(C)/6010(B)**
**** See Tables 6-5,6-6,6-15,6-16,6-17**

(A) Methods for Chemical Analyses of Water and Wastes, EPA 600/4-70-020, revised March 1983.
(B) SW 846 Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods, Third Edition.
(C) Wisconsin State Laboratory of Hygiene Method for Sample Preparation.
(D) USEPA Contract Laboratory Program Statement of Work for Inorganic Analysis, July 1988.
(E) ASTM Method.
(P) Plastic Container.

Sediment Results reported on dry weight basis.
Fish results reported on an "as received" basis.

1 EPA Method No.
2 EPA Parameter No.
3 NIOSH Method taken from USEPA document No. EPA-600/2-77-178.

N/A = Not Applicable

6 Sampling Procedures

Sampling procedures for this project are described in this section of the quality assurance plan.

6.1 Samples/Measurements

Samples to be collected and/or measurements to be made are detailed in Tables 6-1 through 6-18.

6.2 Cleaning/Decontamination Procedures

Sufficient clean equipment should be transported to the field such that field cleaning is minimized. Equipment that is transported to the field shall be precleaned and ready to use.

Equipment is cleaned prior to transportation to the site according to the following scheme:

- Wash with hot, soapy water.
- Scrub with brush (if necessary).
- Rinse thoroughly with tap water.
- Rinse thoroughly with deionized water.
- Air dry completely.
- Store in a manner to minimize contamination.

When decontamination is necessary, the following procedure is to be used:

- Wash thoroughly with Alconox® and water using a brush (if necessary) to remove heavy contamination.
- Rinse with water from a documented source.
- Rinse with deionized water from a documented source.
- Allow equipment to air dry.

Records will be maintained which indicate date and method of cleaning. This documentation will be recorded in the field notebook (when equipment is decontaminated in the field) and in the equipment service/maintenance record when cleaning is performed in-house.

6.3 Sampling Containers

Sample containers (when needed) will be provided by the laboratory. The laboratory will provide new containers for samples and shall be able to substantiate the source(s) of containers used on the project.

Table 6-1

Groundwater Sampling
(Operation Phase)
Flambeau Mining Company

Frequency	Sampling Location	Parameters
Quarterly (January, April, July, October)	MW1000R MW1000P MW1002 MW1002G MW1004 MW1004S MW1004P MW1005 MW1005S MW1005P MW1010P	Groundwater Elevation (Field) Specific Conductance (Field) pH (Field) pH (Lab) Total Dissolved Solids Iron Manganese Sulfate Copper Total Alkalinity Total Hardness Color (Field) Odor (Field) Turbidity (Field)

Table 6-2

Groundwater Elevation
(Operation Phase)
Flambeau Mining Company

Frequency	Measurement Location	Parameters
Quarterly (January, April, July, October)	MW1001 MW1001G MW1001P MW1003 MW1003P PZ1006 PZ1006G PZ1006S PZ1007S PZ1008 PZ1008G PZ1009 PZ1009G PZ1011 PZ1012 PZR1 PZS1 PZS3 Sand Point ST-9-23 ST-9-23A ST-9-26 PZ-1A PZ-1B OW-7 OW-10 OW-39 OW-42 OW-43	Groundwater Elevation

Table 6-3

Type I Lysimeter and Type II Leachate Sampling (Operation Phase) Flambeau Mining Company

Frequency	Sampling Location	Parameters
Quarterly (January, April, July, October)	CL-1	pH (Lab) pH (Field) Specific Conductance (Field) Total Chromium Copper Iron Manganese Sulfate Total Dissolved Solids Total Alkalinity Total Hardness Volume of Liquid Removed
Quarterly (January, April, July, October)	MH-2	pH (Lab) pH (Field) Specific Conductance (Field) Copper Iron Manganese Sulfate Total Dissolved Solids Total Alkalinity Total Hardness Volume of Liquid Removed

Table 6-4

Sediment Sampling
(Operation Phase)
Flambeau Mining Company

Frequency	Sampling Location	Parameters
Annually (May)	S-1	Particle Size
	S-2	% Volatile Solids
	S-3	Iron
		Manganese
		Aluminum
		Arsenic
		Silver
		Nickel
		Cadmium
		Chromium
		Copper
		Lead
		Mercury
		Selenium
		Zinc

Sample Locations: S-1 = Blackberry Lane (Upstream of Site)
S-2 = Old Port Arthur Dam Site (Downstream of Site)
S-3= Sisters Farm (Downstream of Site)

Table 6-5

Fish Sampling
(Operation Phase)
Flambeau Mining Company

Frequency	Sampling Location	Parameters
Annually (Low Flow Period)	F-1 F-2	Fillets (w/skin on) Total Mercury Livers Aluminum Arsenic Cadmium Chromium Copper Lead Mercury Zinc Selenium Nickel Silver Iron Manganese

Number of Walleyes to be Collected by Size at Each Sampling Location:
10"-12" - 1
12"-15" - 2
15"-18" - 3
18"-22" - 2
>22" - 1

Location of Sampling: F-1 = Ladysmith Flowage (Upstream of Site)
F-2 = Thornapple Flowage (Downstream of Site)

Table 6-6

Macroinvertebrate Sampling
(Operation Phase)
Flambeau Mining Company

Frequency	Sampling Location	Parameters
Annually	M-1(1) M-2(1) M-3(1)	Aluminum Arsenic Cadmium Chromium Copper Lead Mercury Zinc Selenium Nickel Silver

(1) - 25 Crayfish or more will be composited at each sampling location.

Location of Sampling: M-1 = Blackberry Lane (Upstream)
M-2 = Above Mouth of Meadowbrook Creek (Downstream)
M-3 = Old Port Arthur Dam Site (Downstream)

Table 6-7

Macroinvertebrate Fauna Sampling
(Operation Phase)
Flambeau Mining Company

Frequency	Sampling Location	Parameters
Annually (Autumn)	M-1 M-2 M-3	Lowest Taxonomic Level(1)

(1) - Sampling and evaluation will follow procedures outlined in Hilsenhoff (1987), "An Improved Biotic Index of Organic Stream Pollution".

Location of Sampling: M-1 = Blackberry Lane (Upstream)
M-2 = Above Mouth of Meadowbrook Creek (Downstream)
M-3 = Old Port Arthur Dam Site (Downstream)

Table 6-8

Wetland Surface Flows
(Operation Phase)
Flambeau Mining Company

Frequency	Measurement Location	Parameters
Monthly (March-December)	WT-1 WT-2 WT-3 WT-4 WT-5	Water Levels

Table 6-9

Groundwater Sampling
(Long-term Care/Maintenance Phase)
Flambeau Mining Company

Frequency	Sampling Location	Parameters
Quarterly (January, April, July, October)	Well Nests: MW1002 MW1004 MW1005 Well: MW1000P MW1000R MW1010P	Specific Conductance (Field) pH (Field) pH (Lab) Total Dissolved Solids Total Alkalinity Total Hardness Iron Manganese Copper Sulfate Groundwater Elevation (Field) Color (Field) Odor (Field) Turbidity (Field)

Table 6-10

Groundwater Sampling
(Long-term Care/Maintenance Phase)
Flambeau Mining Company

Frequency	Sampling Location	Parameters
Annually (July)	Well Nests: MW1002 MW1004 MW1005 Well: MW1000P MW1000R MW1010P	Specific Conductance (Field) pH (Field) pH (Lab) Total Dissolved Solids Total Alkalinity Total Hardness Iron Manganese Copper Sulfate Arsenic Barium Cadmium Total Chromium Lead Mercury Selenium Silver Zinc Groundwater Elevation (Field) Color (Field) Odor (Field) Turbidity (Field)

Table 6-11

Groundwater Quality
(Long-term Care/Maintenance Phase)
Flambeau Mining Company

Frequency	Sampling Location	Parameters
Quarterly	MW1013P	Groundwater Elevation (Field)
(January, April, July, October)	MW1013G	Specific Conductance (Field)
	MW1014P	pH (Field)
For two years (i.e., eight quarters)	MW1014G	pH (Lab)
		Total Dissolved Solids
		Total Alkalinity
		Total Hardness
		Iron
		Manganese
		Sulfate
		Copper
		Color (Field)
		Odor (Field)
		Turbidity (Field)

Table 6-12

Groundwater Monitoring
(Long-term Care/Maintenance Phase)
Flambeau Mining Company

Frequency	Sampling Location	Parameters
Annually (July)	MW1013P MW1013G MW1014P MW1014G	Groundwater Elevation (Field) Specific Conductance (Field) pH (Field) pH (Lab) Total Dissolved Solids Total Alkalinity Total Hardness Iron Manganese Copper Sulfate Arsenic Barium Cadmium Total Chromium Lead Mercury Selenium Silver Zinc Color (Field) Odor (Field) Turbidity (Field)

Table 6-13

Groundwater Elevations
(Long-term Care/Maintenance Phase)
Flambeau Mining Company

Frequency	Measurement Location	Parameters
Quarterly*	MW1001	Groundwater Elevation
(January, April, July, October)	MW1001G	
	MW1001P	
	MW1003	
	MW1003P	
	PZ1006	
	PZ1006G	
	PZ1006S	
	PZ1007S	
	PZ1008	
	PZ1008G	
	PZ1009	
	PZ1009G	
	PZ1011	
	PZ1012	
	PZR1	
	PZS1	
	PZS3	
	Sand Point	
	ST-9-23	
	ST-9-23A	
	ST-9-26	
	PZ-1A	
	PZ-1B	
	OW-7	
	OW-10	
	OW-39	
	OW-42	
	OW-43	

* Until water levels stabilize.

Table 6-14

Sediment Sampling
(Long-term Care/Maintenance Phase)
Flambeau Mining Company

Frequency	Sampling Location	Parameters
Annually* (May) *For two years after cessation of discharge from wastewater treatment facilities.	S-1 S-3	Particle Size % Volatile Solids Iron Manganese Aluminum Arsenic Silver Nickel Cadmium Chromium Copper Lead Mercury Selenium Zinc

Sample Locations: S-1 = Blackberry Lane (Upstream of Site)
S-3 = Sisters Farm (Downstream of Site)

Table 6-15

Fish Sampling
(Long-term Care/Maintenance Phase)
Flambeau Mining Company

Frequency	Sampling Location	Parameters
Annually* (Low Flow Period) *For two years after cessation of discharge from wastewater treatment facilities.	F-1 F-2	Fillets (w/skin on) Total Mercury Livers Aluminum Arsenic Cadmium Chromium Copper Lead Mercury Zinc Selenium Nickel Silver Iron Manganese

Number of Walleyes to be Collected by Size at Each Sampling Location:
10"-12" - 1
12"-15" - 2
15"-18" - 3
18"-22" - 2
>22" - 1

Location of Sampling: F-1 = Ladysmith Flowage (Upstream of Site)
F-2 = Thornapple Flowage (Downstream of Site)

Table 6-16

Macroinvertebrate Sampling
(Long-term Care/Maintenance Phase)
Flambeau Mining Company

Frequency	Sampling Location	Parameters
Annually (Until notice of completion of reclamation is issued.)	M-1(1) M-2(1) M-3(1)	Aluminum Arsenic Cadmium Chromium Copper Lead Mercury Zinc Selenium Nickel Silver

(1) - 25 Crayfish or more will be composited at each sampling location.

Location of Sampling: M-1 = Blackberry Lane (Upstream)
M-2 = Above Mouth of Meadowbrook Creek (Downstream)
M-3 = Old Port Arthur Dam Site (Downstream)

Table 6-17

Wetland Surface Flows
(Long-term Care/Maintenance Phase)
Flambeau Mining Company

Frequency*	Measurement Location	Parameters
Spring Summer Autumn	WT-1 WT-2 WT-3 WT-4 WT-5	Water Levels

* Until water levels in monitored groundwater monitoring wells stabilize.

Table 6-18

TSP and Meteorological Monitoring Sites
Flambeau Mining Company

Site	State Plane Coordinates	
North Site (Rusk Hospital)	593,030 N	1,715,240 E
Northeast Site	590,100 N	1,714,760 E
Northwest Site (Blackberry Lane)	589,730 N	1,711,640 E
Southeast Site	589,550 N	1,714,825 E
Meteorological Station	581,260 N	1,714,730 E

North Site (Rusk County Hospital)

Property Owner:	Rusk County Hospital
Location:	Southwest corner of the intersection of Highway 27 and College Avenue West.
General Description:	The sampler is located on the roof of the hospital. The face plate of the sampler is 45 feet from the ground. College Avenue runs approximately 200 feet on the north side of the hospital complex, and Highway 27 runs approximately 440 feet along the east side. The Flambeau River flows approximately 300 feet to the south. There are woods and adjacent hospital buildings to the west. The sampler is sufficiently high enough and far enough away so that interference will be prevented.

Southeast Site

Property Owner:	Flambeau Mining Company
Location:	Northwest corner of the intersection of Flambeau Mine Access Road and Highway 27.
General Description:	The sampler is located on a wooden platform such that the face plate of the sampler is seven feet from the ground. The sampler is located approximately 180 feet west of Highway 27 and approximately 125 feet north of Flambeau Mine Access Road. The sampler is located outside of the wake effects region created by the Type II stockpile. Sufficient clearance from the trees that stand east and south of the monitoring site will be provided in order to meet siting criteria.

Northeast Site

Property Owner:	Flambeau Mining Company
Location:	Southwest corner of the intersection of Highway 27 and Blackberry Lane.
General Description:	The sampler is located on a platform such that the face plate of the sampler is 16 feet from the ground. The platform is located on the roof of a small garage. This site sits approximately 170 feet west of Highway 27 and approximately 260 feet south of Blackberry Lane.

Table 6-18 *(Cont'd.)*

Blackberry Lane	
Property Owner:	Flambeau Mining Company
Location:	South of Blackberry Lane and east of Kennecott Lane.
General Description:	The sampler is located approximately 650 feet south of Blackberry Lane and 40 feet east of Kennecott Lane. The old gravel pit is approximately 300 feet to the east. Two stands of trees grow approximately 150 feet northeast and 150 feet south of the sampling location.
Meteorological Site	
Property Owner:	Flambeau Mining Company
Location:	The northwest corner of Highways 27 and P. The site is approximately one mile south of the southeast sampling site.
General Description:	The wind speed, temperature sensor and direction sensors are placed on a 35-foot tall tower which will be located approximately approximately 290 feet west of Highway 27 and approximately 470 feet north of Highway P.

The location of the four TSP monitoring sites and the meteorological station are shown in Appendix B.

6.4 Sampling Protocols

Described within this section of the quality assurance plan are those procedures which will be used to collect those samples specified by the monitoring plan.

6.4.1 Wastewater Sampling

Wastewater sampling protocols are addressed in the WPDES Permit.

6.4.2 Surface Water Quality

Two surface water sampling locations (Appendix B) will be monitored quarterly when permitted discharge is occurring.

A grab sample will be taken at each site. Parameters tested, methods and procedures are those included in the WPDES permit issued for the facility discharge.

When collecting a sample, surface water sampling bottles will be inverted, submersed to mid-depth and upright and allowed to fill. The sample bottles will then be removed from the surface water and capped with Teflon® lined caps. Every effort will be made not to disturb the bottom sediments. Samples will be collected so as not to cause cross-contamination; downstream samples will be collected first. Care must be taken to not stir up bottom sediment when sampling surface waters such that any sample loss is minimized. Decontamination and cleaning between surface water sampling points should follow procedures stated in Section 6.2.

6.4.3 Groundwater Sampling

Permanently-installed wells shall be adequately developed at least five calendar days prior to sampling by suction-lift pumping, pressure objectives pumping, submersible pumping, surge blasts, and/or bailing.

Wells shall be purged prior to obtaining samples. Two methods are used to maximize representative aquifer conditions:

1. Bail or pump the well until at least four static well volumes have been removed (or until the well is dewatered). Well volumes are determined and recorded using Figure 6-1, Groundwater Monitoring Field form. The water level depth will be determined using a water level indicator and recorded on the Groundwater Monitoring Field form.

2. Bail or pump the well until the specific conductivity, temperature and pH of the groundwater stabilizes (pH $\pm$0.1 unit, temperature $\pm$0.5°C; conductivity $\pm$10 umhos/cm).

Sampling shall follow purging by no more than six hours for wells which recover quickly. For slowly recovering wells, sampling must be completed with 10 hours of purging. In no case will wells be samples after 10 hours have elapsed following the purging event.

Prior to purging, the depth to water is first determined by weighted tape or a water level indicator. The well is then purged such that the purging will "pull" water from the aquifer into the screened area of the well and up through the casing.

Figure 6-1

Groundwater Monitoring Field Form

GROUNDWATER MONITORING FIELD FORM

Purging Phase

Well I.D.	Date	Time	Depth to SWL (ft.)	Total Depth (ft.)	Length Water Col. (ft.)	Length of Sand Pack(ft.)	Req. Gals. to Purge 4 Vols.*	Amount Purged (gal.)	Depth to SWL After Purge (ft.)
1000R						7			
1000P						7			
1002						12			
1002S						7.5			
1004						14.5			
1004S						7			
1004P						8			
1005						12			
1005S						8.2			
1005P						7.5			
1010P						8.0			

Sampling Phase

Date	Time	pH	Spec. Cond. at 25 C	Temp. (C)	Color Before Filter	Color After Filter	Odor	Turb Before Filter	Turb After Filter	# of Filters

Temperature/Weather:

Other Remarks:

CASING I.D. (INCHES)	GAL/FT/CASING	BOREHOLE DIA.	GAL/FT/WELL VOLUME (V1 + V2)
2	0.16	8"	0.69
4	0.65	10"	1.67

Equipment Used:

Corning Checkmate LCD pH/Cond. Meter
Geotech 0.45 micron Disposable filters
Water Level Indicator

Site Name: Flambeau Mining Company

Personnel:

FLAMBEAU MINING COMPANY

N4100 HWY 27

LADYSMITH, WISCONSIN

54848

Project:

Page:

Prepared by:

Date:

Checked by:

Date:

Samples shall be collected directly into the appropriate containers, when possible. Groundwater samples will be collected using dedicated, Grundfos Redi Flo II pumps or decontaminated PVC bailers with clean nylon rope for lowering the PVC bailer into wells for sampling. Groundwater collected by the Grundfos Redi Flo II pumps or PVC bailers will be poured directly into the sampling containers specified by the laboratory. A transfer container may be needed if in-line filtration cannot take place at the well head.

Metal sample aliquots will be filtered in the field through a 0.45-micron membrane prior to preservation. Conductance, pH, and temperature readings will be performed at the wellhead. Field observations of color, odor, turbidity will be noted on the field monitoring form (Figure 6-1). The field technician shall also note dates, times, personnel, water levels, purge volumes, as well as field pH, conductance and temperature on the field monitoring form.

Documentation of purging and sampling activities shall be accomplished by using the groundwater monitoring field form (Figure 6-1) and field log book as necessary.

6.4.4 Type I Stockpile Exfiltrate/Type II Leachate

Samples collected from the collection lysimeter will be used to determine the characteristics of the exfiltrate from the Type I stockpile.

Samples will be collected from the sampling riser of the collection lysimeter. Samples will be withdrawn from the sampling riser with a dedicated PVC bailer or submersible pump. Water samples will be poured from the bailer or pump into transfer containers. Samples will be prefiltered in the field with 0.45 micron membrane. Metal sample aliquots will be filtered at the site lab with a 0.2 micron membrane prior to preservation. Conductance, pH and temperature readings will be performed at the riser. Observations of color, odor and turbidity will be noted on the field monitoring form (Figure 6-1). The field technicians shall also note dates, times, personnel, water levels in the manhole, purge volumes as well as pH, temperature and conductivity readings.

Prior to sampling and if the lysimeter is generating a large quantity of liquid on a continuous basis (during the monitoring period), the sampling riser and storage space in the manhole sump will be bailed/pumped dry approximately one to two weeks prior to the sampling date. Samples shall be collected for the parameters below. Where only small sample volumes are obtained, samples for analyses shall be collected in the order below:

pH (field and lab)
Specific conductance (field)
Total chromium
Copper
Iron
Manganese
Sulfate
Total dissolved solids
Total alkalinity
Total hardness

Samples collected from Manhole No. 2 will be used to determine the characteristics of the leachate from the Type II storage area.

Samples will be collected from the sampling riser of the collection lysimeter. Samples will be withdrawn from the sampling riser with a dedicated PVC bailer or pump. Water samples will be poured from the bailer or pump into containers. Metal sample aliquots will be filtered in the field through a 0.2 micron membrane prior to preservation. Conductance, pH, and temperature readings will be performed at the riser. Observations of color, odor, and turbidity will be noted on the field monitoring form. The field technicians shall also note dates, times, personnel, water levels in the manhole, pH, temperature and conductivity readings.

Samples shall be collected for the parameters below. Where only small sample volumes are obtained, samples for analyses shall be collected in the order below:

pH (field and lab)
Specific conductance (field)
Copper
Iron
Manganese
Sulfate
Total dissolved solids
Total alkalinity
Total hardness

6.4.5 Sediment Sampling

Three sediment traps will be suspended above the river bed at each sampling location (Appendix B). These traps will be glass cylinders with an opening approximately one-third of the cylinder depth. Sediment samples will be collected from the sediment within the jars for analytical purposes. If WDNR should wish to split samples, WDNR should notify Flambeau in advance so that appropriate arrangements can be made with regard to sample collection. If insufficient sediments are collected by the traps for analysis, a proposal will be made to WDNR to collect sediments in areas near the sediment traps.

6.4.6 Fish Sampling

Fish (walleye) are to be collected once annually during the low flow period of the year at one upstream and one downstream location of the site (Appendix B).

Acceptable sampling methods will include hook and line, electroshocking and fyke nets. The WDNR will be notified of each sampling event prior to mobilization. After a reasonable effort (eight-hour nocturnal) is made to collect individual fish to coincide with the prescribed size range (Table 6-5), Flambeau will consult with the Department to discuss substitution of walleyes with other species or different sized walleyes.

Fillets (with the skin left on) will be tested. Livers of the fish collected will be composited into one sample for each location and analyzed as outlined on Table 6-5. Each fish will be measured for total length, sexed and the stomach contents will be noted. In addition, the age of each fish will be determined by commonly-accepted techniques.

6.4.7 Macroinvertebrate Sampling

Once per year, 25 or more crayfish (similar in size to the extent possible) will be collected from each of three sampling locations (Appendix B). Whole body composites (including the exoskeleton) will be made of those crayfish collected from each site. Each of the three composites will be analyzed as noted on Table 6-6. If an insufficient sample is available after a reasonable effort (eight hours), the tests will be run on the sample that is available.

In the autumn of each year, at each of the three sampling locations (Appendix B), macroinvertebrate fauna will be collected. Suitable substrates will be chosen at each location.

These organisms will be identified to the lowest possible taxonomic level. Sampling and evaluation of the taxonomic data will follow Hilsenhoff (1987), "An Improved Biotic Index of Organic Stream Pollution: The Great Lakes Entomologist, Vol. 20".

6.4.8 Habitat Characteristics

A physical evaluation of the river bottom habitats will be performed annually at a designated location during the summer low-flow period. The evaluation shall note the location of river sediment loss, percent of area that is sand or finer particle size, as well as unusual biological growth.

This procedure will be conducted annually during the low-flow period until permitted discharges from the site cease.

6.4.9 Wetland Monitoring

Water levels will be read and recorded monthly from March through December of each year (see Figure 6-2). These readings will continue until at least the time that the pit is backfilled unless significant drawdown effects on those wetlands attributable to the project occur.

6.4.10 Pit Inflow

Estimates of groundwater inflow into the open pit during stripping of overburden and mining will be calculated on a monthly basis using the following procedure:

- The total estimated amount of water pumped from the open pit will be recorded through the use of either flow measurement equipment or by calculating flow using recorded pump running time and the specific discharge rate versus head relationship for the pumps used to remove the water from the pit.

- Groundwater inflow will be calculated by subtracting precipitation recorded (from precipitation gauge) less evaporation from the volume pumped. Adjustments to the calculation may be made to reflect the volume of runoff that flows into the pit and to reflect overflows from the runoff and surge pond back into the pit.

Figure 6-2

Wetland Monitoring Form

WETLAND STAFF GAUGE FORM

FLAMBEAU MINING COMPANY
LADYSMITH MINE PROJECT
LADYSMITH, WISCONSIN
91F6

DATE	TIME	WEATHER	PERSONNEL	REMARKS	STAFF GAUGE LOCATION WATER LEVEL READING (FT)				
					WT-1	WT-2	WT-3	WT-4	WT-5

NOTE: Staff gauges to be read at one month increments (first of the month) and recorded to the 0.00 decimal place.

6.4.11 TSP Meteorological Monitoring

Flambeau is required to monitor the TSP ambient air concentration using high-volume air samplers at each of four sites (Appendix B). On behalf of Flambeau, Foth & Van Dyke determined the location of the four sites. Site selections were based on USEPA siting criteria as described in the Ambient Monitoring Guidelines for Prevention of Significant Deterioration, EPA 450/4-87-007, as well as WDNR requirements. In addition to the TSP monitors, a meteorological station consisting of wind speed and direction sensors, precipitation gauge, and temperature sensors have also been installed. The location of the meteorological station is the same as that used during baseline sampling. State plan coordinates for each of the five sites are provided in Table 6-18.

6.4.11.1 Total Suspended Particulates (TSP) Monitors

Each of the four sampling sites are equipped with a TSP high volume sampler consisting of the following:

- Sierra-Anderson High Volume Air Sampler (motor and enclosure).
- Pressure Transducer Flow Recorder.
- Combined Flow Controller/Digital Timer-Programmer.
- Glass Fiber Filter Media.
- Wooden Support Platform.

With the high volume air sampler, the flow rate is easily adjusted with an adjustable resistor (potentiometer) mounted in the electronics enclosure. The flow will be adjusted to approximately 50 cfm so that it is in the required range of 40 to 60 cfm.

During the mining phase, each monitor shall be operated once every day (24 hours on and 24 hours off). If after one year of monitoring during the mining and reclamation phases, there have been no exceedances of a TSP standard, the sampling schedule may be reduced to no less than once every six days.

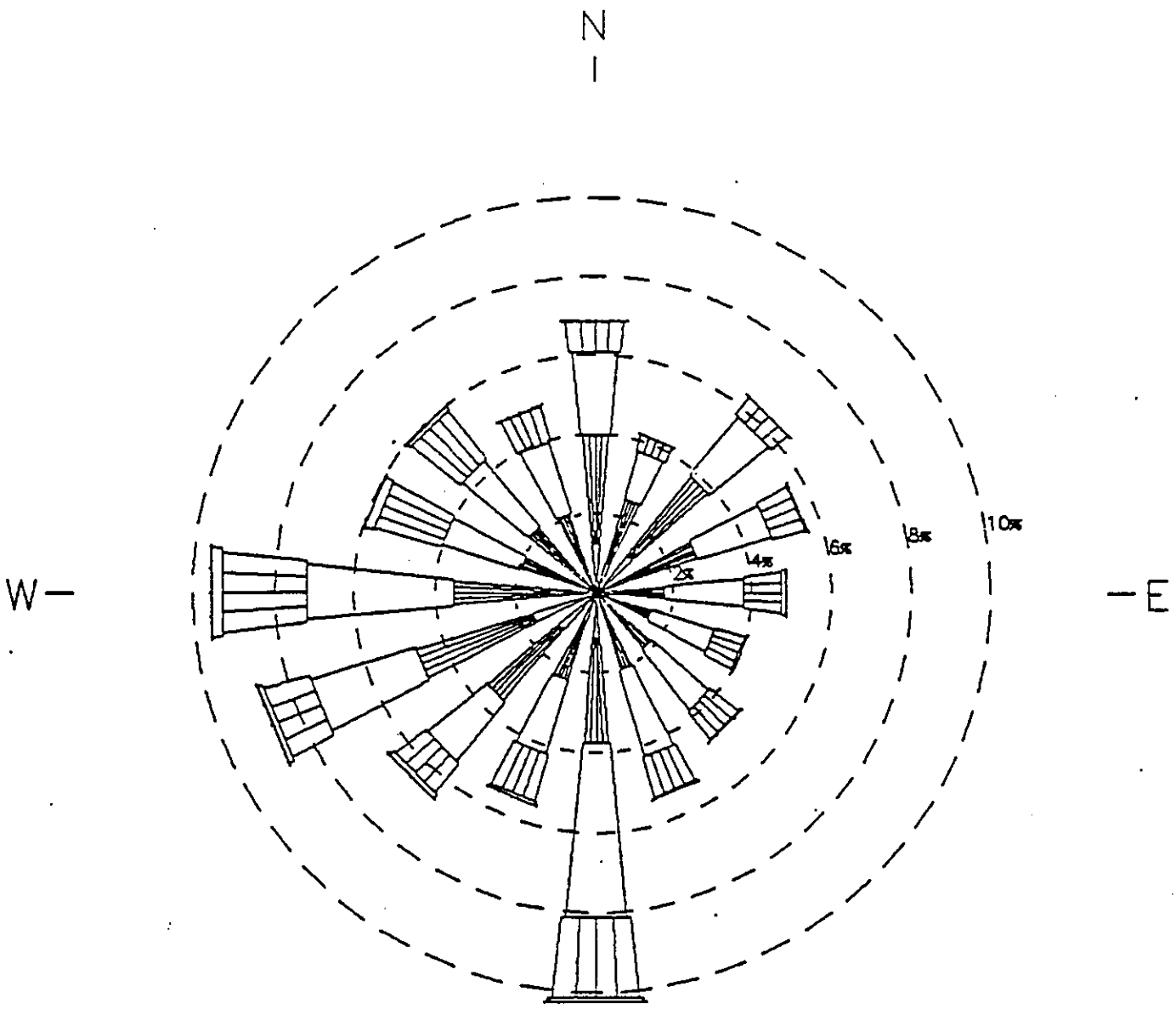
The high volume samplers will operate every third day (24 hours on, commencing at midnight and 48 hours off) during the reclamation phase.

Filters will be installed one day prior and removed one day after the operating day to avoid non-representative particulate loading. The meteorological instruments will operate continuously for the entire 24-hour monitoring period.

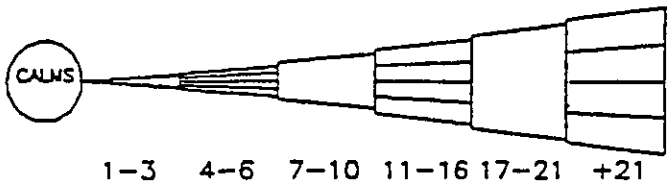
A Sierra-Anderson variable resistance calibration kit which consists of an orifice and a manometer is available for calibration. Calibration procedures for the samplers are contained in Appendix F.

6.4.11.2 Asbestiform Monitors

A separate high volume sampler will be established at the northeast site (southwest corner of the intersection of Highway 27 and Blackberry Lane) to monitor for asbestiform fibers. Figure 6-3 depicts frequency of wind speed and direction for Eau Claire, Wisconsin. This wind rose shows



CALM WINDS .00%



WIND SPEED CLASS
(KNOTS)

WINDROSE
EAU CLAIRE, WI
1982-86

FLAMBEAU MINING COMPANY	
FIGURE 6-3 FREQUENCY OF WIND SPEED AND DIRECTION	
SCALE:	DATE:
PREPARED BY: FOTH & VAN DYKE	BY:

wind direction from the south and west; hence, the northeast site was chosen as the appropriate monitoring site.

A quality assurance plan for asbestiform sampling in ambient air is included as Appendix J. This plan describes the sampling equipment, sample procedures and analytical procedures for asbestiform sampling. If after three years there are no detects of asbestiform fibers, the monitoring will be discontinued.

6.4.11.3 Meteorological Sensors

Meteorological sensors will consist of wind speed, direction sensors, temperature sensor and a precipitation gauge. The wind sensors will be mounted on top of a tower located in the southeast corner of a field. They will be approximately 35 feet off the ground where they will be free of air turbulence caused by ground level obstructions. Any obstructions close enough to cause turbulence will be removed.

Wind speed is sensed by a three-cup anemometer and is converted to an electric signal. Wind direction is sensed by a counterbalanced wind vane coupled to a precision, low-torque potentiometer. The following specifications will be met:

	Accuracy	Range	Threshold
Wind Direction	$\pm 3°$	0-360°	1.0 mph
Wind Speed	± 0.25 mph	0-125 mph	1.0 mph

An external heater will also be provided for the wind sensor.

The heated precipitation gauge has the following characteristics:

- Type - Tipping bucket
- Sensitivity - One tip per 0.01-inch
- Resolution - 0.01-inch
- Accuracy - One percent at two inches per hour

Signals from the wind instruments, precipitation gauge and temperature sensor are recorded on a Datalogger mounted in a weatherproof enclosure at the base of the tower. The Datalogger performs sensor measurement signal conversion, timekeeping, communication, data reduction, data/program storage and control functions. Data is transferred to a remote computer from the station datalogger via a short-haul modem. Battery back-up is provided in the event of a power outage.

6.5 Sample Documentation/Identification

A sample numbering system is used to identify each sample. This numbering system will assure that each sample is uniquely identified. In the case of TSP filters, they will be numbered sequentially and placed in a manila folder. The folder will be placed into a resealable plastic bag to maintain their integrity during transportation and storage.

Project sampling activities will be documented by keeping a written record of daily sampling activities using forms provided in this plan for specific activities and/or implementing the chain-of-custody procedures outlined in Section 7 of this plan.

6.6 Sample Preservation, Holding Time, Container Types, Required Sample Volume

Samples requiring refrigeration will be stored in an ice chest containing sufficient wet ice for transport to the laboratory. Samples requiring pH adjustment will be preserved on-site. Those samples requiring filtration will be preserved after filtration. Preservatives will be provided by NLS and shall be of sufficient purity so as not to interfere with the analysis of the parameters of interest. Field verification of the pH of preserved samples will be accomplished by measuring the pH of a sub sample using pH paper. Sample containers and preservation requirements are listed in Table 5-2.

For TSP monitoring, each of the glass fiber filters will be conditioned and pre- and post-weighed in order to determine particulate loading. A copy of the conditioning and weighing procedures is included in Appendix F. Weighing and conditioning will be performed by Superior Testing Laboratories in Superior, Wisconsin.

6.7 Sampling Procedures

Groundwater and lysimeter sampling is performed in accordance with WDNR guidelines published in WDNR Publ. WR-153-87 "Groundwater Sampling Procedures Guidelines".

Plant and animal samples for tissue analysis will be placed in water-tight plastic bags, which are securely sealed and placed on ice for transport to the laboratory.

TSP or meterologically-related items will be sampled as detailed in Appendix G. Other media will be sampled as described in Section 6 of this quality assurance plan.

6.8 Sample Dispatch

Samples are segregated according to type, i.e., water, air and are packed in separate containers. All samples requiring refrigeration will be packed in ice. When packing the shipping containers, precaution will be taken to minimize sample container breakage during transport to the laboratory. Chain-of-custody documentation will be used to track possession of samples on this project.

After being removed from the sampler, the filter samples will immediately be sent to Superior Testing Laboratories and weighed as soon as possible after reaching the lab. Superior Testing Laboratories will notify Flambeau of the results.

7 Sample Custody

The Chain-of-custody form (Figure 7-1 or equivalent) will be used to document sample possession from the time the sample bottles leave the laboratory until they are received back at the laboratory. Each time custody of a sample is transferred, the new custodian will sign the form and will document the time and date. A sample will be considered in custody if it is:

- in one's actual possession.
- in view, after being in physical possession.
- locked so that no one can tamper with it, after having been in one's physical possession.
- in a secured area, restrictive to authorized personnel.

Upon receipt of samples in the laboratory, the Chain-of-Custody form will be checked and signed. A copy of the form will be retained by the laboratory and the remaining copy returned to the sampling team.

Procedures for preparing and shipping samples will conform with labelling and packing requirements of the United States Department of Transportation.

While awaiting screening or packaging, samples will be stored on wet ice in coolers. Preservatives are added to collected samples such that the physical and/or chemical alterations are minimized. Preservatives must be added immediately upon sample collection. The preservative added will be documented on the Chain-of-Custody form in the "analyses required" or "remarks" portion of the form. If samples cannot be shipped on the same day that they are collected, packaging will be delayed until the following morning so that the samples can be shipped with a full load of ice. These samples will be stored on wet ice in coolers and kept in a secure area.

Each time the custody of the samples is relinquished to another individual (or to the laboratory), the date, time and items transferred are noted on the Chain-of-Custody form. After the samples have been packaged for shipping, the custody will be transferred to a team member who will ship the coolers via overnight courier. Upon shipment, the laboratory will be notified that the sample shipment is scheduled to arrive.

7.1 Laboratory Arrangements

Flambeau Mining Co. will send all samples for analysis to NLS in Crandon, with the exception of the samples associated with particulate monitoring, which will be sent to Superior Testing Laboratories and those for asbestiform, which will be sent to WOHL.

7.2 Laboratory Processing of Samples

Procedures for the receipt and logging of samples by the laboratory are addressed in their individual quality assurance plans. The following minimum requirements will be expected of any laboratory which is used for sample analysis on a given project.

Figure 7-1
Sample Chain of Custody Form

NO. 06017

NORTHERN LAKE SERVICE, INC.

Analytical Laboratory and Environmental Services

400 North Lake Avenue • Crandon, WI 54520
Tel: (715) 478-2777 • Fax: (715) 478-3060

SAMPLE COLLECTION AND CHAIN OF CUSTODY RECORD

Wisconsin Lab Cert. No. 721026460

RETURN THIS FORM WITH SAMPLES.

CLIENT			PROJECT TITLE	
ADDRESS			PROJECT NO.	P.O. NO.
CITY	STATE	ZIP	CONTACT	PHONE

ITEM NO.	NLS LAB. NO.	SAMPLE ID	COLLECTION DATE	COLLECTION TIME	SAMPLE TYPE	GRAB/ COMP.	CONTAINER/PRESERVATIVE					COLLECTION REMARKS
1.												
2.												
3.												
4.												
5.												
6.												
7.												
8.												
9.												
10.												
11.												
12.												

SAMPLE TYPE:
SW = surface water; WW = wastewater; GW = groundwater; DW = drinking water; TIS = tissue; AIR = air; PROD = product; SOIL = soil; SED = sediment
describe others

CONTAINER
P = plastic; G = glass; V = glass vial; B = plastic bag
describe others

PRESERVATIVES & PREPARATION
NP = nothing added; S = sulfuric acid; N = nitric acid; Z = zinc acetate; OH = sodium hydroxide; HA = hydrochloric & ascorbic acid; H = hydrochloric acid; F = field filtered

COLLECTED BY (signatures)		CUSTODY SEAL NO. (IF ANY)	DATE/TIME
RELINQUISHED BY (signature)	RECEIVED BY (signature)		DATE/TIME
RELINQUISHED BY (signature)	RECEIVED BY (signature)		DATE/TIME
DISPATCHED BY (signature)	METHOD OF TRANSPORT		DATE/TIME

RECEIVED AT NLS BY (signature)	DATE/TIME	CONDITION	TEMP.
SEAL INTACT? ☐ YES ☐ NO	SEAL #	REMARKS & OTHER INFORMATION	

IMPORTANT: 1. TO MEET REGULATORY REQUIREMENTS, THIS FORM **MUST** BE COMPLETED IN DETAIL AND INCLUDED IN THE SHIPPER CONTAINING THE SAMPLES DESCRIBED.
2. PLEASE USE ONE LINE PER SAMPLE, **NOT** PER BOTTLE.
3. RETURN THIS FORM WITH SAMPLES - CLIENT MAY KEEP PINK COPY.

ORIGINAL COPY

7.2.1 Receipt of Samples by Laboratory

Upon receipt of samples at the laboratory, the following, at a minimum, shall take place:

7.2.1.1 Non-Air Quality-Related Samples

- Examine all samples and determine if proper temperature has been maintained during shipment. If samples have been damaged during shipment, the remaining samples will be carefully examined to determine whether they were affected. Any samples affected will be considered damaged. It will be noted on the Chain-of-Custody form and reported to laboratory management that specific samples were damaged and that the samples were removed from the sampling program. Field personnel will be notified as soon as possible that samples were damaged.

- Compare samples received against those listed on the Chain-of-Custody and any analysis request forms which may be used. Any discrepancies are to be reported immediately to the project manager.

- Verify that sample holding times have not been exceeded.

- Sign and date the Chain-of-Custody and any analysis request forms.

- Verify temperature of samples. If the temperature is not within specifications, the project manager will be notified so that a decision regarding resampling can be made.

- Verify pH of samples. If the samples have been unpreserved, the project manager will be notified so that a decision regarding resampling can be made.

- Assign laboratory number to each sample.

- Place the samples in adequate laboratory cold storage. This is generally accomplished by placing the samples in a refrigerator or cold storage room where the temperature is maintained at 4°C. A maximum-minimum thermometer or thermomograph is used to verify temperatures present in the refrigerator or cold room.

- Enter the following information in a laboratory sample log-in system:

  - Assigned laboratory numbers.
  - Project name.
  - Date received in laboratory.
  - Chain-of-Custody number.

7.2.1.2 Air Quality-Related Samples

Procedures for sample receipt of air quality-related samples are described in Appendix E and J.

7.2.2 Laboratory Storage of Samples

The primary considerations for sample storage are:

- Maintenance of prescribed temperature, if required, which is typically 4°C.
- Proper preservation to ensure integrity of samples until samples are analyzed.
- Security of the laboratory and the samples.

All extraction and chemical analyses of samples at a given project will conform to the holding times and be maintained at the temperatures given in Table 5-2. Placement of samples in the proper storage environment is the responsibility of the laboratory.

7.3 Sample Disposal

After the testing program is completed, samples, extracts and digestates are handled, stored and/or disposed in accordance with the individual laboratory's procedure in that regard, and within applicable State and/or Federal regulations.

7.4 Documentation

Project sampling activities will be documented by keeping a written record of daily sampling activities and implementing the Chain-of-Custody procedures described in this portion of the quality assurance plan. The information documented will incorporate that which is specified in Section 7.4.2 of the plan, at a minimum. This will provide for the integrity of data by tracking and documenting samples from the time they are collected by the sampling team through receipt at the laboratory.

7.4.1 Sample Numbering System

A sample numbering system will be used to identify each sample. This numbering system will provide a tracking procedure to allow retrieval of information about a particular sample and assure that each sample is uniquely numbered.

7.4.2 Sample Collection Data

Sample collection data will be collected in the field for each sample acquired. Collection data for samples can be documented on the Groundwater Monitoring Field form (Figure 6-1), TSP field data sheet (Appendix G), or other forms adopted for specific activities.

The information to be provided includes that which is required by these forms and any additional information that the field technician deems important.

7.4.3 Sample Labelling

Sample labels must contain sufficient information to uniquely identify the sample in the absence of other documentation. This will include at a minimum:

- Unique sample number.
- Sample location (and depth, if applicable).
- Sampling date and time.
- Individual collecting of the sample (signature).
- Grab or composite.
- Preservation method employed (if any).

7.4.4 Field Notebook

A bound field notebook with pre-numbered pages will be used to record field analytical sampling results. The notebook will be completed in indelible ink and will include (as appropriate) a record of:

- Field screening instrument readings.
- Water sampling field parameters (i.e., temperature, specific conductance and pH).
- Sample identification numbers, and time/date of collection, location and description.
- Sample preservation documentation.
- Instrument adjustments (calibrations) performed in the field.
- Statements pertaining to any problems encountered.
- Field analysts.
- Weather/site conditions.
- Individuals collecting samples and field supervisor's signature.

Mistakes in the notebook will be crossed through with a single line, initialled and dated.

7.4.5 Common Carrier Shipments

Samples may be shipped to the laboratory using common carriers. A copy of the shipping documents which are completed in order to ship samples with a carrier will be maintained as part of the file in order to demonstrate sample custody.

8 Analytical Methods

The field reading methodologies to be taken or analytical methods to be performed are specified in the tables which follow.

8.1 Field Operations

Methods to be used for field operations are listed in Table 8-1.

Table 8-1

Field Methodologies

Parameter	Method	MDL	Standards Methods 17th Edition	Methods*
pH	Meter/ Electrode	0.1	4500-H+	150.1/9040
Conductivity	Meter	1 umho	2510	120.1/9050
Temperature	Thermometer/ Meter	0.1 C	2550	170.1/N/A

* Format used refers to:

Method for Chemical Analysis of Water and Wastes USEPA March 1983 Test Methods for Evaluating Solid Waste (SW846) USEPA September 1986.

8.2 Laboratory Operations

8.2.1 NLS

Analytical methods to be used at NLS are listed in Table 5-2.

8.2.2 Superior Laboratory

Laboratory procedures for particulate filters are detailed in Appendix E.

In addition, after weighing each filter, a portion of it will be saved. Once every three months, these filter sections will be composited and analyzed for arsenic, beryllium, cadmium, chromium, mercury and nickel. These filter sections will be sent by Superior Labs to NLS for metals analysis.

A description of the compositing procedure is provided in Appendix E.

NLS will use a method for sectioning (303A) and digestion of TSP filters (822) taken from "Methods of Air Sampling and Analysis, Third Edition", James P. Lodge, 1989 (included as Appendix I).

TSP filter digestions are performed in accordance with Section 8.4.4, part 822 of "Methods of Air Sampling and Analysis, Third Edition". James P. Lodge 1989. All filter samples are analyzed in accordance with the following EPA methods: As:206.2, Cr:200.7, Cd:200.7, Ni:200.7, Hg:245.1. All TSP filter results are blank corrected with the average of the blank filters.

A microscopic analysis will be conducted on all TSP filters exceeding 150 ug/m^3 averaged over a 24-hour period. A total of three filters will be analyzed per TSP sampler. In the event that less than three filters per monitor exceed 150 ug/m^3, the three filters having the highest concentration will be analyzed, in those instances where at least one exceedance was noted.

8.2.3 Wisconsin Occupational Health Laboratories

Filters collected during asbestiform sampling will be sent to a certified laboratory for analysis. Samples will be analyzed for mineral particles which have parallel sides with aspect ratios which are greater than 3:1. Laboratory results will be reported as:

- Number of asbestos fibers per cubic meter of air sampled.
- Total number of fibers - length, width and aspect ratio.
- Mass concentration of fibers.
- Mineralogical composition based on X-ray analysis (if required)
- Size distribution of asbestos fibers by length.

These procedures are detailed in the Asbestiform QA plan included as Appendix J of this document.

9 Calibration Procedures and Frequency

Standardized calibration of the equipment used is necessary to obtain valid data.

Measuring and test equipment will be calibrated at prescribed intervals and/or prior to each use. The frequency of calibration will be based on the type of equipment, relative stability, manufacturer's recommendation, intended use and experience with a particular piece of equipment. Calibration procedures and frequency of calibration of field equipment that will be used are provided in Table 9-1.

Calibration of the TSP samplers will be performed after motor maintenance, whenever the results of a quality assurance audit do not meet WDNR's criteria (agreement within $\pm$9 percent of the last calibration) and at such other time that the field technician observes conditions that warrant a recalibration. In any event, each sampler shall be calibrated at least every three months. See Appendix E for calibration procedures. Calibration of the meteorological sensors will be conducted on site as necessary as determined by the site technician.

For asbestiform monitoring, less frequent calibrations will occur since monitoring will only be conducted one day per month from May through September. Thus, it is anticipated that the asbestiform sampler will be calibrated prior to and following each sampling event through the reclamation phase.

Flambeau Mining Company anticipates that the WDNR will audit the instruments at the start of the monitoring period and annually thereafter.

Replicate field measurements of samples and laboratory analysis of replicate samples will be performed to document the effectiveness of these calibration procedures.

Calibration records for equipment used will be maintained.

Standards used in calibration procedures will be prepared from pure standard materials or will be purchased as certified solutions (Table 9-2). The standards which are used an/or any preparation of standards by field personnel will be documented. The documentation will contain the following information for equipment used:

- Date of calibration.
- Data pertaining to calibration and/or maintenance procedures.
- An indication of the person performing the calibration and/or maintenance.
- Adjustments made and an indication of accuracy of the equipment readings prior to and following such adjustments (where applicable).
- Records of equipment failure or inability to calibrate to specification (where applicable).

Table 9-1

Field Instrument Calibration

Instrument	Number of Standards Initial Calibration	Acceptance/ Rejection Criteria (Initial)	Frequency	Number of Standards Continual Calibration	Acceptance/ Rejection Criteria (Continuing)	Frequency
pH Meter	2	±0.1 SU	Daily prior to use or failure of continuing calibration.	1	Reading within 5% of known value.	Initial and every ten samples.
Conductivity Meter	2	±1%	Daily prior to use or failure of continuing calibration.	1	Reading within 5% of known value.	Initial and every ten samples.
Thermometer	N/A	±0.1°C	Yearly	N/A	N/A	N/A

Table 9-2

Standard Sources and Preparation

Instrument Group	Standard Source	How Received	Source Storage	Preparation From Source	Preparation Frequency
pH Meter	Commercial Lab Supplier	Certified Solutions	Room Temp.	N/A	N/A
Conductivity	Commercial Lab Supplier	Certified Solution or Standard	Room Temp.	Working stocks are prepared from source stocks	Semiannual or as needed
Thermometer	NIST certified thermometer	N/A	N/A	N/A	N/A

N/A = Not Applicable

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10 Preventive Maintenance

The result of any equipment/instrument readings depends on the inherent accuracy and proper operation, use and function of the instrument. It is essential that the equipment/instruments operate under optimum conditions at all times. Each equipment/instrument user is expected to be familiar with the manufacturer's operations manual on each instrument and routinely performs various service checks.

Each equipment/instrument is calibrated according to the manufacturer's instructions. A maintenance log will be maintained for each instrument. This log will include the following (at a minimum):

- Instrument description.
- Manufacturer, model number and serial number.
- Name, address and telephone number of company which services item.
- Type of service policy.
- Timing and frequency of routine maintenance, servicing and calibration.

Routine field preventive maintenance procedures are found on Table 10-1. Routine laboratory preventive maintenance procedures for NLS are found in Appendix A (see also Table 10-2).

Critical spare parts are stocked where frequent failure or routine wear warrant. Unexpected downtime is unavoidably encountered at times due to equipment failure. In such instances, a protocol will be followed in which steps are taken to either correct the problem and resume measurements or otherwise ensure that samples are properly analyzed within allowable holding times. Regular maintenance of the TSP sampler will allow long periods of operation without system failure. After each sampling period, the motors, the power cords, the filter holder gaskets and the continuous recorder pen will be visually inspected.

The flow controller probe should be cleaned routinely with water followed by isopropyl alcohol. The use of a small camel hair brush is recommended. The motor's carbon brushes must be replaced every 400 to 500 hours of operation, or after 17 days of operation. It is imperative that the brushes be replaced before the brush shunt touches the motor commutator. This maintenance procedure is described in the manufacturers literature.

In addition, the meteorological station will be visually inspected for damage. Routine service and calibration will be provided by the site electrician. A separate manual will be available for operation and maintenance of the met station equipment.

The following contingency plan has been established in the event of equipment malfunction. The steps are carried out in sequence until the analysis of still-valid samples is ensured or provisions are made for resampling.

10.1 Field Preventive Maintenance

1. Attempts made by field technician to correct the problem immediately, by referencing available service information. Samples are returned to proper storage during trouble-shooting.

Table 10-1

Field Preventive Maintenance

Instrument	Activity	Frequency
pH Meter	Rinse electrodes with pH 7 solution.	After each reading.
	Immerse electrodes if required to do so based on type of electrode. pH 7 solution	When not in use.
	Clean electrodes with mild acid or alcohol solution.	When dirty, coated with oil or other precipitate.
	Recondition electrodes by alternately soaking in a 1:10 solution of HCl for one minute and then 1:10 solution NaOH for one minute, for a total of four soakings.	When sensor probe will not calibrate to pH 10 or pH 4 solution.
	Add new KCl solution to sensor probe.	When excess KCl crystal buildup, or when sensor probe will not calibrate to pH 10 or pH 4 or KCl level is less than (25mm) one inch. Keep wetting cap saturated with KCl.
	Check batteries.	Before each use.
Conductivity Meter	Standardization with standard potassium chloride solution.	Prior to each use.
	Rinse probe with deionized water.	After each use.
	Check batteries (if any).	Prior to each use.

Table 10-1 *(Cont'd.)*

Instrument	Activity	Frequency
D.O. Meter	Rinse tip with D.O. electrolyte solution and clean sensor tip with silver/gold polish.	After every two weeks of continuous use.
	Clean tip with silver and gold sensor tip. Replace D.O. electrolyte solution.	After every two weeks of continuous use or inaccurate calibrations.
	Replace membrane cap.	Every four weeks or when damaged.
Grundfos Redi Flo II Pump	Clean impellers. No regular preventive maintenance necessary on dedicated equipment. Keep converter dry.	If pump does not pump and if not electrical problem.
Water Level Indicator	Scrape with knife sensor tip.	When dirty or coated with a precipitate.
	Check batteries.	Prior to each use.

Table 10-2

Laboratory Preventative Maintenance

Instrument	Activity	Frequency
Atomic Absorption (flame)	Clean burner head	Daily
	Check aspiration tubing	Daily
	Clean optics	Every 3 months
	Check gases	Daily
	Check optics	Annually
Autoanalyzer (AAII)	Flush system with DI water	Daily
	Clean pump platen surfaces	Daily
	Flush with Kemwash	Weekly
	Clean pump rollers	Weekly
	Check pump tubing	Weekly
	Replace pump tubing	160-200 hours
	Oil wicks on pump	Every 3 months
	Replace transmission tubing	Every 6 months
Conductivity Bridge	Clean conductivity cell	As needed
	Re-platenize electrodes	As needed
DO Meter	Change probe membrane	As needed
	Clean gold cathode	As needed
Mass Spectrometer	Check cooling system	Weekly
	Check mechanical vacuum pump oil level	Weekly
	Rebuild vacuum pumps	As needed
	Check diffusion pump oil level	Monthly
	Service diffusion pumps	As needed
	Replace source filament	As needed
	Bake out source, analyzer, and manifold	As needed
	Bake out foreline traps	As needed
pH Meter	Inspect electrode junction for air bubbles	As needed
	Check for blocked junction	As needed
	Clean or recondition pH bulb	As needed

Table 10-2 *(Cont'd.)*

Instrument	Activity	Frequency
UV/Visible Spectrophotometer	Flush with DI water after use	Daily
Analytical Balances	Clean pans and compartment Check accuracy	After every use Annually (on contract)
Incubators/Refrigerators	Check temperature Check freon level/leaks	Daily Annually
Ovens	Check temperature	Daily

2. Management is appraised that an equipment malfunction is disrupting normal field sampling activities. Attempts made to correct failure are described.

3. Management decides whether or not to involve outside servicing. This decision is based on the nature of the problem and availability of service assistance and parts.

4. Management assesses time required to restore proper equipment function in relation to remaining sample-holding time.

5. Management selects an approved alternate analytical method, if possible, which will permit completion of field activities within applicable time limits (if any).

6. Management makes arrangements with another equipment source to complete the field measurements within remaining holding time and by approved methodology.

10.2 Laboratory Preventive Maintenance

Routine maintenance activities for NLS laboratory instruments are described in Appendix A.

Recommended maintenance activities for such instruments are found in Table 13-2.

10.3 Documentation

Routine maintenance procedures will be documented and records of maintenance activities will be kept for each instrument. Records of non-routine repairs will be maintained at the laboratory.

11 Quality Control Checks

The quality control checks described in this section are those to be used in conjunction with those sampling events not involving TSP or asbestiform monitoring. The quality control checks for TSP are described in Appendices E, F and G.

11.1 Field QC Checks

11.1.1 Sampling Events Involving Ten or More Samples of Common Matrix

11.1.1.1 Equipment Blanks

At least one equipment blank on clean sampling equipment will be submitted and analyzed for every 20 samples in a matrix group. This blank will be prepared in the field before sampling begins by filling or rinsing the precleaned equipment with analyte-free water, filling the appropriate container(s) and preserving and documenting in the same manner as the collected samples. Suitable blanks for analyte groups of interest will be submitted and analyzed for each type of equipment set to be used in sampling.

11.1.1.2 Field Duplicates

During each independent sampling event, at least one sample, or 10 percent of the samples, whichever is greater, will be collected in duplicate for analysis. This requirement applies to each matrix group that is samples.

11.1.2 Sampling Events Involving Five to Ten Samples of Common Matrix

11.1.2.1 Equipment Blank

If equipment is cleaned in the field, one equipment blank for each matrix group will be collected and analyzed on the field-decontaminated equipment. If no equipment is cleaned, then one equipment blank that is prepared on-site on the precleaned equipment will be collected and analyzed for each matrix group.

11.1.2.2 Field Duplicates

One field duplicate will be collected and analyzed for all matrix groups.

11.1.3 Sampling Events Involving Less than Five Samples of Common Matrix

One equipment blank on either precleaned or field-decontaminated equipment will be collected and analyzed for each matrix group.

11.1.4 QC Checks on Field Measurements

At least one duplicate sample will be analyzed for every 10 field measurements.

11.2 Laboratory QC Checks

11.2.1 Method Reagent Blanks

A method reagent blank is a blank of an appropriate analyte-free matrix that is processed (digested, extracted, etc.) and analyzed with a specified sample set.

Method reagent blanks will be prepared and analyzed at a rate of one per sample set, or five percent, whichever is greater.

11.2.2 Matrix Spikes

Matrix spikes are environmental samples selected from a set (not blanks) that are fortified to a known and validated concentration of analyte(s) before sample preparation. The concentration of each analyte in the spiking solution should be approximately three to five times the level expected in the sample.

At least one matrix spike in a sample set (or five percent, whichever is greater), with common matrices will be prepared and analyzed using the specified method. If a set contains samples of different matrices, matrix spikes should be prepared and analyzed for each matrix type.

11.2.3 Quality Control Check Standards

Quality control check standards are standard solutions from a source other than normal calibration standards that are certified and traceable. These standards are used to check the accuracy of a calibration curve.

QC check standards will be analyzed at a continuing frequency equivalent to five percent of the samples in the analytical set (i.e., one every 20 samples).

11.3 Routine Procedures to Assess Precision and Accuracy

The results of the instrument readings or laboratory results (as appropriate) will be used to evaluate precision and accuracy.

11.3.1 Evaluation of Field Analytical Precision

To determine the precision of the field sampling methods used, a routine program of duplicate measurements/analyses will be performed. The results of duplicate measurements/analyses will be used to calculate the relative percent difference (RPD) to assess the degree of precision associated with field measurement systems.

The RPD is defined as:

$$\% \; RPD \; = \; \frac{D_1 - D_2}{\left(\frac{D_1 + D_2}{2}\right)} \; x \; 100\%$$

where: RPD = relative percent difference
D_1 = first sample value
D_2 = second sample value

Acceptable ranges for field measurements can be found in Table 5-1.

11.3.2 Evaluation of Field Analytical Accuracy

To determine the accuracy of the field sampling methods used, a routine program of evaluating the results of an observed measurement of a check standard against the true concentration of such a standard shall be used. The result of these evaluations will be used to calculate percent recovery (percent R).

The percent R is defined as:

$$\% \; R = \frac{observed}{true} \; x \; 100\%$$

Acceptable ranges for field measurements can be found in Table 5-1.

11.3.3 Evaluation of Field Completeness

Completeness is defined as the percentage of valid data obtained as judged by the data quality objectives compared to the total amount of data required to be collected. Completeness is calculated for each field measurement/analysis in the following manner:

$$C = V/D \; x \; 100$$

where: C = percent completeness
V = number of valid sample measurements/results
D = number of total sample measurements/results required

It is expected that at least 95 percent of the determination will be complete. Certain sample types may require different levels of completeness, which should be identified in specific project plans.

11.3.4 Evaluation of Laboratory Analytical Precision (NLS)

These procedures are described in Appendix A.

11.3.5 Evaluation of Laboratory Analytical Accuracy (NLS)

These procedures are described in Appendix A.

12 Data Reduction, Validation and Reporting

12.1 Data Reduction

The field technician/lab analyst will be responsible for reading charts and/or interpreting instrument output and raw concentration data. Standard curves, determined by linear regression of standard concentration with peak height (or equivalent output), will be used to calculate sample concentrations. Other parameters (e.g., sample dilution, sample weight, extract volume) will be factored in, to arrive at corrected concentration values. Field measurement data will also be entered into spreadsheets for tabulation and analysis. Data entry will be performed by the analyst, technicians or managers. It will be the responsibility of the manager to insure that data are entered accurately and on time.

12.2 Data Validation

12.2.1 Data Integrity

Technicians and ultimately, managers will be responsible for the following tasks associated with checking data integrity:

- Checking raw data entries and calculations.
- Checking sample preparation log books.
- Checking analytical log books.
- Checking calibration integrity.
- Checking internal chain-of-custody.

Some or all of these tasks apply to both field measurements and laboratory analyses.

12.2.2 Data Validation

12.2.2.1 Field and Laboratory Activities

It will be the responsibility of the lab analyst or field technician to properly perform routine QC checks and to identify and report out of control situations. The Supervisor of Environmental Affairs will be responsible for verification of QC checks and resolution of any out of control situations.

12.2.2.2 Project Data

The Supervisor of Environmental Affairs will be responsible for reviewing overall project data before submission. Key areas of review include field and laboratory QC data, review of supporting documentation and review of data for any obvious anomalous values.

12.3 Data Storage

Raw and processed data will be stored on computer disks and/or hard copy. Computer files will be backed-up on separate disks stored in a different location than the original files. Data hard copies, along with strip charts and instrument printouts, will be labelled and stored. Field, laboratory, sample preparation and analytical log books will also be stored. All archived data will

be stored in such a manner that records are easily accessed. All records will be maintained for a minimum of three years.

12.4 Data Reporting

Data entry will be performed by the analyst, project technician or Supervisor of Environmental Affairs. The Supervisor of Environmental Affairs will be responsible for checking data entry. The Supervisor of Environmental Affairs will assure that data on the final report are correct, by performing an informal audit of analytical, data entry and data reduction procedures.

Flambeau Mining Company will submit data consisting of 24-hour average TSP concentrations, hourly average wind speed and direction and daily rainfall to the WDNR within 30 days after completion of the required analyses. In addition, results of the metallic and asbestiform analyses will be submitted within 30 days of completion of these analyses. An annual report will also be submitted which will summarize the year's monitoring activities and any observed trends in the monitoring data.

Data will be submitted in accordance with guidelines provided by the Air Monitoring Section of the Bureau of Air Management. A hard copy transmittal letter and summary of missing data will be included with the data. The letter will contain our explanation relating to any missing data.

Should the TSP 24-hour concentration at a monitoring site exceed 150 micrograms per cubic meter (ug/m^3), Flambeau shall investigate the exceedance and report it to the Department within two working days of having validated the sample concentration. Flambeau will provide an exceedance investigation report to the Department which shall include the following information: an analysis of the monitoring filter; a wind rose or bar chart for the exceedance period; and information about the operating conditions at the mining site during the exceedance period (i.e., number of trucks and mining vehicles in operation; amount of production occurring at the facility, etc.)

The results of the groundwater analytical testing, collection lysimeter testing and groundwater levels will be submitted to the WDNR within 30 days of receipt of validated results.

In March of each year, following the collection of monitoring data for the previous year, an annual surface water monitoring report will be prepared and submitted to WDNR. The inflow to the pit will be calculated on a monthly basis and reported to the WDNR on an annual basis with the surface water monitoring report.

13 Corrective Actions

A nonconformance is any procedure, event, reading or measurement which is outside the limits established for field operations.

As a result of a nonconformance, whether identified by the project quality control officer, by the sampling technician, or by an auditor, a corrective action shall be implemented. Any one of the individuals indicated above can initiate a corrective action, if necessary.

Corrective actions are generally of two kinds:

- Immediate, to recalibrate or repair nonconforming equipment. The need for such an action will most frequently be identified by the field technician.

- Long-term, to eliminate causes of nonconformance and to minimize the possibility of their recurrence. These are usually system-related issues that may be identified as the result of quality control reports associated with one or more projects.

Field corrective action procedures are detailed in Table 13-1. Laboratory corrective action procedures are detailed in Table 13-2.

Depending on the nature of the problem, the corrective action employed may be formal or informal. An informal corrective action consists of an evaluation of a nonconforming situation that threatens the outcome of a procedure, event, reading or measurement. Upon recognition of the problem, the field/lab technician will review his procedure for apparent errors, recalibrate the instrument used for measurement and remeasure.

If this does not result in correction of the problem, the field/lab technician will bring the problem to the attention of the appropriate manager who will determine the proper corrective action. If significant time or costs are involved, the manager will obtain the necessary approval for the corrective action indicated. The corrective action will be incorporated into the appropriate procedures to minimize the possibility of recurrence.

In either case, occurrence of the problem, corrective action taken and verification of problem resolution must be documented. Documentation of corrective action will be made in the field/lab log book. Documentation of corrective actions will be in memos or forms developed for this purpose.

Table 13-1

Recommended Field Corrective Actions

QC Activity	Acceptance Criteria	Recommended Corrective Action
Instrument Zero	Must zero	Reset zero: if same response, determine cause.
Initial Calibration	Standard concentration ±5% of expected value	Reanalyze standards; if still unacceptable, remake standards. If equipment malfunctions, notify manager.
QC Check Standard	±5% of expected value	Reanalyze standard; if still unacceptable, remake standards or use new standards. If equipment malfunctions, notify manager.
Continuing Calibration (cc)	±5% of expected values	Reanalyze standard; if unacceptable, recalibrate equipment and rerun samples from last cc standard check. If equipment malfunctions, notify manager.

Table 13-2

Recommended Laboratory Corrective Actions

QC Activity	Acceptance Criteria	Recommended Corrective Action
Initial Instrument Blank	Instrument response >MDL response	Prepare another blank. If same response, determine cause of contamination: reagents, environment, instrument equipment failure, etc.
Initial Calibration Standards	Coefficient of variation >acceptable limit or standard concentration value (*) deviation from value	Reanalyze standards. If still unacceptable, then remake standards.
QC Check Standard	(*) Deviation from value	Reanalyze standard. If still unacceptable, then remake standards, or use new primary standards if necessary.
Continuing Calibration	(*) Deviation from value	Reanalyze standard. If still unacceptable, then recalibrate and rerun samples from the last cc standard check.
Method Blank	>MDL	Reanalyze blank. If still positive, determine source of contamination. If necessary, reprocess (i.e., digest or extract) sample set.

* ±10% for metals analyses.
±20% for wet lab/nonmetals analyses.
±15% for organic analyses

14 Performance and System Audits

14.1 System Audits

A systems audit determines that each element within an activity is functioning appropriately and is within the guidelines specified by the QA plan. These types of audits may be conducted on field sampling, preservation, shipping and equipment calibration/cleaning procedures. A systems audit will include a review of the sampling/analysis plan, sample collection/measurement methods, sampling protocol, field chain-of-custody procedures, field documentation methods and sample identification methods.

14.2 Performance Audits

These types of audits may be conducted on field or laboratory activities. Flambeau Mining Company reserves the right to audit laboratories used for analyses on a regular basis or if there are inappropriate trends in the laboratory data, major changes in personnel, and/or discrepancies in quality control samples.

15 Quality Assurance Records

Records shall be maintained to provide evidence of quality assurance activities. All activities which indicate an out of control situation will be evaluated. Corrective actions taken will be documented. This documentation will be in the field records or in formal memos, letters or notifications which are part of the file.

Records will be maintained for a minimum period of three years or as specified by permit or regulation.

Appendix A

Northern Lake Service Quality Assurance Plan

NORTHERN LAKE SERVICE, INC.
QUALITY ASSURANCE/QUALITY CONTROL MANUAL

This manual documents the methods and procedures used by Northern Lake Service (NLS) to comply with NR149 Wisconsin Administrative Code. Methods herein are taken from authoritative sources with some modifications recommended by instrument manufacturers to increase analytical performance and ease of instrument operation.

This QA/QC manual is updated annually.

GENERAL INFORMATION

Northern Lake Service began operations in 1974 to provide analytical and consulting support for Wisconsin's Inland Lake Renewal Program. Under that program NLS conducted comprehensive lake studies requiring collection, analysis, and interpretation of groundwater and surface water samples along with hydrological and biological investigations to determine water quality and lake management alternatives for about 30 Wisconsin lakes. It was under this program that our reputation for analytical expertise and accurate results became recognized and grew.

NLS has continued to provide new environmental services in response to client needs. Procedures and methods are chosen or developed to provide the most accurate and precise information in the most efficient and timely manner. Consequently, our ever-expanding list of satisfied clients includes various industries, landfills, municipal waste treatment plants, public water utilities, government agencies, and private parties.

Our modern laboratory is equipped with state-of-the-art instrumentation for analyzing drinking water, groundwater, process water, wastewater, soil, sediments, and tissue for inorganic, organic, and physical constituents. We are Wisconsin certified as an environmental laboratory. In addition, NLS is one of the few labs in Wisconsin to become certified under the Safe Drinking Water Act (SDWA), and by our request, one of the first to undergo the comprehensive lab audit required under this certification program.

While much of our present effort is committed to providing analytical lab services, we also offer a variety of field services. Our groundwater sampling service, which utilizes an efficient in-line field filtering procedure to insure the collection of representative samples, has set the standard for producing reliable groundwater data and has become our primary field service.

The NLS staff take particular pride in producing objective, reliable, accurate, and precise environmental data. Praise and satisfaction, both from our clients and from the regulatory agencies, provide the chief driving force at Northern Lake Service. We strive to grow both in technology and client-base without losing the level of personal service and efficiency associated with being small.

RESUMES OF KEY PERSONNEL

RON K. KRUEGER, President
Ron Krueger founded Northern Lake Service in 1974 and currently provides overall management of the company. He also remains active in various NLS field activities, developing and refining sampling procedures and programs to meet clients' needs.

Ron's environmental experience spans over 25 years and includes: conducting biological and chemical surveys and coordination of waste disposal programs in the paper industry; drainage basin surveys and administration of aquatic nuisance control programs in Wisconsin Department of Natural Resources' Lake Michigan District; lake management consultation and field investigation for over 30 lake districts while at NLS.

Ron holds a B.S. in biology and general science from the University of Wisconsin-Stevens Point. He is a member of the American Water Well Association and the Wisconsin Ground Water Association.

JAMES E. FISHER, Laboratory Director
Jim Fisher provides technical management and overall direction of the organic and inorganic laboratory operations. He helps to develop and establish analytical methodology, oversees the QA/QC program and manages the supervision and training of analytical personnel. Jim is also involved with LIMS computer programming, instrument troubleshooting, and technical liaison with clients and regulatory agencies.

Jim has over ten years of experience in environmental analysis, with half that time in supervision and management roles. Prior to joining NLS, Jim managed an environmental laboratory in Michigan and worked on PCB research projects at a USEPA laboratory. He has a B.S. in Chemistry from Michigan State University.

W. JOSEPH NOSEK, JR., Quality Assurance Officer
Joe Nosek oversees the NLS quality assurance program and the Continuous Quality Improvement Program, which he instituted at NLS. Joe also monitors data quality and adherence to Standard Operating Procedures (SOP's). He interacts with regulatory agencies and is generally responsible for maintaining current laboratory certification by those agencies.

Joe graduated from the University of Minnesota at Duluth with a B.S. in Earth Sciences. He has completed courses in quality assurance from the National Bureau of Standards and the Association of Official Analytical Chemists, in Good Laboratory Practices from the Society of Quality Assurance. He is a member of the American Society for Quality Control and is a Certified Quality Auditor. Joe has over seven years of experience in quality assurance with environmental laboratories.

CHRIS GESKE, LIMS Manager
Chris Geske manages the programming, operation and maintenance of the NLS Laboratory Information Management System. He also oversees the operation and maintenance of other computers and networks, and is the principal computer systems troubleshooter.

Chris works closely with the Laboratory Director and the Quality Assurance Officer, as well as with other departments. He attended the Milwaukee School of Engineering and has an Associate degree in electronics from North Central Wisconsin Technical College.

JERRY BOCK, Organics Supervisor
Jerry Bock provides supervision of the organics department and organics analysis by gas chromatography with various detectors for volatiles, semivolatiles and pesticides/PCBs. He has a strong background in organic chemistry and over 15 years of analytical chemistry experience.

Jerry has a B.S. in Medical Technology from the University of Wisconsin-Eau Claire. He has also attended Hewlett-Packard courses in gas chromatography techniques.

TED JOHNSON, Organic Chemist
Ted Johnson specializes in the analysis of diverse sample matrices for pesticides and PCBs. He has over six years of experience in organic analysis, using several types of instrumentation, at commercial and state laboratories. Ted holds a B.S. degree in Chemistry from the University of Wisconsin - Eau Claire.

JENNIFER A. SCHLUNDT, Organic Chemist
Jennifer Schlundt provides analysis of samples for volatile organic compounds. She has over eight years experience in research and chemical analysis, including polymer chemistry, work in a university setting and in private industry.

Jenny holds a B.S. degree in Chemistry from the University of Wisconsin-Stevens Point, where she earned the Merck Index Award for academic excellence. Presentations include "Factors Affecting Reproducibility in Pyrolysis Gas Chromatography" given at a U.W.-Eau Claire Research Symposium.

JOHN W. BEHRMAN, Organic Chemist
John Behrman conducts analysis for organic compounds by gas chromatography/mass spectrometry. He has over five years of analytical experience working with a variety of environmental matrices. John operates and maintains our Varian Saturn II GC/MS system.

John graduated from the University of Wisconsin Stevens Point, with a B.S. in Water Resources and Chemistry. He also attended Hewlett Packard and Finnegan - sponsored GC/MS operations

courses. John is a member of the American Water Resources Association.

JOSEPH WEIX, Inorganics Chemist
Joe Weix works in the inorganics department, and analyzes samples for metals and nutrients. His primary experience is in analysis for toxic metals in the ppm and ppb range via AA-flame, AA-graphite furnace and cold vapor, and ICP. Joe has a B.S.in Natural Resources and Water Chemistry from the University of Wisconsin-Stevens Point.

PAUL D. KNUTH, Chief Water Quality Technician
Paul Knuth has six years of experience in environmental analysis and field work. At NLS he provides wet chemistry analysis in inorganics and nutrients, as well as some work in analysis for metals. He primarily works with the spectrophotometer, auto analyzer and AA-flame/graphite furnace instruments, and provides field sampling services.

THOMAS R. PRIEBE, Inorganic Supervisor
Tom Priebe provides supervision of the Inorganics department and analysis of samples for metals and inorganic parameters. His background also allows Tom to specialize in troubleshooting analytical interferences in complex waste matrices.

He has experience with a large waste disposal company, as well as with WDNR where he was involved with field sampling, analysis, instrument calibration, and maintenance.

Tom holds a B.S. degree in Water Chemistry from the University of Wisconsin Stevens Point, and has completed the 40 hr training in Health, Safety & Management of Hazardous Materials per 29 CFR 1910.120.

ANDREW J. OSTROWSKI, Environmental Scientist
Andy Ostrowski provides analytical capabilities in inorganics and wet chemistry. He is also a primary resource in NLS field services, ground water monitoring, UST site assessments, and lake management studies.

He holds a B.S. in Water-Resources, Chemistry and Soil Science from the University of Wisconsin-Stevens Point. He has also attended WGWA seminars and has completed OSHA's required 40-hour HazWaste Site Training. Andy is a member of the Wisconsin Ground Water Association.

DATA CONFIDENTIALITY

The results of all analyses are confidential. This data is only released to the client, or to an agent of the client if NLS has received prior written authorization from the client. Unless the data has been subpoenaed by a court action, regulators can only receive copies of this data from the client.

LAB AND FIELD SECURITY

Lab equipment, field equipment, reagents, empty prepared sample bottles, and filled sample bottles are all items which potentially can become contaminated either maliciously or inadvertently through tampering. These items should remain in secure custody to insure the legal credibility of analytical results.

Sample Custody in the Field

There are basically two categories of custody for samples which are collected at various locations and analyzed at Northern Lake Service. The first category includes samples which are collected by Northern Lake Service personnel in whose custody the samples remain until they are received and logged into the data base at the lab. The second category of custody occurs when a client or his assign(s) collect a sample or set of samples and either makes personal delivery or ships the sample(s) to the laboratory using a public or private carrier.

To insure a secure custody of samples collected by NLS personnel, the following policy will be followed by NLS field investigators during sampling and while transporting samples to the lab:

> The names or initials of NLS field personnel will be listed on data sheets or field data records. NLS personnel will insure that secure custody is maintained by keeping all tamperable items either under lock and key or under the direct surveillance of at least one NLS field investigator at all times while in the field. This means that vehicles, buildings, motel rooms, or other locations in which sampling equipment and samples are stored or transported must be securely locked whenever unattended by NLS personnel. Whenever the conditions of this policy are not met, a written report explaining the circumstances of non-compliance is required. If the samples were left in someone else's custody for a period of time, the times and name will be recorded. If samples could not or inadvertently were not securely locked up in the absence of NLS personnel, the circumstances will be recorded. Any comments regarding evidence of tampering or whether the attending NLS personnel feel the samples were tampered with should be recorded. This report will be signed by all NLS personnel present on that sampling trip and attached to the data to which it pertains in NLS files.

Northern Lake Service assumes no responsibility for sample custody prior to delivery at the lab except when NLS personnel have conducted the sampling and transporting. NLS does provide a chain of custody form for its clients. NLS makes no claims regarding the legal propriety of this form; it was designed to be efficient and minimize paperwork, and to identify all sample custodians. A signature is required by each custodian who is

likely to have primary interest in the samples. Transporters are identified only by company name or agency.

Section V of the NLS chain of custody form is completed by NLS personnel when the sample(s) arrive at the lab. The original copy is returned to the client with the final data reports for the samples to which it pertains.

Sample Custody in the Laboratory

Once samples are delivered to the laboratory, sample custody is secure by virtue of the fact that no unauthorized persons are allowed in the laboratory. Visitors and service personnel are allowed only under the supervision of NLS personnel.

The computerized database is self-contained on the premises. The computer system does not allow anyone to login without the proper user-id and password.

All access doors to NLS are locked at all times when the premises are vacated. All lab reagents, sample bottles, and lab equipment are stored on the premises. Only full time employees are allowed unsupervised access to the laboratory. Lab security is an important consideration whenever new employees are hired. While locks on the sample walk-in cooler and reagent cabinets are considered unnecessary at this time, the need for increased sample security is reassessed from time to time.

REFERENCES OF METHODOLOGY

All Northern Lake Service analytical, quality control, and preservation methodologies are taken from the following sources:

1. American Public Health Association, et. al. 1985. Standard Methods for the Examination of Water and Wastewater. 16th Edition. American Public Health Association. Washington, D.C.

2. American Public Health Association, et. at. 1989. Standard Methods for the Examination of Water and Wastewater. 17th Edition. American Public Health Association. Washington, D.C.

3. Federal Register. Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act. Final Rule and Interim Final Rule and Proposed Rule. October 26, 1984. Government Printing Office. Washington, D.C.

4. American Society of Agronomy, et. al. 1982. Methods of Soil Analysis Part 2 - Chemical and Microbiological Properties. 2nd Edition. Edited by A.L. Page, R.H. Miller, D.R. Keeney. Soil Science Society of America. Madison, Wisconsin.

5. Perkin-Elmer. Analytical Methods for Atomic Absorption. 1982. Perkin-Elmer Corporation.

6. Technicon Industrial Systems. Technicon Autoanalyzer II Operation Manual. 1983. Technicon Instrument Corporation. Tarrytown, New York.

7. United States Environmental Protection Agency. Handbook for Analytical Quality Control in Water and Wastewater Laboratories. March, 1979. E.P.A.-600/4-79-019. Revised 1983. Government Printing Office. Washington, D.C.

8. United States Environmental Protection Agency. Methods for the Chemical Analysis of Water and Wastes. March, 1983. E.P.A.-600-4-79-020. Government Printing Office. Washington, D.C.

9. United States Environmental Protection Agency. Methods for Organic Analysis of Municipal and Industrial Wastewater. July 1982. EPA-600/4-82-057. Government Printing Office. Washington, D.C.

10. United States Environmental Protection Agency. Test Methods for Evaluating Solid Waste. July, 1986. SW-846. Third Edition. Government Printing Office. Washington, D.C.

11. Varian Techtron Pty. LTD. Analytical Methods for Flame Spectroscopy. 1979. Varian Techtron. Springvale, Australia.

12. Varian Techtron Pty.LTD. Analytical Methods for Graphite Tube Atomizer. 1982. Varian Techtron. Mulgrave Victoria, Australia.

REPORTING WATER CHEMISTRY DATA

Significant Digits
All results are reported to two significant digits, unless otherwise specified.

Rounding
Digits 6, 7, 8, & 9 are rounded up; 1, 2, 3, & 4 are rounded down. 5's are rounded to nearest even number; e.g., 4.25 = 4.2; 4.35 = 4.4.

LABORATORY CHEMICALS AND GASES

High quality results are a function of the reagents used. In general, most reagents are of AR quality or better. All preservative chemicals meet a minimum quality of ACS analytical grade. All laboratory water used in the analytical methods is distilled and deionized. All acids used in graphite furnace analysis are of J.T. Baker Instra-Analyzed quality or better. Acetylene used in atomic absorption is the purified form. Nitrous oxide is U.S.P. grade. Air for atomic absorption analysis is filtered to remove particulates and passed through silica gel to remove moisture prior to its introduction into the atomic absorption spectrophotometers. All chromatography gases meet a minimum purity of 99.99%. Standards may be purchased or made up by NLS staff. Chemicals used to make standards are of primary standard grade. If purchased, standards are obtained from a reputable supplier. All reagents are dated, and appropriate shelf lives are recorded. Reagents are discarded prior to their expiration date. Matrix modifiers meet ACS Grade. Matrix modifiers for graphite furnace analysis may be extracted with

ADPC/MIBK to remove trace metal contaminants. GC gases are purified using moisture, carbon, and oxygen traps when necessary.

IN-HOUSE BOTTLE CHECKS

New Bottles:
Northern Lake Service utilizes an in-house bottle check procedure to rule out the sample container as a source of contamination. Upon receipt of new sample bottles, each box is given a lot number. Lot numbers are assigned by size of bottle and type of preservative to be used. Bottles are immediately capped to prevent contamination. A random sampling is then pulled from each lot of bottles. These bottles are given a sample number and logged into the database for the specific parameters each bottle is used for during analysis. The appropriate preservative along with distilled water is added to each bottle. These samples are then analyzed according to EPA protocol and holding times. If a lot is proven to be contaminated, the whole lot is rinsed in the appropriate manner to remove the contamination.

Reuse of Bottles:
Northern Lake Service reuses bottles for specific parameters. The following are the parameters and the cleaning procedures for each parameter:

Oil and Grease - glass bottle:
1. Soap and water wash
2. Rinse three times with tap water
3. Hydrochloric acid wash with 20% HCL
4. Rinse three times with distilled - deionized water
4. Dry well
5. Replace cap with a new cap

Fecal Coliform - Polypropylene bottle:
1. Soap and water wash with low phosphorus lab detergent
2. Rinse three times with tap water
3. Rinse three times with distilled - deionized water
4. Add sodium thiosulfate if necessary
5. Autoclave for 30 minutes at 15 pounds of pressure

PCBs, Pesticides, and PAHs - amber glass bottle:
1. Soap and water wash with low phosphorus lab detergent
2. Rinse three times with tap water
3. Acid wash with Chromic-Sulfuric Acid
4. Rinse three times with tap water
5. Solvent rinse with Methylene Chloride
6. Rinse three times with distilled - deionized water
7. Dry
8. Replace cap with a new cap

SAMPLE PRESERVATIVE AND HOLDING TIMES

Sample preservation methods are taken from the following source:

American Public Health Association, et. al., 1989. Standard Methods for the Examination of Water and Wastewater. 17th Edition. American Public Health Association. Washington, D.C.

Sample preservation is difficult because almost all preservatives interfere with some types of tests. Immediate analysis is ideal. Storage at low temperature (4 degrees C) is perhaps the best way to preserve most samples until the next day. Chemical preservatives are used only when they are shown not to interfere with the analysis being conducted. When used, preservatives are added to the sample bottle initially, so that all sample portions are preserved as soon as collected.

No single method of preservation is entirely satisfactory; the preservative must be chosen with due regard to the determinations to be made. All methods of preservation may be inadequate when applied to suspended matter.

Methods of preservation are relatively limited and are generally intended to retard biological action, retard hydrolysis of chemical compounds and complexes, and reduce volatility of constituents.

Preservation methods are limited to pH control, chemical addition, refrigeration, and freezing. Table I contains holding times and preservation techniques currently employed by Northern Lake Service.

ANALYTICAL RECORDS

The following records are maintained for a minimum of three years by Northern Lake Service:

1. Sample log book.
2. Samples processed so that any sample may be traced back to the analyst, date collected, date analyzed, method used, raw data, calculations, results and final report.
3. Quality control data for spikes, duplicates, reagent blanks, reference samples, calibration standards, and known standards.
4. Quality control records for precision and accuracy.
5. Instrument maintenance records.
6. Sample preservation procedures for specific methods.
7. Status of samples on arrival.
8. Log books, bench sheets, and method demonstration.
9. Chain-of-custody.
10. If NLS does the sampling, the following records are kept on file:
    - A. Preservation techniques.
    - B. Grab or composite sample for wastewater.
    - C. Whether sample was equal volume, time-proportionate or composited-proportionate to flow.
    - D. Whether groundwater samples were field filtered, and the pore size dia. of the filter, i.e., 0.45 um.
    - E. Any unusual circumstances which may affect the results.
    - F. Field sample results.
    - G. Calibration curves for field instruments, standard conditions, and appropriate maintenance.
    - H. Location and time of sampling.

Analytical methods for the analysis of groundwater, surface water, industrial and municipal wastewaters comply with Wisconsin

Statutes NR101, NR140, NR149, NR180, NR181, NR204, NR214, NR219, NR508. NOTE: This section does not address NR109 Wisconsin Safe Drinking Water statute.

METHODOLOGY

In order to insure accurate and consistent results, Northern Lake Service uses methods that have been studied and proven to be reliable by the USEPA. Detection limits used by Northern Lake Service are updated frequently. Detection limits are derived by conducting a replicate analysis with a minimum of seven samples. These samples are spiked and diluted to the proper volume. The samples are extracted (if necessary) and analyzed as if they were an actual sample. The average response and standard deviation is calculated and the method detection limit is calculated using a student-t table with 99% confidence level. The reported detection limits are generally a multiple of two or three times this calculated detection limit. Detection limits and methods used for each parameter are shown in Table 2.

GENERAL QUALITY CONTROL

Quality assurance in the laboratory has come to mean many things. To some, it is merely equated with such factors as:

1. Adequately trained and experienced personnel
2. Good physical facilities and equipment
3. Certified reagents and standards
4. Frequent servicing and calibration of instruments
5. Use of replicate and known-addition analysis

While all of these are important, none in itself assures reliability of laboratory data. A good analytical quality control program consists of three factors:

1. Using only methods that have been studied collaboratively and found acceptable (this generally implies "Standard Methods," EPA, etc.)
2. Routinely analyzing control samples regularly during runs on which unknown samples are being analyzed
3. Confirming the ability of a laboratory to produce acceptable results by requiring analysis of reference samples several times a year

Additional considerations which supplement those above, may be designated as internal or statistical quality control, as well as external quality control, proficiency testing, or laboratory evaluation. In the following discussion, internal quality control is emphasized. It is based on a system developed for the control of general production processes and product quality although the same concepts are adapted readily to laboratory operations.

LABORATORY QUALITY CONTROL LIMITS

In industrial applications, control limits are recommended for each product, each machine, and each operator. In the laboratory

environment, the parameter of interest, the instrument, and the operator are analogous system variables. However, environmental laboratories routinely have to contend with a variable that has no industrial counterpart - the true concentration level of the parameter of interest, which may vary considerably among samples. Unfortunately, the statistics that work well in industrial applications are sensitive to the variability in true concentration that is found in environmental analysis. This variability in true concentration means that there are no expected values for randomly selected samples, so that the accuracy of testing methodology must be evaluated indirectly through the recovery of known standards and spikes. As a result, it is somewhat difficult to apply industrial quality control techniques to the environmental laboratory.

Accuracy Control Limits

Accuracy is defined as the ability to obtain a result with minimal deviation from the actual amount. Control limits for accuracy are calculated after running a minimum of thirty analyses on spiked samples. The accuracy of the analysis is recorded as percent recovery. Percent recovery (P) can be calculated using the following equation:

$$P = \frac{\text{(observed result - background)}}{\text{(amount of spike)}} \times 100\%$$

After collecting a minimum of thirty data points for percent recovery, the average percent recovery (P_a) is calculated using the following equation:

$$P_a = \frac{\sum P}{\text{(number of points)}}$$

The standard deviation (P_s) is calculated using the following equation:

$$(P_s)^2 = \frac{n\sum P^2 - (\sum P)^2}{n(n-1)}$$

where n = number of points

The warning and control limits are calculated using the following equations:

$$\text{Upper Control Limit} = UCL = P_a + 3(P_s)$$
$$\text{Upper Warning Limit} = UWL = P_a + 2(P_s)$$
$$\text{Lower Warning Limit} = LWL = P_a - 2(P_s)$$
$$\text{Lower Control Limit} = LCL = P_a - 3(P_s)$$

These control limits will stand until another set of data points are collected (minimum of 30). During an analytical run, every one out of ten samples are spiked and analyzed. If the recovery of these samples is out of control, the last ten samples are reran until the spiked sample is in control.

Precision Control Limits

Precision is defined as the ability to obtain the same result every time a sample is analyzed. Control limits for precision are calculated after a minimum of thirty analyses on duplicate samples. The precision of the analysis is recorded as the difference in the results of the duplicate samples. The duplicate difference is calculated using the following equation:

$$D = |(\text{Result of 1st Analysis}) - (\text{Result of 2nd Analysis})|$$

Precision of the analysis can also be recorded as percent difference in the results of the duplicate samples. Percent difference ($D_\%$) is calculated using the following equation:

$$D_\% = \frac{(\text{Result of 1st Analysis}) - (\text{Result of 2nd Analysis})}{(\text{Result of 1st Analysis}) + (\text{Result of 2nd Analysis})} \times 200\%$$

Because the characteristics of precision for samples with a low concentration of analyte as compared to samples with a high concentration of analyte are different, control limits for individual analytes are divided into three ranges of concentrations. Samples with a low concentration of analyte must meet the control limits for the low concentration range. Samples with a high concentration of analyte must meet the control limits for the high concentration range. There is also an intermediate range of analyte concentration. The following is an example of this:

Range 1: 0 - 20 mg/l Maximum Duplicate Difference = 1 mg/l
Range 2: 20 - 40 mg/l Maximum Duplicate Difference = 2 mg/l
Range 3: 40 - 100 mg/l Maximum Duplicate Difference = 3 mg/l

After collecting a minimum of thirty data points for duplicate difference, the average duplicate difference (D_a) for a particular range can be calculated using the following equation:

$$D_a = \frac{\sum D}{\text{(number of points)}}$$ where D = duplicate difference

The standard deviation (D_s) is calculated using the following equation:

$$(D_s)^2 = \frac{n\sum D^2 - (\sum D)^2}{n(n-1)}$$ where n = number of points

The warning and control limits for a particular concentration range are calculated using the following equations:

Upper Control Limit = UCL = $D_a + 3(D_s)$
Upper Warning Limit = UWL = $D_a + 2(D_s)$
Lower Warning Limit = LWL = $D_a - 2(D_s)$
Lower Control Limit = LCL = $D_a - 3(D_s)$

These control limits will stand until another set of data points are collected (minimum of 30). During an analytical run, one out of ten samples are run in duplicate. Many of these duplicate analysis involve the spiking of the samples to provide a non-zero result. If the difference between the duplicate analyses is out of control, the last ten samples are reran until the duplicates are in control.

Sample Matrix

Since accuracy and precision data is more likely to vary with sample matrix, control limits have been established for the different matrices. There are seperate control limits for clean, solid, and waste matrices.

Control Charts and Benchsheets

Accuracy and precision data can be best observed on a control chart. A control chart is a graphical representation of the data. An example of a control chart can be seen in Figure 1. This is a plot of Range 1 duplicate data and accuracy data for Hardness (clean matrix).

When benchsheets are printed for an individual parameter, the control limits for that parameter are printed on the first page. Therefore, the analyst knows immediately if a spike or duplicate analysis is out of control.

Computer-Aided Data Entry and Limit Calculation
To assist in the tracking and entry of quality control data, customized computer programs are incorporated into the quality assurance program. Individual analytes are assigned a test code specific to Northern Lake Service requirements. All quality control data make reference to these testcodes. After the completion of every analytical run, the quality control data for that run is entered into the database. Any out of control results are flagged immediately, and the samples reran. Control limits are automatically recalculated every three months. Only those parameters with a minimum of thirty data points are recalculated. All data and past control limits are stored in the new database for ten years.

FIELD SAMPLING QUALITY CONTROL

In addition to laboratory quality control, NLS has standardized field sampling techniques and field quality control. Each time our field sampling crew conducts groundwater sampling, a field equipment check is performed to determine cross contamination between wells.

NLS has devised the following procedure:

1. All equipment is triple rinsed with distilled-deionized water. NOTE: This is the standard clean up procedure between well samples.

2. 500 ml of distilled-deionized water is run through the Geofilter pump and filter holder which contain a 0.45 um membrane filter to flush and remove any residual COD, TOC, MBAS, or other trace analytes.

3. An appropriate volume of water is placed in the bailer, filtered through the Geofilter filtering system, and collected into new bottles containing the proper preservatives. These samples are then iced.

4. Appropriate field analyses are run and recorded immediately after sample collection. Examples would be conductivity, pH, and temperature.

5. Date, time, weather conditions, etc. are recorded for each sample collected.

6. The field equipment check is logged into the database when received at the lab with all the parameters to be performed on the corresponding samples. This is done to insure there is no possibility of cross-contamination.

7. All meters for field analysis are standardized prior to and after sample collection. Both the pH and conductivity meters are calibrated before sample collection and at four hour intervals.

Field determination for odor, color, and turbidity on water samples might be expected to vary from observer to observer on the same sample. In an attempt to reduce this variability and

produce the most definitive and repeatable results, the terminology shown in Table 3 will be used for these determinations by NLS personnel in the field. All records acquired during field sample collection are kept for a minimum of three years.

ANALYTICAL EQUIPMENT

Northern Lake Service always strives to utilize the most modern equipment available in the environmental analysis field. Many hours of evaluation and testing go into any equipment purchase. The following is a list of analytical equipment used at Northern Lake Service:

1. Technicon Auto Analyzer II
2. Varian Atomic Absorption Spectrometer AA-1475
3. Varian Graphite Tube Analyzer GTA-95
4. Perkin Elmer Zeeman Atomic Absorption Spectrometer 4100ZL
5. Thermo Jarrell Ash AtomScan 25 ICP
6. Cetac U-5000AT Ultrasonic Nebulizer
7. Sartorius Analtyical Balance
8. Mettler AT200 Analytical Balance
9. Milton Roy Spectronic 1201 Spectrometer
10. Blue-M Magni-Whirl Constant Temperature Water Bath (two)
11. American Scientific Products Model DX-38 Drying Oven (three)
12. Blue-M Single Wall Transite Oven
13. Linberg Laboratory Box Furnace Model 51748 Muffle Furnace
14. Technicon BD-20/40 Digestion Block and Controller
15. Orion Model 820 Oxygen Meter (two)
16. Hach Ratio/XR Turbidimeter
17. Orion Specific Ion Electrode Meter Model 920A
    Flouride, ph/temperature, redox, single junction,
    and double junction electrodes.
18. Precision Scientific Inc. Steam Bath
19. Baxter S/P Brand Ultrasonic Cleaners (two)
20. Hewlett Packard 5890 Gas Chromatograph with
    Electronic Capture Detector (two)
21. Hewlett Packard 5890A Gas Chromatograph with
    Flame Ionization Detector
    Nitrogen/Phosphorus Detector
22. Varian 3400 Gas Chromatograph with
    Flame Ionization Detector
    Photo-Ionization Detector
23. Varian 3400 Gas Chromatograph with
    Hall Detector
    Photo-Ionization Detector
24. Varian 3300 Gas Chromatograph with
    Hall Detector
    Photo-Ionization Detector
25. Varian Saturn II GC / Mass Spectrometer
26. Tekmar LSC 2000 Purge and Trap with
    ALS 2016 16-position autosampler (four)
27. Tekmar 7000 Headspace Analyzer with
    Tekmar 7050 50-position autosampler
28. Hewlett Packard High Performance Liquid Chromatograph with
    1046A Flouresence Detector
    1040 Diode Array Detector
    1050 Autosampler
    1050 Quaternary Pump
29. Hewlett Packard 3365 Dos Chemstation Software
30. Hewlett Packard 3D Win Chemstation for HPLC Software

31. Varian DS654 Chemstation
32. Varian Saturn Mass Spectrometer Software

INSTRUMENT CALIBRATION

All instruments are calibrated on the day of analysis. A minimum of three calibration standards is used to calibrate every instrument. Some methods allow the use of a continuing calibration check standard to assure the calibration from the previous day is still intact. In which case, the recovery of the check standard must fall within predetermined limits. If this check standard does not meet the limits, the instrument must be recalibrated using three calibration standards. The following are summaries of the calibration procedures for all instruments:

1. Furnace Atomic Absorption analysis on Varian AA Furnace: All standard calibration curves consist of a blank and three standards. All samples in run duplicate. Spike 1/10 samples. Reslope acceptable after every 10th sample (maximum).

2. Flameless Atomic Absorption for Hg on Varian AA Furnace: All standard calibration curves consist of the following: 2 blanks, 2-0.05 ug, 2-0.10 ug, 2-0.2 ug, 2-0.5 ug, and 2-1.0 ug standards. All samples are run in duplicate; different dilutions acceptable. Spike 1/10 samples.

3. Metals by Thermo Jarrel Ash ICP model Atomscan 25: All standard calibration curves consist of a blank and a minimum of three calibration standards. All samples are scanned a minimum of three times per element. Duplicate and spike 1/10 samples.

4. Metals by Perkin Elmer Zeeman Atomic Absorption Furnace model 4100ZL: All standard calibration curves consist of a blank and a minimum of three standards run in duplicate. All samples are run in duplicate. Spike 1/10 samples.

5. Wet chemistry determined on Technicon AA II: All standard calibration curves consist of a blank and a minimum of three calibration standards run in duplicate. Duplicate and spike 1/10 samples.

6. Wet chemistry determined on Milton Roy 1201 and Bausch & Lomb Spec 88: All standard calibration curves consist of a blank and a minimum of three standards. Duplicate and spike 1/10 samples.
7. Conductivity meter: Meter standardized using 0.010 Molar solution of Potassium Chloride at 1413 Michromhos/cm @ 25C

8. pH meter: Calibrated using a pH 7.00 buffer and one other buffer to bracket the expected sample pH range. Meter is recalibrated after every 20th sample and at the end of the pH run. If standards differ by greater than 0.05 pH units from the true concentration, meter is recalibrated and samples rerun.

9. Titrations:
   Titration analysis for alkalinity and calcium consists of a titrated blank and a 100 mg/l standard as CaCO3, followed by the samples. Duplicate and spike 1/10 samples.

10. Gasoline Range Organics and PVOCs run on Varian 3400 GC:
    Standard curve consists of a blank and five calibration standards. A continuing calibration is utilized on this instrument for GRO and PVOCs. After the instrument has been initially calibrated, the curve can be used until the check standard recoveries are out of the 80-120% range. Duplicate and spike 1/10 samples. Check standards run a minimum of 1/20 samples.

11. Diesel Range Organics run on HP5890A GC:
    Standard curve consists of a blank and five calibration standards. A continuing calibration is utilized on this instrument for DRO. After the instrument has been initially calibrated, the curve can be used until the check standard recoveries are out of the 80-120% range. Duplicate and spike 1/10 samples. Check standards run a minimum of 1/20 samples.

12. PCBs and Pesticides run on HP5890 GC:
    Standard curve consists of a blank and five calibration standards. A continuing calibration is utilized on this instrument. After the instrument has been initially calibrated, the curve can be used until the check standard recoveries are out of the 80-120% range. Duplicate and spike 1/10 samples. Check standards run a minimum of 1/20 samples.

13. VOCs run on Varian 3300 GC and Varian 3400 GC:
    Standard curve consists of a blank and five calibration standards at the beginning of every analytical run. Duplicate and spike 1/10 samples.

14. VOCs run on Varian Saturn GC/MS:
    Standard curve consists of a blank and five calibration standards. A continuing calibration is utilized on this instrument. After the instrument has been initially calibrated, the curve can be used until the check standard recoveries are out of the 80-120% range. Duplicate and spike a minimum of 1/10 samples. Check standards run a minimum of 1/10 samples.

Calculations performed by NLS staff to reduce raw data into final form are performed twice. (Once by the analyst and checked by a senior chemist. The lab director periodically spot-checks rough data calculations. The preferred mode of operation entails instruments reading directly in concentration.

PREVENTATIVE MAINTENANCE

Refrigerators are monitored daily for temperature; the temperature is kept at 4 degrees C. The BOD-5 incubator is kept at 20 degrees C, and temperature is monitored daily. Glucose or glutamic acid checks are run monthly for BOD. BOD blanks should have a depletion drop of <0.20 mg/l. If depletion exceeds 0.20

mg/l, BOD bottles, storage bottles, and dilution water beakers are washed with concentrated chromic acid and rinsed six times with distilled deionized water. Analytical balances and triple beam balances are cleaned frequently and checked annually by B&B Scale. Balances are checked with class S weights daily. Scheduled maintenance is performed on all analytical equipment. Maintenance procedures for individual instruments are performed according to instructions in the specific owner and operation manual for that piece of equipment. Conductivity, pH, and specific ion electrodes are rinsed with distilled and deionized water after each use. Probes are also cleaned according to cleaning procedure in operation manual. Records outlining daily measurements are kept for a minimum of three years. The following list outlines the type of measurements recorded:

1. Sample storage refrigeration temperatures.
2. Standards storage refrigeration temperatures.
3. Laboratory oven temperatures.
4. Laboratory digestion block temperatures.
5. Standardization of pH and conductivity meters.
6. Water bath systems temperatures.
7. Turbidity Meter calibration.
8. Conductivity of distilled and deionized water.
9. Standardization of field meters.
10. pH of preserved samples.
11. Calibration of laboratory thermometers.
12. Sample extraction data and procedures.
13. Sources and lot numbers of standards used.
14. Maintenance logs for all analytical instruments.
15. Records of computer archived raw data.

LABORATORY INFORMATION MANAGEMENT SYSTEM

In order to efficiently manage the large amount of data produced by an analytical laboratory, Northern Lake Service uses an Altos Multiuser System 5000 computer operating under the Unix V3.2 operating system and an Oracle database Version 6.0. The Altos 5000 incorporates the latest 32-bit microprocessor technology in the Intel 80486 CPU. The operating system allows for up to 200 simultaneous users, local area ethernet network, and wide area networking. Every user must have a login name and password to access the database.

The versatility of the Unix operating system and the Oracle database allows us to conform to the various needs of our customers. Data can be transferred to the customer via disk or modem. Data format can be adjusted so it can be imported into various types of software.

The database is used in almost every step of the analytical process. After receiving a project from a customer at the laboratory, the samples are logged into the database. The corresponding customer information and analytical parameters to perform on the samples are entered into the database. Sample labels and login reports are automatically printed. The analysts can then print benchsheets for the individual tests to perform.

After completing the analytical run, the analyst enters all results and corresponding quality control information into the database. A list of completed projects is automatically printed every morning. The final reports are then printed for these projects, reviewed, and sent to the client. Quality control limits for all parameters can be calculated on command and are generally recalculated every three months. Results for every project are stored in the computer for a minimum of ten years after the receipt of samples. A number of reports can also be run to help in the scheduling process. All customer data is backed up every night onto a tape drive.

ANALYSIS OF QUALITY CONTROL SAMPLES

Laboratory Certification

Northern Lake Service participates in the Wisconsin Laboratory Certification and Registration Program. NLS is currently enrolled and certified in two USEPA Performance Evaluation Programs: the Water Supply and the Water Pollution Programs. The Wisconsin Department of Natural Resources grants certification depending on the results of these programs. Certified laboratories must comply with the rules and regulations established in NR149.

Performance Evaluation Samples (Reference Samples)

Wisconsin certified laboratories are required to analyze reference samples for each test category in which they wish to be certified. In order to be certified for a test category, the reference sample results must meet the acceptable limits established by the provider. If certification of a test category depends on more than one analyte, the laboratory must have 80% of the results within acceptable limits. For test categories in which reference samples are not required, the laboratory must demonstrate acceptable precision and accuracy based on replicate and spiked sample analysis. Table XXX displays the test categories in which Northern Lake Service is certified or pending certification.

Blind Standards

Wisconsin certification also requires the analysis of blind standards. Blind standards must be analyzed a minimum of three times per year. The known amount of analytes and the acceptable ranges are shipped along with the blind standard ampules. If the result of any test category is not within the acceptable range, corrective action must be taken and the standard must be reanalyzed until the corrective action proves to be successful.

SAFE DRINKING WATER ACT

This section outlines QA/QC required for certification under the Safe Drinking Water Act (SDWA). Wisconsin has addressed the necessary requirements under the Wisconsin administrative code

NR109. Except where noted, this section only addresses SDWA protocol.

Sample Handling Procedures for Drinking Water
A chain-of-custody form accompanies all drinking water samples. All such samples are collected in bottles provided by NLS. These bottles come from a certified bottle check lot, and contain the proper preservatives as listed in Table 1. When a sample is received at NLS, whether collected by a client or by NLS staff, it is logged into the Laboratory Database Management Program. When all analyses are complete, a data report is printed, reviewed by the laboratory technical director, then sent to the client. Completed samples may be discarded by NLS staff two weeks after completion of the final analytical report.

Sample Collection, Handling, and Preservation procedure:
The sample tap must be representative of the potable water system. The water tap is sampled after maintaining a steady flow for two to three minutes to clear the service line. The sample is taken prior to any water purification or water softening devices, if possible. The tap must be free of aerator, strainer, and hose attachments. Samples are preserved according to Table 1. Analyses are then completed prior to maximum holding times. When maximum holding times cannot be met, the sample is discarded and a new sample collected. If a Safe Drinking Water Act sample exceeds the maximum contaminant level for a primary drinking water standard parameter, this sample is analyzed in both duplicate and spike.

Safe Drinking Water Methodology
Table 4 contains the approved methodology for drinking water parameters.

TABLE I
SUMMARY OF SPECIAL SAMPLING OR HANDLING REQUIREMENTS

Test Name	Container Type	Size (ml)	Preservation	Regulatory Holding Time
Acidity	P,G	100	Refrigerate	14 days
Alkalinity	P,G	200	Refrigerate	14 days
BOD-5	P,G	1000	Refrigerate	48 hrs
Boron	P,G	100	*6	6 months
Bromide	P,G	100	None required	28 days
Carbon, tot. Organic	P,G	100	*4	28 days
Carbon dioxide	P,G	100	None required	Immediately
COD	P,G	100	*4	28 days
Chloride	P,G	30	None required	28 days
Chlorine, Residual	P,G	500	None required	Immediately
Chlorine, Dioxide	P,G	500	None required	Immediately
Chlorophyll	P,G	500	*2	28 days
Color	P,G	500	Refrigerate	48 hrs
Conductivity	P,G	500	Refrigerate	28 days
Cyanide, tot.	P,G	500	*3	14 days
Fluoride	P	300	None required	28 days
Grease & Oil	G	1000	*4	28 days
Hardness	P,G	100	*6	6 mos
Iodine	P,G	500	None required	Immediately
Metals	P(A),G(A)	---	*5, *6	6 mos
Chromium, Hexavalent	P(A),G(A)	300	Refrigerate	24 hrs
Mercury	P(A),G(A)	500	*6	28 days
Nitrogen, Ammonia	P,G	500	*1	28 days
Nitrogen, Nitrate	P,G	100	Refrigerate	48 hrs
Nitrogen, N02+N03	P,G	200	*4	28 days
Nitrogen, TKN	P,G	500	*4	28 days
Odor	G	500	None required	48 hrs
Phenols, (4AAP)	G only	500	*4	28 days
Purgeables, purge & trap	G(C)	40	*9	7 days
Pesticides-GC	G(D)	1000	Refrigerate	E7-A40
Nitrotoluenes	G(D)	1000	Refrigerate	E7-A40
PAHs-GC	G(D)	1000	Refrigerate	E7-A40
Chlorinated Hydrocarbons	G(D)	1000	Refrigerate	E7-A40
DRO (water)	G(D)	1000	Refrigerate	E7-A40
DRO (soil)	G(D)	25 g	Refrigerate	E7-A40
GRO (soil)	G(D)	25 g	Refrigerate	14 days
GRO (water)	G(D)	40	Refrigerate	14 days
Oxygen, dis. (electrode)	G(E)	300	None required	Immediately
pH	P,G	50	None required	2 hrs
Phosphorus, elemental	G	100	Refrigerate	48 hrs
Phosphorus, total	P,G	100	*4	28 days
Salinity	G(F)	240	None required	Immediately
Silica	P	50	Refrigerate	28 days
Solids	P,G	250	Refrigerate	7 days
Sulfate	P,G	50	Refrigerate	28 days
Sulfide	P,G	300	*8	7 days
Taste	G	500	None required	Immediately
Temperature	P,G	500	None required.	Immediately

For determinations not listed, glass or plastic containers are used; preferably refrigerated during storage and analyzed as soon as possible.

Refrigeration = storage at 4 degrees C, in darkness.
P = plastic
G = glass
G(A) = glass, acid rinsed or QA/QC checked
G(B) = glass, borosilicate
G(C) = glass, VOC vial
G(D) = glass, teflon lined cap
G(E) = glass, BOD bottle
G(F) = glass, wax seal
G(S) = glass, rinsed with organic solvents.

E7-A40 = extraction in 7 days, analysis in 40 days
*1 = Analyse immediately, or refrigerate and add H2SO4 to ph < 2.
*2 = 30 days in dark freezer
*3 = Add NaOH to pH > 12, refrigerate, store in dark
*4 = Add H2SO4 to pH < 2, refrigerate
*5 = Dissolved metals need to be filtered immediately
*6 = Add HNO to pH < 2, refrigerate
*7 = Analyze as soon as possible, refrigerate, or freeze at 20 C
*8 = Refrigerate, add 4 drops 2N zinc acetate/100ml
*9 = Refrigerate, add 100mg ascorbic acid if residual Cl present add 1:1 HCL to pH < 2.

TABLE 2
DETECTION LIMITS
REPORTED BY NORTHERN LAKE SERVICE
AND CORRESPONDING METHODS

Parameter	Detection Limit	Method
Alkalinity	2.0 mg/l	EPA 310.1
B.O.D. (5 days)	2.0 mg/l	EPA 405.1
Chloride	1.0 mg/l	EPA 325.2
C.O.D.	5.0 mg/l	EPA 410.1
Color (APHA)	2.0 C.P.U.	EPA 110.2
Conductivity	1.0 umohs/cm	EPA 120.1
Cyanide	0.001 mg/l	EPA 335.1
Dissolved Oxygen	0.1 mg/l	EPA 360.2
Fluoride	0.1 mg/l	EPA 340.1,.2,.3
Hardness (tot. as CaCO3)	2.0 mg/l	EPA 130.2, 200.7
Nitrogen, Ammonia	0.05 mg/l	EPA 350.1
Nitrogen, Kjeldahl	0.05 mg/l	EPA 351.2
Nitrogen, Nitrite	0.01 mg/l	EPA 354.1
Nitrogen, Nitrate + Nitrite	0.05 mg/l	EPA 353.1
Oil & Grease	5.0 mg/l	EPA 413.1
pH	0.1 su	EPA 150.1
Phenol (Distillation 4AAP)	0.01 mg/l	EPA 420.1,.2
Phosphorus Tot., Dis., Reactive	0.004 mg/l	EPA 356.2
Solids-Total,	2.0 mg/l	EPA 160.3
Solids-Volatile Dissolved	2.0 mg/l	EPA 160.4
Solids-Volatile Total	2.0 mg/l	EPA 160.4
Solids-Volatile Suspended	2.0 mg/l	EPA 160.4
Solids-Dissolved	2.0 mg/l	EPA 160.2
Solids-Organic	0.1 %DWB	EPA 160.3
Solids-Percent	0.1 %DWB	EPA 160.3
Sulfate	2.0 mg/l	EPA 375.1
Sulfide	0.1 mg/l	EPA 376.1
Turbidity	0.5 NTU	EPA 180.1
Furnace AA Metals		
Aluminum	3.0 ug/l	EPA 202.2
Antimony	3.0 ug/l	EPA 204.2
Arsenic	1.0 ug/l	EPA 206.2
Barium	2.0 ug/l	EPA 208.2
Beryllium	0.2 ug/l	EPA 210.2
Cadmium	0.1 ug/l	EPA 213.2
Chromium	1.0 ug/l	EPA 218.2
Cobalt	2.0 ug/l	EPA 219.2
Copper	1.0 ug/l	EPA 220.2
Iron	1.0 ug/l	EPA 236.2
Lead	1.0 ug/l	EPA 239.2
Manganese	0.2 ug/l	EPA 243.2
Mercury, Cold Vapor	0.2 ug/l	EPA 245.1
Molybdenum	1.0 ug/l	EPA 246.2
Nickel	3.0 ug/l	EPA 249.2
Selenium	2.0 ug/l	EPA 270.2
Silver	0.5 ug/l	EPA 272.2
Thallium	1.0 ug/l	EPA 279.2
Tin	5.0 ug/l	EPA 282.2
Vanadium	2.0 ug/l	EPA 286.2
Zinc	0.5 ug/l	EPA 289.2

TABLE 2 CONTINUED: Methods and Detection Limits

Metals by ICP	Detection Limit	Method
Aluminum	0.034 mg/l	EPA 200.7
Arsenic	0.134 mg/l	EPA 200.7
Barium	0.015 mg/l	EPA 200.7
Beryllium	0.480 mg/l	EPA 200.7
Boron	0.022 mg/l	EPA 200.7
Calcium	0.006 mg/l	EPA 200.7
Cadmium	0.006 mg/l	EPA 200.7
Cobalt	0.016 mg/l	EPA 200.7
Chromium	0.014 mg/l	EPA 200.7
Copper	0.012 mg/l	EPA 200.7
Iron	0.015 mg/l	EPA 200.7
Lead	0.048 mg/l	EPA 200.7
Magnesium	0.008 mg/l	EPA 200.7
Manganese	0.004 mg/l	EPA 200.7
Molybdenum	0.020 mg/l	EPA 200.7
Nickel	0.016 mg/l	EPA 200.7
Potassium	0.600 mg/l	EPA 200.7
Silver	0.010 mg/l	EPA 200.7
Sodium	0.034 mg/l	EPA 200.7
Strontium	0.009 mg/l	EPA 200.7
Tin	0.052 mg/l	EPA 200.7
Vanadium	0.012 mg/l	EPA 200.7
Zinc	0.003 mg/l	EPA 200.7

Metals by ICP - Ultra Sonic Nebulizer (Low Level)		
Antimony	10.0 ug/l	EPA 200.7
Cadmium	0.4 ug/l	EPA 200.7
Chromium	2.0 ug/l	EPA 200.7
Copper	2.0 ug/l	EPA 200.7
Lead	3.0 ug/l	EPA 200.7
Molybdenum	2.0 ug/l	EPA 200.7
Silver	2.0 ug/l	EPA 200.7
Thallium	7.0 ug/l	EPA 200.7

VOCs by EPA 8010, 8020, 8021, 502.2, 601, 602 Parameter	(water 5ml)	(soil 0.5g)
Benzene	0.30 ug/l	7.0 ug/kg
Bromobenzene	0.50 ug/l	57 ug/kg
Bromochloromethane	1.00 ug/l	28 ug/kg
Bromodichloromethane	0.50 ug/l	7.0 ug/kg
Bromoform	1.00 ug/l	21 ug/kg
Bromomethane	2.00 ug/l	70 ug/kg
n-Butylbenzene	1.50 ug/l	14 ug/kg
sec-Butylbenzene	1.00 ug/l	28 ug/kg
tert-Butylbenzene	1.00 ug/l	28 ug/kg
Carbon Tetrachloride	0.50 ug/l	7.0 ug/kg
Chlorobenzene	0.50 ug/l	7.0 ug/kg
Chloroethane	1.00 ug/l	43 ug/kg
Chloroform	0.50 ug/l	7.0 ug/kg
Chloromethane	3.00 ug/l	43 ug/kg
2-Chlorotoluene	1.00 ug/l	57 ug/kg
4-Chlorotoluene	1.00 ug/l	57 ug/kg
Dibromochloromethane	0.50 ug/l	7.0 ug/kg
1,2-Dibromo-3-Chloropropane	1.50 ug/l	28 ug/kg
Ethylene Dibromide	1.00 ug/l	28 ug/kg
Dibromomethane	1.00 ug/l	57 ug/kg
1,2-Dichlorobenzene	0.50 ug/l	14 ug/kg
1,3-Dichlorobenzene	0.80 ug/l	14 ug/kg

TABLE 2 CONTINUED: Methods and Detection Limits

Parameter	(water 5ml)	(soil 0.5g)
1,4-Dichlorobenzene	0.50 ug/l	7.0 ug/kg
Dichlorodifluoromethane	1.00 ug/l	43 ug/kg
1,1-Dichloroethane	0.50 ug/l	7.0 ug/kg
1,2-Dichloroethane	0.50 ug/l	7.0 ug/kg
1,1-Dichloroethene	0.50 ug/l	7.0 ug/kg
cis-1,2-Dichloroethene	2.00 ug/l	28 ug/kg
trans-1,2-Dichloroethene	0.40 ug/l	7.0 ug/kg
1,2-Dichloropropane	0.50 ug/l	7.0 ug/kg
1,3-Dichloropropane	2.00 ug/l	57 ug/kg
2,2-Dichloropropane	1.00 ug/l	28 ug/kg
1,1-Dichloropropene	1.50 ug/l	28 ug/kg
Ethylbenzene	0.50 ug/l	7.0 ug/kg
Hexachlorobutadiene	0.50 ug/l	14 ug/kg
Isopropylbenzene	0.50 ug/l	28 ug/kg
p-Isopropyltoluene	1.00 ug/l	14 ug/kg
Methylene Chloride	1.00 ug/l	14 ug/kg
Naphthalene	1.50 ug/l	28 ug/kg
n-Propylbenzene	1.50 ug/l	57 ug/kg
Styrene/O-xylene	1.00 ug/l	30 ug/kg
1,1,1,2-Tetrachloroethane	0.50 ug/l	28 ug/kg
1,1,2,2-Tetrachloroethane	0.50 ug/l	7.0 ug/kg
Tetrachloroethene	0.50 ug/l	7.0 ug/kg
Toluene	0.50 ug/l	7.0 ug/kg
1,2,3-Trichlorobenzene	0.50 ug/l	14 ug/kg
1,2,4-Trichlorobenzene	0.70 ug/l	14 ug/kg
1,1,1-Trichloroethane	0.50 ug/l	7.0 ug/kg
1,1,2-Trichloroethane	0.50 ug/l	7.0 ug/kg
Trichloroethene	0.50 ug/l	7.0 ug/kg
Trichlorofluoromethane	1.00 ug/l	28 ug/kg
1,2,3-Trichloropropane	1.50 ug/l	28 ug/kg
1,2,4-Trimethylbenzene	0.50 ug/l	14 ug/kg
1,3,5-Trimethylbenzene	0.50 ug/l	14 ug/kg
Vinyl Chloride	0.20 ug/l	2.9 ug/kg
Meta/Para-xylene	1.00 ug/l	28 ug/kg
tert-Butylmethyl ether	1.00 ug/l	28 ug/kg
cis-1,3-Dichloropropene	0.50 ug/l	
trans-1,3-Dichloropropene	0.50 ug/l	
Isopropyl ether		14 ug/kg

VOCs by GC/MS EPA 8240, 8260, 524.2, 624

Parameter	(Water 5ml)
Benzene	0.1 ug/l
Bromobenzene	0.1 ug/l
Bromochloromethane	0.1 ug/l
Bromodichloromethane	0.1 ug/l
Bromoform	0.1 ug/l
Bromomethane	0.1 ug/l
n-Butylbenzene	0.1 ug/l
sec-Butylbenzene	0.1 ug/l
tert-Butylbenzene	0.1 ug/l
Carbon Tetrachloride	0.1 ug/l
Chlorobenzene	0.1 ug/l
Chloroethane	1.0 ug/l
Chloroform	0.1 ug/l
Chloromethane	0.1 ug/l
2-Chlorotoluene	0.1 ug/l
4-Chlorotoluene	0.1 ug/l
Dibromochloromethane	0.1 ug/l
1,2-Dibromo-3-Chloropropane	0.1 ug/l
Ethylene Dibromide	0.1 ug/l

TABLE 2 CONTINUED: Methods and Detection Limits

Parameter	(Water 5ml)
Dibromomethane	0.1 ug/l
1,2-Dichlorobenzene	0.1 ug/l
1,3-Dichlorobenzene	0.1 ug/l
1,4-Dichlorobenzene	0.1 ug/l
Dichlorodifluoromethane	0.1 ug/l
1,1-Dichloroethane	0.1 ug/l
1,2-Dichloroethane	0.1 ug/l
1,1-Dichloroethene	0.1 ug/l
cis-1,2-Dichloroethene	0.1 ug/l
trans-1,2-Dichloroethene	0.1 ug/l
1,2-Dichloropropane	0.1 ug/l
1,3-Dichloropropane	0.1 ug/l
2,2-Dichloropropane	0.1 ug/l
1,1-Dichloropropene	0.1 ug/l
Ethylbenzene	0.1 ug/l
Hexachlorobutadiene	0.1 ug/l
Isopropylbenzene	0.1 ug/l
p-Isopropyltoluene	0.1 ug/l
Methylene Chloride	0.1 ug/l
Naphthalene	0.1 ug/l
n-Propylbenzene	0.1 ug/l
Styrene/O-xylene	0.1 ug/l
1,1,1,2-Tetrachloroethane	0.1 ug/l
1,1,2,2-Tetrachloroethane	0.1 ug/l
Tetrachloroethene	0.1 ug/l
Toluene	0.1 ug/l
1,2,3-Trichlorobenzene	0.1 ug/l
1,2,4-Trichlorobenzene	0.1 ug/l
1,1,1-Trichloroethane	0.1 ug/l
1,1,2-Trichloroethane	0.1 ug/l
Trichloroethene	0.1 ug/l
Trichlorofluoromethane	0.1 ug/l
1,2,3-Trichloropropane	0.1 ug/l
1,2,4-Trimethylbenzene	0.1 ug/l
1,3,5-Trimethylbenzene	0.1 ug/l
Vinyl Chloride	0.15 ug/l
Meta/Para-xylene	0.1 ug/l
tert-Butylmethyl ether	0.1 ug/l
cis-1,3-Dichloropropene	0.1 ug/l
trans-1,3-Dichloropropene	0.1 ug/l
Acetone	1.0 ug/l
Carbon Disulfide	0.1 ug/l
2-Butanone	0.2 ug/l
4-Methyl-2-Pentanone	0.1 ug/l
2-Hexanone	0.2 ug/l
Acrolein	1.0 ug/l
Acrylonitrile	0.1 ug/l
Vinyl Acetate	0.1 ug/l

PVOCs by EPA 8020

Parameter	(water 5ml)	(soil 0.5g)
tert-Butylmethyl ether	1.0 ug/l	30 ug/kg
Benzene	0.5 ug/l	30 ug/kg
Toluene	0.5 ug/l	30 ug/kg
Ethyl Benzene	0.5 ug/l	30 ug/kg
Meta/Para-xylene	1.0 ug/l	30 ug/kg
O-xylene	0.5 ug/l	30 ug/kg
1,3,5-Trimethylbenzene	0.5 ug/l	30 ug/kg
1,2,4-Trimethylbenzene	1.0 ug/l	30 ug/kg

TABLE 2 CONTINUED: Methods and Detection Limits

Gasoline and Deisel Range Organics by Wisconsin GRO/DRO

Parameter	(water)	(soil)
GRO	0.02 mg/l (5ml sample)	2 mg/kg (25g sample)
DRO	0.10 mg/l (1000ml sample)	5 mg/kg (25g sample)

Organochlorine Pesticides by EPA 508, 608, 8080

Parameter	(water 1000ml)	(soil)
Alpha-BHC	0.05 ug/l	2.5 ug/kg
Beta-BHC	0.05 ug/l	2.5 ug/kg
Gamma-BHC	0.05 ug/l	2.5 ug/kg
Delta-BHC	0.05 ug/l	2.5 ug/kg
Heptachlor	0.05 ug/l	2.5 ug/kg
Heptachlor Epoxide	0.05 ug/l	2.5 ug/kg
DDE	0.05 ug/l	2.5 ug/kg
DDD	0.05 ug/l	2.5 ug/kg
DDT	0.05 ug/l	2.5 ug/kg
Aldrin	0.05 ug/l	2.5 ug/kg
Dieldrin	0.05 ug/l	2.5 ug/kg
Endrin	0.05 ug/l	2.5 ug/kg
Endrin Aldehyde	0.05 ug/l	2.5 ug/kg
Endrin Ketone	0.05 ug/l	2.5 ug/kg
Endusulfan I	0.05 ug/l	2.5 ug/kg
Endosulfan II	0.05 ug/l	2.5 ug/kg
Endosulfan Sulfate	0.05 ug/l	2.5 ug/kg
Methoxychlor	0.05 ug/l	2.5 ug/kg
Chlordane	0.20 ug/l	10.0 ug/kg
Toxaphene	0.50 ug/l	25.0 ug/kg

Polychlorinated Biphenols (PCB) by EPA 508, 608, 8080

Parameter	(water 1000ml)	(soil)
1016 PCB	0.50 ug/l	25.0 ug/kg
1221 PCB	0.50 ug/l	25.0 ug/kg
1232 PCB	0.50 ug/l	25.0 ug/kg
1242 PCB	0.50 ug/l	25.0 ug/kg
1248 PCB	0.50 ug/l	25.0 ug/kg
1254 PCB	0.50 ug/l	25.0 ug/kg
1260 PCB	0.50 ug/l	25.0 ug/kg
1262 PCB	0.50 ug/l	25.0 ug/kg

Nitrogen/Phosphorus Pesticides by EPA 507

Parameter	(water 1000ml)	(soil)
Atrazine	0.5 ug/l	25.0 ug/kg
Simazine	0.5 ug/l	25.0 ug/kg
Diazinon	0.5 ug/l	25.0 ug/kg
Alachlor	0.5 ug/l	25.0 ug/kg
Cyanazine	0.5 ug/l	25.0 ug/kg
Metolachlor	0.5 ug/l	25.0 ug/kg
Methyl Parathion	1.0 ug/l	50.0 ug/kg
Ethyl Parathion	1.0 ug/l	50.0 ug/kg

TABLE 3 - FIELD SAMPLE CHARACTERISTICS

ODOR
Observe immediately upon collection.

intensity:
not detected (ND)
slight (slt.)
moderate (mod.)
strong

description:
musty
sulfide
smokey
oily
sour
sweet
putrid
pulpy
mineral
other (specify)

COLOR
Observe filtered sample immediately after filtering, prior to preservation.

intensity:
not detected (ND)
light (lt.)
medium (med.)
dark (dk.)

description:
reddish brown (red br.)
yellow
gray
amber
green
salmon
purple
red
tan or natural
other (specify)

TURBIDITY
Observe filter after about 0.3 to 0.5 liters are filtered.

quantity:
not detected (ND)
slight
moderate (mod.)
extreme

texture:
very fine - slimy feel, no observable particles, clay.
fine - floury feel, no observable particles, silt.
medium (med.) - fine gritty feel, tiny observable particles, v.fine sand.
coarse - definite sandy feel; fine, med., coarse sand.
mixed texture (mxd.tx.) - mixture of above.

color:
state color

TABLE 4 - CERTIFICATION PARAMETERS

Category	Analyte		
Oxygen Utilization	Biological Oxygen Demand		
	Carbonaceous Biochemical Oxygen Demand		
Nitrogen	Nitrate		
	Nitrite		
	Ammonia		
	Kjeldahl		
Phosphorus	Orthophosphate		
	Phosphorus		
Physical	Total Solids		
	Dissolved Solids		
	Volatile Solids		
	Total Suspended Solids		
	Oil and Grease		
General I	Alkalinity/Acidity		
	Bromide		
	Chlorophyll a		
	Color		
	Hardness		
	Silica		
	Silicate		
	Sulfide		
	Sulfite		
	Surfactants		
General II	Chemical Oxygen Demand		
	Chloride		
	Cyanide		
	Fluoride		
	Sulfate		
	Total Phenolic Compounds		
General III	EP Toxicity		
	Ignitability		
	Toxicity Characteristic Leaching Procedure		
Metals I	Aluminum	Iron	Strontium
	Antimony	Lead	Thallium
	Arsenic	Magnesium	Tin
	Barium	Manganese	Vanadium
	Beryllium	Mercury	Zinc
	Boron	Molybdenum	
	Cadmium	Nickel	
	Calcium	Potassium	
	Chromium	Selenium	
	Cobalt	Silver	
	Copper	Sodium	
Metals II	Bismuth	Palladium	Titanium
	Gold	Platinum	Tungsten
	Iridium	Rhodium	Zirconium
	Lithium	Ruthenium	
	Osmium	Silicon	

TABLE 4 CONTINUED: Certification Parameters

Category	Analyte
Organics; Purgeable by Gas Chromatography or Gas Chromatography-Mass Spectrometry	Purgeable Halocarbons Purgeable Aromatics Acrolein Acrylonitrile
Organics; Extractables by Liquid Chromatography	Polynuclear Aromatic Hydrocarbons
Organics; Acid Extractable Pesticide	2,4-D 2,4,5-T Picloram Chloramben
Organics; Petroleum Hydrocarbons	Gasoline Range Organics Diesel Range Organics Petroleum Volatile Organic Compounds
Organics; Organochlorine Compounds	Polychlorinated Biphenyls Organochlorine Pesticides

TABLE 5
SAFE DRINKING WATER METHODS

Primary Inorganic Contaminants	Method
Antimony	EPA 200.9
Arsenic	EPA 206.2, 200.7
Barium	EPA 208.2, 200.7
Beryllium	EPA 210.2, 200.7
Cadmium	EPA 213.2, 200.7
Copper	EPA 220.2, 200.7
Chromium	EPA 218.2, 200.7
Cyanide	EPA 335.1,.2,.3
Fluoride	EPA 340.1,
Lead	EPA 239.2
Mercury	EPA 245.1
Nickel	EPA 249.2, 200.7
Nitrate	EPA 353.1
Nitrite	EPA 354.1
Selenium	EPA 270.2
Sulfate	EPA 375.1,.2
Thallium	EPA 279.2
Turbidity	EPA 180.1

Physical, Residual Chlorine, Sodium, Corrosivity and Secondary Inorganic Contaminants	Method
Alkalinity	EPA 310.1
Aluminum, total	EPA 202.2, 200.7
Calcium	EPA 215.2, 200.7
Chloride	EPA 325.2
Chlorine dioxide residual	Standard Methods (17ed) 4500-ClO_2
Color	EPA 110.2
Conductivity	EPA 120.1
Corrosivity, Langelier index	Standard Methods (17ed) 2330
Foaming Agents	EPA 425.1
Free Chlorine Residual	Standard Methods (17ed) 4500-Cl
Iron, total	EPA 236.2, 200.7
Manganese, total	EPA 243.2, 200.7
Odor	EPA 140.1
Orthophosphate	EPA 365.2,.3
Ozone	n/a
pH	EPA 150.1
Silica	EPA 200.7
Sodium, total	EPA 273.2, 200.7
Silver, total	EPA 272.2, 200.7
Sulfide	EPA 376.1
Temperature	EPA 170.1
Total Filterable Residue	EPA 160.1
Total Residue	EPA 160.3
Turbidity	EPA 180.1
Zinc, total	EPA 289.2, 200.7

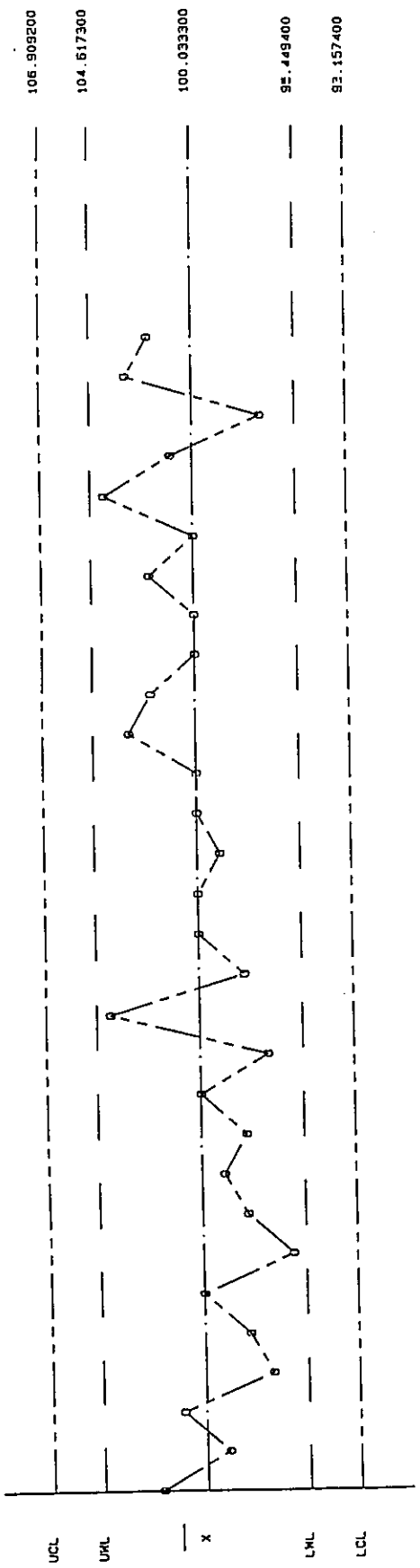
Organic Contaminants Regulated Parameters	Method
Alachlor	EPA 505, 507, 525.1
Adicarb	EPA 531.1
Aldicarb sulfone	EPA 531.1
Aldicarb Sulfoxide	EPA 531.1
Atrazine	EPA 505, 507, 525.1
Benzo(a)pyrene	EPA 550, 550.1, 525.1
Carbofuran	EPA 531.1
Chlordane	EPA 505, 508, 525.1
Dalapon	EPA 515.1

TABLE 5 CONTINUED: Safe Drinking Water Methods

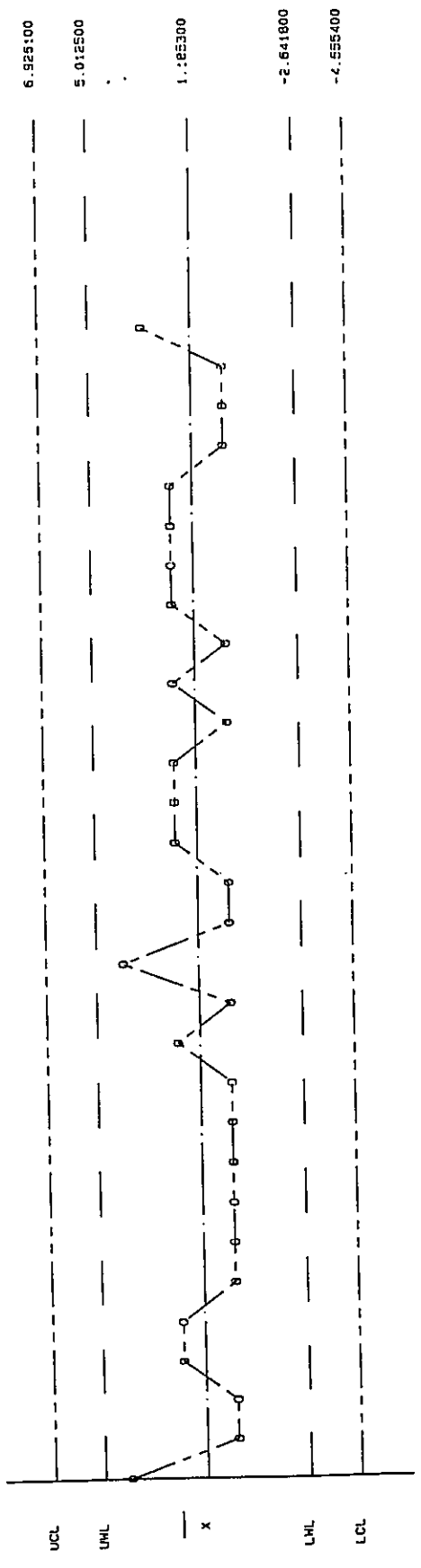
Organic Contaminants Regulated Parameters (cont.)	Method
Dibromochloropropane	EPA 504
Di(2-ethylhexyl)adipate	EPA 506, 525.1
Di(2-ethylhexyl)phthalate	EPA 506, 525.1
Dinoseb	EPA 515.1
Diquat	EPA 549
2,4-D	EPA 515.1
Endothall	EPA 548
Endrin	EPA 505, 508, 525.1
Ethylene Dibromide (EDB)	EPA 504
Glyphosate	EPA 547
Heptachlor	EPA 505, 508, 525.1
Heptachlor Epoxide	EPA 505, 508, 525.1
Hexachlorobenzene	EPA 505, 508, 525.1
Hexachlorocycolpentadiene	EPA 505, 525.1
Lindane	EPA 505, 508, 525.1
Methoxychlor	EPA 505, 508, 525.1
Oxamyl	EPA 531.1
Picloram	EPA 515.1
Polychlorinated Biphenyls	EPA 505, 508, 508A
Pentachlorophenol	EPA 515.1, 525.1
Total Trihalomethanes (TTHM)	EPA 502.1, 502.2, 524.1, 524.2
Simazine	EPA 505, 507, 525.1
Toxaphene	EPA 505, 508
2,3,7,8-TCDD (Dioxin)	EPA 1613A
2,4,5-TP	EPA 515.1
Volatile Organic Chemicals (VOCs)	EPA 502.1, 502.2, 503.1, 524.1, 524.2

Organic Contaminants Unregulated Parameters	Method
Aldrin	EPA 505, 508, 525.1
Butachlor	EPA 507, 525.1
Carbaryl	EPA 531.1
Dicamba	EPA 515.1
Dieldrin	EPA 505, 508, 525.1
3-Hydroxycarbofuran	EPA 531.1
Methomyl	EPA 531.1
Metolachlor	EPA 507, 525.1
Metribuzin	EPA 507, 508, 525.1
Propachlor	EPA 507, 525.1

Figure 1
Quality Control Charts



2050 - Hardness, tot. as Ca
RANGE 1 SPK (.0000 - 200.0000 %) CALC'D ON: 08-JAN-93



2050 - Hardness, tot. as Ca
RANGE 1 DUP (.0000 - 200.0000 mg/l) CALC'D ON: 22-JUL-92

TEST
Metals by Atomic Absorption by Flame or Furnace.

REFERENCE
Methods for Chemical Analysis of Water and Wastes. EPA March, 1983.

INSTRUMENTATION
Varian AA-1475 Atomic Absorption Spectrophotometer.
Varian GTA-95 Graphite Tube Atomizer.
Starna Boost Control for Super Lamps.
Perkin Elmer 4100ZL Zeeman Atomic Absorption Spectrophotometer.

SCOPE AND APPLICATION
This method can be used for the determination of dissolved, suspended, or total elements in drinking water, surface water, waste water, and waste material. Dissolved metals are determined from filtered and acid preserved samples. Total metals are determined after appropriate digestion procedures have been performed. Drinking waters free of particulate matter may be analyzed directly. Domestic and industrial wastes require processing to solubilize suspended matter. Sludges, sediments and other solid samples can be analyzed after appropriate treatment.

Detection limits, sensitivity and optimum ranges will vary with various models of atomic absorption spectrophotometers. Table 1 and Table 2 contain the detection limits for the various metals analyzed on the Varian AA-1475 and the Perkin Elmer 4100ZL. Detection limits by direct aspiration may be extended through concentration of the sample and/or through solvent extraction techniques. Lower concentrations can also be determined through the furnace technique. When using the furnace technique, the analyst should be cautioned as to possible chemical reactions occurring at elevated temperatures which may interfere with the metals analysis. In order to provide valid data with furnace techniques, the analyst must examine each matrix for possible interference effects. If interference does occur in a particular matrix, the sample should be analyzed accordingly either through dilution, matrix modification, or the method of standard addition.

In samples where direct aspiration does not provide adequate sensitivity, the furnace technique may be used. Other specialized procedures are also available such as gaseous hybride method for arsenic and selenium, cold vapor method for mercury, and the chelation-extraction procedure for specific metals. Approved colorimetric methods for many elements are also available.

SUMMARY OF METHOD
The following is a summary of the direct aspiration atomic absorption spectroscopy method and the furnace atomic absorption spectroscopy method. Lower detection limits can be determined with the furnace technique.

Direct Aspiration
In direct aspiration atomic absorption spectroscopy, a sample is aspirated into a flame. The heat of the flame causes the sample to atomize. A light beam from a hollow cathode lamp with a cathode made of the element of interest is directed through the flame into a monochromator. A detector in the monochromator measures the amount of light absorbed by the atomized sample. The amount of absorption depends on the presence of free unexcited ground state atoms in the flame. The light produced by the cathode lamp has a wavelength characteristic of the metal being analyzed. An increase in the element of interest in the flame causes more light to be absorbed. The detector monitors this absorption and a determination of the amount of element in a sample can be derived.

Furnace Technique
When using the furnace technique, a known amount of sample is placed in a graphite tube in the furnace. The graphite tube is then heated, causing the sample to evaporate, char, and finally atomize. Since a greater percentage of

the atoms are atomized in the tube than in the flame, the detection of very low concentrations of elements is possible. The principle is very similiar to flame technique, except a furnace is used to atomize the sample instead of a flame. Light of a specific wavelength is directed through the vapor of the atomized sample. The intensity of the transmitted light decreases as the amount of ground state element increases. A monochromator isolates the wavelength of interest and transmits this to the photosensitive detector. The detector monitors the amount of absorption and a determination of the amount of element in the sample can be derived.

General Sample Characteristics
The atomic absorption method is generally limited to the analysis of metals in solution or solubilized through some form of processing. Wastewater and industrial effluents usually require some form of digestion because of the complexity and variability of the matrix. A digestion is required when the breakdown of organic material is necessary.

DEFINITIONS
Optimum Concentration Range - A range below which scale expansion must be used and above which curve correction should be considered. This range will vary with the sensitivity of the instrument and the operating conditions.

Sensitivity - The concentration in milligrams of metal per liter that produces an absorption of 1%.

Detection Limit - Detection limits can be expressed as either instrument detection limits or method detection limits. Instrument detection limit is defined as the concentration equivalent to a signal, due to the analyte, which is equal to three times the standard deviation of a series of ten replicate measurements of a reagent blank signal at the same wavelength. Method detection limit is defined as the

Dissolved Metals - Those constituents (metals) which will pass through a 0.45 um membrane filter.

Suspended Metals - Those constituents (metals) which are retained by a 0.45 um membrane filter.

Total Metals - The concentration of metals determined on an unfiltered sample following vigorous digestion, or the sum of the concentrations of metals in both the dissolved and suspended forms.

Total Recoverable Metals - The concentration of metals in an unfiltered sample following treatment with hot dilute minteral acid.

SAFETY
The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined. Each chemical compound should be treated as a potential health hazard. Exposure to these chemicals must be reduced to the lowest possible level by whatever means available. A reference sheet for material handling is available for all chemicals used in this method. These sheets available to all analysts.

INTERFERENCES IN FLAME ATOMIZATION
The most common type of interference is chemical interference. This occurs when there is a lack of absorption of atoms bound in molecular combination in the flame. This can occur when the flame is not sufficiently hot enough to dissociate the molecules. The addition of lanthanum into the sample matrix will overcome the phosphate interference in the Magnesium, Calcium, and Barium determinations. The addition of Calcium will eliminate the Silica interference with Manganese. Chemical interferences may also be eliminated by separating the metal from the interfering material. While complexing agents are used to increase the sensitivity of the analysis, they may also be used to eliminate interferences.

INTERFERENCES IN FLAMELESS ATOMIZATION
Although the use of flameless atomization greatly reduces oxide formation, it is still subject to chemical and matrix interferences. Gases produced in the furnace during analysis may have molecular absorption bands that overlap the analytical wavelength. The use of a background correction or an alternate wavelength should eliminate this problem.

Interferences from a smoke producing sample matrix can be reduced by extending the charring time at a higher temperature, or using an ashing cycle in the presence of air. Samples with high concentrations of organic material should be oxidized by a digestion procedure prior to analysis. Nitric acid is preferred for the digestion procedure. If the addition of other acids is required, use minimal amounts. This particularly applies to Hydrochloric acid.

EQUIPMENT
The following is the equipment used to analyze water and waste samples for trace elements:

1. Varian AA-1475 Atomic Absorption Spectrophotometer.
2. Varian GTA-95 Graphite Tube Atomizer.
3. Starna Boost Control for Super Lamps.
4. Perkin Elmer 4100ZL Zeeman Atomic Absorption Spectrometer.
5. Hollow Cathode Lamps (element specific).
6. Arsenic and Selenium Super Lamps.
7. Strip Chart Recorder, used primarily during Hg analysis.
8. Glassware.

REAGENTS AND STANDARDS
The following is the required chemicals for atomic absorption analysis:

1. Distilled and deionized water.
2. Nitric Acid, concentrated.
3. Nitric Acid, (1:1) Add 500 ml of concentrated HNO_3 to 500 ml deionized, distilled water.
4. Hydrochloric Acid, (1:1) Add 500 ml of concentrated HCL to 500 ml deionized, distilled water.
5. Stock standard metal solutions used for calibration and sample spiking.
6. Fuel and oxidant.

SAMPLE HANDLING AND PRESERVATION
All laboratory glassware used in this procedure must be thoroughly washed with detergent and tap water; rinsed with (1:1) nitric acid; and final rinsed three times with distilled and deionized water. Chromic acid may be used to remove organic deposits from glassware, but extreme care must go into the final rinse in order to remove all traces of Chromium.

Before collection of the sample, a decision must be made as to what types of data is desired. For the determination of dissolved parameters, the sample must be filtered throught a 0.45 um membrane filter as soon as practical after

collection and acidified to a pH <2.0 with (1:1) Nitric acid. For the determination of total or total recoverable parameters, the sample must be acidified to a pH <2.0 with (1:1) Nitric acid as soon as possible after the time of collection. For determinations of suspended parameters, a measured volume of nonpreserved sample must be filtered through a 0.45 um membrane filter as soon as possible after collection. The filter should then be transferred to a suitable container for storage. Drinking water samples containing suspended and setteable material should be prepared as a total recoverable parameter.

SAMPLE PREPARATION
For the determination of dissolved parameters, the filtered, preserved sample may often be analyzed as received. Digestion is usually not required for a filter sample. The acid matrix and concentration of the samples and calibration standards must be the same. If a precipitate has formed upon acidification of the sample, the precipitate must be redissolved before analysis through the addition of more acid or by heat. If the precipitate can not be redissolved, the sample must be digested for total recoverable parameters.

Samples requiring total parameters for ground water, waste water, soils, and sludges must be digested prior to analysis. Follow the digestion procedures given on page DIG - 1.

PROCEDURE
Instrument parameters specific to each element analyzed by atomic absorption are given in individual operating procedures in this manual. Refer to these procedures for instrument setups. The general start-up and analysis procedures for samples ran on the Varian AA-1475 and the Perkin Elmer 4100ZL are given below.

I) Start-up procedure for Varian AA-1475 and GTA-95.

1. Turn on exhaust fume hood.
2. Turn argon carrier/purge gas on at tank requlator.
3. Turn printer on.
4. Turn power on to AA-1475 and GTA-95.
5. Select program to run on furnace.
   A. Pick 1 of 8 preset programs on instrument panel.
   B. Manually program element specific parameters.
   C. Element specific parameters begin on page AAM - 1.
6. Select proper Hollow Cathode lamp and insert into turret.
7. Adjust lamp current to proper setting.
8. Allow lamp to warm up and stabilize for 45 minutes.
9. Check graphite tube appearance.
   A. Clean furnace head and quartz window if necessary.
   B. Insert pyrolytic platform or partition tube if replacement is necessary.
10. Select and optimize for element specific wavelength.
11. Optimize furnace workhead for maximum light throughput.
12. Optimize lamp for maximum light throughput using axial adjustment on lamp turret and recheck workhead alignment.
13. Change water in reagent blank/autosampler flush reservoir.
14. Purge air bubbles from autosampler syringe.
15. Insert appropriate modifiers, blanks, and standards into autosampler. Use the loading order list given below.
    A. Verify auto sampler positions and sample pickup, adjust if necessary.
    B. Verify sample injection into graphite tube. Adjust depth if necessary. Adjust autosampler if necessary.
16. When verification of autosampler is complete, reset the autosampler and restart the program with the appropriate samples inserted in the autosampler. Use the loading list

given below.
17. Press run to initiate program.
18. Furnace will run a standard curve for the element of choice, followed by a verification standard and a blank.
19. If the results obtained for the calibration data and the from the analysis of the blank are in control, continue to analyze samples loaded according to loading list given below.
20. Follow QC requirements given at the end of this SOP.

II) Shutdown procedure for Varian AA-1475 and GTA-95.

1. Verify completion of last cycle.
2. Push STOP button on AA-1475.
3. Turn down lamp current if applicable.
4. Turn off GTA-95.
5. Turn off AA-1475.
6. Turn off Printer.
7. Turn off Super Lamp power supply of applicable.
8. Turn off Argon gas at regulator.
8. Turn off fume hood.

III) Start-up procedure for Perkin Elmer 4100ZL.

1. Turn Argon gas on at tank regulator.
2. Turn printer on.
3. Turn computer on and start furnace software by executing AA-INSTRUMENT file.
3. Turn 4100ZL on.
4. Prepare fume extraction unit.
   A. Empty scrubber water container and refill with distilled, deionized water.
   B. Remove scrubber filter paper and replace with new filter.
5. Prepare distilled, deionized water reservoir and waste containers.
   A. Fill water reservoir.
   B. Drain waste reservoir and replace.
6. The EDL II source is now active.
7. Turn on the voltage supply and adjust to the proper voltage.
8. Allow 45 minutes for the EDL II's / HC's to warm up and stabilize.
9. Select the method to load into the furnace.
10. Pull down the <Align Lamps> menu and select the element to analyze. Select the <AGC/AIC> icon to get the intensity reading for the element. Align lamp for maximum intensity.
11. Select <Wavelength Scan> to verify the peak of interest.
12. Exit the <Align Lamps> window.
13. Prepare standards, blanks, modifiers, and verification standards and insert them in the proper locations in the autosampler. Use the loading list given below for sequence.
14. Select the <AS-70> window, and then select <Sampler Standby> and verify the sipper probe is entering the graphite tube properly. Use the X-Y Axis adjustments if needed.
15. Select <Flush Sampler> and remove impurities from the sipper.
16. Select <Calibrate> to initiate the run of the calibration curve. Visibly inspect and ensure proper sample deposition. Run the standard curve and observe peak shapes and correlation coefficients.
17. If the proper peak shapes are observed and the correlation

coefficient is observed, calculate characteristic mass to verify proper sensitivity.
18. Select the <AS-70> window and enter the positions required for the analysis.
19. Select <Run Samples> to initiate the run.
20. Use the loading list given below.
21. Verification standards recovery limits, QC limits, spikes recovery limits, and duplicate spike limits, are all preprogrammed in the method. They will be run automatically. If any deviations from the limits are encountered, the instrument automatically executes the corrective action required by the method.
22. Follow QC requirements given at the end of this SOP.

IV) Shutdown Procedure for Perkin Elmer 4100ZL.

1. Select the <AS-70> window, verify the current run has been completed, or select terminate run from the menu.
2. Turn down the voltage to the EDL II's.
3. Exit furnace software program.
4. Turn 4100ZL off.
5. Turn printer off.
6. Turn off Argon gas supply at regulator.

IV) Sample Loading List AA-1475 and 4100ZL.

1. The following is the loading list for the autosampler. These positions are relative to initial calibration and blank reagent samples.

Sample Position	Sample Type
1	Blank
2	Check Standard
3	Sample
4	Sample 3 spiked
5	Sample 3 duplicate spike
6 - 10	Samples
11	Blank
12	Check Standard
13	Sample
14	Sample 13 spiked
15	Sample 13 duplicate spike
16 - 20	Samples

2. The same pattern holds true for samples 21 through 40, samples 41 through 60, etc. A blank and a check standard will be analyzed before every group of six samples.

CALCULATIONS
Direct determination of liquid samples can be derived from calibration curve linear regression analysis or from the direct readout of the instrument.

If dilution of the sample was required:

ug/l metal in sample = A((C + B) / C)

where A = ug/l of metal in the diluted aliquot from curve,
B = ml of deionized water used for dilution,
C = ml of sample aliquot.

If sample contains particulates:

ug/l metal in sample = A(V / C)

where A = ug/l of metal in the sample from curve,
V = final volume of the processed sample,
C = ml of sample processed.

For dry solid samples (reported as mg/kg dry weight basis):

mg metal / kg sample = (A x V) / D

where A = mg/l of metal in processed sample from curve,
V = final volume of the processed sample in ml,
D = weight of dry sample in grams.

For wet solid samples (reported as mg/kg dry weight basis):

mg metal / kg sample = (A x V) / (W x P)

where A = mg/l of metal in processed sample from curve,
V = final volume of the processed sample in ml,
W = weight of wet sample in grams,
P = percent solids.

QUALITY CONTROL

Instrument standardization is checked initially and throughout the analytical run by the analysis of an appropriate check standard containing the elements of interest. This check standard is analyzed once for every six samples. If the response for any of these elements is out of control, the previous six samples are reanalyzed with a new calibration curve until an acceptable response is acquired.

A calibration blank is analyzed once for every six samples. If the response for any element in this blank is unacceptable, the previous six samples are reanalyzed with a new calibration curve until an acceptable response is acquired.

One out of every six samples is analyzed in duplicate. The duplicate difference for the elements in these samples must meet quality control limits established in the Northern Lake Service Quality Control Database for that specific element. If the duplicate difference exceeds the established control limits, the next six samples are reanalyzed with a new calibration curve until an acceptable response is acquired.

One out of six eight samples is spiked with the elements of interest to monitor instrument accuracy. The recovery of the elements in this spiked sample must meet quality control limits established in the Northern Lake Service Quality Control Database. If the response for an element does not meet the established control limits, the next six samples are reanalyzed with a new calibration curve until an acceptable response is acquired.

If it appears there is a sample matrix problem, perform the appropriate procedure to improve element response. Samples that are ran in duplicate are spiked to provide positive results for each element of interest.

All quality control results from an analytical run must be entered into the Northern Lake Service Quality Control database. Control limits are recalculated every three to six months. Only those parameters with a minimum of thirty data points will be recalculated.

INSTRUMENT MAINTENANCE

Procedures for general maintenance on the Varian AA-1475, the Varian GTA-95, and the Perkin Elmer 4100ZL are given in the owners manual for the instrument. Refer to these manuals for maintenance procedures.

METALS DIGESTION FOR ICP AND FLAME AA

Aqueous Sample Preparation - Dissolved Metals

For the determination of dissolved constituents, the sample must be filtered through a 0.45 um membrane filter as soon as practical after collection. Use the first 50-100 ml to rinse the filter flask. Discard this portion and collect the required volume of filtrate. Acidify the filtrate with (1:1) redistilled HNO_3 to a pH less than 2. Normally, 3ml of (1:1) Nitric Acid per liter should be sufficient to preserve the sample. If hexavalent Chromium is to be included in the analytical scheme, a portion of the filtrate should be transferred before acidification to a separate container and analyzed as soon as possible using Method 218.4.

1. Transfer 100 ml of sample to beaker.
2. Add 2 ml of (1:1) Nitric Acid to sample.
3. Add 1 ml of (1:1) Hydrochloric Acid to sample.
4. Sample is now ready for analysis.
   Allowance for sample dilution should be made in calculations.

Note: If a precipitate is formed during acidification, transport, or storage, the sample aliquot must be treated using the total recoverable digestion procedure.

Aqueous Sample Preparation - Total Metals

For the determination of total metals, the sample is acidified with (1:1) Nitric Acid to a pH of less than 2 at the time of collection. The sample is not filtered before processing.

1. Transfer 50 ml of sample to Griffin beaker.
2. Add 3 ml of concentrated Nitric Acid to sample.
3. Place beaker on hot plate.
4. Evaporate to near dryness. Do not boil.
5. Cool the beaker.
6. Add another 3 ml of concentrated Nitric Acid to sample.
7. Cover beaker with watch glass.
8. Return sample to hot plate.
9. Increase temperature so that a gentle reflux action occurs.
10. Continue heating, adding additional acid if necessary, until the digestion is complete. This is generally indicated when the digestate is light in color or does not change in appearance with continued refluxing.
11. Evaporate to near dryness.
12. Cool the beaker.
13. Add a small quantity of (1:1) Hydrochloric Acid and warm beaker to dissolve any precipitate or residue resulting from evaporation.
14. Wash down the beaker walls and watch glass with distilled, deionized water.
15. Filter the sample to remove silicates and insoluble matter.
16. Adjust the volume to 50 ml in a volumetric flask.
17. Transfer sample to appropriately labeled 60 ml plastic bottle.
18. The sample is ready for analysis.

Aqueous Sample Preparation - Total Recoverable Metals

For the determination of total recoverable metals, the sample is acidified with (1:1) Nitric Acid to a pH of less than 2 at the time of collection. The sample is not filtered before processing.

1. Transfer 50 ml of sample to Griffin beaker.
2. Add 2 ml of (1:1) Nitric Acid to sample.
3. Add 1 ml of (1:1) Hydrochloric Acid to sample.
4. Place sample on hot plate at 85 degrees Celsius.

5. Heat until volume is reduced to approximately 20 ml.
6. Do not boil.
7. Cover the beaker with a watch glass.
8. Increase temperature.
9. Reflux sample for 30 minutes. Slight boiling may occur.
10. Cool beaker and watch glass.
11. Transfer sample to 50 ml volumetric flask.
12. Dilute to volume with distilled - deionized water.
13. Transfer sample to appropriately labeled 60 ml plastic bottle.
13. Centrifuge sample or allow to sit overnight.
14. Sample is now ready for analysis.

Aqueous Sample Preparation - Suspended Metals

For the determination of suspended metals, a representative volume of unpreserved sample must be filtered through a 0.45 um membrane filter. When considerable suspended material is present, as little as 100 ml of a well mixed sample is filtered. Record the volume filtered.

1. Transfer membrane filter to a 250 ml Griffin beaker.
2. Add 3 ml concentrated Nitric Acid to sample.
3. Cover the beaker with a watch glass.
4. Place sample on hot plate.
5. Heat gently.
6. Once filter has dissolved, increase temperature of hot plate.
7. When acid has nearly evaporated, add 3 ml concentrated Nitric Acid to sample.
8. Continue heating, adding additional acid if necessary, until the digestion is complete. This is generally indicated when the digestate is light in color or does not change in appearance with continued refluxing.
9. Evaporate to near dryness.
10. Add 5 ml Hydrochloric Acid and warm beaker gently to dissolve any soluble material.
11. Wash down the watch glass and beaker wall with distilled, deionized water.
12. Filter sample to remove silicates and insoluble matter.
13. Transfer sample to 50 ml volumetric flask.
14. Dilute to volume with distilled, deionized water.
15. Transfer sample to appropriately labeled 60 ml plastic bottle.
16. Sample is ready for analysis.

Solid Sample Preparation - Total Recoverable Metals

For determination of total recoverable elements in solid samples (sludge, soils, and sediments), mix the sample thoroughly to achieve homogeneity before processing. The following procedure is used for samples with a high percentage of solids. If a particular sample is found to have a low percentage of solids, increase the sample portion to be digested.

1. Weigh accurately a 1.0 gram portion of the sample.
2. Transfer sample to a 250 ml Phillips beaker.
3. Add 4 ml (1:1) Nitric Acid to sample.
4. Add 10 ml (1:4) Hydrochloric Acid.
5. Cover beaker with a watch glass.
6. Heat sample on a hot plate and gently reflux for 30 minutes.
7. Cool beaker and watch glass.
8. Wash down the watch glass and beaker walls with distilled, deionized water.
9. Transfer sample to 100 ml volumetric flask.
10. Dilute to volume with distilled, deionized water.
11. Transfer sample to appropriately labeled 100 ml plastic bottle.
12. Centrifuge sample or allow to sit overnight.
13. Sample is now ready for analysis.

Note: Determine the percent solids in the sample for calculating and reporting data on a dry weight basis.

Solid Sample Preparation - Total Metals

For the determination of total elements in solid samples (sludge, soils, and sediments), mix the sample thoroughly to achieve homogeneity before processing. The following procedure is used for samples with a high percentage of solids. If a particular sample is found to have a low percentage of solids, increase the sample portion to be digested.

1. Weigh accurately a 1.0 gram portion of the sample.
2. Transfer sample to a 250 ml Phillips beaker.
3. Add 10 ml of (1:1) Nitric Acid to sample.
4. Mix, and cover with watch glass.
5. Heat the sample to 95 degrees Celsius.
6. Reflux for 10 to 15 minutes without boiling.
7. Allow beaker and watch glass to cool.
8. Add 5 ml of concentrated Nitric Acid to sample.
9. Cover with watch glass.
10. Reflux sample for 30 minutes.
11. Add 5 ml of concentrated Nitric Acid to sample.
12. Cover with watch glass.
13. Reflux sample for 30 minutes.
14. Allow sample to evaporate down to 5 ml without boiling.
15. Cool beaker and watch glass.
16. Add 2 ml of water to sample.
17. Add 3 ml of 30% Hydrogen Peroxide.
18. Cover with watch glass.
19. Heat sample to start the peroxide reaction.
20. Continue heating until effervescence subsides.
21. Cool beaker and watch glass.
22. Continue to add 30% Hydrogen Peroxide in 1 ml aliquots with warming until the effervescence is minimal or until the sample appearance is unchanged.
23. Do not add more than a total of 10 ml 30% Hydrogen Peroxide.
24. Add 5 ml of concentrated Hydrochloric Acid to sample.
25. Add 10 ml of distilled, deionized water to sample.
26. Reflux for additional 15 minutes without boiling.
27. Wash down beaker walls and watch glass with water.
28. Filter sample to remove insoluble matter.
29. Transfer sample to 100 ml volumetric.
30. Dilute to volume with distilled, deionized water.
31. Transfer sample to appropriately labeled 100 ml plastic bottle.
32. The sample is ready for analysis.

Note: Determine the percent solids in the sample for calculating and reporting data on a dry weight basis.

TEST
Metals Digestion for analysis by atomic absorption, inductively coupled plasma, or colorimetric procedures.

REFERENCE
Methods for Chemical Analysis of Water and Wastes. EPA March, 1983.

Test Methods for Evaluating Solid Waste, Physical/Chemical Methods. SW846 - EPA November, 1986.

SCOPE AND APPLICATION
This operating procedure outlines the methods required to prepare a sample for the analysis of metals. This method can be used for the preparation and digestion of drinking water, waste water, surface water, ground water, process water, soils, sludges, industrial wastes, and tissue.

SUMMARY OF METHOD
Colorless samples with a turbidity of <1 NTU, no odor, and of single phase may be analyzed directly by atomic absorption or inductively coupled plasma techniques for total and dissolved parameters. Samples that do not meet the above criteria require a pretreatment to remove particulates and organically bound metals. This pretreatment is generally called a digestion. The digestion reduces interference by organic matter and converts metals associated with particulates to a form that can be determined by atomic absorption or ICP techniques. There are a number of digestion techniques, but the least vigorous procedure that provides complete and consistent recovery should be used. Nitric acid will digest most samples adequately. Nitrate is an acceptable matrix for atomic absorption techniques. Some samples require the addition of perchloric, hydrochloric, or sulfuric acid for complete digestion. Hydrochloric acid is required in the digestion of metals analyzed by inductively coupled plasma techniques, but interferes with analysis by furnace techniques. Hydrochloric acid will not be used in the digestion procedure for metals analyzed by furnace.

Seperate digestion methods are given for trace metals analysis of metals by inductively coupled plasma and atomic absorption.

DEFINITIONS
Dissolved - Those elements that will pass through a 0.45 um membrane filter.

Suspended - Those elements which are retained by a 0.45 um membrane filter.

Total - The concentration determined on an unfiltered sample following vigorous digestion, or the sum of the dissolved plus suspended concentrations.

Total Recoverable - The concentration of an analyte determined in an unfiltered sample following treatment by refluxing with hot, dilute mineral acid.

Laboratory Reagent Blank - An aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, reagents, and acids that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or apparatus.

Laboratory Fortified Blank - An aliquot of reagent water spiked with the appropriate levels of analytes that is treated exactly as a sample including exposure to all glassware, equipment, reagents, and acids that are used with other samples. The LFB is used to determine if method analytes are being lost during the method procedure.

Laboratory Fortified Blank Spiking Solution - A mixture of the elements of interest at the appropriate level of concentration to provide a result in the

midrange of the calibration range used to spike the reagent water to provide a LFB.

EQUIPMENT
The following is the equipment required to prepare samples for trace metals analysis:

1. Griffin Beakers, 250 ml
2. Phillips Beakers, 250 ml conical
3. Pipet, 0.1 to 2500 ul
4. Pipet tips
5. Analytical Balance, accurate to nearest 0.0001 grams
6. Hot plate, graduated dial 90 to 450 degrees Celsius
7. Centrifuge (optional)
8. Volumetric Flasks, 50 and 100 ml
9. Filters, Whatman GF/A Glass Microfibre Filters
10. Filter apparatus and vacuum source

REAGENTS
The following is the reagents required to prepare samples for trace metals analysis:

1. Nitric Acid, concentrated
2. Nitric Acid, (1:1) with distilled, deionized water
3. Hydrochloric Acid, concentrated
4. Hydrochloric Acid, (1:1) with distilled, deionized water
5. Hydrogen Peroxide, 30%
6. Distilled, deionized laboratory grade water
7. Spiking Solution, see Table 1

SAFETY
The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined. Each chemical compound should be treated as a potential health hazard. Exposure to these chemicals must be reduced to the lowest possible level by whatever means available. A reference sheet for material handling is available for all chemicals used in this method. These sheets are available to all analysts.

SAMPLE HANDLING AND PRESERVATION
All laboratory glassware used in this procedure must be thoroughly washed with detergent and tap water; rinsed with (1:1) nitric acid; and final rinsed three times with distilled and deionized water. Chromic acid may be used to remove organic deposits from glassware, but extreme care must go into the final rinse in order to remove all traces of Chromium.

Before collection of the sample, a decision must be made as to what types of data is desired. For the determination of dissolved parameters, the sample must be filtered through a 0.45 um membrane filter as soon as practical after collection and acidified to a pH < 2.0 with (1:1) Nitric acid. For the determination of total or total recoverable parameters, the sample must be acidified to a pH < 2.0 with (1:1) Nitric acid as soon as possible after the time of collection. For determinations of suspended parameters, a measured volume of nonpreserved sample must be filtered through a 0.45 um membrane filter as soon as possible after collection. The filter should then be transferred to a suitable container for storage.

QUALITY CONTROL
A laboratory reagent blank and laboratory fortified blank will be digested along with each set of digested samples. The data obtained from the analysis of the LRB will be used to assess contamination from the laboratory environment. If an analyte value in the reagent blank exceeds its determined MDL, then laboratory or reagent contamination should be expected. Any determined source of contamination should be corrected and the samples reanalyzed. The data obtained from the analysis of the LFB will be used to

assess the accuracy of the results obtained for the samples digested with that LFB. If the recovery of any analyte in the LFB falls outside of the control limits established in the NLS QC Database, the source of the problem should be identified and resolved before continuing analysis.

A minimum of 10% of the actual samples must be digested in duplicate. These duplicate analysis will be spiked with the same solution used to spike the LFB. If the recoveries of these matrix spikes does not meet the control limits established in the NLS QC Database, the source of the problem should be identified. If it is determined that the source of the problem is system related, the set of ten samples digested prior to the matrix spike will be redigested. If it is determined that the source of the problem is matrix related, the sample will be analyzed using the method of standard addition.

Table 1 contains the elements and corresponding concentration levels for the spiking solution used for inductively coupled plasma and furnace techniques.

TABLE 1
COMPOUNDS AND CORRESPONDING
CONCENTRATIONS FOR DIGESTION SPIKING SOLUTIONS

Compound	ICP Level	Furnace Level

METALS DIGESTION - FURNACE

Aqueous Sample Preparation - Dissolved Elements
For the determination of dissolved constituents, the sample must be filtered through a 0.45 um membrane filter as soon as practical after collection. Use the first 50-100 ml to rinse the filter flask. Discard this portion and collect the required volume of filtrate. Acidify the filtrate with (1:1) redistilled HNO_3 to a pH less than 2. Normally, 3ml of (1:1) Nitric Acid per liter should be sufficient to preserve the sample. Sample is now ready for analysis by furnace technique. If hexavalent Chromium is to be included in the analytical scheme, a portion of the filtrate should be transferred before acidification to a separate container and analyzed as soon as possible using Method 218.4.

If a precipitate is formed upon acidification, the filtrate should be digested using the procedure for total metals.

Aqueous Sample Preparation - Total Metals
For the determination of total metals, the sample is acidified with (1:1) Nitric Acid to a pH of less than 2 at the time of collection. The sample is not filtered before processing.

1. Transfer 50 ml of sample to Griffin Beaker.
2. Add 3 ml of concentrated Nitric Acid to sample.
3. Place beaker on hot plate.
4. Evaporate to near dryness. Do not boil.
5. Cool the beaker.
6. Add another 3 ml of concentrated Nitric Acid to sample.
7. Cover beaker with watch glass.
8. Return sample to hot plate.
9. Increase temperature so that a gentle reflux action occurs.
10. Continue heating, adding additional acid if necessary, until the digestion is complete. This is generally indicated when the digestate is light in color or does not change in appearance with continued refluxing.
11. Evaporate to near dryness.
12. Cool the beaker.
13. Add a small quantity of (1:1) Nitric Acid and warm beaker to dissolve any precipitate or residue resulting from evaporation.
14. Wash down the beaker walls and watch glass with distilled, deionized water.
15. Filter the sample to remove silicates and insoluble matter.
16. Adjust the volume to 50 ml in a volumetric flask.
17. Transfer sample to appropriately labeled 60 ml plastic bottle.
18. The sample is ready for analysis.

Aqueous Sample Preparation - Total Recoverable Metals
For the determination of total recoverable metals, the sample is acidified with (1:1) Nitric Acid to a pH of less than 2 at the time of collection. The sample is not filter before processing.

1. Transfer 50 ml of sample to Griffin Beaker.
2. Add 2 ml of (1:1) Nitric Acid to sample.
3. Place sample on hot plate at 85 degrees Celsius.
4. Heat until volume is reduced to approximately 20 ml.
5. Do not boil.
6. Cover the beaker with watch glass.
7. Increase temperature.
8. Reflux sample for 30 minutes. Slight boiling may occur.
9. Cool beaker and watch glass.
10. Transfer sample to 50 ml volumetric flask.
11. Dilute to volume with distilled, deionized water.

12. Transfer sample to appropriately labeled 60 ml plastic bottle.
13. Centrifuge sample or allow to sit overnight.
14. Sample is now ready for analysis.

Aqueous Sample Preparation - Suspended Metals

For the determination of suspended metals, a representative volume of unpreserved sample must be filtered through a 0.45 um membrane filter. When considerable suspended material is present, as little as 100 ml of a well mixed sample is filtered. Record the volume filtered.

1. Transfer the membrane filter to a 250 ml Griffin beaker.
2. Add 3 ml concentrated Nitric Acid to sample.
3. Cover the beaker with a watch glass.
4. Place sample on hot plate.
5. Heat gently.
6. Once filter has dissolved, increase temperature of hot plate.
7. When acid has nearly evaporated, add 3 ml of concentrated Nitric Acid to sample.
8. Continue heating, adding additional acid if necessary, until the digestion is complete. This is generally indicated when the digestate is light in color or does not change in appearance with continued refluxing.
9. Evaporate to near dryness.
10. Add 1 ml Nitric Acid and warm beaker gently to dissolve any soluble material.
11. Wash down the watch glass and beaker walls with distilled, deionized water.
12. Filter sample to remove silicates and insoluble material.
13. Transfer sample to 50 ml volumetric flask.
14. Dilute to volume with distilled, deionized water.
15. Transfer sample to appropriately labeled 60 ml plastic bottle.
16. Sample is ready for analysis.

Solid Sample Preparation - Total Recoverable Metals

For determination of total recoverable elements in solid samples (sludge, soils, and sediments), mix the sample thoroughly to achieve homogeneity before processing. The following procedure is used for samples with a high percentage of solids. If a particular sample is found to have a low percentage of solids, increase the sample portion to be digested.

1. Weigh accurately a 1.0 gram portion of the sample.
2. Transfer sample to a 250 ml Phillips beaker.
3. Add 4 ml (1:1) Nitric Acid to sample.
4. Cover beaker with a watch glass.
5. Heat sample on a hot plate and gently reflux for 30 minutes.
6. Cool beaker and watch glass.
7. Wash down the watch glass and beaker walls with distilled, deionized water.
8. Transfer sample to 100 ml volumetric flask.
9. Dilute to volume with distilled, deionized water.
10. Transfer sample to appropriately labeled 100 ml plastic bottle.
11. Centrifuge sample or allow to sit overnight.
12. Sample is now ready for analysis.

Note: Determine the percent solids in the sample for calculating and reporting data on a dry weight basis.

Solid Sample Preparation - Total Metals

For the determination of total elements in solid samples (sludge, soils, and sediments), mix the sample thoroughly to achieve homogeneity before processing. The following procedure is used for samples with a high percentage of solids. If a particular sample is found to have a low percentage of solids, increase the sample portion to be digested.

1. Weigh accurately a 1.0 gram portion of the sample.
2. Transfer sample to a 250 ml Phillips beaker.
3. Add 10 ml of (1:1) Nitric Acid to sample.
4. Mix, and cover with watch glass.
5. Heat the sample to 95 degrees Celsius.
6. Reflux for 10 to 15 minutes without boiling.
7. Allow beaker and watch glass to cool.
8. Add 5 ml of concentrated Nitric Acid to sample.
9. Cover with watch glass.
10. Reflux sample for 30 minutes.
11. Add 5 ml of concentrated Nitric Acid to sample.
12. Cover with watch glass.
13. Reflux sample for 30 minutes.
14. Allow sample to evaporate down to 5 ml without boiling.
15. Cool beaker and watch glass.
16. Add 2 ml of water to sample.
17. Add 3 ml of 30% Hydrogen Peroxide.
18. Cover with watch glass.
19. Heat sample to start the peroxide reaction.
20. Continue heating until effervescence subsides.
21. Cool beaker and watch glass.
22. Continue to add 30% Hydrogen Peroxide in 1 ml aliquots with warming until the effervescence is minimal or until the sample appearance is unchanged.
23. Do not add more than a total of 10 ml 30% Hydrogen Peroxide.
24. Cool beaker and watch glass.
25. Wash down beaker walls and watch glass with water.
26. Filter sample to remove insoluble matter.
27. Transfer sample to 100 ml volumetric.
28. Dilute to volume with distilled, deionized water.
29. Transfer sample to appropriately labeled 100 ml plastic bottle.
30. The sample is ready for analysis.

Note: Determine the percent solids in the sample for calculating and reporting data on a dry weight basis.

TEST
Inductively Coupled Plasma - Atomic Emission Spectrometric Method for Trace Element Analysis of Water and Wastes.

REFERENCE
Methods for Chemical Analysis of Water and Wastes. EPA March, 1983. Method 200.7.

INSTRUMENTATION
Thermo Jarrell Ash ATOMSCAN 25 ICP Emission Source.
Cetac Ultrasonic Nebulizer Model U-5000AT.
ThermoScan Software Version 5.02 on 80386 Computer

SCOPE AND APPLICATION
This method can be used for the determination of dissolved, suspended, or total elements in drinking water, waste water, and surface water. Dissolved elements are determined from filtered and acid preserved samples. Total elements are determined after appropriate digestion procedures have been performed. The following table contains the list of elements for which this method applies and the recommended wavelengths and estimated detection limits:

TABLE 1

Element	Wavelength (nm)	Estimated Detection Limit (ug/l)
Aluminum	308.215	45
Antimony	206.833	53
Arsenic	193.696	32
Barium	455.403	2
Beryllium	313.042	0.3
Boron	249.773	5
Cadmium	226.502	4
Calcium	317.933	10
Chromium	267.716	7
Cobalt	228.616	7
Copper	324.754	6
Iron	259.940	7
Lead	220.353	42
Magnesium	279.079	30
Manganese	257.610	2
Molybdenum	202.030	8
Nickel	231.604	15
Potassium	766.491	na
Selenium	196.026	75
Silica	288.158	58
Silver	328.068	7
Sodium	588.995	29
Thallium	190.864	40
Vanadium	292.402	8
Zinc	213.856	2

The estimated instrument detection limits in the above table are derived from conventional pneumatic nebulization. Actual detection limits and wavelengths are instrument dependent and vary with sample matrix. Table 2 contains the calibration standards and detection limits used for analysis of trace metals on the Thermo Jarrell Ash ICP.

SUMMARY OF METHOD
The following method is for the simultaneous or sequential multielement analysis of trace elements in solution. The method involves the measurement of atomic emission of excited atoms by an optical spectroscope. The emission source in the ATOMSCAN 25 spectrometer is an inductively coupled argon plasma (ICAP). The electron source is powered by a 2kW crystal controlled radio frequency (RF) generator operating at 27.12 MHz. The output of the radio frequency generator is coupled to a water cooled copper induction coil that is wrapped around a quartz torch assembly. Plasma ignition occurs when an argon gas flow is seeded with electrons from an external spark source. These

seed electrons are accelerated in a torroidal path by the RF electromagnetic field. As the electrons collide with the argon atoms, the argon becomes ionized and more electrons are produced. This process continues until the gas becomes highly ionized and a plasma is produced. At this point, the plasma is completely stable and self-sustaining as long as the RF field is applied. The plasma temperature can reach as high as 10000 degrees Kelvin.

Liquid samples can then be introduced into the plasma as an aerosol suspended in argon gas. As the aerosol passes through the center of the torch, the sample becomes atomized. The resulting atoms have their outer shell electrons excited by the plasma source. After excitation, the atoms emit photons (light) at their characteristic wavelength. This light is transmitted to the optical system. The argon plasma source is close to the ideal excitation source. It provides a high degree of excitation, resulting in a number of excitation lines to monitor for each element. The high density of free electrons ensures that the portion of ionized elements remains constant despite sample matrix. The extremely high temperature reduces anion interferences.

Light from the plasma emission source is focused onto the entrance slit of the optical system. The incoming light is then dispersed by a diffraction grating. A narrow range of wavelengths is passed through an exit slit onto the detector. The wavelength passed to the detector is controlled by varying the angle of incidence and the angle of reflection of the incoming light. These angles are controlled by changing the position of the diffraction grating. The position of the grating is controlled by an electric stepper motor under computer control. The measurement of the intensity of light at a particular wavelength is very accurate once the optical system is calibrated. Calibration is achieved by scanning for the maximum emission lines of a Mercury lamp. These maximum emission lines are known and constant over a linear range. The detector consists of a photo-multiplier tube that converts light energy into an electrical current, of which the magnitude is proportion to the light intensity. The current produced by the detector is monitored and integrated over a predefined period of time and passed onto the host computer. As long as sample aerosol is continuously passed through the plasma torch, the sample can be analyzed for a number of elements. Elements are analyzed sequentially by setting the diffraction grating to reflect the optimum wavelength for each element (one at a time) onto the detector.

DEFINITIONS

Dissolved - Those elements which will pass through a 0.45 um membrane filter.

Suspended - Those elements which are retained by a 0.45 um membrane filter.

Total - The concentration determined on an unfiltered sample following vigorous digestion, or the sum of the dissolved plus suspended concentrations.

Instrument detection limit - The concentration equivalent to a signal, due to the analyte, which is equal to three times the standard deviation of a series of ten replicate measurements of a reagent blank signal at the same wavelength.

Sensitivity - The slope of the analytical curve. The functional relationship between emission intensity and concentration.

Instrument check standard - A multielement standard of known concentrations prepared by the analyst to monitor and verify instrument performance on a daily basis.

Interference check sample - A solution containing both interfering and analyte elements of known concentration that can be used to verify background and interelement correction factors.

Quality control sample - A solution obtained from an outside source having known concentration values to be used to verify the calibration standards.

Calibration standards - A series of known standard solutions used by the analyst for calibration of the instrument.

Linear dynamic range - The concentration range over which the analytical curve remains linear.

Reagent blank - A volume of deionized, distilled water containing the same acid matrix as the calibration standards carried through the entire analytical scheme.

Calibration blank - A volume of deionized, distilled water acidified with HNO_3 and/or HCL.

Method of standard addition - The standard addition technique involves the use of the unknown and the known amount of standard.

SAFETY
The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined. Each chemical compound should be treated as a potential health hazard. Exposure to these chemicals must be reduced to the lowest possible level by whatever means available. A reference sheet for material handling is available for all chemicals used in this method. These sheets are available to all analysts.

INTERFERENCES
Several type of interferences can contribute to inaccuracies in the analysis of trace elements. The following discussion separates these interferences into individual topics.

Spectral Interferences
The spectral line from another element in the sample matrix may overlap the spectral line of the required element. This interference can be compensated by utilizing a computer correction of the raw data, which requires the monitoring of the interfering element. The unresolved overlap of molecular band spectra may interfere with the spectra of the required element. This interference may require the monitoring of another wavelength. Background contribution from stray light and from continuous or recombination phenomena also contributes to spectral interference. Background interference can be compensated by a background correction adjacent to the analyte spectral line.

Physical Interferences
Physical interferences are generally related to sample nebulization and sample delivery to the plasma torch. Variations in sample viscosity and surface tension can cause significant changes in analyte response. The use of a peristaltic pump decreases the chance of variation in samples with high concentration of dissolved solids and/or acids. Samples with a high degree of physical interferences usually require the analysis of a dilution or require analysis by standard addition.

Chemical Interferences
Molecular compound formation, ionization effects, and solute vaporization effects are all considered chemical interferences. These interferences are not common in the ICP method. When chemical interferences do occur, they can be minimized by careful selection of operating conditions. Incident power, observation position, sample buffering, matrix matching, and standard addition are factors that should be considered to minimize chemical interference.

EQUIPMENT
The following is the equipment required to analyze water and waste samples for trace elements:

1. Thermo Jarrell Ash Inductively Couple Plasma Spectrometer.
2. Argon gas supply, welding grade or better.
3. Cetac Ultrasonic Nebulizer Model U-5000AT (optional for low level analysis).

REAGENTS AND STANDARDS
The following is the required chemicals for ICP analysis:

1. Acetic Acid, concentrated

2. Hydrochloric Acid, concentrated

3. Hydrochloric Acid, (1:1) Add 500 ml of concentrated HCL to 400 ml deionized, distilled water and dilute to 1 liter.

4. Nitric Acid, concentrated

5. Nitric Acid, (1:1) Add 500 ml of concentrated HNO_3 to 400 ml deionized, distilled water and dilute to 1 L.

6. Deionized, distilled water.

7. Standard stock solutions, (purchased or prepared). Concentration of standard solutions for each element for the calibration curve are given in Table 2.

SAMPLE HANDLING AND PRESERVATION
All laboratory glassware used in this procedure must be thoroughly washed with detergent and tap water; rinsed with (1:1) nitric acid; and final rinsed three times with distilled and deionized water. Chromic acid may be used to remove organic deposits from glassware, but extreme care must go into the final rinse in order to remove all traces of Chromium.

Before collection of the sample, a decision must be made as to what types of data is desired. For the determination of dissolved parameters, the sample must be filtered through a 0.45 um membrane filter as soon as practical after collection and acidified to a pH < 2.0 with (1:1) Nitric acid. For the determination of total or total recoverable parameters, the sample must be acidified to a pH < 2.0 with (1:1) Nitric acid as soon as possible after the time of collection. For determinations of suspended parameters, a measured volume of nonpreserved sample must be filtered through a 0.45 um membrane filter as soon as possible after collection. The filter should then be transferred to a suitable container for storage.

SAMPLE PREPARATION
For the determination of dissolved parameters, the filtered, preserved sample may often be analyzed as received. Digestion is usually not required for a filtered sample. The acid matrix and concentration of the samples and calibration standards must be the same. If a precipitate has formed upon acidification of the sample, the precipitate must be redissolved before analysis through the addition of more acid or by heat.

Samples requiring total parameters for ground water, waste water, soils, and sludges must be digested prior to analysis. Follow the digestion procedures given on page XXXXXXXX.

PROCEDURE
Standard curves, optimum wavelengths, and detection limits for metals ran by EPA Method 200.7 are given in Table 2. The following is the operating procedures for the Thermo Jarrell Ash ICP and the Cetac U-5000AT Ultra Sonic Nebulizer:

I) Start-up Procedure

1. Turn fume hood on (switch on north wall).
2. Turn cooling pump on (switch on floor below fume hood).
3. Turn on computer and printer.
4. Open nebulizer compartment door.
   A. Disconnect argon carrier tubing from teflon nebulizer.
   B. Disconnect sample carrier tubing.
   C. Carefully pull teflon nebulizer cap off of the quartz tube and dry the inside using kimwipes. Blow out with

microduster if necessary.
D. Pull teflon flow spoiler out of quartz tube using forceps. Clean with soapy water and rinse with distilled, deionized water. Dry off with kimwipes.
E. Dry the inside of quartz tube with kimwipes using forceps. Periodic dismantling and cleaning of this equipment is necessary. This will be performed by the metals chemists.
F. Reinstall the flow spoilers and position v-shaped groove at the bottom of the quartz tube. This allows excess water to escape from the chamber into the drain tubing.
G. Carefully reinstall teflon nebulizer cap and reattach argon tubing.
H. Replace sample peristaltic pump tubing with new tubing and attach to nebulizer.
I. Route all tubing out of nebulizer compartment and secure with black rubber stopper.
J. Clip pump tubing harness down onto peristaltic pump. Tension adjustment lever should be at 45 degrees from horizontal position.
K. Close nebulizer compartment.

II) Instrument Calibration

1. On power-up, the computer will automatically load and run the Thermospec software.
2. Use the cursor keys and pull down the menu for <SET-UP>.
3. Select <Plasma Control Panel> from the menu.
   A. Press <F1> to ignite plasma.
   B. When prompted, press <F9> to continue with ignition. The torch enclosure will then purge for 90 seconds with argon.
   C. After plasma ignition, press <enter> to continue.
   D. Press <F2> to adjust pump rate. Enter a value of 100 for pump rate and press <enter>.
   E. Press <esc> to return to main menu.
4. Select <Wavelength Calibration> from the menu. Date calibrated and current date will appear on the screen. Press <F1> and the computer will display "Wavelength Calibration is recommended", if recalibration is necessary. When wavelength calibration is completed, press <F9> to return to main menu.
5. Allow 45 minutes for the instument to stabilize before running any samples.
6. Select <Development> from the menu.
   A. Select <Methods> from the development menu. Enter the name of the method to use and press <enter>, or press <F6> to list all of the methods available.
   B. Press <F8> to show method options. Press <F2> to show print options. Press <F9> to print method.
   C. The Methods Options menu will now be displayed. Press <F9> twice to return to main menu.
7. Select <Peak Search> from the main menu.
   A. Press <enter> to initiate the peak search process.
   B. Manually aspirate the standard displayed and press <F1> to start the peak search. The monitor will display 'done' next to the standard when it is completed.
   C. Press <F9> to save peak search information and return to main menu.
8. Select <Operations> from the main menu.
   A. Select <Analsys> from the operations menu.
   B. Type in the appropriate method name and press <enter>.
   C. Press <F3> to begin calibration procedure.

The monitor will display:
Blank
std1
std2
std3

D. Use the cursor keys to move the cursor to the appropriate standard.
E. Manually aspirate the standard and press <F1> to begin calibration procedure for that standard.
F. The monitor will display the intensity counts for the standard that was just ran. Press <F9> to commit that data to the calibration table.
G. Select and aspirate the next standard and continue this process until all standards have been analyzed.
H. When the last standard is completed and committed, press <F9> to commit all calibration data.
I. Press <F4> to review the data, <F2> to print the data, <F9> when completed.

9. Press <F1> to analyze a blank sample.
   A. Enter <blank> for name of sample.
   B. Press <F1> to begin run.
   C. Aspirate blank into nebulizer.
   D. Results will be printed.
   E. Verify a result of zero.
10. Press <F1> to analyze a verification sample.
   A. Enter <chkstd> for name of sample.
   B. Press <F1> to begin run.
   C. Aspirate verification standard into nebulizer.
   D. Results will be printed.
   E. Verify results are in control.
   F. If blank and verification standard are good, then
11. Press <F9> to select autosampler control.
   A. Connect autosampler to aspiration tube.
   B. Press <F1> when ready to run.

III) Autosampler Loading List

1. The following is the loading order for the autosampler:

Sample Position	Sample Type
1	Sample 1
2	Sample 1 spiked
3	Sample 1 duplicate spike
4 - 10	Samples
11	Blank
12	Check Standard
13	Sample 13
14	Sample 13 spiked
15	Sample 13 duplicate spike
16 - 22	Samples
23	Blank
24	Check Standard

2. The same pattern holds true for samples 25 through 48, samples 49 through 72, and samples 73 through 96. Check standards will be in positions 12, 24, 36, 48, 60, 72, 84, and 96.

IV) Instrument Shutdown Procedure

1. Use the cursor keys and pull down the menu for <SET-UP>.
2. Select <Plasma Control Panel> from the menu.
3. Press <F7> to turn off the torch. The torch will turn off, and the cool down process will begin.
4. After the instrument has cooled down, power can be removed from all components if desired. Power to all components may be left on, but the computer monitor should be turned off to prevent screen burn-in.

V) Use of Cetac Ultrasonic Nebulizer for Low Level Analysis

1. If the constant temperature cooling system is off, turn it on and let the temperature stabilize for approximately 90 minutes. The cooling system may be left on while not in use to minimize the cool-down time.
2. Connect the output aspiration tube of the Cetac to the input aspiration tube of the ICP.
3. The sample will now be aspirated into the ultrasonic nebulizer before entering the ICP. A sample can be fed to the Cetac either manually or through the output of the autosampler.
4. Turn on the U-5000AT. The U-tube temperature should stabilize at 140 degrees celcius in about 10 minutes.
5. Initiate the plasma according to the startup procedure.
6. Press the operate switch on the Cetac to turn on the ultrasonic nebulizer transducer.
7. Turn on the sample peristaltic pump and deliver deionized water to the transducer. The ultrasonic nebulizer should stabilize in about 15 minutes. If necessary, aspirate a dilute hydrofluric solution to achieve a dense aerosol. The ultrasonic nebulizer is now ready for routine analysis.

VI) Shutdown Procedure for the Cetac Ultrasonic Nebulizer.

1. Aspirate deionized water for at least 3 minutes.
2. Turn off the sample peristaltic pump and let the nebulizer run dry for about 15 seconds.
3. Turn off the operate switch on the Cetac.
4. Press the fast pump switch on the Cetac and allow the pump to drain liquid from the system until no liquid can be seen flowing out of the drain tubing.
5. Turn off the fast pump switch on the Cetac.
6. Turn off the power switch on the Cetac.
7. Disconnect sample input and output delivery tubes on the Cetac.

CALCULATIONS

Reagent blanks should be subtracted from all samples. This is important for digested samples requiring large quantities of acids to complete the digestion. If dilutions were performed, the appropriate factor must be applied to sample values.

QUALITY CONTROL

Instrument standardization is checked initially and throughout the analytical run by the analysis of an appropriate check standard containing the elements of interest. This

check standard is analyzed once for every eight samples. If the response for any of these elements is out of control, the previous eight samples are reanalyzed with a new calibration curve until an acceptable response is acquired.

A calibration blank is analyzed once for every eight samples. If the response for any element in this blank is unacceptable, the previous eight samples are reanalyzed with a new calibration curve until an acceptable response is acquired.

One out of every eight samples is analyzed in duplicate. The duplicate difference for the elements in these samples must meet quality control limits established in the Northern Lake Service Quality Control Database for that specific element. If the duplicate difference exceeds the established control limits, the next eight samples are reanalyzed with a new calibration curve until an acceptable response is acquired.

One out of every eight samples is spiked with the elements of interest to monitor instrument accuracy. The recovery of the elements in this spiked sample must meet quality control limits established in the Northern Lake Service Quality Control Database. If the response for an element does not meet the established control limits, the next eight samples are reanalyzed with a new calibration curve until an acceptable response is acquired.

If it appears there is a sample matrix problem, perform the appropriate procedure to improve element response. Samples that are ran in duplicate are spiked to provide positive results for each element of interest.

Control limits are established by the Northern Lake Service Quality Control Database. All quality control results from an analytical run must be entered into this database. Control limits are recalculated every four to six months. Only those parameters with a minimum of thirty data points will be recalculated.

INSTRUMENT MAINTENANCE
Procedures for general maintenance on the TJA Atomscan ICP are given in the ow the instrument maintenance procedure given in the operators manual for the TJA Atomscan ICP. Procedures for general maintenance on the Cetac U-5000AT Ultrasonic Nebulizer are given in the operators manual for the Cetac USN.

TABLE 2
CALIBRATION STANDARDS AND DETECTION LIMITS ON THE TJA ATOMSCAN 25 SPECTROMETER

Element	Standard Curve (ppm)	Detection Limit
Aluminum	0.5 - 1.0 - 5.0	0.034 ppm
Barium	0.1 - 0.5 - 5.0	0.015 ppm
Beryllium	0.010 - 0.025 - 0.050	1.000 ppm
Boron	0.1 - 0.5 - 1.0 - 5.0	0.022 ppm
Cadmium	0.1 - 0.5 - 1.0 - 5.0	0.006 ppm
Cobalt	0.05 - 0.50 - 5.00	0.006 ppm
Chromium	0.1 - 0.5 - 1.0 - 5.0	0.014 ppm
Copper	0.1 - 0.5 - 1.0 - 5.0	0.012 ppm
Iron	0.1 - 0.5 - 1.0 - 5.0	0.015 ppm
Lead	0.25 - 0.50 - 1.0 - 5.0	0.048 ppm
Magnesium	1.0 - 5.0 - 10 - 20 - 50	0.008 ppm
Manganese	0.1 - 0.5 - 1.0 - 5.0	0.004 ppm
Molybdenum	2.0 - 5.0 - 10.0	0.020 ppm
Nickel	0.1 - 0.5 - 1.0 - 5.0	0.016 ppm
Potassium	0.5 - 5.0 - 50 - 100	0.600 ppm
Silver	0.1 - 0.25 - 0.50	0.010 ppm
Sodium	0.5 - 5.0 - 50 - 100	0.034 ppm
Strontium	0.25 - 0.50 - 1.0	0.009 ppm
Tin	0.25 - 0.50 - 1.0	0.052 ppm
Zinc	0.1 - 0.5 - 1.0 - 5.0	0.003 ppm
Cadmium (USN)	0.010 - 0.025 - 0.050 - 0.10	0.400 ppb

Chromium (USN)	0.010 - 0.025 - 0.050 - 0.10	2.000 ppb
Copper (USN)	0.010 - 0.025 - 0.050 - 0.10	2.000 ppb
Lead (USN)	0.010 - 0.025 - 0.050 - 0.10	3.000 ppb
Molybdenum (USN)	0.05 - 0.10 - 0.25	2.000 ppb
Silver (USN)	0.010 - 0.025 - 0.050 - 0.10	2.000 ppb
Thallium (USN)	0.025 - 0.050 - 0.10	7.000 ppb
Antimony (USN)	0.10 - 0.25 - 0.50	10.00 ppb

Note: The designation (USN) means the element was analyzed with an ultrasonic nebulizer. These method detection limits were approved on 3/3/93. Detection limits are recalculated frequently and the above limits may not be up to date. Ask the Quality Control Officer for current detection limits.

The State of Wisconsin

DEPARTMENT OF NATURAL RESOURCES

Hereby grants

Certification

under the provisions of ch. NR 149, Wisconsin Administrative Code to:

Northern Lake Service Inc
400 North Lake Avenue
Crandon, WI 545201286

721026460
Laboratory ID Number

Issued: September 17, 1993

Expires: June 30, 1994

for the following test categories:

* Oxygen Utilization
* Nitrogen
  Ammonia
  Nitrite
  Nitrate
  Kjeldahl Nitrogen
* Phosphorus
* Physical
* General I
* General II
  Chloride
  Cyanide
  COD
  Fluoride
  Phenolics
  Sulfate
* General III
  EP Toxicity
  Ignitability
  TCLP
* Metals I
  Silver
  Aluminum
  Arsenic
  Boron
  Barium
  Beryllium
  Calcium
  Cadmium
  Cobalt
  Chromium
  Copper
  Iron
  Hexavalent Chromium
  Mercury
  Potassium
  Magnesium
  Manganese
  Molybdenum
  Sodium
  Nickel
  Lead
  Antimony
  Selenium
  Strontium
  Thallium
  Vanadium
  Zinc
* Organics; Purgeable
* Liquid Chromatography
  Polynuclear Aromatic Hc
* Petroleum Hydrocarbons
  Diesel Range Organics
  Gasoline Range Organics
  Petroleum VOCs
* Organics; Organochlorine
  PCBs
  Pesticides
* Any Single Analyte
  Atrazine

George E. Meyer
Secretary

Administrator, Division for Environmental Quality

Director, Office of Technical Services

This certificate is valid unless revoked or suspended and supercedes all previous certificates.

Form 4800-10 Rev. 2-93

The State of Wisconsin

DEPARTMENT OF NATURAL RESOURCES

Hereby grants

Safe Drinking Water Certification

under the provisions of ch. NR 149, Wisconsin Administrative Code to:

Northern Lake Service Inc
400 North Lake Avenue
Crandon, WI 545201286

721026460
Laboratory ID Number

Issued: September 10, 1993

Expires: June 30, 1994

for the following test categories:

Arsenic
Barium
Cadmium
Chromium
Fluoride
Mercury
Nitrite
Nitrate
Lead
T. Trihalomethanes
Volatile Organics

George E. Meyer
Secretary

Administrator, Division for Environmental Quality

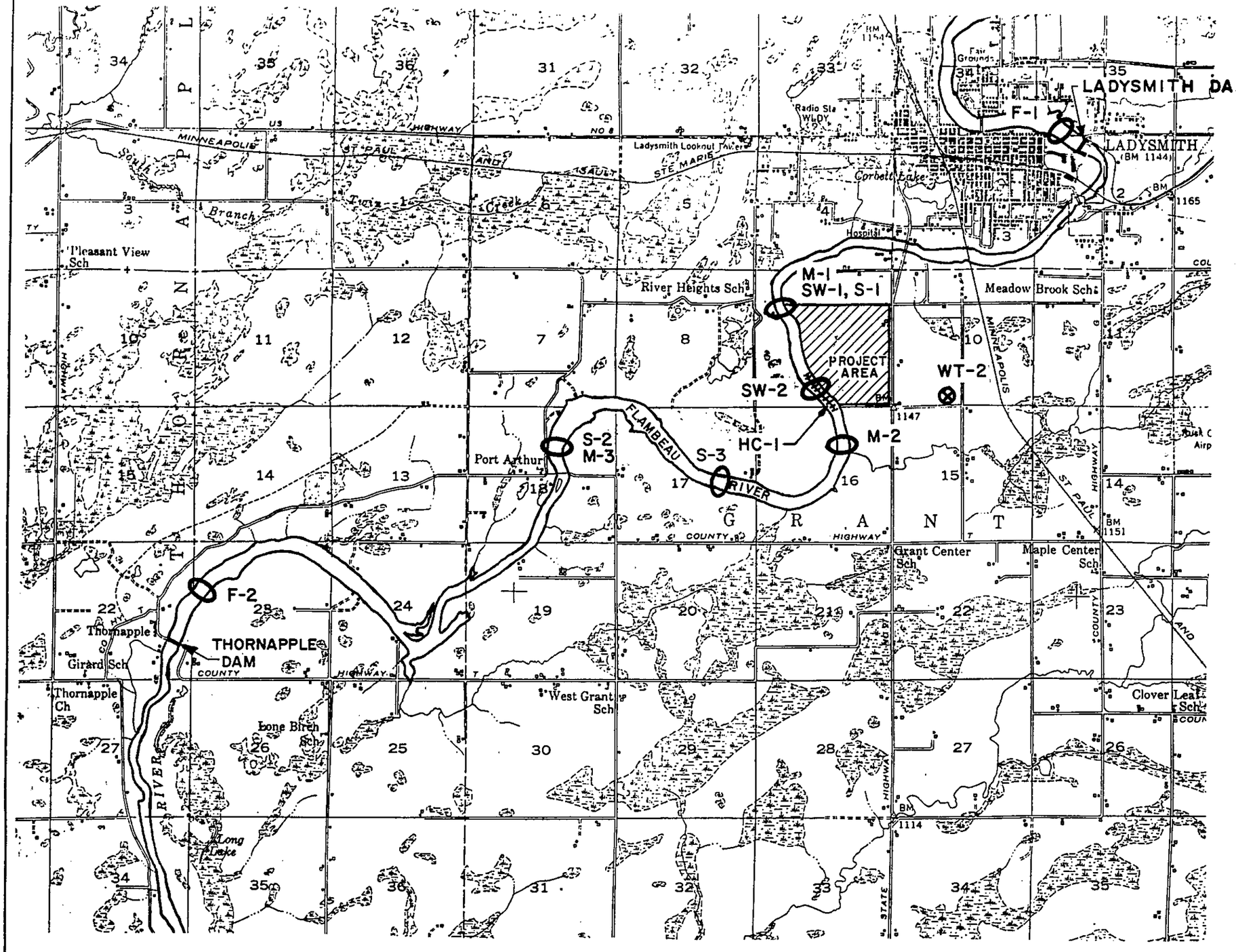
Director, Office of Technical Services

This certificate is valid unless revoked or suspended and supercedes all previous certificates.

Form 4800-10 Rev. 2-93

Appendix B

Sampling Location Maps



NOTE: SEE FIGURE NO. 7-1 FOR THE LOCATION OF WETLAND STAFF GAUGES WT-1, WT-3, WT-4 AND WT-5.

N

0 4000' 8000'

SCALE

LEGEND

- SW-1 — SAMPLING LOCATIONS FOR SURFACE WATER SAMPLES
- S-1 — SAMPLING LOCATION FOR SEDIMENTS
- M-1 — SAMPLING LOCATION FOR MACRO-INVERTEBRATES
- F-1 — SAMPLING LOCATION FOR FISH
- HC-1 — LOCATION FOR HABITAT CHARACTERISTICS OBSERVATIONS
- WT-2 — WETLAND STAFF GAUGE

MAP SOURCE: U.S.G.S. LADYSMITH, WI. 15 MINUTE QUADRANGLE

FOTH & VAN DYKE
GEOSCIENCES & ENVIRONMENTAL MANAGEMENT DIVISION
GREEN BAY, WISCONSIN

FLAMBEAU PROJECT
LADYSMITH, WISCONSIN

KENNECOTT MINERALS COMPANY
1515 MINERAL SQUARE
SALT LAKE CITY, UTAH 84112

FIGURE NO. 7-7
CONSTRUCTION AND OPERATION
SURFACE WATER MONITORING
SITE LOCATIONS

	BY	DATE
DESIGN		
DRAWN	DHS	12/89
CHK'D		
DES. ENG'R		
SECT ENG'R		

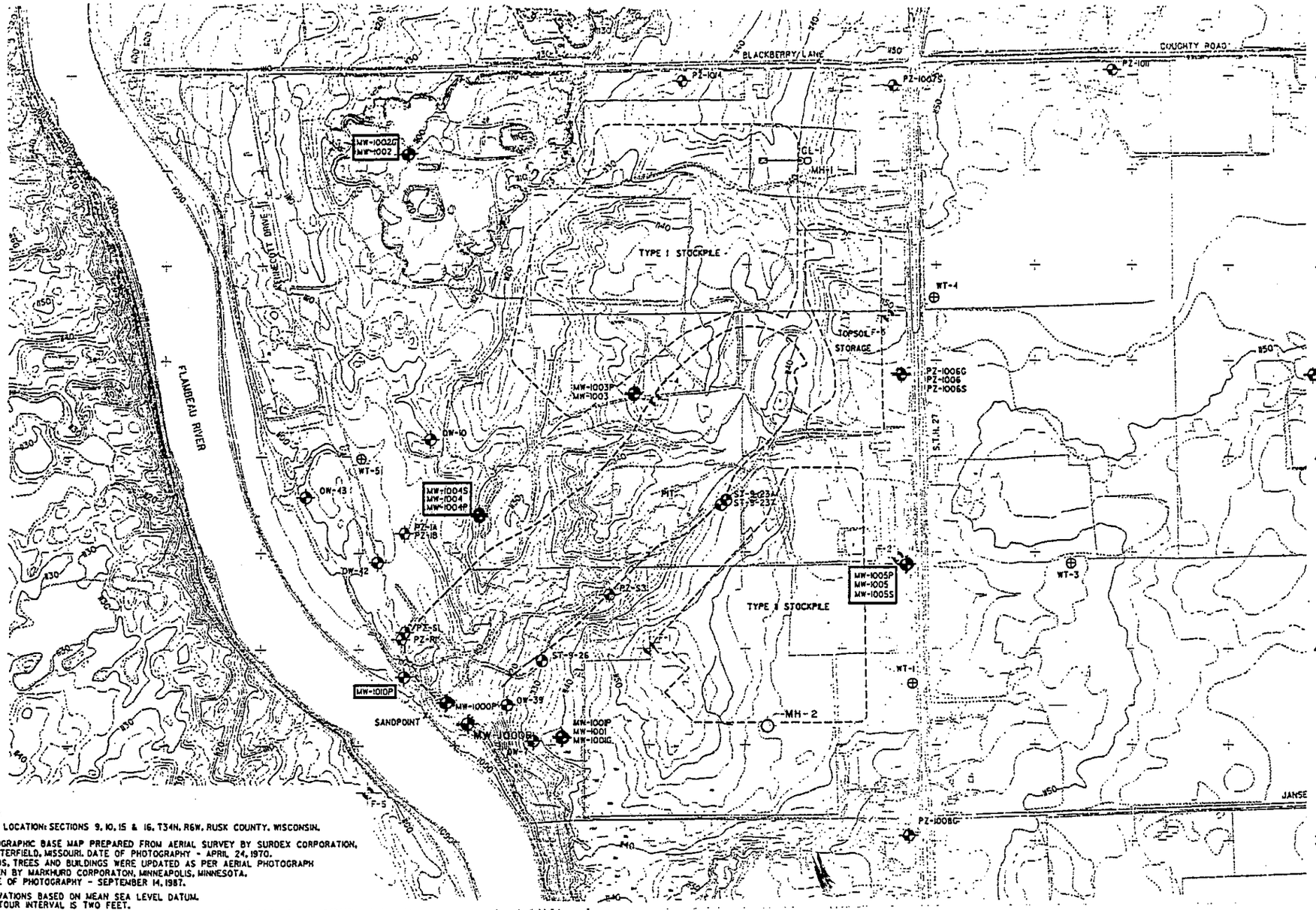
MICROFILM | JOB
DRAWING NO. | REV.
DIVISION DRAWING NO.
SCALE

REFERENCES

DWG. NO.	DESCRIPTION

NO.	DATE	REVISIONS	BY	CH'D	ENG'R	DES ENG'R

B1



GROUNDWATER AND COLLECTION LYSIMETER CONSTRUCTION AND OPERATION MONITORING PROGRAM

COLLECTION LYSIMETER/ WELL/PIEZOMETER NUMBER	ELEVATION OF SCREENED INTERVAL (FT. MSL)	GEOLOGIC UNIT	PARAMETER*
MW-1000R	1095-1085	PRECAMBRIAN, TILL	1, 2
MW-1000P	1049-1044	PRECAMBRIAN	1, 2
MW-1001	1118-1108	TILL	1
MW-1001G	1095-1090	TILL, SANDSTONE	1
MW-1001P	1051-1046	PRECAMBRIAN	1
MW-1002	1096-1086	SAND & GRAVEL	1, 2
MW-1002G	1055-1050	SAND & GRAVEL	1, 2
MW-1003	1113-1103	SANDSTONE	1
MW-1003P	1062-1057	PRECAMBRIAN	1
MW-1004	1112-1102	SAND & GRAVEL	1, 2
MW-1004S	1093-1088	SANDSTONE	1, 2
MW-1004P	1042-1037	PRECAMBRIAN	1, 2
MW-1005	1134-1124	TILL	1, 2
MW-1005S	1097-1092	SANDSTONE	1, 2
MW-1005P	1056-1051	PRECAMBRIAN	1, 2
PZ-1006	1143-1138	TILL	1
PZ-1006G	1119-1114	TILL	1
PZ-1006S	1101-1096	SANDSTONE	1
PZ-1007S	1110-1105	SANDSTONE	1
PZ-1008	1138-1128	TILL	1
PZ-1008G	1096-1091	SAND & GRAVEL	1
PZ-1009	1144-1134	TILL	1
PZ-1009G	1107-1102	TILL	1
MW-1010P	995- 990	PRECAMBRIAN	1, 2
PZ-1011	1114-1104	TILL	1
PZ-1012	1111-1101	TILL	1
PZ-R1	901- 881	PRECAMBRIAN	1
PZ-S1	1067-1062	PRECAMBRIAN	1
PZ-S3	1100-1095	SANDSTONE	1
SANDPOINT	1084-1082	SAND & GRAVEL	1
ST-9-23	1106-1101	SANDSTONE	1
ST-9-23A	1125-1120	SAND & GRAVEL	1
ST-9-26	1106-1101	TILL	1
PZ-1A	1089-1087	SAND & GRAVEL	1
PZ-1B	1103-1101	SAND & GRAVEL	1
OW-7	1088-1078	TILL	1
OW-10	1069-1059	TILL	1
OW-39	1107-1073	TILL	1
OW-42	1090-1058	SAND & GRAVEL	1
OW-43	1080-1022	SAND & GRAVEL	1
MH-2	N.A.	N.A.	3
CL-1	N.A.	N.A.	3

*1 GROUNDWATER ELEVATION (QUARTERLY).

*2 SPECIFIC CONDUCTIVITY (FIELD), PH (FIELD AND LAB), TDS, IRON, MANGANESE, SULFATE, COPPER, TOTAL ALKALINITY, TOTAL HARDNESS (ALL QUARTERLY).

*3 PH (FIELD AND LAB), SPECIFIC CONDUCTANCE (FIELD), TOTAL CHROMIUM, COPPER, IRON, MANGANESE, SULFATE, TOTAL DISSOLVED SOLIDS, TOTAL ALKALINITY, TOTAL HARDNESS, VOLUME OF LIQUID REMOVED (ALL QUARTERLY).
(NO TOTAL CHROMIUM FOR MH-2)

NOTES:

1. SITE LOCATION: SECTIONS 9, 10, 15 & 16, T34N, R6W, RUSK COUNTY, WISCONSIN.
2. TOPOGRAPHIC BASE MAP PREPARED FROM AERIAL SURVEY BY SURDEX CORPORATION, CHESTERFIELD, MISSOURI. DATE OF PHOTOGRAPHY - APRIL 24, 1970. ROADS, TREES AND BUILDINGS WERE UPDATED AS PER AERIAL PHOTOGRAPH TAKEN BY MARKHURD CORPORATON, MINNEAPOLIS, MINNESOTA. DATE OF PHOTOGRAPHY - SEPTEMBER 14, 1987.
3. ELEVATIONS BASED ON MEAN SEA LEVEL DATUM. CONTOUR INTERVAL IS TWO FEET.
4. HORIZONTAL DATUM BASED ON PROJECT SITE GRID SYSTEM. SITE GRID COORDINATES CORRELATION TO STATE PLANE COORDINATES DERIVED AS FOLLOWS:

SITE GRID COORDINATES CONTROL MONUMENT F-1	STATE PLANE COORDINATES
40000 N =	587,257.8887 N
40000 E =	1,713,516.1229 E

THE ANGULAR ROTATION FROM STATE PLANE BEARINGS TO SITE GRID BEARINGS IS 359°-13'-23" RIGHT WITH CONTROL POINT F-1 AS THE BASE POINT.

5. SEE FIGURE NO.'S 7-1 AND 7-7 FOR THE LOCATION OF WETLAND STAFF GAUGE WT-2 AND FOR SURFACE WATER MONITORING LOCATIONS.

LEGEND

- —800— EXISTING CONTOUR
- EXISTING PAVED ROADWAY
- EXISTING TRAIL/GRAVEL SURFACE
- TREES AND/OR BRUSH
- FENCE
- F-1 CONTROL MONUMENT
- MW-1005 MONITORING WELL
- PZ-R3 PIEZOMETER
- MW-1005 WELL ON THE WATER QUALITY MONITORING PROGRAM
- WT-5 WETLAND STAFF GAUGE
- MH-2 LEACHATE MANHOLE

N

0 300' 600'
SCALE

FOTH & VAN DYKE
GEOSCIENCES & ENVIRONMENTAL MANAGEMENT DIVISION
GREEN BAY, WISCONSIN

FLAMBEAU PROJECT
LADYSMITH, WISCONSIN

KENNECOTT MINERALS COMPANY
55 MINERAL SQUARE
SALT LAKE CITY, UTAH
84112

FIGURE NO. 7-1
CONSTRUCTION AND OPERATION
GROUNDWATER AND COLLECTION
LYSIMETER MONITORING PROGRAM

MICROFILM | JOB
DRAWING NO. | REV.
DIVISION DRAWING NO.
SCALE : SEE BAR SCALE

REFERENCES	CHG. NO.	DESCRIPTION

REFERENCES	CHG. NO.	DESCRIPTION

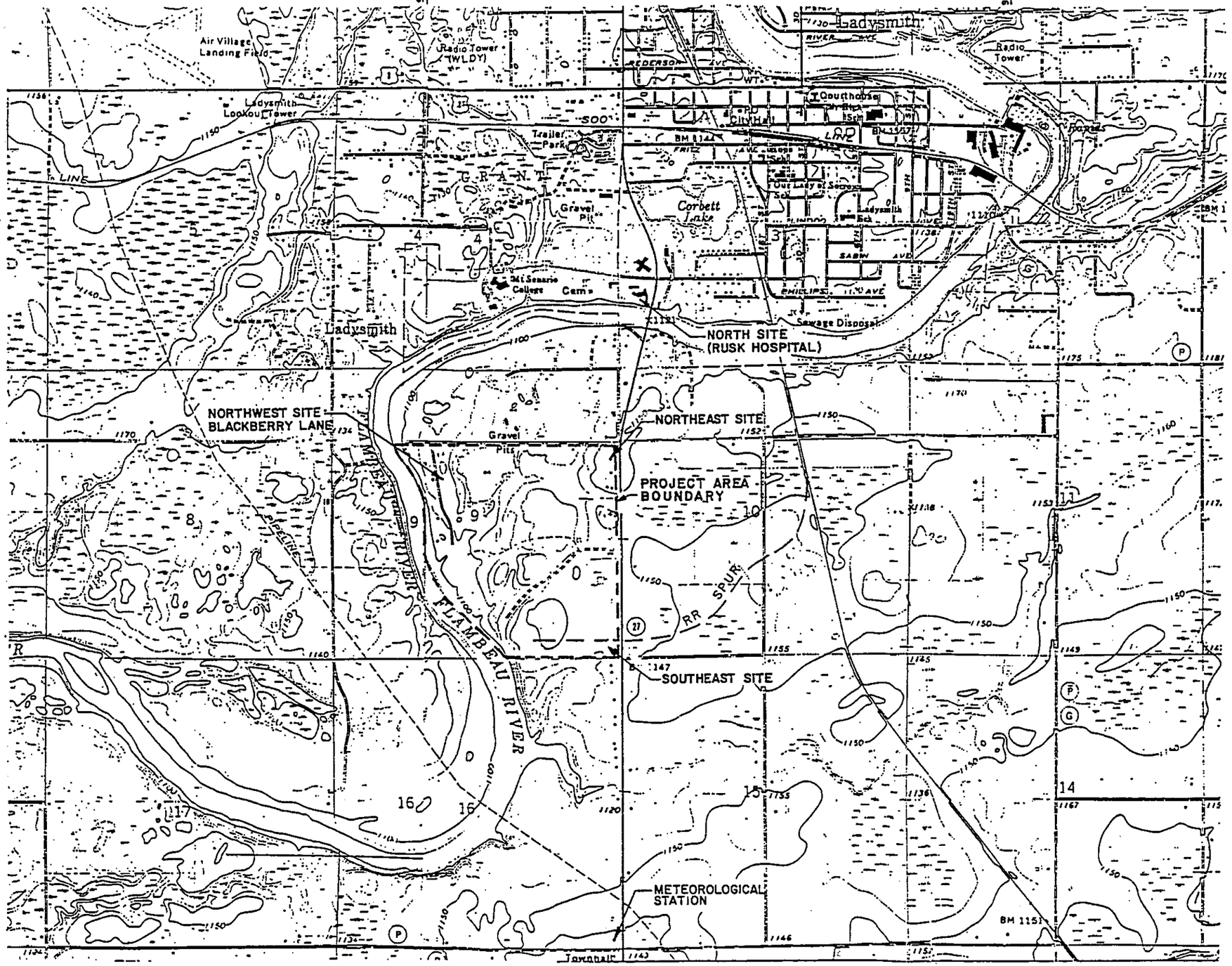
NO.	DATE	REVISIONS	BY	CHK'D	ENG'R	CHIEF W.R.

NO.	DATE	REVISIONS	BY	CHK'D	ENG'R	CHIEF W.R.

	BY	DATE
PROJ. ENGR		
MGR. PROCESS DEV.		
ENGR MGR.		

	BY	DATE
DESIGN		
DRAWN	DHS	12/89
CHK'D	GWS	12/89
DES. ENGR		
SECT. ENGR		

B2



NOTE: BASE MAP PREPARED FROM U.S.G.S. MAPS 7.5 MINUTE SERIES, LADYSMITH AND THORNAPPLE WISCONSIN QUADRANGLES

B3

FOTH & VAN DYKE
GEOSCIENCES & ENVIRONMENTAL MANAGEMENT DIVISION
GREEN BAY, WISCONSIN

FLAMBEAU PROJECT
LADYSMITH, WISCONSIN

KENNECOTT MINERALS COMPANY
1515 MINERAL SQUARE
SALT LAKE CITY, UTAH
84112

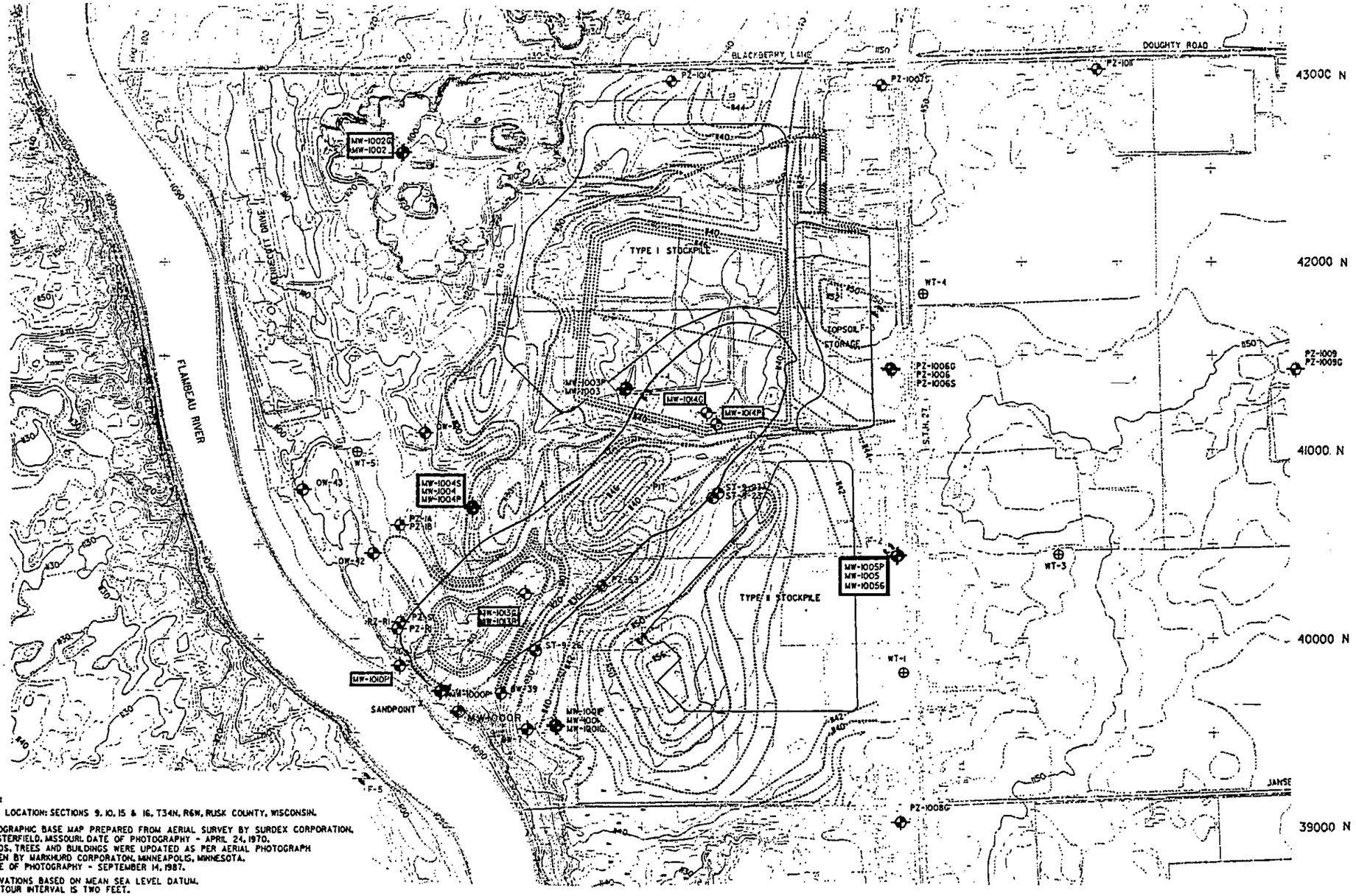
FIGURE 1
TSP AND METEOROLOGICAL SITES

REFERENCES	DWG. NO.	DESCRIPTION
	B3	

REFERENCES	DWG. NO.	DESCRIPTION	NO.	DATE	REVISIONS	BY	CHK'D	ENG'R	NO.	DATE	REVISIONS	BY	CHK'D	ENG'R
	B3													

	BY	DATE
DRAWN	SJL	12/89
CHK'D	GWS	1/3/89

MICROFILM | JOB
DRAWING NO. | REV.
DIVISION DRAWING NO.
SCALE 1" = 2000'



NOTES:

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3. ELEVATIONS BASED ON MEAN SEA LEVEL DATUM. CONTOUR INTERVAL IS TWO FEET.
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40000 E =	1,713,516.1229 E

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5. SEE FIGURE NO.'S 7-1 AND 7-7 FOR THE LOCATION OF WETLAND STAFF GAUGE WT-2 AND FOR SURFACE WATER MONITORING LOCATIONS.

LEGEND

- EXISTING CONTOUR
- EXISTING PAVED ROADWAY
- EXISTING TRAIL/GRAVEL SURFACE
- TREES AND/OR BRUSH
- FENCE
- CONTROL MONUMENT
- MONITORING WELL
- PIEZOMETER
- WELL ON THE WATER QUALITY MONITORING PROGRAM
- WETLAND STAFF GAUGE

N

0 300' 600'
SCALE

40 YEAR LONG TERM CARE AND MAINTENANCE PLAN

	TIMES PER YEAR	DURATION
1. INSPECTIONS INSPECT RECLAIMED SITE FOR EROSION, VEGETATION GROWTH, SETTLING, AND MONITORING DEVICE INTEGRITY		
PHASE I	SPRING & FALL	4 YEARS
PHASE II	LATE SUMMER	36 YEARS
2. MAINTENANCE		
A. LANDFORM	AS NEEDED	40 YEARS
B. VEGETATION	AS NEEDED	40 YEARS
C. MONITORING DEVICE	AS NEEDED	40 YEARS
3. GROUNDWATER MONITORING		
A. OUTSIDE BACKFILLED PIT WELL NESTS-MW-1000, 1002, 1004, 1005 WELL-MW-1010P	QUARTERLY[1] ANNUALLY[2]	40 YEARS
B. INSIDE BACKFILLED PIT WELL NESTS - 1013S1013		
PHASE I	QUARTERLY[3] ANNUALLY[3]	2 YEARS
PHASE II	ANNUALLY (JUNE)[3][2]	SEE FOOTNOTE 3
PHASE III	EVERY FIFTH YEAR (JUNE)[3][2]	REMAINDER OF PERIOD
C. WATER LEVELS		
PHASE I	QUARTERLY[4]	UNTIL WATER LEVELS STABILIZE
PHASE II	QUARTERLY[5]	REMAINDER OF PERIOD
4. SURFACE WATER[6]		
A. SEDIMENTS, MACROINVERTEBRATES & FISH		
PHASE I	ANNUALLY	2 YEARS
PHASE II (CRAY FISH ONLY)	ANNUALLY	UNTIL ISSUANCE OF NOTICE OF COMPLETION
PHASE III (FISH ONLY)	ONCE	10 YEAR CERTIFICATE OF COMPLETION IS ISSUED
B. WATER QUALITY	THREE IN TWO YEAR PERIOD	2 YEARS
C. WETLAND SURFACE FLOWS[7]	SPRING, SUMMER & AUTUMN	UNTIL WATER LEVELS STABILIZE
5. VEGETATION & WILDLIFE		
A. PERCENT COVER	SEE FOOTNOTE 8	UNTIL ISSUANCE OF CERTIFICATE OF COMPLETION
B. BIOMASS	SEE FOOTNOTE 8	UNTIL ISSUANCE OF CERTIFICATE OF COMPLETION
C. DIVERSITY	SEE FOOTNOTE 8	UNTIL ISSUANCE OF CERTIFICATE OF COMPLETION
D. SURVIVORSHIP OF WOODY PLANT STOCK	SEE FOOTNOTE 8	UNTIL ISSUANCE OF CERTIFICATE OF COMPLETION
E. WETLAND VEGETATION	SEE FOOTNOTE 8	UNTIL ISSUANCE OF CERTIFICATE OF COMPLETION
F. HABITAT EVALUATION	SEE FOOTNOTE 8	UNTIL ISSUANCE CERTIFICATE OF COMPLETION
6. TERRESTRIAL ECOLOGY		
PHASE I	ANNUALLY (LATE SUMMER)[9]	4 YEARS
PHASE II	EVERY FIVE YEARS (LATE SUMMER)[9]	36 YEARS

[1] PARAMETERS: SPECIFIC CONDUCTANCE (FIELD), PH (FIELD AND LAB), TOTAL DISSOLVED SOLIDS, TOTAL ALKALINITY, TOTAL HARDNESS, IRON, MANGANESE, COPPER, SULFATE.

[2] PARAMETERS: ARSENIC, BARIUM, CADMIUM, TOTAL CHROMIUM, LEAD, MERCURY, SELENIUM, SILVER, ZINC (JUNE QUARTERLY ROUND).

[3] ANNUAL SAMPLING WILL CONTINUE UNTIL WATER-LEVELS IN MW-1013P AND 1014P INDICATE THAT WATER LEVELS HAVE RISEN TO BOTTOM OF SAPROLITE LAYER IN THE BACKFILLED PIT.

[4] LOCATIONS: SEE TABLE NO. 7-1 OF REPORT.

[5] LOCATIONS: WELL NESTS MW-1000, 1002, 1004 AND 1005. WELL MW-1010P.

[6] SEE SECTION 7.4 OF REPORT FOR SAMPLING LOCATIONS AND ANALYTICAL PARAMETERS.

[7] MONITORING TO BE CONDUCTED ONLY IF WATER LEVEL MEASUREMENTS DURING THE CONSTRUCTION AND OPERATION MONITORING PROGRAM INDICATE A SIGNIFICANT DRAWDOWN EFFECT ON A MONITORED WETLAND WHICH IS ATTRIBUTABLE TO THE PROJECT.

[8] AT DISCRETION OF APPLICANT TO DEMONSTRATE THAT MINIMUM STANDARDS HAVE BEEN MET BEFORE ISSUANCE OF NOTICE OF COMPLETION OF RECLAMATION BY THE APPLICANT AND ISSUANCE OF CERTIFICATE OF COMPLETION OF RECLAMATION BY WDNR. SEE SECTION 5.11 OF REPORT FOR MINIMUM STANDARDS AND MONITORING PROCEDURES.

[9] AERIAL AND COLOR INFRARED PHOTOGRAPHY.

NOTE: THIS FIGURE EXCERPTED FROM MINING PERMIT APPLICATION

B4

REFERENCES	DRG. NO.	DESCRIPTION

REFERENCES	DRG. NO.	DESCRIPTION
	B4	

NO.	DATE	REVISIONS	BY	CHKD	ENGR	SUPT

NO.	DATE	REVISIONS	BY	CHKD	ENGR	SUPT

	BY	DATE
PROJ ENGR		
W.A. PROCESS ENGR		
ENGR MGR		

	BY	DATE
DESIGN		
DRAWN	DHS	12/89
CHKD	GWS	12/89
RES ENGR		
SECT ENGR		

FOTH & VAN DYKE
GEOSCIENCES & ENVIRONMENTAL MANAGEMENT DIVISION
GREEN BAY, WISCONSIN

KENNECOTT MINERALS COMPANY
865 MINERAL SQUARE
SALT LAKE CITY, UTAH 84102

FLAMBEAU PROJECT
LADYSMITH, WISCONSIN

FIGURE NO. 10-1
LONG TERM CARE
AND MAINTENANCE PLAN

MICROFILM | JOB
DRAWING NO. | REV.
DIVISION DRAWING NO.
SCALE : SEE BAR SCALE

Appendix C

Quality Assurance/Quality Control Biomonitoring Study Plan
October 1992

Foth & Van Dyke

REPORT

Quality Assurance/Quality Control Biomonitoring Study Plan

Scope ID: 91F6

Flambeau Mining Company
Ladysmith, Wisconsin

October 1992

Foth & Van Dyke

2737 S. Ridge Road
P.O. Box 19012
Green Bay, WI 54307-9012
414/497-2500
Fax: 414/497-8516

October 29, 1992

Mr. Tom Bauman
Industrial Wastewater Section
Department of Natural Resources WW/2
P.O. Box 7921
Madison, WI 53707-7921

Dear Tom:

RE: Flambeau Project - Quality Assurance/Quality Control, Biomonitoring Study Plan

On behalf of the Flambeau Mining Company (Flambeau), Foth & Van Dyke is submitting two copies of the attached pursuant to Part I, E(4) of the WPDES Permit (Permit No. WI-0047376-1, Docket No. IH-89-14) for the Flambeau project in Rusk County, Wisconsin.

If you have any comments or questions regarding this submittal, please contact Jim Hutchison at (414) 497-2500.

Sincerely,

Foth & Van Dyke

James B. Hutchison, P.E.
Project Engineer

Jerry W. Sevick, P.E.
Group Vice President

JBH:JWS:jef

{A3S10}91F6.51

Distribution List

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7	Lawrence E. Mercando Vice President Flambeau Mining Company Ladysmith Office 105 West Lake Avenue Ladysmith, WI 54848
1	Henry J. Handzel DeWitt, Port, *et al.* 121 South Pinckney Street Madison, WI 53707
1	Bernice Dukerschein, Chairman Rusk County Board 114 West Miner Avenue Ladysmith, WI 54848
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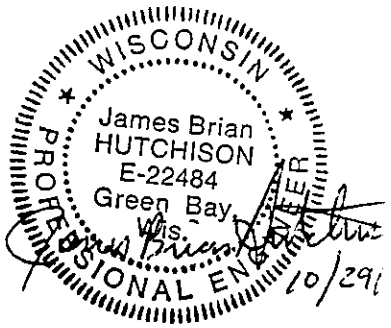
Quality Assurance/Quality Control Biomonitoring Study Plan

Scope ID: 91F6



Prepared for
Flambeau Mining Company
Ladysmith, Wisconsin

Prepared by
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October 1992

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Quality Assurance/Quality Control Biomonitoring Study Plan

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1 Description of Activities

The Quality Assurance/Quality Control Biomonitoring Study Plan is being submitted in accordance with the requirements of Section E(4) of Part I of the WPDES Permit No. WI-0047376-1 for the Flambeau Mining Co. Section E(4) requires Flambeau Mining Co. (Flambeau) to perform effluent toxicity test batteries. All toxicity tests required by the permit shall be conducted according to the QA/QC plan.

Flambeau is required to perform the effluent toxicity test batteries as follows:

a. Flambeau shall conduct an acute toxicity test battery using the procedure described in the QA/QC plan twice each year following commencement of discharging effluent from outfall 001 (wastewater treatment plant effluent). Flambeau will conduct these tests between the months of May-September and November-April.

b. Flambeau shall conduct an acute toxicity test battery using the procedure described in the QA/QC plan once during the first year of permit issuance and twice each year thereafter for effluent discharged from outfall 002 (settling pond effluent). Flambeau will conduct these tests between the months of May-September and November-April.

c. Flambeau shall conduct a chronic toxicity test battery using the procedure described in the QA/QC plan once each year between the months of June-September upon commencement of discharging effluent from outfall 001.

2 Acute/Chronic Bioassay Study Plan

Flambeau has selected Integrated Paper Services, Inc. (IPS) as the laboratory to perform this effluent toxicity testing. A copy of the IPS Study Plan for Flambeau is found in Appendix A. The plan and use schedules for hand delivery and overnight delivery are found in Tables 2-1 and 2-2 respectively. IPS standard operating procedures (SOP) and quality assurance practices are incorporated in the plan by reference to their SOP document which is approved and on file with the Wisconsin Department of Natural Resources.

Table 2-1

Sample Acquisition/Hand Delivery/ Use Schedules for Flambeau Mining Co.

Sample	Sample Type	Volume (gal)	Delivery[a]	Test Use
Acute(s):				
River: Tuesday	Grab	3.5	Tuesday	Ac(1-4)
Effluent: Monday-Tuesday	001 Comp. 002 Comp.	2 2	Tuesday Tuesday	Ac(1-2) Ac(1-2)
Effluent: Wednesday-Thursday	001 Comp. 002 Comp.	2 2	Thursday Thursday	Ac(3-4) Ac(3-4)
Chronic:				
River: Tuesday	Grab	6	Tuesday	Ch(1-7)
Effluent: Monday-Tuesday	001 Comp.	1	Tuesday	Ch(1-2)
Effluent: Wednesday-Thursday	001 Comp.	1	Thursday	Ch(3-4)
Effluent: Thursday-Friday	001 Comp.	2	Friday	Ch(5-7)
Acute/Chronic:				
River: Tuesday	Grab	10	Tuesday	Ac(1-4)/Ch(1-7)
Effluent: Monday-Tuesday	001 Comp. 002 Comp.	2.5 2	Tuesday Tuesday	Ac(1-2)/Ch(1-2) Ac(1-2)
Effluent: Wednesday-Thursday	001 Comp. 002 Comp.	2.5 2	Thursday Thursday	Ac(3-4)/Ch(3-4) Ac(3-4)
Effluent: Thursday-Friday	001 Comp.	2	Friday	Ch(5-7)

[a] Delivery by 10:30 a.m.

Table 2-2

Sample Acquisition/Overnight Delivery/ Use Schedules for Flambeau Mining Co.

Sample	Sample Type	Volume (gal)	Delivery[a]	Test Use
Acute(s):				
River: Monday	Grab	3.5	Monday/Tuesday	Ac(1-4)
Effluent: Sunday-Monday	001 Comp. 002 Comp.	2 2	Monday/Tuesday Monday/Tuesday	Ac(1-2) Ac(1-2)
Effluent: Tuesday-Wednesday	001 Comp. 002 Comp.	2 2	Wednesday/Thursday Wednesday/Thursday	Ac(3-4) Ac(3-4)
Chronic:				
River: Monday	Grab	6	Monday/Tuesday	Ch(1-7)
Effluent: Sunday-Monday	001 Comp.	1	Monday/Tuesday	Ch(1-2)
Effluent: Tuesday-Wednesday	001 Comp.	1	Wednesday/Thursday	Ch(3-4)
Effluent: Thursday-Friday	001 Comp.	2	Friday/Saturday	Ch(5-7)
Acute/Chronic:				
River: Monday	Grab	10	Monday/Tuesday	Ac(1-4)/Ch(1-7)
Effluent: Sunday-Monday	001 Comp. 002 Comp.	2.5 2	Monday/Tuesday Monday/Tuesday	Ac(1-2)/Ch(1-2) Ac(1-2)
Effluent: Tuesday-Wednesday	001 Comp. 002 Comp.	2.5 2	Wednesday/Thursday Wednesday/Thursday	Ac(3-4)/Ch(3-4) Ac(3-4)
Effluent: Thursday-Friday	001 Comp.	2	Friday/Saturday	Ch(5-7)

[a] Delivery by 10:30 a.m.

3 Statement of Effluent Sampling Specifics

Flambeau will be responsible for effluent and receiving water sampling, handling and transportation to IPS for testing. Samples to be collected for toxicity testing include the receiving water (Flambeau River), Outfall 001 (wastewater treatment plant effluent) and Outfall 002 (settling pond effluent).

3.1 Sample Type

The receiving water sample will be a grab sample. The sample from Outfall 001 will be a flow-proportional composite sample collected over a 24-hour period. The sample from Outfall 002 will be a time-proportional composite sample collected over a 24-hour period.

3.2 Sample Volume and Frequency

The sample volume and frequency of collection will be as shown in the Plan and Use Schedules (Tables 2-1 and 2-2).

3.3 Sample Location

The receiving water sample will be collected from the Flambeau River at the west end of Blackberry Lane. This location is upstream from and out of contact with Outfalls 001 and 002. The sample will be collected by inverting the sample containers and submerging them below the water surface to about mid-depth. The sample bottles will then be turned upright and allowed to fill. Care will be taken not to disturb the river bottom sediments.

The sample from Outfall 001 will be collected from a stationary refrigerated composite sampler (ISCO Model 2910R or equal) located downstream from the wastewater treatment plant process but prior to discharge to the Flambeau River.

The sample from Outfall 002 will be collected from a similar composite wastewater sampler located downstream from the settling ponds but prior to discharge to the Flambeau River.

3.4 Sample Containers and Shipping Coolers

IPS will provide Flambeau with sample containers (new cubitainers) and shipping coolers for the toxicity testing. Flambeau will notify IPS several weeks in advance of the anticipated testing in order that the containers and coolers can be shipped in a reasonable time frame.

3.5 Sample Labeling

Each sample collected will contain a label with the following minimum information:

- Client identification
- Individual collecting the sample
- Sample identification (001, 002 or receiving water)
- Date and time of sampling
- Sample type (grab or composite)

Care will be taken when labeling samples such that the label cannot be washed off or smeared when ice is added to the cooler.

3.6 Sample Preservation

The samples from Outfalls 001 and 002 will be refrigerated during the 24 hours they are being composited. The temperature of the refrigerators will be maintained at 4°C. A thermometer will be placed in each unit to ensure that the 4°C temperature is maintained.

Upon completion of the 24-hour sample collection period, the samples will be transferred from the polyethylene sample container inside the refrigerator to the labeled sample containers provided by IPS. These samples, along with the grab sample from the receiving water, will be placed inside the IPS coolers for shipment. The coolers will then be filled with a sufficient amount of wet ice to maintain the temperature of the samples at, or less than, 10°C until receipt by IPS the following day.

3.7 Chain-of-Custody Record and Custody Seal

An IPS chain-of-custody record will be completed for all samples to be shipped to IPS. See Figure 3-1. At a minimum, the chain-of-custody record will include the following information:

- Client identification
- Samplers signature
- Sample identification (001, 002 or receiving water)
- Number of containers
- Sample type (grab or composite)
- Date and time of sampling
- Initial temperature and pH of sample (if known)
- Carrier identification (UPS, Federal Express, etc.)
- Shippers signature, date and time

The shipper will keep a copy of the completed chain-of-custody record for Flambeau files in order to demonstrate sample custody. The shipper will place the completed chain-of-custody record inside a sealed plastic bag and place the sealed bag inside the cooler with the samples. The cooler will then be securely fastened for shipment to IPS. An IPS custody seal will be placed around the cooler to ensure that no tampering of the samples takes place.

3.8 Sample Transportation

Flambeau will select a common carrier, who will guarantee delivery by 10:30 a.m. the next day, to transport the samples to IPS. The samples will be collected, shipped and delivered to IPS according to the IPS overnight delivery schedule found in Table 2-2. Flambeau will retain a copy of the shipping documents for their files to demonstrate sample custody. Flambeau will also notify IPS in advance of the shipment. In return, IPS will notify Flambeau upon receipt of the samples.

FIGURE 3.1

Chain-of-Custody Record

Client _____

IPS
Environmental and Analytical Services

Return Samples To: Integrated Paper Services, Inc.
Aquatic Toxicology Lab
101 W. Edison Ave., Suite 250
Appleton, WI 54915

Sampled by: _____
(signature)

Sample Identification	# Containers	Grab	Composite		Collection				Receipt					
		Date/Time	Start Date/Time	End Date/Time	Temp. (°C)	pH	NH_3-N	Cl_2	Ice	Temp. (°C)	pH	DO	Cl_2	NH_3-N
1														
2														
3														
4														
5														

Remarks:

Custody Seal: OK / Broken

Laboratory ID:
1 _____
2 _____
3 _____
4 _____
5 _____

Reliquished by: _____ _____
(to carrier) Date/Time

Received by: _____ _____
Date/Time

Reliquished by: _____ _____
Date/Time

Received for lab: _____ _____
Date/Time

As an alternate, Flambeau may also choose to hand deliver the samples to IPS by 10:30 a.m. on the day of sample collection. In this case, the samples will be collected and delivered according to the IPS hand delivery schedule found in Table 2-1. Upon delivery of the samples to IPS, Flambeau will receive a signed copy of the chain-of-custody record from sample receiving personnel at IPS.

Appendix A

Acute/Chronic Bioassay Study Plan for Flambeau Mining Co.

Acute/Chronic Bioassay Study Plan for Flambeau Mining Co.

This plan, when accompanied by a detailed description of methods for effluent and receiving water sampling, handling, and transportation to the IPS laboratory comprises the QA/QC biomonitoring study plan required as per Section E(4)(a) of WPDES Permit No. WI-0047376-1. This plan is intended for submission to the Wisconsin Department of Natural Resources.

Prescreen Tests

Date: Within two weeks prior to definitive tests.

Samples: 0.5 gallon Flambeau River water (grab sample from upstream and outside of all influence of the outfall) and/or 0.25 gallon effluent (grab sample)

Definitive Tests

Type: Acute tests using fathead minnows (96 hour), Daphnia magna, and Daphnia pulex (48 hour)

Seven-day fathead minnow and C. dubia chronic tests

Date: Acute - Outfall 001 effluent twice annually (November-April and May-September) following commencement of discharge for term of permit; Outfall 002 effluent once during year of permit issuance and twice annually (November-April and May-September) following commencement of discharge for term of permit.

Chronic - Outfall 001 effluent once annually (June-September) following commencement of discharge for term of permit

Test Organisms: Acute - Fathead minnows (20-40 days old), Daphnia magna and Daphnia pulex (<24 hours old at test initiation)

Chronic - Fathead minnows (<24 hours old at test initiation) and Ceriodaphnia dubia (<24 hours old and within 8 hour window at test initiation)

Treatments: Acute - 100% (v:v) Outfall 001 and Outfall 002 effluents, Flambeau River water (primary control/diluent), and laboratory water (secondary control/diluent)

Chronic - 1% (IWC) and 100% (v:v) Outfall 001 effluent, Flambeau River water (primary control/diluent), and laboratory water (secondary control/diluent)

Samples: See Tables 2 and 3

Reporting: Formal report issued within ten business days after completion of the test

Laboratory Identification: Integrated Paper Services, Inc.
P.O. Box 446
101 W. Edison Avenue, Suite 250
Appleton, WI 54912-0446

Applicable SOP Documentation: Sections 4, 5.2, 5.3, 5.4.1, 5.4.3, 5.5.1, 5.5.2, 6 and 7 of, and amendments to, Standard Operational Procedures document dated February 1, 1990.

Appendix D

Biotic Index Sorting Procedures

BIOTIC INDEX SORTING PROCEDURE - 1983

1. Place contents of the jar into a large pan or tray containing a grid of 2-inch, consecutively numbered squares. The grid pattern may be on the bottom of the tray or on some suitable material placed under a transparent tray. If desired, alcohol can be removed by placing the sample in a US #30 mesh seive and washing with water before transferring to the pan.

2. Distribute the debris and arthropods as evenly as possible in the tray. Remove any large debris, being careful to not discard any arthropods with it. Samples with large numbers of organisms can be divided and sub-sampled.

3. Remove all arthropods from one grid at a time and place them in a jar containing 70 percent alcohol. Arthropods can be sorted to an identifiable taxonomic level and placed in separate jars. An arthropod is considered to lie within a grid if more than one-half of it is within the grid. The grids to be picked should be selected from a random number table and picked individually. Continue picking until at least 100 arthropods with B.I. values have been removed. The last grid should be totally picked, no matter how many arthropods end up in the sample.

3a. Alternative sorting procedure: A random number table works well on some samples, but not those with a lot of debris and few insects. Under these circumstances the following is suggested:

   a. randomly select a corner of the pan to start picking from,
   b. randomly select a direction to proceed (vertical or horizontal),
   c. pick grids in line.

   This semi-random method allows the debris to be pushed aside as sorting progresses.

4. Avoid sorting arthropods less than 3 mm in length, except for adult riffle beetles (Elmidae). Collect, but do not count, adult insects except for riffle beetles (Elmidae and Dryopidae). Adult beetles (Dytiscidae, Gryinidae, Hydrophilidae) and adult bugs (especially Corixidae) are frequently found in some samples but cannot be used in the HBI analysis.

2660A

MACROINVERTEBRATE/BIOTIC INDEX SAMPLING GUIDELINES - 1983

The following macroinvertebrate sampling guidelines are designed as standard operating procedures for routine investigations, basin assessments, pre and post studies, etc. The objective of these guidelines is to provide minimum requirements to assure data quality, and to assure that future data can be reliably compared to past data. These guidelines do not cover all possible sampling situations. However, investigators are expected to conform as closely as possible to these guidelines in all routine sampling programs which use the Hilsenhoff Biotic Index analysis system.

SAMPLING STRATEGY

Site Selection

The basic site selection criterion is that most sampling sites within a stream reach should have similar habitat characteristics. Of particular importance is substrate and current velocity.

Riffles, where flow is rapid and the substrate is composed of gravel or small stones, is the preferred sampling habitat. However, if riffles are not available at most sampling sites, the next best habitat which is available at most sites should be sampled. A variety of habitats found in most streams are suitable for macroinvertebrate sampling. The only exception is that nonflowing areas should not be sampled. In streams with poor habitat, artificial substrate samplers can be used.

General site selection criteria include:

1. Sample similar habitat at most sites (for example, do not sample a gravel riffle upstream and debris in a slower velocity area downstream);

2. Riffles with gravel or stone substrates are preferred;

3. Sample areas with a flow velocity of at least 0.5 ft/sec., preferably with gravel or stone substrates;

4. If areas with gravel or stone substrates are not available, sample debris in the fastest turbulent current;

5. Leaves, grass and other debris clinging to branches or snags are acceptable if nothing better can be found;

6. Avoid areas directly downstream from impoundments or bridges;

7. Avoid sampling silty substrates;

8. Streams without suitable habitat should be sampled with artificial substrates.

Replicate Sampling

For routine investigations three replicate samples should be taken at a control, or upstream site, and no replicates at other sites within a stream reach.

When conducting investigations for enforcement purposes or other potentially sensitive situations, three replicate samples at each site are suggested. It may not be necessary to process all samples, but replicates should at least be available if needed.

Sampling Seasons

Macroinvertebrate sampling in Wisconsin should generally be done from October to May. Because of ice conditions, autumn sampling should be done as late as possible before freeze up, and spring sampling should be done as soon after ice out and return to normal flow conditions as possible.

For routine investigations, sampling only one season is recommended. Spring sampling is preferred in most situations. However, there are situations where autumn sampling may be preferred.

To insure any future sampling can be correlated with past data it is important to collect water temperature and flow, or stage data when macroinvertebrate samples are taken. Future samples should be taken under similar physical conditions.

SAMPLING PROCEDURES

Sampling Methods

Sample with a D-frame net by holding the net firmly against the substrate and disturbing the substrate upstream from the net with your feet to dislodge arthropods. Do not try to push the net through the substrate. Let the arthropods wash downstream into the net. A few rocks, sticks or pieces of vegetation should be examined and sampled if necessary, to ensure that firmly attached insects are included in the sample.

Try to sample all suitable niches at each sampling site with equal effort. Do not sample areas at the site with flow velocity less than 0.5 ft/sec., or areas with substrate composed of sediment. In some situations, sampling along a transect is appropriate, in others an expanded effort at a site may be required.

When replicate samples are to be taken, sample from downstream to upstream to insure that an undisturbed area is sampled. A stream reach should also be sampled from downstream to upstream if sites are close together.

Number of Arthropods

A minimum of 100 arthropods that have Biotoc Index values should be sampled at each site. Sample all suitable habitat at each site no matter how many arthropods are collected.

Sample Handling and Preservation

1. After the sample is collected rinse sediment from the net by forcefully running the net through the water a few times.

2. Visually inspect the net contents to insure that at least 100 arthropods with Biotic Index values were collected. Insufficient numbers may indicate a water quality problem and should be noted.

3. Transfer the debris and arthropods to a wide-mouth jar of sufficient size. Remove any arthropods clinging to the net and include them in the sample. Add enough 70 percent alcohol to the jar to cover the debris (use 95 percent alcohol if enough water remains in the sample to dilute the alcohol to 70 percent).

Field Data

1. Fill out the Macroinvertebrate Field Sampling Data sheet (Form 3200-52) when samples are taken. Use a different sheet at each site within a stream reach.

2. Describe, in detail, the exact location of each sampling site. Use landmarks such as bridges, rock outcroppings, etc. Record distances, directions (east, west -- NOT left, right). Be precise as possible to insure someone else can find the same site in the future.

3. Record water temperature and flow, or stage for future reference.

4. Record sampling methods, i.e., D-frame net, number of replicates, number of transects or other sampling pattern, etc.

5. Record the time spent taking each sample.

6. Record an estimate of the abundance of arthropods at each site as follows:

   Abundant - large number of arthropods found at the site, greater than 1,000 collected in a short time.

   Common - no difficulty in collecting 100 arthropods, sampling resulted in 200 to 1,000 arthropods.

   Uncommon - had difficulty, but managed to collect at least 100 arthropods with Biotic Index values.

   Rare - could not obtain 100 arthropods.

Appendix E

Laboratory Handling Procedures for Particulate and Asbestiform Filters

1.0 LABORATORY HANDLING PROCEDURES FOR PARTICULATE FILTERS

1.1 Introduction

Precise and reproducible laboratory procedures are an essential aspect of producing accurate particulate concentrations via the high volume sampling technique. The laboratory procedures to be employed by Foth & Van Dyke are in compliance with the procedures and quality assurance requirements established by the U.S. Environmental Protection Agency (USEPA) in the following guideline documents:

> "Quality Assurance Handbook for Air Pollution Measurement System, Vol. II - Ambient Air Specific Methods," EPA-600/4-77-027A, May 1977.
>
> "Reference Method for the Determination of Suspended Particulate Matter in the Atmosphere," 40 CFR 50, Appendix B.

1.2 Filter Media and Selection

Filters for the measurement of particulates will consist of an 8 inch by 10 inch mat of binderless glass fiber material. This is the normal or traditional filter grade. Surface alkalinity should be between a pH of approximately 6.5 and 7.5. Since commercially available filters frequently have alkaline pH valves greater than pH 7.5, they will be checked at a sampling frequency of 7 percent (approximately one out of every fourteen) to make certain they meet the specified maximum pH.

Only filters having a collection efficiency of at least 99 percent for particles of 0.3 um diameter, as measured by the DOP test (ASTM-D2986-71), are to be used. The manufacturer shall be required to furnish proof of the collection efficiency of a batch of new filters when purchased.

Each filter will be visually inspected with the aid of a light table. Filters with pinholes and other defects such as tears, creases, or lumps shall be discarded or returned to the supplier. Loose particles shall be removed with a soft brush.

1.3 Filter Handling and Identification

Standard procedures require that any laboratory personnel handling the filters during any stage of the laboratory analysis must wear plastic gloves such that dirt and perspiration are not transferred to the filter.

Filters will be numbered and weighed by the lab in batch quantities of sufficient size to accommodate at least a three month period for each sampler (120 filters during the proproduction and reclamation phases and 180 filters during the first year of the mining phase). Filters will be numbered sequentially using an ink stamp along an edge of each filter that is not part of the sampling surface. To avoid misidentification of filters, the filter I.D. numbers will be prefixed with a code unique to this project (i.e. FMC _____). Each filter will be placed in its own (dedicated) manila folder.

Each folder will be marked with the following information:

SUPERIOR TESTING LABORATORY
Project_____
Inst. #_____Site #_____
Filter #_____
Date Sampled_____

The above information will be logged on an independent lab data sheet that will be kept in the laboratory files in the event the filter label or folder is lost or destroyed. Enter the filter

number only at this time. Each folder will then be placed into a resealable plastic bag. The sealed filters will then be arranged in numerical order and stored in the original or a similar container.

1.4 Filter Equilibrium and Weighing

1.4.1 Equilibrium

The filter shall equilibriate (desiccate) in a conditioning environment for a minimum of 24 hours prior to weighing to minimize errors in measuring the weight. Longer periods of equilibrium will not affect accuracy. The conditioning environment shall have an average temperature between 20°C and 30°C. Temperature must not vary more than ±3°C. Relative humidity (RH) must be below 50 percent and vary by not more than ±5 percent. A convenient working RH is 40 percent. Clean filters are usually processed in lots, that is, several at one time.

This procedure ensures that each filter has a uniformly low moisture content and that the effects of variable atmospheric humidity are minimized when each individual filter is weighed.

1.4.2 Weighing

Before weighing the first filter, a balance check shall be performed by weighing a standard Class "S" weight of between three and five grams. The actual and measured weights, the date, and the operator's initials shall be recorded in the lab log book. If the actual and measured values differ by more than ±0.5 mg. (0.0005 g), it shall be reported to the project manager before proceeding.

If the actual and measured values agree to within ±0.5 mg., each filter shall be weighed to the nearest mg. Each filter shall be weighed within 30 seconds after removal from the equilibration

chamber. The initial weight and serial number of each filter shall be recorded on the Particulate Sample Data Sheet. Clean filters shall not be folded or creased prior to weighing or use. The following procedure shall be used for weighing the filters:

1. Each filter shall be weighed to the nearest ten-thousandth of a gram on a Sartorius Model A200S Air analytical balance. This balance is referenced to Class S weights traceable to the National Bureau of Standards (NBS). The filter number, date weighed, project number, person weighing, and initial weight of each filter shall be recorded on a Particulate Sample Data Sheet (see Figure E-1 attached), which will be supplied to the laboratory. This sheet will be mailed to the site with the individual filter. As a backup, information for each filter shall also be recorded on a laboratory data sheet. This summary sheet shall be stored in the project file.

2. In order to check that the proper weighing procedures were followed and that the initial weight of the filter was accurate, every tenth filter shall be independently audited by an individual not responsible for the initial weighing of the filter. If the audit weight of the filter differs by greater than .0005 grams from the initial weight of the filter, then the filter must be reweighed and, if necessary, redesiccated for another 24-hours. Enter this information on the Particulate Sample Data Sheet.

3. Each individual filter shall be placed in a separate manila folder which is then placed into a resealable plastic bag. These precautionary procedures shall be followed to protect the filters from damage either in mailing or on-site handling. For identification and data recording purposes, the Particulate Sample Data Sheet shall be placed in the plastic bag. The filter shall then be mailed to the sampling site.

1.5 Post Sampling Filter Processing and Analysis

Upon arrival of the filter at Superior Testing Laboratories, the date of receipt and the person receiving the filter is immediately entered on the Particulate Sample Data Sheet and the lab data form. The filter shall then be placed in a desiccator for a minimum of 24 hours before the final weighing. The conditioning environment shall have a temperature between 20°C and 30°C. Temperature must not vary by more than ±3°C. Relative humidity must be below 50 percent and not vary by more than ±5 percent. A convenient working RH is 40 percent. The desiccation process minimizes the effect of the varying moisture content of the atmosphere between the site and laboratory conditions when the final weight of the filter is determined.

The filter is then weighed to the nearest ten-thousandth of a gram on the same analytical balance on which it was preweighed. The final weight of the filter, date weighed, person weighing, and particulate weight (Pwt) is recorded on both the Particulate Sample Data Sheet and on the lab data form. As in the preweighing procedures, the final weight of every tenth filter shall be independently audited to check that the proper procedure was followed in the weighing technique.

1.5.1 Calculations

Calculations shall then be performed to determine the actual particulate concentration, in ug/m^3, on each filter. The following formula is used:

$$\frac{W_F - W_I}{Qa \times t \times (0.02832\ m^3/ft^3) \times CF}$$

where W_F = Final Weight of the filter, ug
W_I = Initial weight of the filter, ug
Qstd = Ambient Volumetric flowrate of the sampler, scfm
t = Total sampling time, min.
Cf = Seasonal correction factor

The flow rate of air through the filter at site conditions shall be determined using the most recent calibration information available. An on-site calibration of the sampler shall be performed every three months using a certified calibration orifice, traceable to the NBS, with a known response curve (see Appendix A). The timer on the sampler will control the sampling time to within 15 minutes.

The site flow rate is adjusted to an equivalent flow rate at standard atmospheric conditions (25°C and 1.0 atmospheric pressure) with the use of the seasonal correction factor. These correction factors are as follows:

Dec/Jan/Feb	-	1.050
Mar/Apr/May	-	1.021
Jun/Jul/Aug/Sep	-	1.000
Oct/Nov	-	1.024

Such an adjustment is necessary in order to compare the particulate loading on the filter to the National Ambient Air quality Standards, which are referenced to standard conditions.

Finally, the calculations for every tenth filter shall be independently audited by an individual not responsible for calibrating the samplers in order to check that the proper techniques, calibration curves, and mathematical procedures were followed.

1.6 Data Archives

The collected particulate samples shall be stored in airtight containers (plastic resealable bags) after final weighing. Once every three months, a portion of each filter will be composited and analyzed for metals. Therefore, the samples shall be protected from contamination or alteration. Where chemical analysis is required, the procedure described in Section 2.0 herein should be followed.

All input data, calculation methods, and results shall be stored permanently in the project files.

2.0 CHEMICAL ANALYSIS

When chemical analysis of the collected particulates is required, several filters will generally have to be combined to have a sufficient sample for the analysis. Particulates will be analyzed for heavy metals content as described in Section 8.2.2. This procedure requires about 0.5 - 1.0 gm of sample. Each filter to be submitted is cut in half, and half of each submitted to the laboratory along with an equivalent number of unexposed blank filters. The following procedure describes the process of compositing filters for chemical analysis.

2.1 Preweighing

1. When preweighing a series of particulate filters for the project, one additional filter shall be set aside for each filter weighed. Those filters which have been set aside shall be used as blanks in the subsequent chemical analysis. They need not be preweighed.

2. Place each filter that is set aside in a plastic bag and label it:

   Blanks for Filters XX to YY

   (where XX to YY are the inclusive numbers of the series of filters being weighed).

3. The blank filters shall be stored until needed for chemical analysis.

4. The other filters shall be weighed as described in Section 1.4.2.

2.2 Compositing Exposed Filters

1. All filters exposed at the site during a composite period (3 months) shall be collected. A composite sample shall be prepared by cutting each filter in half, with half going in the composite resealable plastic bag and half being retained in its original resealable plastic bag as described below.

2. The precautions described in Section 1.3 shall be taken while handling filters. The filter to be cut shall be placed on the cutting board with the exposed surface up. A non-metal straightedge and a cutting wheel shall be used to cut the filter in half at the line scribed on the cutting board.

3. The half of the filter that has been touched by the straightedge shall be placed in the plastic bag for the composite sample. Any sample adhering to the straightedge shall also be transferred to the composite sample plastic bag.

4. The other half of the filter shall be placed back in its original plastic bag. Care shall be taken as not to touch the exposed surface of the filter because it may need to be examined later microscopically.

5. The plastic bag that contains the composite sample shall be marked with the months of the quarter included, project number, date composited, filter I.D., and date exposed. The same information shall be entered on a lab data sheet that will be retained at the lab.

2.3 Compositing Blank Filters

1. The blank filters that were set aside when the exposed filters were preweighed shall be assembled.

2. The blank filters shall be composited in the same manner as the exposed filters - half of each filter shall be retained in the composite blank bag and half shall be retained in its original plastic bag.

3. The plastic bag that contains the composite blank shall be marked with the months of the quarter included, project number, and date composited.

FIGURE E-1

PARTICULATE SAMPLE DATA SHEET

Flambeau Mining Company

Lab:

Filter No. :_____

Project Number :_____

Intital Weight (grams) :_____

Final Weight (grams) :_____

Particulate Weight (P_{wt}, grams) :_____

Date Received :_____

Person Receiving :_____

Date Weighed : Initial:_____ Final:_____

Person Weighing : Initial:_____ Final:_____

Audited : Yes:_____ No.:_____

Audited by : Initial:_____ Final:_____

Audit Date : Initial:_____ Final:_____

Audit Remarks:_____

_____

_____

Field:

Date of Sampling :_____

Site I.D. :_____

Standard Volume (m^3) :_____

Foth & Van Dyke

Appendix F

High-Volume Air Sampler Calibration Procedures

High Volume Air Sampler Calibration Procedures

Calibration will be done in the field using the following procedures:

1. Shut off motor, and attach the variable resistance orifice (vari-flow calibrator) and place the calibrator on the first setting.

2. Check that the flow recorder is properly zeroed. Adjust the set screw on the front of the recorder as necessary.

3. Record the site location, sampler I.D., date and the operators initials on the back of a clean recorder chart.

4. Record the following parameters on the calibration data sheet (see Figure A-1):

   a. Site I.D.,
   b. Date,
   c. Sampler No.,
   d. Orifice No.,
   e. Ambient Temperature (^{o}C),
   f. Station barometric pressure (mmHg)

5. Disable the flow controller by unplugging it from the power source. Restart motor by plugging it in directly to the power source. Allow it to warm up.

6. Record the following on a calibration sheet:

   a. Manometer reading or pressure change ($\triangle P$) for the vari-flow calibrator position.

   b. Transducer reading (I) for the resistance position.

   c. Measured air flow rate (Qa) for the measured $\triangle P$ from the orifice calibration curve.

7. Change the calibrator position and repeat Step 6 for all other resistance positions.

8. Calculate and record the flow event recorder actual correction (IC) for each calibration point as:

$$I\ (Pa/Pstd \times Tstd/Ta)^{1/2}$$

   where: IC = actual correction
   I = recorder response, arbitrary units

9. On a sheet of graph paper, plot the sampler corrected recorder units, IC (y-axis), versus the corresponding calculated orifice flow rates, Qa (x-axis), to obtain a

visual calibration curve and indication of the calibration linearity. A five-point calibration should yield a regression equation with a correlation coefficient of $r > 0.990$.

Using a programmable calculator, determine the best-fit straight line by the method of least squares. The equation for this fit is:

$$IC = m(Qa) + b$$

10. The slope, m, and intercept, b, are then calculated.

11. Calculate and record on the calibration data sheet the set point flow rate (SFR).

$$SFR = (1.42 \times m) + b$$

where: SFR = sampler's seasonally adjusted set point flow rate, $ft^{3/min}$

12. Reconnect the motor to the mass flow controller.

13. Install a clean filter (within a filter cartridge) in the sampler. Tighten the four wing nuts to ensure an even seal, do not overtighten or the gasket may warp.

14. Install a clean recorder chart in the flow recorder and verify that the recorder is zeroed (the pen rests on the innermost circle of the chart). Gently tap on side of sampler to seat ink pen. Rotate chart with coin or screwdriver until chart indicates correct time.

15. Energize the sampler and allow it to warm up to operating temperature. Adjust the flow rate potentiometer on the mass flow controller until the recorder response indicates the set point flow rate (SFR) as calculated in Step 11.

16. Verify that the flow controller will maintain this flow rate for at least ten minutes. Turn off the sampler. The sampler can now be prepared for the next sampler run day.

17. Complete any required maintenance or adjustments.

18. Repeat steps 1, 2 and 3 for the post adjustment portion of calibration.

19. Record the data on the Hi-Vol Calibration Sheet. Store the completed forms in the project file with the other completed forms.

Figure F-1

HI-VOL CALIBRATION DATA SHEET
Flambeau Mining Company

City _____ Date _____

Site No. _____ Site I.D. _____

Orifice No. _____ Instrument No. _____

Temperature (T) _____ °K

Pressure (P) _____ mm Hg

Calibrator Position	Sampler Response I	Corrected Response IC Y-Axis	ΔP (in. H_2O)	Qa X-Axis

I = Instrument Reading b= _____

IC = $I(Pa/Pstd \times Tstd/Ta)^{1/2}$ m= _____

ΔH = Water Manometer Reading r= _____

Qa = Flow from Orifice Calibration Curve

SFR = _____ m^3/min SFR = (1.42 x m) + b

Pre-Maintenance _____ Post-Maintenance _____

Calibrated by _____

[32-34191F6,51/HI-VCALI.FOR

Appendix G

TSP Field Operation Procedures

1.0 TSP FIELD OPERATING PROCEDURES

The sampling procedures used in this network are in accordance with those found in the Federal Reference Method for the Determination of Total Suspended Particulate Matter in the atmosphere.

1.1 Sampling Operations

The procedure for TSP sampling is as follows:

1. Remove a clean filter from the bag and inspect it for holes, tears or any other irregularities. If any of these are found, discard filter and select another.

2. Fill out the top portion of the TSP Field Data Sheet (Figure G-1) and enter the sampling date and the site I.D. on the particulate Sample Data Sheet that is enclosed with the filter.

3. Record the sampling date, sampler I.D., site I.D., date started and time started on the manila folder.

4. Record the sampling date, sampler I.D., site I.D., and filter number on the back side of the flow recorder chart.

5. Record initial counter reading.

6. Load the filter cartridge with standard filter.

    a. Loosen the four nuts that clamp the cartridge together and remove the upper portion of the filter cartridge.

    b. Inspect the filter cartridge screen for deposits for foreign material. Clean if necessary. Ensure that the cartridge gasket is not damaged or compressed.

c. Center the filter on the cartridge support screen.

d. Replace the top cover and tighten the nuts.

e. If the cartridge is equipped with a protective, snap-on screen cover the cartridge.

7. Transport the monitoring equipment to the sampler location.

8. Raise the sampler inlet and inspect the sampler's filter screen and remove any deposits or foreign matter.

9. Inspect the filter holder sealing gasket located beneath the filter screen for compression or damage. Replace, if necessary.

10. Remove the filter cartridge protective cover and center the cartridge on the sampler's filter screen. Tighten the four swing bolts.

11. Open the shelter door and the flow event recorder. Install the annotated recorder chart. Set the chart at 12 midnight.

12. Make sure that the flow recorder is connected to the motor housing pressure tap and it is properly zeroed (the pen rests on the innermost circle of the chart). Adjust the zero by rotating the small set screw located on the bottom right of the recorder.

13. Energize the sampler. Ensure that the recorder pen is inking and indicates that the sampler is operating at its correct set-point.

    Allow the sampler to operate for three to five minutes. If necessary, adjust the potentiometer on the MFC until the correct set-point is indicated.

14. Turn off the sampler and close the recorder and shelter doors. Lower the sampler roof. Set timer to activate the sampler on the next scheduled run day.

1.2 Post-Sampling Procedures

After the 24-hour sample has been taken, the site technician must:

1. Remove the filter cartridge by reversing the installation procedures. Replace the snap-on cover.

2. Open the shelter and recorder doors. Remove and examine the recorder chart. The trace should be stable without peaks or interruptions. Irregularities may result from:

   - Power failure or fluctuations.
   - Pen failure.
   - Motor brush failure.

3. Complete the Field Data sheet. Record any unusual weather or site conditions that may have affected the sample.

   Record:

   - Sample stop time (24-hour clock basis).
   - Total elapsed sampling time (minutes).
   - Seasonal or ambient temperature (Ts or Ta, °F).
   - Seasonal or ambient pressure (Ps or Pa, mmHg).
   - Final counter reading.

4. Transport the filter cartridge to a protected area.

5. Carefully remove the filter from the cartridge. Handle the filter only by the edges to avoid disturbing any of the deposit. Remove insects loosely attached to the filter with a pin or with Teflon^{R}-tipped tweezers. If they are embedded in the particulates, note this and do not try to remove them. Fold the filter lengthwise aligning the deposit edges (inward toward the "dirty" side) and place it

in the appropriate manila folder and resealable plastic bag. Place the Particulate Sample Data Sheet form in the same bag. Note any problems with the filter resulting from air leakage on the Field Data Sheet. Mail filters to Superior Testing Laboratories. Mail copies of the Field Data Sheets to Foth & Van Dyke in St. Louis.

1.3 Data Validation

If any of the following conditions exist, the sample should be voided in the field. "VOID" should be written in large letters in the remarks section of the Field DAta Sheet followed by the reason for voiding the sample.

Flow

If the instrument reading every indicates a flow outside the flow rate range of 40 cfm to 60 cfm for more than six hours, the sample must be voided. Corrective action should be taken.

Time

Whenever the sampling time is less than 23 hours or greater than 25 hours, or whenever the start and stop times are not within one hour of midnight, the sample must be voided.

Filter

The number on the filter must correspond to the number on the Particulate Sample Record sheet. If there is no tare mass on the sheet, the filter is invalid. Check the filter visually for defects before and after use. Look for rips, holes, and gasket leaks. Note any defects and record them on the Field Data Sheet. Physical damage to the filter after sampling does not always invalidate the sample as long as all pieces of the filter are included in the folder. However, any loss of sample due to leakages during the sampling period caused by holes or tears in the exposed portion of the filter or to

loss or loose particulates from the filter after sampling (e.g., loss of particulates when folding the filter) invalidates the sample.

FIGURE G-1
TSP FIELD DATA SHEET
Flambeau Mining Company

Operator _____ Filter No. _____

Sampler I.D. _____ Date _____ Counter Reading

Site Location _____ Time Off _____ _____

Time On _____ _____

Total Elasped Time _____ _____

Recorder Response (I) = _____

bs = _____ From most recent calibration

ms = _____ From most recent calibration

SQa = _____ = (I-bs)/ms

Qstd = _____ = SQa x (Pa/Pstd) x (Tstd/Ta)

Total Volume = _____ = Qstd x Min.

Remarks_____

_____

_____

Average Wind		Visibility		Sky		Humidity		Temp. °F		Barometric Pressure
Direction	_____	Clear	_____	Clear	_____	Dry	_____	Below 20	_____	_____inHg
Calm	_____	Hazy	_____	Scattered	_____	Moderate	_____	20 - 40	_____	
Light	_____			Overcast	_____	Humid	_____	40 - 60	_____	
Gusty	_____					Rain	_____	60 - 80	_____	
						Snow	_____	Above 80	_____	

Operator Signature _____ Date _____

Appendix H

Monitoring Plan for Asbestiform Sampling

ASBESTIFORM SAMPLING IN THE AMBIENT AIR

Flambeau Mining Company
Ladysmith, Wisconsin

Foth & Van Dyke

11970 Borman Drive, Suite 110
St. Louis, MO 63146
314/434-5700
FAX: 314/434-7071

May 30, 1991

Mr. Julian Chazin
Chief, Air Monitoring Section
Wisconsin Department of Natural Resources
101 South Webster Street
Madison WI 53707

Dear Mr. Chazin:

RE: Asbestiform Sampling at Flambeau Mining Company

Please find attached the monitoring plan for Abestiform Sampling in the Ambient Air at Flambeau Mining Company in Ladysmith, Wisconsin. This plan outlines the process to be followed for sampling during the mining phase of the project. The procedures and schedule we had agreed to during our previous meeting of April 5, 1991, and telephone conversation of May 3, 1991, are presented in this plan.

Please review the proposed plan and return comments to me so that Foth & Van Dyke on behalf of Flambeau may initiate the plan. If you have questions or comments, please address them to me at the above address or phone number.

Sincerely,

Christa D. Andrew

Christa Andrew
Chemical Engineer

CDA/jmk

Attachment

91F6
CHAZDEPT.LET

MONITORING PLAN FOR ASBESTIFORM SAMPLING IN THE AMBIENT AIR 91F6

Prepared for:

Flambeau Mining Company
105 West Lake Avenue
Ladysmith, WI 54848

Prepared by:

Foth & Van Dyke and Associates, Inc.
11970 Borman Drive
Suite 110
St. Louis, Missouri 63146

MAY, 1991

Foth & Van Dyke
11970 Borman Drive, Suite 110
St. Louis, Missouri 63146
314/434-5700
FAX: 314/434-7071

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SECTION 1.0

INTRODUCTION

1.0 INTRODUCTION

Flambeau Mining Company, located in Ladysmith, Wisconsin, has been required by the Wisconsin Department of Natural Resources (DNR) to monitor for asbestiform fibers for one month during each 12 month period for the first three years or throughout the operating life of the mine if found necessary. Pursuant to the approved Mining Permit Conditions, Part 4, Section 5, this monitoring plan is submitted for approval by the Wisconsin Department of Natural Resource's air monitoring section. Contained herein are methodologies for asbestiform fiber sample collection and analyses and descriptions of sampling equipment. The sampling schedule and locations are also presented.

SECTION 2.0

OVERVIEW

2.0 OVERVIEW

2.1 Sampling

Samples will be collected at three sites around the mine. Each sample will be collected over an eight hour sampling period per sampling event. A measured volume of air will be drawn through a 25 mm diameter, 0.8 um pore size mixed cellulose ester (MCE) membrane filter. A high volume pump, equipped with a critical orifice to maintain a controlled flow rate, will be employed at each site to collect the required samples.

2.2 Analytical

The MCE filters will be analyzed first by phase contrast microscopy (PCM) in order to screen out samples with small amounts of asbestiform fiber on them. Transmission electron microscopy (TEM) will be used to analyze filters with a concentration of greater than or equal to 0.01 fibers per cubic centimeter (f/cc) as analyzed by PCM. When the concentration is less than 0.01 f/cc, only the filter from the downwind site with the highest fiber concentration will be analyzed by TEM.

A concentration of 0.01 f/cc was selected as the level at which TEM will be performed because it is the limit for reliable quantification by PCM. It was also selected because this is the level at which asbestos removal contractors are released following an abatement action as specified by the Quality Assurance Division of the USEPA.

SECTION 3.0

AIR SAMPLING PROCEDURES

3.0 AIR SAMPLING PROCEDURES

3.1 Sampling Locations and Schedule

Asbestiform samples will be collected at three of the sites where total suspended particulate samples will also be collected. These are the northeast, northwest (Blackberry Lane) and southeast sites as shown on Figure 3-1.

Samples will be collected one day a month during the period May through September for a total of five samples per year. One sample will be coordinated with a blasting day at the mine or during another significant material handling procedure. This monitoring will be conducted only once if no asbestiform fibers are detected. The remaining samples will be collected according to the commonly employed national sampling schedule.

Each monitoring event will be conducted over an eight hour duration coincident with the normal daily operating schedule of the mine. Two samples will be collected at each site, one at a low flow rate and the other at a high flow rate. Two flow rates will be used in order to prevent voiding a sampling event due to overloaded or underloaded samples.

Monitoring shall begin when the mining phase begins and shall be repeated annually. If monitoring during the first three years of active mining does not detect asbestiform fibers from the mining operations, monitoring will be discontinued.

3.2 Sampling Equipment

In the sampling process, air is drawn through a filter at a known rate by a flow-controlled pump. The sampling components are described below.

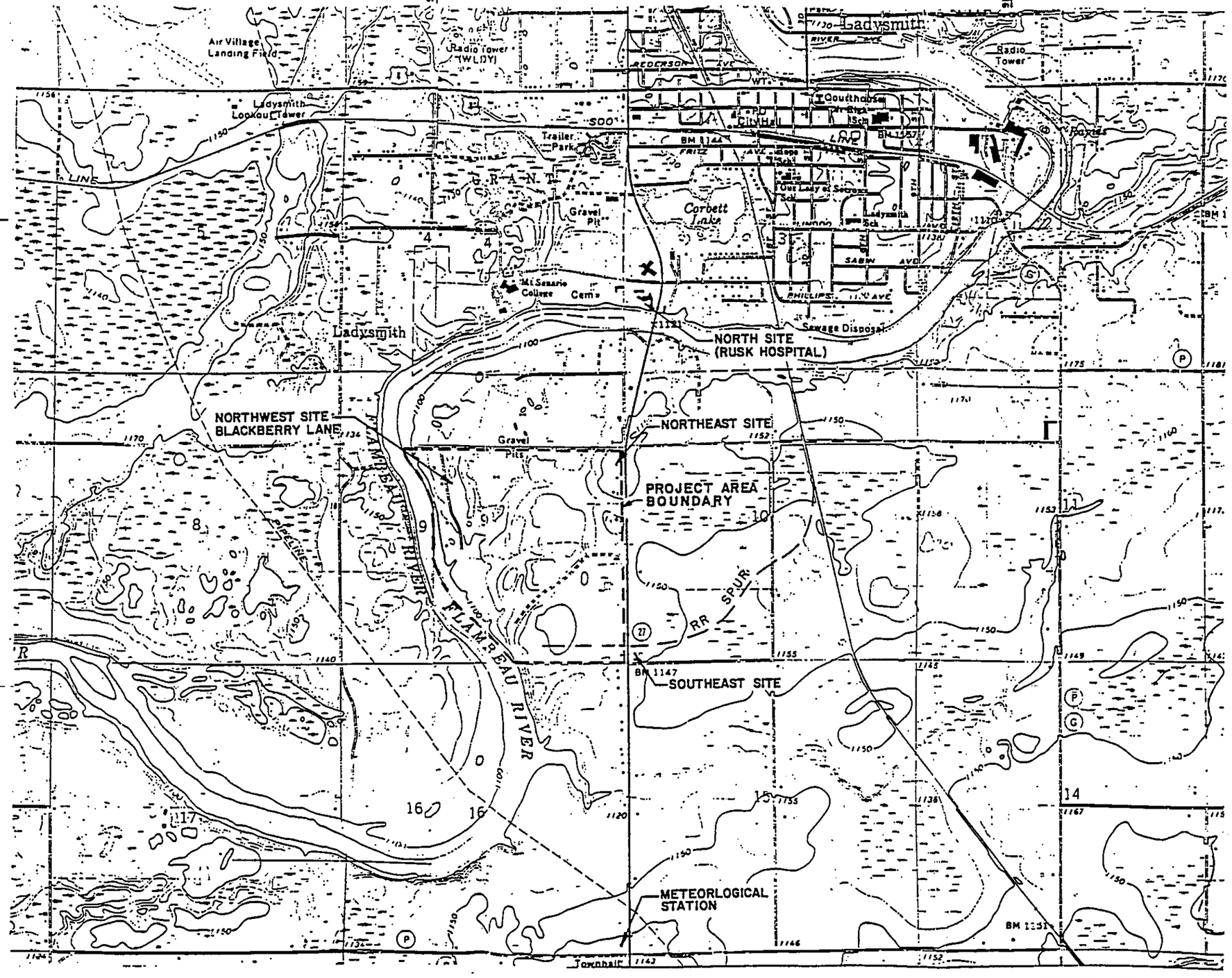
3.2.1 Filter Media and Cassettes

Commercially available filters comprised of the filter media and cassettes will be used for sample collection. The cassette shall be loaded with a 25 mm diameter mixed cellulose ester filter of pore size 0.8 um. The filter shall be backed with a 5.0 mm pore size MCE filter followed by a cellulose support pad. The support pad is provided so that distortion of the filter caused by differential pressure across it does not occur during sampling. The cassettes shall be purchased with the required filters in position. The cassettes will be sealed by the manufacturer to prevent air leakage.

The movement of air through the filter may cause a significant buildup of static charge on the cassettes. The static charge, in turn, is likely to affect the distribution of fibers on the filter and may cause fibers to collect on the cassette walls rather than on the filter. To guard against static buildup, a metal cowl or electrically conductive cassette shall be used in conjunction with the sampling train.

3.2.2 Sampling Pump

The sampling pump shall be capable of achieving flow rates of 2-12 liters per minute (lpm) and of pumping over an eight hour duration. A typical pump and sampling train is shown in Figure 3-2. Flexible tubing shall be used to connect the filter cassette to the sampling pump. The sampling pump shall provide a non-fluctuating air-flow through the filter, and shall maintain the initial flow rate to within ±10% throughout the sampling period. A



NOTE: BASE MAP PREPARED FROM U.S.G.S. MAPS 7.5 MINUTE SERIES, LADYSMITH AND THORNAPPLE WISCONSIN QUADRANGLES

H11 4

DWG. NO.	DESCRIPTION

REFERENCES

DWG. NO.	DESCRIPTION

NO.	DATE	REVISIONS	BY	CHK'D	DWG'D	CHK'D BY

NO.	DATE	REVISIONS	BY	CHK'D	DWG'D	CHK'D BY

	BY	DATE
FINAL CHK'D		
WORK PACKAGE MGR		
CHK'D WOR		

	BY	DATE
DESIGN		
DRAWN	SJL	2/89
CHK'D	GWS	3/89
DES. ENGR		
SECT CHIEF		

FOTH & VAN DYKE
GEOSCIENCES & ENVIRONMENTAL MANAGEMENT DIVISION
GREEN BAY, WISCONSIN

FLAMBEAU PROJECT
LADYSMITH, WISCONSIN

KENNECOTT MINERALS COMPANY
1515 MINERAL SQUARE
SALT LAKE CITY, UTAH 84112

FIGURE 3-1
ASBESTIFORM SITES AND TSP SAMPLING

MICROFILM | JOB
DRAWING NO. | REV.
DIVISION DRAWING NO.
SCALE 1" = 2000'

critical orifice will be used to meet this requirement. Because slight changes in size and shape of the orifice (due to wear or accumulation of particles) will change the orifice characteristics, orifices shall be inspected during each sampling event.

3.2.3 Rotameter

A high quality rotameter with arbitrary unit graduations shall be used to monitor the sample flow rate through the sampling apparatus. The flow measuring device shall be inserted downstream of the filter and the pump assembly. The rotameter shall be accurate to ±5% of the expected sampling flow rate. The rotameter shall be calibrated before and after each sampling event against a NBS traceable primary flow standard with an accuracy of ±1%.

3.3 Sampling Procedures

3.3.1 Air Volume

The sampling rate and the period of sampling shall be selected to yield as high a sampled volume as possible. Two samples will be collected over an eight hour period; one at 3-4 lpm and the other at 6-8 lpm in order to collect an optimum volume of air per unit area of filter. This will minimize the potential that filters will have to be rejected for analysis due to overloading or underloading.

3.3.2 Sampling Operation

Before air samples are collected, unused filters shall be analyzed to determine the mean background asbestos structure count for the analytical procedure. Air samples shall be collected using the cassettes described in Section 3.2.1. Each cassette assembly will be visually checked for leaks both before and after each sampling event.

Sampling shall be conducted with the cassette open-face. During sampling, the filter cassette shall be supported on a stand so that it is isolated from the vibrations of the pump. The cassette shall be held facing vertically downward at a height of approximately 2.1 meters above ground level and connected to the pump with a flexible tube. It may be sufficient to collect samples with a standard cassette configuration. If conditions dictate the need for additional protection, however, an extension cowl may be affixed to the front of the cassette.

The sampling pumps will be calibrated with a loaded cassette in line. A rotameter which has been calibrated against a primary standard will be inserted downstream of the filter and the pump assembly. Once the sampling equipment is in place, as shown in Figure 3-2, and has been calibrated, the sampling site location, start time, filter number, pump number and other pertinent information will be recorded. The pump will be started and the flow rate recorded. Flow will be verified after 15-30 minutes of sampling. The critical orifice should maintain the set flow rate. The rate will be verified at least every 2 hours. If at any time the measurement indicates that the flow rate has decreased by more than 30%, the sampling will be terminated. The mean value of these flow rate measurements will be used to calculate the total air volume sampled.

At the end of each sampling event, the final flow rate and the stop time will be recorded. A cap will be placed over the open end of the cassette, and the cassette will be packed in a

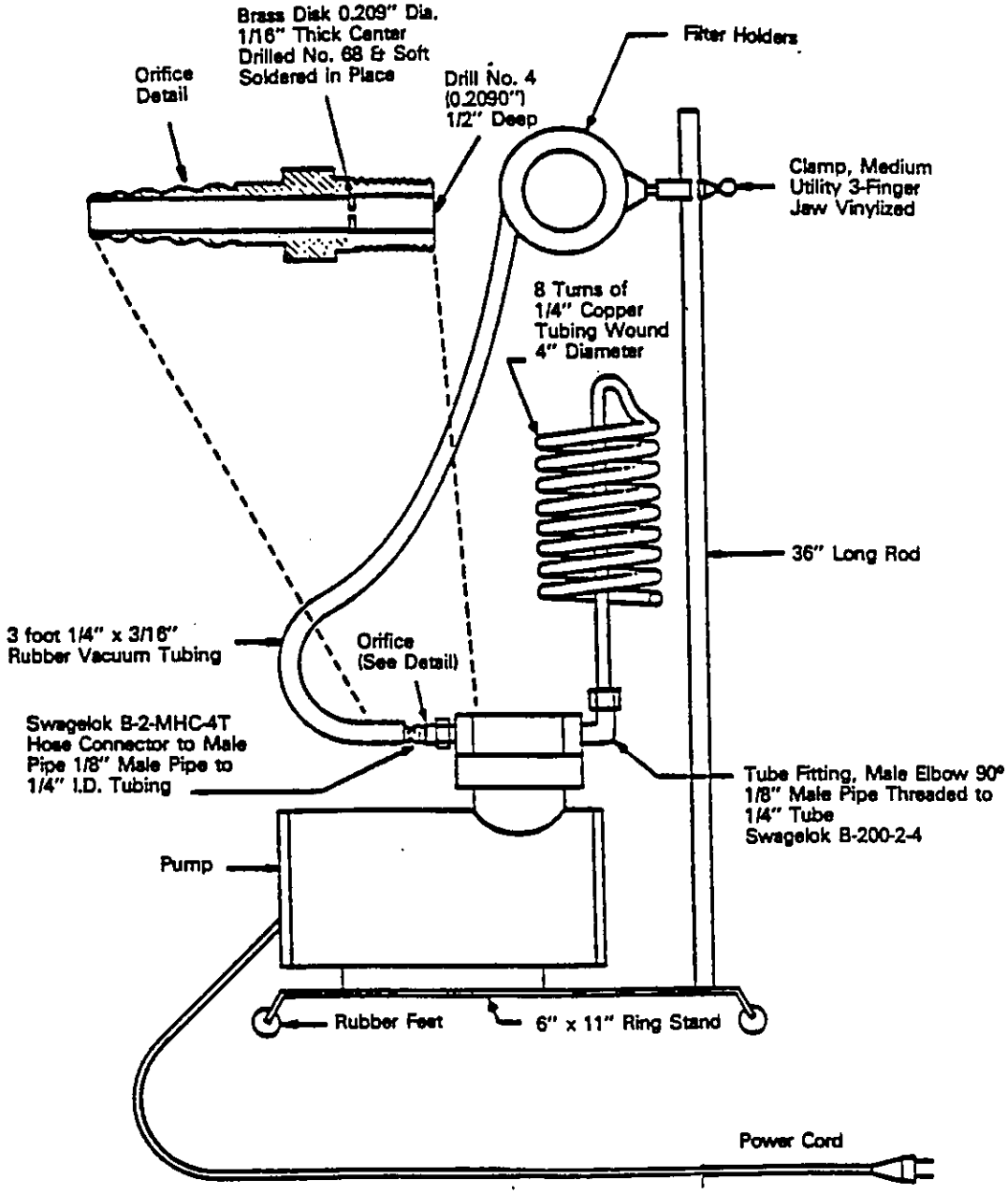


FIGURE 3-2		
ASBESTIFORM SAMPLING TRAIN Flambeau Mining Company Ladysmith, Wisconsin		
SCALE: N/A	DATE: May, 1991	
PREPARED BY: FOTH & VAN DYKE	BY:	

clean plastic bag for return to the laboratory. Field blank filters will also be included in the shipment to the laboratory, as described in Section 5.2, and will be processed through the remaining analytical procedures along with the samples.

SECTION 4.0

ANALYTICAL PROCEDURES

4.0 ANALYTICAL PROCEDURE

As previously discussed, samples will first be screened by PCM. Filters from the downwind site which have a concentration of 0.01 fibers per cubic centimeter (f/cc) as detected by PCM will be further analyzed by TEM as a confirmatory analysis. This analysis will be performed because PCM does not differentiate between asbestos and other fibers. Any particle meeting the counting criteria will be counted. When the results for all filters indicate concentrations of less than 0.01 f/cc, the sample with the highest concentration from the downwind site will be analyzed by TEM. The PCM analytical method will be based on NIOSH Method 7400. A copy of this method is presented in Appendix A. The equipment used, and the sample preparation, calibration, quality control and measurement procedures and calculations are described in the method. The TEM method is taken from USEPA document No. EPA-600/2-77-178, "Electron Microscope Measurement of Airborne Asbestos Concentrations, A Provisional Methodology Manual". Excerpts from this USEPA manual are provided in Appendix B.

SECTION 5.0

QUALITY CONTROL

5.0 QUALITY CONTROL

Reliable results can be obtained only if the collection, transfer, handling and analysis of the filters, and collection and documentation of the data follow specified procedures. The following discussion presents the key elements of a comprehensive QC program.

5.1 Training

Everyone involved with measuring airborne asbestos (field technicians, microscopists, etc.) will be properly trained in applicable procedures. Only trained analytical laboratories will be hired. If possible, the laboratories will participate in NIOSH's Proficiency Analytical Testing Program. The laboratories will provide information on:

. The laboratory's quality control program;
. The lowest fiber counts in f/cc that are routinely reported;
. The thinnest fibers that are routinely detected.

5.2 Blanks

Before air samples are collected, a minimum of two unused MCE filters from each lot of 100 filters shall be sectioned and analyzed by PCM to determine the mean background asbestos structure concentration. If the mean concentration for all types of asbestos structures, expressed as the concentration per unit area of the sample collection filter, is found to be more than 7 structures/mm^2, the reasons for the high blank values will be determined and the situation corrected before scheduled air samples are collected.

To ensure that contamination by extraneous asbestos structures during specimen preparation is insignificant compared with the results reported on samples, it is essential that a continuous program of blank measurements be established. The number of field blanks incorporated into the program will be at least 10% of the total number of samples collected. All of these field blanks will be analyzed. The caps from the field blank cassettes will be removed and then the caps and cassettes will be stored in a clean area (bag or box) during each sampling event. The caps on the blank cassettes will be replaced when the sampling event is completed.

It is further recommended that laboratory blanks be collected intermittently at all critical phases of the laboratory program. The mean of the field blank counts and laboratory blank counts will be calculated and these values will be subtracted from each sample count before reporting the results.

5.3 Analytical Checks

Since there is a subjective component in the structure counting procedure, it is necessary that re-counts of some specimens be made by different microscopists in order to minimize the subjective effects. Such recounts provide a means of maintaining comparability between counts made by different microscopists. Variability between microscopists will be characterized. These quality assurance measurements will be made for a minimum of approximately 10% of all scheduled analyses. Repeat results shall not differ by more than 5%. If they do, appropriate action, e.g., reanalysis, retraining, equipment inspection, etc., will be taken.

5.4 Sample Transport and Chain-of-Custody

After collecting each sample, precaution must be taken to ensure its integrity and prevent contamination until it is analyzed. The plastic top cover and small end caps will be replaced on the monitor immediately after sampling. Collected samples will be shipped in a rigid container with sufficient packing material to prevent damage. Each step in the transfer of the samples from the field to the laboratory will be recorded on a chain-of-custody form. An example of the Chain-of-Custody Form is presented in Figure 5-1.

CHAIN OF CUSTODY

Client: _____ Scope I.D.: _____
Project: _____ Page: _____
Prepared by: _____ Date: _____
Sampler(s): _____ Date: _____
(Signature)

Sta. No.	Date	Time	Comp	Grab	Station Location	Serial Tag Number	No. of Con-tain-ers	Lab Numbers	Analysis Required	Remarks

Signature	Company	Date	Time	Carrier
Relinquished By:				
Received By:				
Relinquished By:				
Received By:				
Relinquished By:				
Received by Lab:				

Foth & Van Dyke

Remarks:

H20
11

FIGURE 5-1
CHAIN-OF-CUSTODY

Flambeau Mining Company
Ladysmith, Wisconsin

SCALE: N/A | DATE: May, 1991
PREPARED BY: FOTH & VAN DYKE | BY:

APPENDIX A

NIOSH METHOD 7400 - FIBERS

FIBERS

FORMULA: various

M.W.: various

METHOD: 7400
ISSUED: 2/15/84

OSHA: 0.5 asbestos fibers (> 5 μm long)/mL
NIOSH: 0.1 asbestos f/mL [1]; 3 glass fibers (>10 μm x <3.5 μm)/mL [2]
ACGIH: 0.2 crocidolite; 0.5 amosite; 2 chrysotile and other asbestos, f/mL

PROPERTIES: solid, fibrous

SYNONYMS: asbestos (actinolite [CAS #13768-00-8], grunerite (amosite) [CAS #12172-73-5], anthophyllite [CAS #17068-78-9], chrysotile [CAS #12001-29-5], crocidolite [CAS #12001-28-4], tremolite [CAS #14567-73-8]); fibrous glass.

SAMPLING

SAMPLER: FILTER
(0.8-1.2 μm cellulose ester membrane, 25-mm diameter)

FLOW RATE*: ≥ 0.5 L/min

VOL-MIN*: 400 L @ 0.1 fiber/mL
-MAX*: 1920 L @ 0.1 fiber/mL
*Adjust for 100 to 1300 fibers/mm² (step 4)

SHIPMENT: routine

SAMPLE STABILITY: indefinite

BLANKS: 10% of samples (minimum 2) [3]

ACCURACY

RANGE STUDIED: 80 to 100 fibers counted

BIAS: see EVALUATION OF METHOD

OVERALL PRECISION (s_r): 0.115 to 0.13 [3] (A Rules)

MEASUREMENT

TECHNIQUE: MICROSCOPY, PHASE CONTRAST

ANALYTE: fibers (manual count)

SAMPLE PREPARATION: acetone/triacetin method

COUNTING RULES: Set A (P&CAM 239 [3,4]) or Set B (modified_CRS [5])

EQUIPMENT: 1. phase-contrast microscope
2. Walton-Beckett graticule (100 μm field diameter): A Rules use G-22; B Rules use Type G-24
3. phase-shift test slide (HSE/NPL)

CALIBRATION: phase-shift detection limit about 3 degrees [7]

RANGE: 100 to 1300 fibers/mm² filter area [5]

ESTIMATED LOD: 7 fibers/mm² filter area

PRECISION: 0.10 to 0.12 [3] (A Rules)

APPLICABILITY: The working range is 0.02 fiber/mL (1920-L air sample) to 1.25 fibers/mL (400-L air sample). The method gives an index of airborne asbestos fibers but may be used for other materials such as fibrous glass by inserting suitable parameters into the counting rules. The method does not differentiate between asbestos and other fibers. Asbestos fibers less than ca. 0.25 μm diameter will not be detected by this method [7].

INTERFERENCES: Any other airborne fiber may interfere since all particles meeting the counting criteria are counted. Chain-like particles may appear fibrous. High levels of non-fibrous dust particles may obscure fibers in the field of view and raise the detection limit.

OTHER METHODS: This method introduces changes for improved sensitivity and reproducibility and replaces P&CAM 239 [3,4].

REAGENTS:

1. Acetone.*
2. Triacetin (glycerol triacetate), reagent grade.

*See Special Precautions.

EQUIPMENT:

1. Sampler: field monitor, 25 mm, three-piece cassette with 50-mm extension cowl with cellulose ester filter, 0.8 to 1.2-μm pore size and backup pad.
   NOTE: Analyze representative filters for fiber background before use and discard the filter lot if more than 5 fibers/100 fields are found.
2. Personal sampling pump, ≥ 0.5 L/min (see step 4 for flow rate), with flexible connecting tubing.
3. Microscope, phase contrast, with green or blue filter, 8 to 10X eyepiece, and 40 to 45X phase objective (total magnification ca. 400X); numerical aperture = 0.65 to 0.75.
4. Slides, glass, single-frosted, pre-cleaned, 25 x 75 mm.
5. Cover slips, 25 x 25 mm, no. 1-1/2, unless otherwise specified by microscope manufacturer.
6. Knife, #10 surgical steel, curved blade.
7. Tweezers.
8. Flask, Guth-type, insulated neck, 250 to 500 mL (with single-holed rubber stopper and elbow-jointed glass tubing, 16 to 22 cm long).
9. Hotplate, spark-free, stirring type; heating mantle; or infrared lamp and magnetic stirrer.
10. Syringe, hypodermic, with 22-gauge needle.
11. Graticule, Walton-Beckett type with 100 μm diameter circular field at the specimen plane (area = 0.00785 mm^2) (Type G-22 for A Rules; Type G-24 for B Rules). Available from Graticules Ltd., Morley Road, Tonbridge TN9 1RN, Kent, England (Telephone 011-44-732-359061).
    NOTE: The graticule is custom-made for each microscope. Specify disc diameter needed to fit exactly the ocular of the microscope and the diameter (mm) of the circular counting area (see step 11).
12. HSE/NPL phase contrast test slide, Mark II. Available from PTR Optics Ltd., 145 Newton Street, Waltham, MA 02154 (Telephone (617) 891-6000).
13. Telescope, ocular phase-ring centering.
14. Stage micrometer (0.01 mm divisions).

SPECIAL PRECAUTIONS: Acetone is an extremely flammable liquid and precautions must be taken not to ignite it. Heating of acetone must be done in a ventilated laboratory fume hood using a flameless, spark-free heat source.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line [3].
2. Fasten the sampler to the worker's lapel as close as possible to the worker's mouth. Remove the top cover from the end of the cowl extension (open face) and orient face down. Wrap the joint between the extender and monitor body with shrink tape to prevent air leaks.

3. Submit at least two field blanks (or 10% of the total samples, whichever is greater) for each set of samples. Remove the caps from the field blank cassettes and store the caps and cassettes in a clean area (bag or box) during the sampling period. Replace the caps in the cassettes when sampling is completed.
4. Sample at 0.5 L/min or greater [8]. Do not exceed 1 mg total dust loading on the filter. Adjust sampling flow rate, Q (L/min), and time to produce a fiber density, E (fibers/mm^2), of 100 to 1300 fibers/mm^2 [3.85 • 10^4 to 5 • 10^5 fibers per 25-mm filter with effective collection area (A_c= 385 mm^2)] for optimum counting precision (see step 21). Calculate the minimum sampling time, t_{min} (min), at the action level (one-half the current standard), L (fibers/mL), of the fibrous aerosol being sampled:

$$t_{min} = \frac{(A_c)(E)}{(Q)(L)10^3}.$$

5. Remove the field monitor at the end of sampling, replace the plastic top cover and small end caps, and store the monitor.
6. Ship the samples in a rigid container with sufficient packing material to prevent jostling or damage.

   NOTE: Do not use polystyrene foam in the shipping container because of electrostatic forces which may cause fiber loss from the sampler filter.

SAMPLE PREPARATION:

NOTE: The object is to produce samples with a smooth (non-grainy) background in a medium with a refractive index equal to or less than 1.46. The method below collapses the filter for easier focusing and produces permanent mounts which are useful for quality control and interlaboratory comparison. Other mounting techniques meeting the above criteria may also be used (e.g., the non-permanent field mounting technique used in P&CAM 239 [1,3,4]).

7. Ensure that the glass slides and cover slips are free of dust and fibers.
8. Place 40 to 60 mL of acetone into a Guth-type flask. Stopper the flask with a single-hole rubber stopper through which a glass tube extends 5 to 8 cm into the flask. The portion of the glass tube which exits the top of the stopper (8 to 10 cm) is bent downward in an elbow which makes an angle of 20 to 30° with the horizontal.
9. Place the flask on a stirring hotplate or wrap in a heating mantle. Heat the acetone gradually to its boiling temperature (ca. 58 °C).

   CAUTION: The acetone vapor must be generated in a ventilated fume hood away from all open flames and spark sources. Alternate heating methods can be used, providing no open flame or sparks are present.
10. Mount either the whole sample filter or a wedge cut from the sample filter on a clean glass slide.
    a. Cut wedges of ca. 25% of the filter area with a curved blade steel surgical knife using a rocking motion to prevent tearing.
    b. Place the filter or wedge, dust side up, on the slide. Static electricity will usually keep the filter on the slide until it is cleared.
    c. Hold the glass slide supporting the filter approximately 1 to 2 cm from the glass tube port where the acetone vapor is escaping from the heated flask. The acetone vapor stream should cause a condensation spot on the glass slide ca. 2 to 3 cm in diameter. Move the glass slide gently in the vapor stream. The filter should clear in 2 to 5 sec. If the filter curls, distorts or is otherwise rendered unusable, the vapor stream is probably not strong enough. Periodically wipe the outlet port with tissue to prevent liquid acetone dripping onto the filter.

d. Using the hypodermic syringe with a 22-gauge needle, place 1 to 2 drops of triacetin on the filter. Gently lower a clean 25-mm square cover slip down onto the filter at a slight angle to reduce the possibility of forming bubbles. If too many bubbles form or the amount of triacetin is insufficient, the cover slip may become detached within a few hours.

e. Glue the edges of the cover slip to the glass slide using a lacquer or nail polish [9].

NOTE: If clearing is slow, the slide preparation may be heated on a hotplate (surface temperature 50 °C) for 15 min to harten clearing. Counting may proceed immediately after clearing and mounting are completed.

CALIBRATION AND QUALITY CONTROL:

11. Calibration of the Walton-Beckett graticule. The diameter, d_c (mm), of the circular counting area and the disc diameter must be specified when ordering the graticule.
    a. Insert any available graticule into the eyepiece and focus so that the graticule lines are sharp and clear.
    b. Set the appropriate interpupillary distance and, if applicable, reset the binocular head adjustment so that the magnification remains constant.
    c. Install the 40 to 45X phase objective.
    d. Place a stage micrometer on the microscope object stage and focus the microscope on the graduated lines.
    e. Measure the magnified grid length, L_o (µm), using the stage micrometer.
    f. Remove the graticule from the microscope and measure its actual grid length, L_a (mm). This can best be accomplished by using a stage fitted with verniers.
    g. Calculate the circle diameter, d_c (mm), for the Walton-Beckett graticule:

$$d_c = \frac{L_a}{L_o} \times D.$$

    Example: If L_o = 108 µm, L_a = 2.93 mm and D = 100 µm, then d_c = 2.71 mm.
    h. Check the field diameter, D(acceptable range 100 µm ± 2 µm) with a stage micrometer upon receipt of the graticule from the manufacturer. Determine field area (mm^2).
12. Microscope adjustments. Follow the manufacturer's instructions and also the following:
    a. Adjust the light source for even illumination across the field of view at the condenser iris.
    NOTE: Köhler illumination is preferred, where available.
    b. Focus on the particulate material to be examined.
    c. Make sure that the field iris is in focus, centered on the sample and open only enough to fully illuminate the field of view.
    d. Use the telescope ocular supplied by the manufacturer to ensure that the phase rings (annular diaphragm and phase-shifting elements) are concentric.
13. Check the phase-shift detection limit of the microscope periodically.
    a. Remove the HSE/NPL phase-contrast test slide from its shipping container and center it under the phase objective.
    b. Bring the blocks of grooved lines into focus.
    NOTE: The slide consists of seven sets of grooves (ca. 20 grooves to each block) in descending order of visibility from sets 1 to 7. The requirements for asbestos counting are that the microscope optics must resolve the grooved lines in set 3 completely, although they may appear somewhat faint, and that the grooved lines in sets 6 and 7 must be invisible. Sets 4 and 5 must be at least partially visible but may vary slightly in visibility between microscopes. A microscope which fails to meet these requirements has either too low or too high a resolution to be used for asbestos counting.

c. If the image quality deteriorates, clean the microscope optics and if the problem persists, consult the microscope manufacturer.

14. Quality control of fiber counts.
    a. Prepare and count field blanks along with the field samples. Report the counts on each blank. Calculate the mean of the field blank counts and subtract this value from each sample count before reporting the results.
       NOTE 1: The identity of the blank filters should be unknown to the counter until all counts have been completed.
       NOTE 2: If a field blank yields fiber counts greater than 7 fibers/100 fields, report possible contamination of the samples.
    b. Perform blind recounts by the same counter on 10% of filters counted (slides relabeled by a person other than the counter).
15. Use the following test to determine whether a pair of counts on the same filter should be rejected because of possible bias. This statistic estimates the counting repeatability at the 95% confidence level. Discard the sample if the difference between the two counts exceeds 2.77 $(F)s_r$, where F = average of the two fiber counts and s_r = relative standard deviation, which should be derived by each laboratory based on historical in-house data.
    NOTE: If a pair of counts is rejected as a result of this test, recount the remaining samples in the set and test the new counts against the first counts. Discard all rejected paired counts.
16. Enroll each new counter in a training course which compares performance of counters on a variety of samples using this procedure.
    NOTE: To ensure good reproducibility, all laboratories engaged in asbestos counting should participate in an asbestos proficiency testing program such as the NIOSH Proficiency Analytical Testing (PAT) Program and routinely participate with other asbestos fiber counting laboratories in the exchange of field samples to compare performance of counters.

MEASUREMENT:

17. Place the slide on the mechanical stage of the calibrated microscope with the center of the filter under the objective lens. Focus the microscope on the plane of the filter.
18. Regularly check phase-ring alignment and Köhler illumination [7].
19. Select one of the following sets of counting rules:
    NOTE: The two sets of rules have been demonstrated to produce equivalent mean counts on a variety of asbestos sample types [5] and must be strictly followed in order to obtain valid results. No hybridizing of the two sets of rules is permitted. The calibration of the microscope with the HSE/NPL test slide determines the minimum detectable fiber diameter (ca. 0.25 µm).
    a. A Rules (same as P&CAM 239 rules [1,3,4]).
       NOTE: The A Rules are required for monitoring asbestos for compliance purposes under OSHA or NIOSH standards.
       1. Count only fibers longer than 5 µm. Measure the length of curved fibers along the curve.
       2. Count only fibers with a length-to-width ratio equal to or greater than 3:1.
       3. For fibers which cross the boundary of the graticule field, do the following:
          a. Count any fiber longer than 5 µm which lies entirely within the graticule area.
          b. Count as 1/2 fiber any fiber with only one end lying within the graticule area.
          c. Do not count any fiber which crosses the graticule boundary more than once.
          d. Reject and do not count all other fibers.

4. Count bundles of fibers as one fiber unless individual fibers can be identified by observing both ends of a fiber.
5. Count enough graticule fields to yield 100 fibers. Count a minimum of 20 fields. Stop at 100 fields regardless of fiber count.

b. B Rules

NOTE: The B Rules are preferred analytically because of their demonstrated ability to improve the reproducibility of fiber counts [5].

1. Count only ends of fibers. Each fiber must be longer than 5 µm and less than 3 µm diameter.
2. Count only ends of fibers with a length-to-width ratio equal to or greater than 5:1.
3. Count each fiber end which falls within the graticule area as one end, provided that the fiber meets rules b.1 and b.2.
4. Count visibly free ends which meet rules b.1 and b.2 when the fiber appears to be attached to another particle, regardless of the size of the other particle.
5. Count the free ends of fibers emanating from large clumps and bundles up to a maximum of 10 ends (5 fibers), provided that each segment meets rules b.1 and b.2.
6. Count enough graticule fields to yield 200 ends. Count a minimum of 20 fields. Stop at 100 fields, regardless of the fiber count.
7. Divide the total end count by 2 to yield fiber count.

NOTE: Split fibers will normally be counted as more than two ends if the free ends meet the rules b.1. and b.2.

20. Start counting from one end of the filter and progress along a radial line to the other end, shift either up or down on the filter and continue in the reverse direction [10]. Select fields randomly by looking away from the eyepiece briefly while advancing the mechanical stage. When an agglomerate covers ca. 1/6 or more of the field of view, reject the field and select another. Do not report rejected fields in the number of total fields counted.

NOTE: When counting a field, continuously scan a range of focal planes by moving the fine focus knob to detect very fine fibers which have become embedded in the filter. The small-diameter fibers will be very faint but are an important contribution to the total count.

CALCULATIONS:

21. Calculate and report fiber density on the filter, E (fibers/mm^2), by dividing the total fiber count, F, minus the mean field blank count, B, by the number of fields, n, and the field area, A_f (0.00785 mm^2 for a properly calibrated Walton-Beckett graticule):

$$E = \frac{(F - B)}{(n)(A_f)}, \text{ fibers/mm}^2.$$

22. Calculate the concentration, C (fibers/mL), of fibers in the air volume sampled, V (L), using the effective collection area of the filter, A_c (385 mm^2 for a 25-mm filter):

$$C = \frac{(E)(A_c)}{V \cdot 10^3}$$

NOTE: Periodically check and adjust the value of A_c, if necessary.

EVALUATION OF METHOD:

This method is a revision of NIOSH Method P&CAM 239 [1,3,4]. A summary of the revisions is as follows:

A. Sampling

The change from a 37-mm to a 25-mm filter size was incorporated to improve sensitivity and reduce problems associated with non-uniform fiber loading reported on the 37-mm filters [10]. The change in flow rates allows for 2 m^3 full-shift samples to be taken, providing that the filter is not overloaded with non-fibrous particulates. The collection efficiency of the sampler is not affected by changes in flow rate in the range 0.5 to 16 L/min [8].

B. Sample Preparation Technique

The acetone vapor-triacetin preparation technique has been incorporated in the method as a faster, more permanent mounting technique than the dimethyl phthalate/diethyl oxalate method of P&CAM 239 [1,3,4,11].

C. Measurement

1. The inclusion of the Walton-Beckett graticule in the method was made to standardize the field area observed through the eyepiece [6,11].
2. The introduction of the HSE/NPL test slide was made to standardize microscope optics for sensitivity to fiber diameter [7,11].
3. A recent international collaborative study involved 16 laboratories using prepared slides from the asbestos, cement, milling, mining, textile, and friction material industries [5]. The relative levels of count by different counting rules were:

Sample Type	Number of Samples	Aspect Ratio > 3:1		Aspect Ratio > 5:1	
		AIA	Mod. CRS*	AIA	Mod. CRS*
Mining	10	100	127	74	92
Milling	10	100	112	84	95
Asbestos Cement	14	100	146	90	137
Textile Chrysotile	10	100	109	89	99
Friction Material	10	100	130	87	116
Others (Insulation, Amosite)	6	100	127	92	118
TOTAL: 60	MEAN:	100	125	86	110

*Arithmetic means of counts made by different laboratories relative to the AIA counts.

The modified CRS (NIOSH B) Rules were found to be more precise than the AIA (NIOSH A)* Rules. The ranges of relative standard deviations (s_r) which varied with sample type and laboratory were:

	s_r		
	Intralaboratory	Interlaboratory	Overall
AIA (NIOSH A Rules)*	0.12 to 0.40	0.27 to 0.85	0.46
Modified CRS (NIOSH B Rules)	0.11 to 0.29	0.20 to 0.35	0.25

*Under AIA rules, only fibers having a diameter less than 3 μm are counted and fibers attached to particles larger than 3 μm are not counted. NIOSH A Rules are otherwise similar to the AIA rules.

The B Rules have also been favorably received by analysts as less ambiguous and simpler to use; these rules also showed the least bias relative to AIA rules in the collaborative study. An independent NIOSH laboratory study using amosite fibers reported a relative standard deviation, including within- and between-sample

variability, of 0.157 for the B Rules [12]. Adding an estimated sampling pump error, s_r, of 0.05 [13] to the within-sample variability in this study results in an estimate of overall precision, s_r, of 0.102 for the B Rules.

4. Because of past inaccuracies associated with low fiber counts, the minimum loading has been increased to 100 fibers/mm^2 filter area (80 fibers total count). This level yields an overall $s_r = 0.13$, as indicated in Figure 3 (revised) of P&CAM 239 [3,4] which corresponds to a measurement $s_r = 0.12$ after removal of pump error [13]. Similarly, at the maximum count of 100 fibers, overall $s_r = 0.115$ and measurement $s_r = 0.10$ are obtained.

D. Evaluation of the method using the A and B counting rules will proceed on a continuing basis through the NIOSH Proficiency Analytical Testing (PAT) Program. The new PAT reporting form allows for reporting of results by either set of rules as of January, 1984.

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METHOD REVISED BY: James W. Carter, David G. Taylor, Ph.D., CIH, and Paul A. Baron, Ph.D., NIOSH/DPSE; based on the revised Method P&CAM 239 [1,3,4].

APPENDIX B

ELECTRON MICROSCOPE MEASUREMENT OF AIRBORNE ASBESTOS CONCENTRATIONS

U.S. DEPARTMENT OF COMMERCE
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PB-285 945

Electron Microscope Measurement of Airborne Asbestos Concentrations A Provisional Methodology Manual

IIT Research Inst, Chicago, IL

Prepared for

Environmental Sciences Research Lab, Research Triangle Park, NC

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ELECTRON MICROSCOPE MEASUREMENT OF AIRBORNE ASBESTOS CONCENTRATIONS

A Provisional Methodology Manual

H32 ...

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16. ABSTRACT

This manual describes a provisional optimum electron microscope (EM) procedure for measuring the concentration of asbestos in air samples. The main features of the method include depositing an air sample on a polycarbonate membrane filter, examining an EM grid specimen in a transmission electron microscope (TEM), and verifying fiber identity by selected area electron diffraction (SAED).

This provisional manual results from a study to develop an optimum EM procedure for airborne asbestos determination. The analytical data supporting the provisional methodology are included in a separate final report.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
*Air pollution *Asbestos *Serpentine *Amphiboles Measurement *Electron microscopy *Electron diffraction	Chrysotile	13B 08G 11E 14B

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FOREWARD

Asbestos or asbestiform minerals include several types or groups of fibrous crystalline substances with special thermal and electrical properties that have long encouraged their use in the manufacture of such products as roofing, insulation, brake linings, fireproof curtains, etc. Their occurrence as pollutants in the ambient air and in supplies of food and drinking water has caused considerable concern because occupational exposures to asbestos have been found to induce mesothelioma of the pleura and peritoneum, as well as cancer of the lung, esophagus, and stomach, after latent periods of about 20 to 40 years.

Electron microscopy is currently the principal technique used to identify and characterize asbestos fibers in ambient air and water samples. Because of the poor sensitivity and specificity of conventional bulk analytical methods, electron microscopy is also being used for routine measurement of airborne or waterborne asbestos concentrations. The several laboratories that perform such analyses generally have reasonable internal self consistency. However, interlaboratory comparisons have shown that the results obtained by the separate laboratories are often widely different.

This manual describes a <u>provisional</u> optimum electron microscope procedure for measuring the concentration of asbestos in air samples. It results from a study, carried out under EPA Contract No. 68-02-2251, to evaluate the various methods currently in use in the various laboratories. Statistical analysis was used to evaluate the effects of the many interacting sub-procedures and arrive at an optimum composite procedure.

This manual does not provide the vast amount of data that supports the provisional methodology. These data are included in the final report on EPA Contract No. 68-02-2251.

Jack Wagman
Project Officer

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ELECTRON MICROSCOPE MEASUREMENT OF AIRBORNE ASBESTOS CONCENTRATIONS

A Provisional Methodology Manual

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ABSTRACT

This manual describes a provisional optimum electron microscope (EM) procedure for measuring the concentration of asbestos* fibers** in air samples. The main features of the method include depositing an air sample on a polycarbonate membrane filter, examining an EM grid specimen in a transmission electron microscope (TEM), and verifying fiber identity by selected area electron diffraction (SAED).

This provisional manual results from a study to develop an optimum EM procedure for airborne asbestos determination. The analytical data supporting the provisional methodology are included in a separate final report.

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* Asbestos is used as a collective term for the six minerals: chrysotile, amosite, crocidolite, and the asbestiform varieties of anthophyllite, actinolite and tremolite.

** The term fiber is used for a particle with an aspect ratio 3:1 or greater and with substantially parallel sides.

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ELECTRON MICROSCOPE MEASUREMENT OF AIRBORNE ASBESTOS CONCENTRATIONS

A Provisional Methodology Manual

1. PROVISIONAL METHODOLOGY - SUMMARY

(1) Take an air sample on a polycarbonate membrane filter, 0.4 um, using a high-volume or personal sampler.

(2) Coat the filter with a 40 nm thick film of carbon using a vacuum evaporator.

(3) Transfer the deposit from the polycarbonate filter to an electron microscope grid using a modified Jaffe washer. The Jaffe washer is prepared as follows. A 60 or 100 mesh stainless steel mesh is placed on top of a paper filter stack or foam sponge contained in a petri dish. Chloroform is carefully poured into the petri dish until the level is just touching the stainless steel mesh. A 1 mm x 2 mm portion of carbon coated polycarbonate filter is placed particle side down on a 200 mesh carbon coated copper electron microscope (EM) grid and this pair is placed on the steel mesh. The 1 mm x 2 mm portion is wetted with a 5 ul drop of chloroform. The polycarbonate filter will dissolve in about 24 to 48 hours.

(4) Examine the EM grid under low magnification in the TEM to determine its suitability for high-magnification examination. Ascertain that the loading is suitable and is uniform, that a high number of grid openings have their carbon film intact, and that the sample is not contaminated.

(5) Systematically scan the EM grid at a magnification of about 20,000X (screen magnification 16,000X) for chrysotile and possibly a lower magnification for cases where predominant amphibole fibers are present. Record the length and breadth of all fibers that have an aspect ratio of greater than 3:1 and have substantially parallel sides. Observe the morphology of each fiber through the 10X binocular and note whether a

tubular structure characteristic of chrysotile asbestos is present. Switch into SAED mode and observe the diffraction pattern. Note whether the pattern is typical of chrysotile or amphibole, or whether it is ambiguous or neither chrysotile nor amphibole.

(6) Count 100 fibers in several grid openings, or alternatively, count all fibers in at least 10 grid openings. If more than 300 fibers are observed in one grid opening, then a more lightly loaded filter sample should be used. If no other filter sample can be obtained, the available sample should be transferred onto a 400 mesh grid. Processing of the sample using ashing and sonification techniques should be avoided wherever possible.

(7) Fiber number concentration is calculated from the following equations

$$\text{Fibers/m}^3 = \frac{\text{Total No. of Fibers}}{\text{No. of EM Fields}} \cdot \frac{\text{Total Effective Filter Area, cm}^2}{\text{Area of an EM Field, cm}^2} \cdot \frac{1}{\text{Volume of Air Sampled, m}^3}$$

Fiber mass for each type of asbestos in the sample is calculated by assuming that the breadth measurement is a diameter; thus, the mass can be calculated from

$$\text{Mass } (\mu g) = \frac{\pi}{4} \cdot (\text{length, } \mu m) \cdot (\text{diameter, } \mu m)^2 \cdot (\text{density, g/cm}^3) \cdot 10^{-6}$$

The density of chrysotile is assumed to be 2.6 g/cm^3, and of amphibole 3.0 g/cm^3. The mass concentration for each type of asbestos is then calculated from

$$\text{Mass Concentration } (\mu g/m^3) \text{ of a Particular Type} = \frac{\text{Total Mass of all Fibers of that Type } (\mu g)}{\text{Volume of Air Sampled } (m^3)}$$

(8) Other characterizing parameters of the asbestos fibers are:

(a) Length and width distributions of chrysotile fibers

(b) Volume distribution of chrysotile fibers

(c) Fiber concentration of other asbestos minerals

(d) Relative proportion of chrysotile fibers with respect to total number of fibers.

2. METHODOLOGY

2.1 Air Sampling

Collect the sample of airborne asbestos on 0.4 μm pore size polycarbonate filters using the shiny smooth side as the particle capture surface. In cases where polycarbonate filters cannot be used, the air sample may be collected on a high efficiency membrane filter, e.g. cellulose acetate, which can then be prepared by using an ashing procedure described in Section 2.8. Use the high-volume air sampler [1]*, or in certain instances, the personal dust sampler.[2] When 110V, 60 cycle power supply is available, a variety of other combinations of pumps and filters and other techniques can be used for air sample collection.[3-5]

2.1.1 Air Sampling Parameters

Sampling rates vary with the type and model of sampler and with the type and pore size of filter used to collect an air sample. Typically, a high-volume air sampler fitted with a 20 cm x 25 cm, 0.4 μm pore size, polycarbonate filter will have a flow rate of about 700 ℓ/min (25 cfm) at a pressure drop of 145 cm of water across the filter. By comparison, a

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* Numbers in brackets denote the literature references.

personal dust sampler, operated with a 37 mm diameter, 0.4 µm pore size, polycarbonate filter, is set, by a flow controller, to sample at a flow rate of 2 ℓ/min. The pressure drop across the filter is 20.9 cm of water.

The two types of samplers can be compared by dividing the volumetric flow rate by the effective filtration area of the filters. The high-volume sampler, with an effective filtration area of 406.5 cm^2, operates at a rate of 28.7 $cm^3/cm^2/sec$ while the personal dust sampler, with an effective filtration area* of 6.7 cm^2, operates at a rate of 5.0 $cm^3/cm^2/sec$. Thus, the filtering rate of the high-volume sampler is about five times higher than that of the personal sampler. Some research investigators contend that the higher face velocity of the high-volume sampler results in a lower fiber retention efficiency. These investigators expect the fibers to align perpendicular to the collection filter, and hence, better able to penetrate through the pores in the filter. They recommend collecting air samples at as low a face velocity as feasible and proportionately extending the sampling time. The optimization study, upon which this provisional methodology is based, tends to support the contention but the reason remains obscure.

Personal dust samplers are used frequently to assess respirable dust levels. When used in this mode, they are preceeded with a nylon cyclone that collects fibers and other particles with aerodynamic diameters in excess of 10 µm. To be comparable with the results of the high-volume sampler, it is recommended that the personal sampler be operated without the cyclone.

It is recommended that a cellulose acetate membrane filter with a pore size of 5 µm be used to support the polycarbonate filter in the samplers. It should be placed between

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* The effective filtration area varies with the style or manufacturer and hence should be measured.

the polycarbonate filter and the wire mesh filter support of the high-volume sampler, or the glass frit filter support of the personal sampler. The cellulose acetate membrane acts as a diffusion plate and aids in obtaining a uniform deposit on the polycarbonate filter. It also decreases the possibility of contaminating the filter with particles from the sampler frame.

It is recommended that flow rate meters be checked periodically during sampling to ascertain constancy of flow rate.

2.1.2 Sample Time Periods

As a guide, the following time periods are suggested for the sampling of airborne asbestos. It is recommended that samples be collected at all three of the suggested time periods until experience dictates otherwise. Sampling at the three time periods increases the probability that one of the samples will be suitably loaded with asbestos to permit quantification of the asbestos by the direct transfer technique.

Table 1

SUGGESTED SAMPLING TIMES FOR DETERMINING AIRBORNE ASBESTOS CONCENTRATIONS

Proximity to Source	Sampler Type	Suggested Sampling Times, min
Point Source 90 m	High-volume Personal	15, 30, 60 75, 150, 300
Near Source 90-180 m	High-volume Personal	30, 120, 480 150, 600
Distant Source 0.8-1.6 km	High-volume Personal	240, 480, 1440 not recommended

2.2 Sample Storage and Transport

After acquiring the sample, every precaution must be taken to assure its integrity and prevent contamination and loss of fibers until the sample is examined under the electron microscope. The polycarbonate filter should be removed immediately from the filter holder with great care and tacked, with cellophane tape, to the bottom of a clean plastic petri dish. The dish cover should then be secured and all necessary sample identifying marks and symbols applied to the cover. With the 20 cm x 25 cm high-volume filters, it may be necessary to cut the filter into 5 cm x 5 cm segments and store each segment in separate petri dishes. A consistent notation must be used so that the location and orientation of each segment with respect to the original filter is not lost. It is recommended that the petri dishes containing the filters be maintained in a horizontal position at all times during storage and transportation to the analyzing laboratory. At the present time, there are no reliable estimates on the loss of fibers from polycarbonate filters prior to carbon coating the filters in the laboratory.

If other membrane filters, such as cellulose acetate, are used for collecting airborne particles, it is generally believed that the storage and transport do not affect these filters because of their high retention efficiency. However, there are no reliable data for comparing retention efficiency of polycarbonate filters and other membrane filters.

Suitable blank and standard filters should be introduced at this stage in the analytical process and carried through the remaining procedures along with the samples.

2.3 Carbon Coating the Filter

The polycarbonate filter with the sample deposit and suitable blanks and standards should be coated with carbon as soon after sampling is completed as possible. The carbon

coating forms an almost continuous film over the filter and bonds the collected particles to the filter surface. Losses are thus reduced during subsequent handling of the filter, and during the transfer process to the electron microscope grid. A carbon film of about 40 nm thickness is most suitable. All experimental equipment and supplies are listed in Appendix A.

It is highly recommended that the handling and processing of the filters after their receipt by the analyzing laboratory be conducted in a clean room or clean bench to reduce the possibility of contamination. Tweezers should be used for handling the filters; static charge eliminators will facilitate handling of the polycarbonate filters by neutralizing the surface electrostatic charge.

Because a thin, uniform, carbon film is desired, the coating of the filter deposit with carbon should be carried out in a vacuum evaporator. Carbon sputtering devices should be avoided because they produce a film of uneven thickness. Too thick a film can lead to problems during the subsequent steps in the procedure, particularly filter dissolution, fiber sizing, and fiber identification. Electron diffraction patterns tend to be faint when operating the TEM at less than 100 KV.

Typically, vacuum evaporators accept samples as large as 10 cm in diameter. Thus, if the personal sampler was used for sample collection, the entire filter may be carbon coated at one time. It is convenient to use the petri dish in which the polycarbonate filter is being stored. After inspecting the filter to be sure it is securely tacked to the bottom of the petri dish, remove the cover and place the bottom of the dish containing the filter in the vacuum evaporator for coating. If the airborne asbestos was collected on the 20 cm x 25 cm polycarbonate filter using the high-volume sampler, the entire filter cannot be coated at once. Portions, about 2.5 cm x 2.5 cm,

should be cut from the central region of the filter using scissors or scalpel. The portions should be tacked with cellophane tape to a clean glass microscope slide and placed in the vacuum evaporator for coating.

Any high-vacuum, carbon evaporator may be used to carbon coat the filters (caution again: carbon sputtering devices should not be used). Typically, the electrodes are adjusted to a height of 8-10 cm from the level of the turn-table upon which the filters are placed. A spectrographically pure carbon electrode sharpened to a 0.1 cm neck is used as the evaporating electrode. The sharpened electrode is placed in its spring-loaded holder so that the neck rests against the flat surface of a second graphite electrode. The samples, in either a petri dish bottom or on a glass slide, are attached to the turn-table with double-sided cellophane tape.

The manufacturer's instructions should be followed to obtain a vacuum of about 1×10^{-5} torr in the bell jar of the evaporator. With the turn-table in motion, the carbon neck is evaporated by increasing the electrode current to about 15 amperes in 10 seconds, followed by 25-30 seconds at 20-25 amperes. If the turn-table is not used during carbon evaporation, the particulate matter is not coated from all sides and there is a shadowing effect which is not desirable. The evaporation should proceed in a series of short bursts until the neck of the electrode is consumed. Continuous prolonged evaporation is not recommended since overheating and consequent polymerization of the polycarbonate filter may easily occur and impede the subsequent step of dissolving the filter. The evaporation process may be observed by viewing the arc through welders goggles. (CAUTION: never look at the arc without appropriate eye protection.) A rough calculation shows that a graphite neck of 5 mm^3 volume, when evaporated over a spherical surface of 10 cm radius, will yield a carbon layer 40 nm thick.

After carbon coating, the vacuum chamber is slowly returned to atmospheric pressure, the filters are removed and placed in clean, marked petri dishes, and stored in a clean bench.

2.4 Transfer of the Sample to the EM Grid

The transfer of the collected airborne asbestos from the coated polycarbonate filter to an electron microscope grid is accomplished in a clean room or bench using a Jaffe washer technique [6] with some modification.

Transfer is made in a clean glass petri dish about 10 cm diameter and 1.5 cm high. A stack of 40 clean, 5½ cm diameter paper filter circles is placed in the dish; alternatively, a 3 cm x 3 cm x 0.6 cm piece of polyurethane foam (like those used as packing in Polaroid film boxes) may be used. Spectroscopic grade chloroform is poured into the petri dish until it is level with the top surface of the paper filter stack or the foam. On top of the stack or foam a piece of (about 0.6 cm x 0.6 cm) 60-mesh stainless steel screen is placed. Several transfers may be completed at one time and a separate piece of mesh is used for each grid. Details of the modified Jaffe washer and the washing process are illustrated in Figure 1.

Sections of the carbon-coated polycarbonate filter on which the sample is deposited are obtained either by using a punch to punch out 2.3 mm discs or sharp scissors to cut out approximately 1 mm x 2 mm rectangles. A section is laid carbon side down on a 200-mesh carbon-coated electron microscope (TEM) grid. (Alternatively, one may use formvar-coated grids or uncoated TEM grids. Here, the carbon coat on the polycarbonate filter forms the grid substrate.) Minor overlap or underlap of the grid by the filter section can be tolerated since only the central 2-mm portion of the grid is scanned in the microscope. This pair (TEM grid and filter section) is picked up with tweezers and carefully placed on the moist

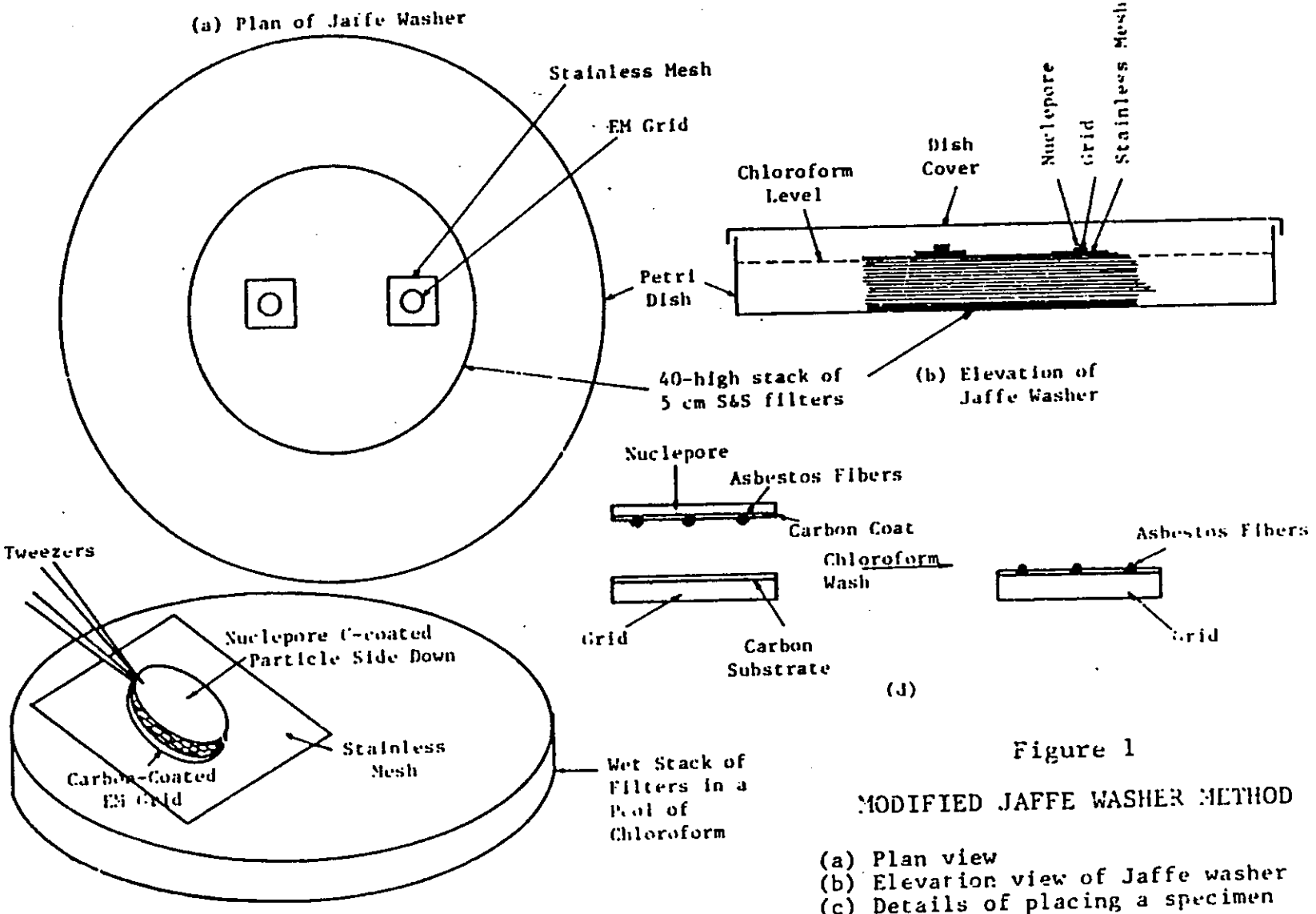


Figure 1

MODIFIED JAFFE WASHER METHOD

(a) Plan view
(b) Elevation view of Jaffe washer
(c) Details of placing a specimen for washing
(d) Principle of the Jaffe method

stainless steel mesh of the Jaffe washer. The 1 mm x 2 mm section is wetted immediately by a 5 µl drop of chloroform.

When all the samples are in place in the washer, more chloroform is carefully added to increase the level back to where it just touches the top of the paper filter stack. Raising the chloroform level any higher may float the TEM grid off the mesh or displace the polycarbonate filter section; neither is desirable. The cover is placed on the washer and weighted to improve and seal and reduce the evaporation of the chloroform.

More chloroform should be added periodically to maintain the level within the washer. After a minimum of 24 hours, the polycarbonate filter should be completely dissolved. The TEM grid is removed by picking up the stainless steel mesh with tweezers and placing it on a clean filter. When all traces of chloroform have evaporated, the grid may be lifted from the mesh and examined in the electron microscope or stored for future examination.

2.5 Examination of the Grid by Transmission Electron Microscopy

2.5.1 Low Magnification

The grid is observed in the transmission electron microscope at a magnification of 500X to determine its suitability for detailed study at high magnification. The grid is rejected if:

(a) The carbon film over a majority of the grid opening is damaged and not intact. If so, the transfer step 2.4 must be repeated to obtain a new grid.

(b) The fibers give poor images and poor diffraction patterns due to organic contamination or interference due to non-fibrous particles. If so, the filter may be ashed, redispersed, and refiltered (see Section 2.8). Ashing step allows elimination of organic matter and facilitates diluting to minimize the interference from other particles.

2.5.2 High Magnification

2.5.2.1 Calibrating Magnification at Fluorescent Screen

It is important to know the exact value of magnification at the fluorescent screen for the most common settings of the electron microscope. The method for calibrating magnification is illustrated in Appendix B.

2.5.2.2 Loading Levels

The method for examining the grid for fiber counting is a function of the fiber loading on the filter. Three generalized loading levels may be encountered.

(a) Low Loading -- less than 50 fibers in a full grid opening (80 μm x 80 μm).

(b) Medium Loading -- 50 to 300 fibers in a full grid opening.

(c) High Loading -- more than 300 fibers per full grid opening.

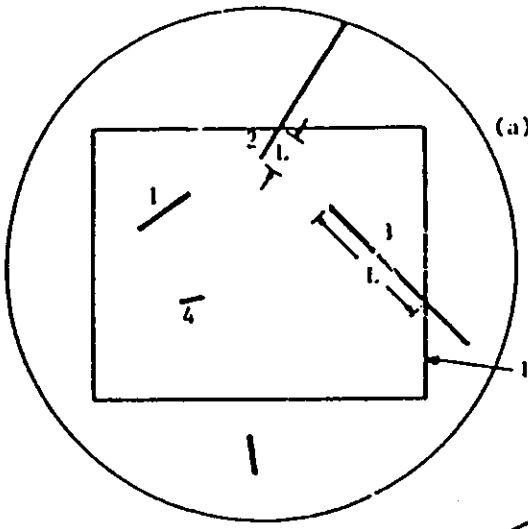
2.5.2.3 Fiber Counting Rules

In making a fiber count, the following rules are to be observed:

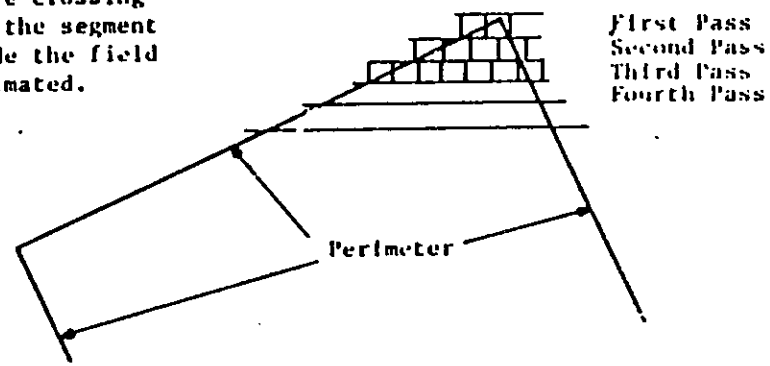
(a) A field of view is defined. In some microscopes, it is convenient to use the central rectangular portion of the fluorescent screen which is lifted for photographic purposes [see Figure 2(a)]. On other microscopes, a scribed circle or the entire circular screen may be used as the field of view. The area of the field of view must be accurately measurable.

(b) All fibers within the field of view are counted and their length and width estimated and noted.

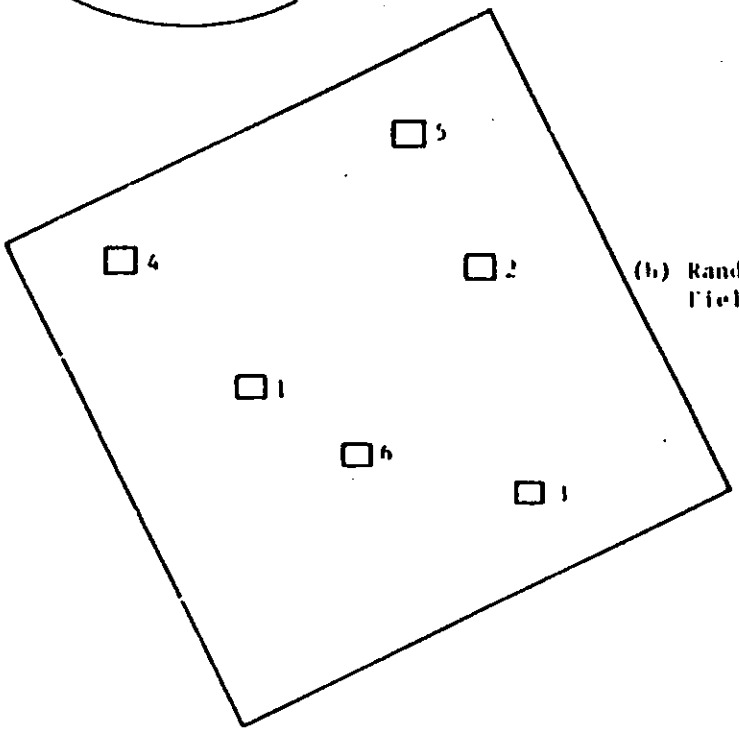
(c) Fibers which extend beyond the perimeter of the field of view are counted. The width of these fibers is measured but their length is measured as only that portion which lies within the field of view. Such fibers are noted by the letter "L" as the length information is recorded, indicating that it is a limit case [see Figure 2(a)]. In the final analysis, such fibers are treated as half-fibers (half-counts).



(a) Field of View:
Fibers 2 & 3 are crossing the perimeter; the segment of length inside the field of view is estimated.



(c) Full Grid Opening:
Method of scanning.



(b) Random Choice of Field of View

Figure 2

TWO METHODS OF EXAMINING A GRID

(d) Tightly bound bundles of fibers are counted as a single fiber and an estimate made of their average length and width. Fibers which touch or cross are counted separately. Some subjective judgement is required but fortunately, borderline cases are rare. Notation is also made in recording the data that the fiber was a bundle.

(e) Selection of the grid opening and the selection of a field of view within a grid opening should be done on a random basis [see Figure 2(b)]. This is important for avoiding biases and to ensure the statistical validity of the results.

(f) Morphological comparison with standard specimens is used as a basis for rejecting non-asbestos particles such as plant parts and diatoms. Where doubt exists, the electron diffraction pattern of the particles should be examined.

2.5.2.4 Fiber Classification Rules

Fibers are classified by observation of their morphology and electron diffraction patterns. It is recommended that both morphological and diffraction pattern study be done at zero degree tilt angle.

The following rules should be followed when classifying a fiber:

(a) Observe a fiber at a TEM screen magnification of about 16,000X through a 10X binocular. At such high magnifications, the tubular structure of chrysotile is usually apparent (compare with standard specimens). Fibers showing the tubular structure may be classified tentatively as chrysotile. A few other minerals, e.g. halloysite, show tubular structure. but can be recognized from chrysotile by electron diffraction. Amorphous matter can get inside the tube or cover the chrysotile fiber, and thus obscure the tubular structure. Therefore, non-tubular structure does not rule out chrysotile.

Amphibole asbestos fibers usually have a lath or plate-like shape, are more electron dense, and show thickness contours and other diffraction contrasts which change due to beam heating. Morphological features alone may not be a sufficient basis for distinguishing chrysotile from amphiboles and other fibrous minerals.

(b) Electron diffraction patterns from single fibers of asbestos minerals fall into distinct groups. The chrysotile asbestos pattern has characteristic streaks on layer lines other than the central line and some streaking also on the central line. There are spots of normal sharpness on the central layer line and on alternate lines (2nd, 4th, etc.). The repeat distance between layer lines is about 0.53 nm.

Amphibole asbestos fiber patterns show layer lines formed by very closely spaced dots, and the repeat distance between layer lines is also about 0.53 nm. Streaking in layer lines is occasionally present due to crystal structure defects.

(c) Transmission electron micrographs and selected area electron diffraction patterns obtained with standard samples should be used as guides to fiber identification.[7-9]

From the examination of the electron diffraction patterns, fibers are classified as belonging to one of the following categories:

- Chrysotile
- Amphibole group (includes amosite, crocidolite, anthophyllite, tremolite and actinolite)
- Ambiguous (incomplete spot patterns)
- Non-asbestos (minerals other than the six asbestos minerals)
- Unknown (no spot pattern)

It should be noted that other particles with fibrous morphology also give layer patterns; for example, pyroxenes. The complete quantitative indexing and deriving interplanar d-spacings from diffraction patterns is a time consuming and complex undertaking and is not feasible for routine analysis.

It is not possible to inspect electron diffraction patterns for some fibers. There are several reasons for the absence of a recognizable diffraction pattern. These include contamination of the fiber, interference from nearby particles, too small a fiber, too thick a fiber, and non-suitable orientation of the fiber. Some chrysotile fibers are destroyed in the electron beam resulting in patterns that fade away within seconds of

being formed. Some patterns are very faint and can be seen only under the binocular microscope. In general, the shortest available camera length must be used and the objective lens current may need to be adjusted to give optimum pattern visibility for correct identification. Use of a 20 cm camera length and a 10X binocular to inspect the SAED pattern on the tilted screen is recommended.

2.5.2.5. Counting at Low Loading Level

When fewer than 50 fibers per grid opening are encountered, the preferred counting method is to scan the entire grid opening and defining the full grid opening as one field. With the microscope magnification at 20,000X, a series of parallel scans across the grid square are made starting with the top corner of the square and ending at the bottom [see Figure 2(c)]. (With the tilting section of the fluorescent screen used as a single field of view, approximately 300-400 fields will be observed if the entire grid opening is scanned.) Fibers noted in each full grid opening (or single field) are classified in accordance with the procedure described above.

Additional grid openings are selected, scanned, and counted until the total number of fibers counted exceeds 100, or a minimum of 10 grid openings have been scanned, whichever occurs first.

2.5.2.6 Counting at Medium Loading Level

When the loading on the filter is in the range of 50 to 300 fibers per grid opening, counting is done on randomly selected fields of view. At a nominal magnification of 20,000X, fields are randomly selected within a grid opening until a total of 20 fibers have been counted, sized, and classified. (Generally 20-40 fields of view are observed per grid opening.) After about 20 fibers have been counted, another grid opening is selected and an additional 20 fibers (approx.) are counted. This procedure is repeated for 5 grid openings until a minimum

of 100 fibers are counted. (When estimating fibers of a particular type of asbestos, counting is continued until 50-100 fibers of that type are counted.)

2.5.2.7 Counting at High Loading Level

When the fiber loading exceeds 300 fibers per grid opening, the filter should ideally be rejected in favor of a filter sample taken for a shorter time period.

If no other filter sample is possible and the number of fibers above 300 is not too great (up to 400), then a filter section should be transferred to a 400 mesh grid and the procedure repeated as for medium filter loading levels. The 400 mesh grid opening is much smaller in area than a 200 mesh grid opening, and hence can be scanned much faster with less fatigue for the operator.

When the loading level is so high that fibers touch and overlap and no other sample is available, then the filter should be ashed, dispersed, and refiltered to yield a lower concentration level. Details for this procedure are given in Section 2.8.

2.6 Recording of Data

It is advantageous to record the TEM data in a systematic form so that it can be transferred to computer data cards for statistical analysis.

2.6.1 Recording Format

A suggested data sheet format is shown in Table 2. The entries at the top describe the sample (identification, the storage box, and storage location), the sampling parameters (volume of air sampled, total effective area of the filter), and the TEM parameters (screen magnification, area of one field of view in cm^2, etc.).

Column 1 -- EM grid opening identification number

Column 2 -- Identification number for the field of view

Table 2

DATA RECORDING SHEET

Sample: _____ Vol. of Air Sampled: 9.2 m^3

Storage Box No.: _____ Effective Area of Membrane: 406.5 cm^2

Location in Box: _____

Magnification: 17,000

Area of One Field: 0.182 x 10^{-6} cm^2

Grid Opening I.D.	Field of View Number	Fiber Number	Cumulative Fiber Count	Fiber Width, mm	Fiber Length, mm	Fiber Identification by Morphology and Electron Diffraction
1	1	1	1	1.0	20	Chrysotile
		2	2	0.25	7	Ambiguous
	2	1	3	0.5	17	Ambiguous
		2	4	1.0	10	Chrysotile
		3	5	1.0	18	Chrysotile
		4	6	0.75	22	Chrysotile
		5	7	1.0	12	Chrysotile
		6	8	0.5	10	No Pattern
	3	1	9	0.25	24	Chrysotile
		2	10	0.75	18	Ambiguous
		3	11	1.0	10	Chrysotile
		4	12	1.0	8	Chrysotile
		5	13	0.25	10	No Pattern
	4	1	14	0.25	6	Chrysotile
		2	15	0.25	20	Ambiguous
		3	16	0.5	5	No Pattern
	5	1	17	2.0	65	Chrysotile
		2	18	1.0	10	Ambiguous
		3	19	0.5	4	No Pattern

and so on.

Column 3 -- Fiber sequence number within a given field of view

Column 4 -- Cumulative number of fibers counted

Column 5 -- Fiber width in mm

Column 6 -- Fiber length in mm

Column 7 -- Fibers extending beyond the perimeter of the field, marked with L (limiting case)

Column 8 -- Fiber identification, chrysotile, amphibole, ambiguous, or no pattern or non-asbestos

2.6.2 Computer Coding Forms

A Fortran program has been developed (see Appendix C) to analyze the data obtained from the electron microscope study. In order to use this Fortran program, it is recommended that data from the notes be transferred to IBM computer coding sheets to facilitate key punching. The coding scheme is given in Table D-1 and an illustration is presented in Table D-2 of Appendix D. The scheme is sufficiently broad to keep all relevant information, such as sample code number, laboratory code number, operator code number, TEM grid number, etc. Ashing factor refers to the dilution or concentration resulting from the ashing and reconstitution step. It is defined as the ratio of the redeposition filter area to the area of the filter segment ashed. For example, if a segment of 5 cm^2 area was ashed and the ash suspension deposited on 25 mm diameter final filter (effective area 2 cm^2), the ashing factor is 0.4. The area of the field of view when multiplied by the ashing factor gives the corrected area of the field.

2.7 EM Data Analysis

2.7.1 Checking Data on Key Punch Cards

Key punch cards are checked by obtaining a printout of all cards as illustrated in Table D-3 of Appendix D. This printout helps in detecting key-punching errors by comparison with the coding forms.

2.7.2 Separating Very Large Sized Bundles

At present, separating bundles of fibers from the data is done by inspection of printout of the input data. The computer program can be modified to exclude the very large sized fibers from the analysis.

2.7.3 Fortran Program for Obtaining Characterizing Parameters

Each analyzing laboratory can develop its own computer program to facilitate statistical analysis and to obtain the necessary characterizing parameters. One Fortran program called CONLAB was specially developed at IITRI for obtaining several important characterizing parameters. The listing for this program is given in Appendix C. The program gives characterizing parameters for each TEM grid used.

2.7.4 Printout of Results on each TEM Grid

A typical printout of results on each TEM grid (for the data in Table D-3) is given in Tables D-4 and D-5. The parameters shown are:

Fiber counts for each category

Fiber concentration per cm^2 of filter
Fiber concentration per m^3 of air

Mass concentration per cm^2 of filter
Mass concentration per m^3 of air

Length (μm) Mean
Std. Deviation

Diameter (μm) Mean
Std. Deviation

Volume $(\mu m)^3$ Mean
Std. Deviation

2.7.5 Summary of Results for a Typical Air Sample

Summaries of the results are obtained using relevant quantities from the printouts in Tables D-4 and D-5. Shown

in Table D-6 are the characterizing parameters for all fibers and for chrysotile fibers.

2.7.6 Precision of TEM Estimates

When more than one TEM grid is used, it is possible to obtain the mean values and 95% confidence levels on the means. This is done for each important parameter. The method consists of obtaining the mean, $\bar{x}$, the standard error of the mean, SEm, and t-value [10] (0.025, n - 1) for n - 1 degrees of freedom, where n = number of TEM grids examined and hence n replicates available. The 95% confidence limits are given by $\bar{x} \pm t \cdot (SEm)$.

In the illustrative case, Table D-6, the following four parameters are given:

(1) Fiber number concentration of all fibers, $10^6/m^3$ of air

(2) Volume concentration of all fibers, 10^{-9} cm^3/m^3 of air

(3) Fiber number concentration of chrysotile, $10^6/m^3$ of air

(4) Mass concentration of chrysotile fibers, $\mu g/m^3$ of air

The t-value decreases sharply with greater replication. For example, t = 12.7 for n = 2 and decreases to 4.3 for n = 3 and to 2.77 for n = 5 and so on. The standard error of the mean also decreases with greater replication. Hence, to increase the precision of the TEM estimates, 3 or 4 replicates per sample should be analyzed.

2.7.7 Analyzing Data on Very Large Bundles of Fibers

Fiber bundles should be reported separately as the number concentration of large bundles or fiber aggregates (greater than 1 μm^3 each) per m^3 of air. In general, these are few and these computations can easily be done using a desk calculator.

No attempt is made to compute either the volume or the mass of bundles because of the large uncertainty in assigning dimensions to aggregates.

2.8 Ashing, Sonification, and Reconstitution

Some air samples (especially samples collected over several hours) may contain high levels of organic contaminant. This organic matter obscures the fibrous particles, and interferes with the proper counting, sizing, and identification. Such samples should be ashed and reconstituted. In cases where a flat, polycarbonate filter cannot be used for initial sample collection, and a depth filter (cellulose acetate) with high retention efficiency must be used, the ashing step may be used to reconstitute the particles on a flat filter for TEM analysis. The procedure for ashing is as follows:

A section of known area (e.g. 1 cm x 1 cm) is cut from the polycarbonate or cellulose acetate filter used to collect the air sample and is placed in a clean glass vial (30 mm diameter x 80 mm high). The membrane is positioned such that the particle collection side (shiny side) faces the glass wall. The vial is placed in an upright position in a low-temperature asher. Using manufacturer's instructions, vacuum is obtained and the filter is ashed at 40 watts power in oxygen plasma. Oxygen is admitted at 2 psi pressure. Though the membrane vanishes in about a half-hour, the ashing is continued for about 3-4 hours to ensure complete ashing. The ashing chamber is allowed to slowly reach atmospheric pressure. The vial is removed and 10 ml of filtered distilled water containing 0.1 percent filtered Aerosol OT is added. The vial is placed in a 100 ml beaker containing 50 ml of water, and this beaker is placed in a low-energy, ultrasonic bath. Ultrasonic energy is applied for 15 minutes to disperse all of the ash.

A 25 mm diameter filtering apparatus is assembled with a 25 mm diameter, 0.1 μm pore size polycarbonate filter with 5 μm pore size cellulose ester filter backing on the glass frit. Suction is applied and the filters are recentered if necessary. The filter funnel is mounted, the vacuum is turned off and suction is allowed to cease. Two ml of distilled water is added to the funnel followed by the careful addition of the water containing

the dispersed ash. Suction is applied to filter the sample. The vial should be rinsed with 10 ml of 0.1 percent Aerosol OT at least twice and the contents carefully transferred to the filtration funnel before the funnel goes dry. At the end of filtration, the suction is stopped. The filter is then dried in still air and stored in a disposable petri dish. After drying, the filter is ready for carbon-coating (see Section 2.3) and transfer of the sample to an EM grid (see Section 2.4).

The effective area of the redispersion filter and the area of the section cut for ashing from the original membrane must be taken into account when computing the fiber concentration, etc., in the TEM data analysis.

2.9 Limits of Detection

The minimum detection limit of the electron microscope method for the counting of airborne asbestos fibers is variable and depends upon the amount of total extraneous particulate matter in the sample and the contamination level in the laboratory environment. This limit also depends on the air sampling parameters, loading level, and the electron microscope parameters used.

In this provisional method, 100 fields, each with an area 0.18×10^{-6} cm^2 are scanned. Assuming that a fiber count has an accuracy of ± 1 fiber, then the detection limit is

$$\text{Detection Limit} = \frac{1}{100} \cdot \frac{\text{Area of Filter } (cm^2)}{0.18 \times 10^{6} \ (cm^2)} \cdot \frac{1}{\text{Vol. of Air } (m^3)}$$

In some cases (for very lightly loaded samples) when four full grid openings are scanned, each grid opening with an area of 0.72×10^{-4} cm^2, the detection limit is

$$\text{Detection Limit} = \frac{1}{4} \cdot \frac{\text{Area of Filter } (cm^2)}{0.72 \times 10^{-4} \ (cm^2)} \cdot \frac{1}{\text{Vol. of Air } (m^3)}$$

Table 3 gives an indication of the magnitude of the detection limit, calculated for the high-volume sampler method. It is seen that the minimum detection limit is lower for very dilute samples. Examining full grid openings leads to a lower value of minimum detection limit because of the large area scanned, as compared with the field of view method. With a given sample, the detection limit can be lowered consideraoly but the experimental effort required also increases. The guidelines of using 100 fields of view or four full grid openings represent a judicious compromise, between a reasonable experimental effort and a fairly low value of the detection limit. Also, using two or more TEM grids will reduce the detection limit further and also improve the precision of the estimates.

3. PREPARATION OF BLANKS

Even after taking utmost precautions to avoid asbestos contamination, one cannot rule out the possiblity of some contamination. It is a good practice to check contamination periodically by running blank samples.

A blank sample may consist of a clean filter, subjected to all the processing conducted with an actual air sample. These may include ashing, resuspension, redeposition, carbon coating, transferring to TEM grid, and TEM examination.

When analyses of blank samples show significant background levels of asbestos, these should be subtracted from the values obtained for field samples. Also, the minimum detection limit may be calculated as twice or three times the standard deviation of the blank or background value.

Table 3

MINIMUM DETECTION LIMIT USING HIGH-VOLUME AIR SAMPLER

	Sampling Duration	Vol. of Air Sampled m^3	Field of View Method* (1 fiber in 100 fields) million fibers/m^3	Full Grid Opening** (1 fiber in 4 grid openings) million fibers/m^3
Point Source	½ hr	21	1.07	0.07
Near Source	2 hr	84	0.27	0.02
Distant Source	8 hr	336	0.067	0.005

* $$\text{Detection Limit} = \frac{1 \text{ Fiber}}{100 \text{ fields}} \cdot \frac{406 \text{ cm}^2}{0.18 \times 10^{-6} \text{ cm}^2/\text{field}} \cdot \frac{1}{\text{Vol. of Air Sampled, m}^3}$$

** $$\text{Detection Limit} = \frac{1 \text{ Fiber}}{4 \text{ Grids}} \cdot \frac{406 \text{ cm}^2}{0.72 \times 10^{-4} \text{ cm}^2/\text{grid}} \cdot \frac{1}{\text{Vol. of Air Sampled, m}^3}$$

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Appendix A

INSTRUMENTATION AND SUPPLIES

A. INSTRUMENTATION

1. Transmission Electron Microscope

A transmission electron microscope should be capable of 100 kv of accelerating voltage, 1 nm resolution, and a magnification range of 300 to 100,000X. The instrument should be capable of selected area electron diffraction analysis on areas 300 nm diameter. The fluorescent screen should have either a millimeter scale, concentric circles of 1, 2, 3, and 4 cm radii, or other devices to estimate the length and width of fibrous particles. All modern transmission electron microscopes meet these requirements.

2. Vacuum Evaporation

A vacuum evaporator is required for depositing a layer of carbon on the polycarbonate filters and for preparing carbon-coated EM grids. The evaporator should have a turntable for rotating the specimen during coating.

3. Low-Temperature Plasma Asher

A low-temperature plasma asher is required when the quantities of organic matter in the air sample are very high and interfere with the detection and identification of asbestos. Oxygen should be used for plasma ashing. The sample chamber should be at least 10 cm diameter, so that glass vials can be positioned vertically (e.g., Plasmod, Tegal Corporation, Richmond, CA or equivalent).

B. SUPPLIES

1. Jaffe Washer: For dissolving polycarbonate filters. This item is not available commercially. The assembly is described in Section 2.4 and illustrated in Figure 1.

2. Filtering Apparatus: 47 mm filtering funnel (e.g., Cat. No. XX1504700, Millipore Corp. Order Service Dept., Bedford, MA 01730). 25 mm filtering funnel (Cat. No. XX1002500, Millipore Corp. Order Service Dept., Bedford, MA 01730). These are used to filter dispersed ash samples.

3. Vacuum Pump: A vacuum pump is needed to filter ash suspensions. It should provide up to 20 in. of mercury. Such vacuum pumps are available from any general laboratory supply house.

4. EM Grids: 200-mesh copper or nickel grids with carbon substrate are needed. These grids may be purchased from manufacturers of electron microscopic supplies (e.g., Cat. No. 1125, E.F. Fullam, Schenectady, NY) or prepared by standard electron microscopic grid preparation procedures. Finder grids may be substituted and are useful if the re-examination of a specific grid opening is desired (e.g., Cat. No. 1458, H-2 London 200 Finder grids, E.F. Fullam, Schenectady, NY or Cat. No. 17420 200 mesh carbon-coated nickel grids, Ladd Research Industries, P.O. Box 901, Burlington, VT 05401).

5. Membrane Filters: Polycarbonate

   (a) 47 mm diameter, 0.4 μm pore size Nuclepore® membranes or equivalent.

   (b) 37 mm diameter Nuclepore® membranes for use with the personal dust samplers.

   (c) 25 mm diameter, 0.4 μm pore size Nuclepore® membranes or equivalent to filter dispersed ash suspension.

   (d) 20 cm x 25 cm, 0.4 μm pore size Nuclepore® membranes or equivalent for collecting air samples using the high-volume sampler.

6. Membrane Filters: Cellulose acetate (to be used as backing filters)

   (a) 47 mm diameter, 5.0 μm pore size Millipore® or equivalent.

(b) 37 mm diameter, 5 μm pore size Millipore® filters or equivalent for use with personal dust samplers.

(c) 25 mm diameter, 5 μm pore size Millipore® filters or equivalent.

(d) 20 cm x 25 cm, 5 μm pore size Millipore® filters or equivalent for use with the high-volume sampler.

7. Air Samplers:

(a) High-volume sampler, see reference 1 (e.g., Sierra Instruments, Model 305, 3756 N. Dunlap St., St. Paul, Mn. 55112 or equivalent).

(b) Personal dust sampler, see reference 2 (e.g., MSA Gravimetric Dust Sampling Kit, MSA Co., Pittsburgh, Pa. 15208 or equivalent).

8. Glass Vials: 30 mm diameter x 80 mm long; for holding filter during ashing. 50 ml beakers can be used instead of vials.

9. Glass Slides: 5.1 cm x 7.5 cm; for support of filters during carbon evaporation.

10. Scalpels: With disposable blades and scissors.

11. Tweezers: Several pairs for the many handling operations.

12. Doublestick Cellophane Tape: To hold filter section flat on glass slide while carbon coating.

13. Disposable Petri Dishes: 50 mm diameter and 100 mm diameter for storing membrane filters.

14. Static Eliminator: 500 microcuries PO-210. (Nuclepore Cat. No. V090POL00101) or equivalent. To eliminate static charges from membrane filters.

15. Carbon Rods: Spectrochemically pure, 3.0 mm diameter, 4.6 mm long with 1.0 mm neck. For carbon coating

(Cat. No. 42350, Ladd Research Industries, P.O. Box 901, Burlington, VT 05401 or equivalent).

16. Ultrasonic Bath: (50 watts, 35 KHz). For dispersing ashed sample and for general cleaning.

17. Graduated Cylinder: 500 ml

18. 10 µl Microsyringe: For administering drop of solvent to filter section during sample preparation.

19. Carbon Grating Replica: 2160 lines/mm. For calibration of EM magnification (e.g., Cat. No. 1002, E.F. Fullam, Schenectady, NY or equivalent).

20. Specimen Grid Punch: For punching 3 mm diameter sections from membranes (e.g., Cat. No. 1178, E.F. Fullam, P.O. Box 444, Schenectady, NY 12301 or Cat. No. 16250, Ladd Research Industries, P.O. Box 901, Burlington, VT 05401).

21. Screen Supports: Copper or stainless steel; 6 mm x 6 mm, 60-100 mesh. To support specimen grid in Jaffe washer.

22. Filter Paper: S&S #589 Black Ribbon or equivalent (5½ cm circles). For preparing Jaffe washer.

23. Chloroform: Spectro grade, doubly distilled. For dissolving polycarbonate filters.

24. Acetone: Reagent grade or better. For cleaning the various tools.

25. Asbestos: Chrysotile (Canadian), crocidolite, amosite. UICC (Union International Contre le Cancer) standards. Reference asbestos samples available commercially (e.g., Duke Standards Company, 455 Sherman Avenue, Palo Alto, CA 94306 or Particle Information Service, 600 South Springer Road, Los Altos, CA 94022 or equivalent).

26. Petri Dish: Glass (100 mm diameter x 25 mm high). For modified Jaffe washer.

27. Cleanser: Alconox, Inc., New York, NY 10003 or equivalent. For cleaning glassware. Add 7.5 g Alconox to a liter of distilled water.

28. Aerosol OT: 0.1% solution (Cat. No. So-A-292, Fisher Scientific Co., 711 Forbes Ave., Pittsburgh, PA 15219). Used as a dispersion medium for ashed filters. Prepare a 0.1% solution by diluting 1 ml of the 10% solution to 100 ml with distilled water. Filter through 0.1 µm pore size polycarbonate filter before using.

29. Parafilm: American Can Company, Neenah, WI Used as protective covering for clean glassware.

30. Pipettes: Disposable, 5 ml and 50 ml.

31. Distilled or Deionized Water: Filter through 0.1 µm pore size polycarbonate filter. Used for making all reagents and for final rinsing of glassware, and for preparing blanks.

31. Storage Box for TEM Grids: Cat. No. E-0174 Grid Holders, JEOL U.S.A., Inc., 477 Riverside Avenue, Medford, Mass. 02155 or equivalent.

33. Squeeze Bottles: For keeping double-filtered distilled water and 0.1 percent Aerosol OT solution.

34. Welders Protective Goggles

Appendix B

MAGNIFICATION CALIBRATION

(1) Align the electron microscope using the instruction manual provided by the manufacturer.

(2) Insert mag-calibration grating replica (with 54864 lines per inch, or 2160 lines per mm, e.g., Cat. No. 1002, E.F. Fullam, Schenectady, NY) in the specimen holder.

(3) Switch on the beam, obtain the image of the replica grating at 20,000X magnification (or the magnification at which the asbestos samples will be analyzed) and focus.

(4) If the fluorescent screen has scribed circles of known diameters, proceed as follows. Using stage control, align one line tangentially to circumference of one circle. Count the number of lines in a diameter perpendicular to the lines. In most cases, the other end of the diameter will be in-between the N^{th} and $N + 1^{th}$ line. You can estimate the fractional spacing by eye. Alternatively, one can estimate the separation between lines using the scribed circles.

(5) If X line spacings span Y mm on the fluorescent screen using this grating replica, the true magnification is given by

$$M = \frac{Y \times 2160}{X}$$

The readings should be repeated at different locations of the replica and the average of about 6 readings should be taken as the representative or true magnification for that setting of the electron microscope.

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Line Spacings X	mm on Screen Y	Magnification M
9.5	83	18871
9.3	80	18580
7.0	60	18514
8.8	80	19636
9.0	80	19200
9.0	80	19200
		Average 19000

On most electron microscopes with large (18 cm dia.) fluorescent screens, the magnification is substantially constant only within the central 8-10 cm diameter region. Hence, calibration measurements should be made within this small region and not over the entire 18 cm diameter.

Appendix C

LISTING FOR THE FORTRAN PROGRAM CONLAB FOR OBTAINING CHARACTERIZING PARAMETERS

```
C       PROGRAM CONLAB
C       ANALYZE FIBER AND MASS CONCENTRATIONS
C
        REAL SUMX(7,6),SUMX2(7,6),CONCT(6),CONMAS(6),VOLCT(6),VOLMAS(6)
        REAL FIBCT(6),QTY(7),DEN(2),SDEV(7,6),SLOGV(7,6),GMN(7,6)
        REAL CVAR(7,6),MEAN(7,6),MEAN2(7,6)
        DATA I,ICT,PI/1,0,3.14159/
        DATA DEN/2.6,3.0/
C       QTY(1) = LENGTH
C       QTY(2) = DIAM
C       QTY(3) = MASS OR VOL
C       QTY(4) = LOG LENGTH
C       QTY(5) = LOG DIAM
C       QTY(6) = LOG MASS
C
C       READ LENGTH,DIAM,COMPUTE OTHER DATA, STORE
        READ(5,110,END=190) IGRID,IFLD,IFSEG,ICSEG,DIAM,ALEN,IOUT,
       *INFIB,ILAB,IFIL,IPUN,XMAG,AREA,XASH,XVOL,TAREA,ICASE
 050    TOTAR=0
        TOTCT=0
        LCT=60
        LCASE=ICASE
        LLAB=ILAB
        LFIL=IFIL
        LPUN=IPUN
        DO 080 I=1,6
        FIBCT(I)=0.0
        VOLCT(I)=0.0
        VOLMAS (I)=0.0
        CONCT(I)=0.0
        CONMAS(I)=0.0
        DO 080 J=1,7
        SDEV(J,I)=0.0
        SLOGV(J,I)=0.0
        GMN(J,I)=0.0
        CVAR(J,I)=0.0
        QTY(J)=0.0
        MEAN(J,I)=0.0
        MEAN2(J,I)=0.0
        SUMX(J,I)=0.0
        SUMX2(J,I)=0.0
 080    CONTINUE
        GOTO 1101
 100    READ(5,110,END=190) IGRID,IFLD,IFSEG,ICSEG,DIAM,ALEN,IOUT,
       *INFIB,ILAB,IFIL,IPUN,XMAG,AREA,XASH,XVOL,TAREA,ICASE
 110    FORMAT (I2,2I3,I4,2F6.0,1X,I1,2X,I1,1X,3I1,2X,2F7.1,3F5.1,5X,I2)
        IF  ((ICASE.NE.LCASE).OR.(ILAB.NE.LLAB)
       *  .OR.(IFIL.NE.LFIL).OR.(IPUN.NE.LPUN))
       * GOTO 200
 1101   AVOL=XVOL
        FILAR=TAREA
        JLAB=ILAB
        JPUN=IPUN
        JFIL=IFIL
        IF ((IGRID.EQ.LGRID).AND.(IFLD.EQ.LFLD)) GOTO 1110
        TOTAR=TOTAR+AREA*XASH*1.0E-6
        WRITE (6,1102)
 1102   FORMAT(132X)
        LCT=LCT+2
        LFLD=IFLD
```


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```
      LGRID=IGRID
1110  IF(LCT.LE.50) GOTO 1112
      WRITE (6,1111) ILAB,IFIL,IPUN,LCASE
1111  FORMAT('1',40X,'FIBER AND MASS CONCENTRATION',15X,'LAB ',I1,
     *'  SAMP ',I1,'  GRID ',I2,'  CASE ',I2/
     *50X,'DATA LIST'//
     *1X,'FIB=SEQ FIELD  FLD-SEQ    DIAM',6X,
     *'LENGTH    OUT-COD    FIB-COD    FLD-MAG    ',
     *'FLD-AREA     ASH-MAG     VOL     FILT-AREA'/)
      LCT=0
1112  IF (INFIB.EQ.0) GOTO 1120
      IFIB=INFIB
      IF((INFIB.GE.2).AND.(INFIB.LE.5)) IFIB=INFIB+1
      IF(INFIB.EQ.5) IFIB=2
      IF(INFIB.GE.6) IFIB=5
1120  WRITE(6,1113) ICSEQ,IFLD,IFSEQ,DIAM,ALEN,IOUT,INFIB,XMAG,
     *AREA,XASH,XVOL,FILAR
1113  FORMAT(3X,I4,3X,I3,5X,I3,2(5X,F6.2),3(7X,I1),
     *3(5X,F7.3),2(4X,F5.1))
      LCT=LCT+1
112   IF(IFSEQ.EQ.0) GOTO 100
      IF (IOUT.EQ.2) GOTO 115
      FIBCT(IFIB)=FIBCT(IFIB)+1.0
      GOTO 117
115   FIBCT(IFIB)=FIBCT(IFIB)+0.5
      ALEN=ALEN*2.0
117   ALEN=ALEN/XMAG
      DIAM=DIAM/XMAG
      QTY(1)=ALEN
      QTY(2)=DIAM
      QTY(3)=PI*ALEN*DIAM*DIAM*1.0E-12/4.0
      IF(IFIB.GT.2) GOTO 122
      QTY(7)=QTY(3)*DEN(IFIB)
C     FIND LOG OF EACH QTY; SUM QTY AND LOG
122   DO 149 I=1,3
      IF (QTY(I)) 140,140,145
140   QTY(I+3)=0
      GOTO 149
145   QTY(I+3)=ALOG(QTY(I))
149   CONTINUE
150   DO 159 I=1,7
      SUMX(I,IFIB)=SUMX(I,IFIB)+QTY(I)
      SUMX2(I,IFIB)=SUMX2(I,IFIB)+(QTY(I))*(QTY(I))
159   CONTINUE
      GOTO 100
190   ILND=1
200   DO 205 IFIB=1,5
      TOTCT=TOTCT+FIBCT(IFIB)
      DO 205 I=1,7
      SUMX(I,6)=SUMX(I,6)+SUMX(I,IFIB)
      SUMX2(I,6)=SUMX2(I,6)+SUMX2(I,IFIB)
205   CONTINUE
      FIBCT(6)=TOTCT
      DO 599 IFIB=1,6
      IF (FIBCT(IFIB).EQ.0.0) GOTO 599
      CONCT(IFIB)=FIBCT(IFIB)/TOTAR
      VOLCT(IFIB)=CONCT(IFIB)*FILAR/AVOL
      IF (IFIB-2) 220,220,210
210   CONMAS(IFIB)=FIBCT(IFIB)*100.0/TOTCT
      GOTO 230
220   CONMAS(IFIB)=SUMX(7,IFIB)/TOTAR
      VOLMAS(IFIB)=CONMAS(IFIB)*FILAR/AVOL
230   DO 250 I=1,7
206   MEAN(I,IFIB)=SUMX(I,IFIB)/FIBCT(IFIB)
      MEAN2(I,IFIB)=SUMX2(I,IFIB)/FIBCT(IFIB)
250   CONTINUE
```

```
      DO 270 I=1,3
      SDEV(I,IFIB)=SQRT(ABS(MEAN2(I,IFIB)-
     #     (MEAN(I,IFIB))*(MEAN(I,IFIB))))
      SLDEV(I,IFIB)=SQRT(ABS(MEAN2(I+3,IFIB)-
     #          (MEAN(I+3,IFIB))*(MEAN(I+3,IFIB))))
      CVAR(I,IFIB)=EXP(SLDEV(I,IFIB))-1
      GMN(I,IFIB)=EXP(MEAN(I+3,IFIB))
  270 CONTINUE
  599 CONTINUE
      WRITE(6,605) JLAB,JFIL,JPUM,LCASE,TOTAR,FILAR,TOTCT,AVOL
  605 FORMAT(1H1,40X,'FIBER AND MASS CONCENTRATION',
     #15X,' LAB ',I1,'  SAMPLE ',I1,'  GRID ',I2,'  CASE ',I2/
     #50X,'SUMMARY'//
     #1X,'TOTAL AREA SCANNED = ',E12.4,'  SQ CM'/
     #1X,'TOTAL AREA FILTER = ',F7.1,8X,'SQ CM'/
     #1X,'TOTAL FIBER COUNT = ',F7.1,8X,'FIBERS'/
     #1X,'TOTAL VOLUME AIR  = ',F7.1,8X,'CUBIC METERS'///
     #30X,'CHRYSOTILE      AMPHIBOLE       AMBIGUOUS        NO PATTERN',
     #'     NON-ASBESTOS       ALL FIBERS'/)
      WRITE(6,607) (FIBCT(IFIB),IFIB=1,6)
  607 FORMAT(1X,'FIBER COUNT'/
     #1X,'(FIBERS)',21X,6(F8.1,7X)/)
      WRITE(6,610) (CONCT(IFIB),IFIB=1,6),(VOLCT(IFIB),IFIB=1,6)
  610 FORMAT(1X,'FIBER CONCENTRATION'/
     #1X,'(FIBERS PER SQ CM OF FILTER) ',6(E12.4,3X)/
     #1X,'(FIBERS PER CUB METER OF AIR)',6(E12.4,3X)/)
      WRITE(6,615) (CONMAS(IFIB),IFIB=1,5),(VOLMAS(IFIB),IFIB=1,2)
  615 FORMAT(1X,'MASS CONCENTRATION',53X,'PERCENT TOTAL FIBERS'/
     #1X,'(GRAMS PER SQ CM OF FILTER)',
     #2X,2(E12.4,3X),3(F8.1,1X,'%',7X)/
     #1X,'(GRAMS PER CUB METER OF AIR)',1X,2(E12.4,3X)/)
      WRITE(6,620) (MEAN(1,IFIB),IFIB=1,6),
     #(SDEV(1,IFIB),IFIB=1,6),
     #(MEAN(4,IFIB),IFIB=1,6),
     #(GMN(1,IFIB),IFIB=1,6),
     #(CVAR(1,IFIB),IFIB=1,6)
  620 FORMAT(1X,'LENGTH     MEAN',11X,6(F12.4,3X)/
     #1X,'(MICRONS) STD DEV',8X,6(F12.4,3X)/
     #11X,'MEAN LOG',7X,6(F12.4,3X)/
     #11X,'GEOM MN ',7X,6(F12.4,3X)/
     #11X,'COEF VAR',7X,6(F12.4,3X)/)
      WRITE(6,625) (MEAN(2,IFIB),IFIB=1,6),
     #(SDEV(2,IFIB),IFIB=1,6),
     #(MEAN(5,IFIB),IFIB=1,6),
     #(GMN(2,IFIB),IFIB=1,6),
     #(CVAR(2,IFIB),IFIB=1,6)
  625 FORMAT(1X,'DIAMETER   MEAN',11X,6(F12.4,3X)/
     #1X,'(MICRONS) STD DEV',8X,6(F12.4,3X)/
     #11X,'MEAN LOG',7X,6(F12.4,3X)/
     #11X,'GEOM MN ',7X,6(F12.4,3X)/
     #11X,'COEF VAR',7X,6(F12.4,3X)/)
      WRITE(6,630) (MEAN(3,IFIB),IFIB=1,6),
     #(SDEV(3,IFIB),IFIB=1,6),
     #(MEAN(6,IFIB),IFIB=1,6),
     #(GMN(3,IFIB),IFIB=1,6),
     #(CVAR(3,IFIB),IFIB=1,6)
  630 FORMAT(1X,'VOLUME     MEAN',15X,6(E12.4,3X)/
     #1X,'(CUB CM)  STD DEV',12X,6(E12.4,3X)/
     #11X,'MEAN LOG',7X,6(F12.4,3X)/
     #11X,'GEOM MN ',11X,6(E12.4,3X)/
     #11X,'COEF VAR',11X,6(E12.4,3X)/)
      IF (IEND.EQ.1) GOTO 9999
      GOTO 050
 9999 STOP
      END
```

Appendix D

ILLUSTRATIVE TABLES

Table D-1

ELECTRON MICROSCOPE METHODS FOR ASBESTOS DATA ENTRY FORMAT, PER FIBER

Cols.	Description of Coding-Sheet Field	Permissible Values*
1-2	EM grid opening ID	01 to 99
3-5	EM field ID	001 to 999
6-8	Sequence no. of fiber within field**	0 to 999
9-12	Cumulative sequence no. within sample**	0 to 9999
13-18	Diameter in mm (do code decimal point)	0.0 or greater
19-24	Length in mm (do code decimal point)	0.0 or greater
26	2 if fiber extends beyond perimeter	0, 2
28	1 if a fiber bundle	0, 1
30	Fiber type	1, 2, 3, etc.
32-36	Case identification:	
	Col. 32 - lab	0 to 6
	33 - filter - sample	1, 2, etc.
	34 - punch - grid	1, 2
	35 - instrument type	1, 2, 3
	36 - operator within lab	1, 2
37-43	Magnification in multiples of K = 1000 (do code decimal point)	1.0 to 99.9
44-50	Area of EM field identified in cols. 3-5, in 10^{-6} cm^2 (do code decimal point)	0.001 to 999.99
51-55	Ashing factor	0.1 to 10
56-60	Volume of air sampled in m^3	1.0 to 100.0
61-65	Effective area of the original membrane in cm^2	1.0 to 999.9
71-72	Data set code	1 to 99

* Right-justify numbers in all fields unless a decimal point is entered. A blank is equivalent to a zero.

** If no fibers are observed in a field, write a one-line record with:

(1) 0 entered for sequence no. of fiber in field and for cumulative sequence no.
(2) diameter and length fields and also columns 26, 28, and 30 blank
(3) grid opening ID, field ID, case ID, magnification, and area, entered as usual.

Table D-[illegible]

COMPUTER PRINTOUT OF DATA CARDS

Grid Opening	ID of Field	Seq. No. of Fibers Within a Field	Cum. Number of Fibers	Fiber Width, [illegible]	Fiber Length, [illegible]	Limit Cases If Bundle	Fiber Type Identif.	Case ID	Screen Mag. x 1000	Area of one Field of Filter [illegible]	Ashing Factor	Vol. of Air Sampled	Effective Area of Collection Filter	Index of [illegible] Set
1	1	1	1	1.	20.		1	31111	17.	.182	1.0	9.2	406.5	3
1	1	2	2	.25	7.		2	31111	17.	.182	1.0	9.2	406.5	3
1	2	1	3	.5	17.		2	31111	17.	.182	1.0	9.2	406.5	3
1	2	2	4	1.	10.		1	31111	17.	.182	1.0	9.2	406.5	3
1	2	3	5	1.	18.		1	31111	17.	.182	1.0	9.2	406.5	3
1	02	4	06	.75	22.		1	31111	17.	.182	1.0	9.2	406.5	3
1	02	5	07	1.	12.		1	31111	17.	.182	1.0	9.2	406.5	3
1	02	6	08	.5	10.		3	31111	17.	.182	1.0	9.2	406.5	3
1	03	1	09	.25	24.		1	31111	17.	.182	1.0	9.2	406.5	3
1	03	2	10	.75	18.		2	31111	17.	.182	1.0	9.2	406.5	3
1	03	3	11	1.	10.		1	31111	17.	.182	1.0	9.2	406.5	3
1	03	4	12	1.	9.		1	31111	17.	.182	1.0	9.2	406.5	3
1	03	5	13	.25	10.		3	31111	17.	.182	1.0	9.2	406.5	3
1	04	1	14	.25	6.		1	31111	17.	.182	1.0	9.2	406.5	3
1	04	2	15	.25	20.		2	31111	17.	.182	1.0	9.2	406.5	3
1	04	3	16	.5	5.		3	31111	17.	.182	1.0	9.2	406.5	3
1	05	1	17	2.	65.	2	1	31111	17.	.182	1.0	9.2	406.5	3
1	05	2	18	1.	10.		2	31111	17.	.182	1.0	9.2	406.5	3
1	05	3	19	.5	4.		2	31111	17.	.182	1.0	9.2	406.5	3
1	06	1	20	1.	30.		1	31111	17.	.182	1.0	9.2	406.5	3
1	06	2	21	2.	32.		1	31111	17.	.182	1.0	9.2	406.5	3
1	07	1	22	1.	25.		1	31111	17.	.182	1.0	9.2	406.5	3
1	08	1	23	.5	5.		2	31111	17.	.182	1.0	9.2	406.5	3
1	09	1	24	.25	6.		2	31111	17.	.182	1.0	9.2	406.5	3
1	9	2	25	1.	30.	2	1	31111	17.	.182	1.0	9.2	406.5	3
1	10	1	26	1.	16.	2	1	31111	17.	.182	1.0	9.2	406.5	3
1	10	2	27	1.	6.	2	1	31111	17.	.182	1.0	9.2	406.5	3
1	10	3	28	1.	12.	2	1	31111	17.	.182	1.0	9.2	406.5	3
1	10	4	29	.25	10.		2	31111	17.	.182	1.0	9.2	406.5	3
1	10	5	30	.25	4.		3	31111	17.	.182	1.0	9.2	406.5	3
2	11	1	31	1.	8.		1	31111	17.	.182	1.0	9.2	406.5	3
2	11	2	32	1.	6.		1	31111	17.	.182	1.0	9.2	406.5	3
2	11	3	33	.5	5.		2	31111	17.	.182	1.0	9.2	406.5	3
2	11	4	34	1.	8.	2	2	31111	17.	.182	1.0	9.2	406.5	3
2	12	1	35	1.	4.		1	31111	17.	.182	1.0	9.2	406.5	3
2	12	2	36	.2	4.		2	31111	17.	.182	1.0	9.2	406.5	3
2	12	3	37	.25	5.		3	31111	17.	.182	1.0	9.2	406.5	3
2	13	1	38	1.	18.		1	31111	17.	.182	1.0	9.2	406.5	3
2	13	2	39	.2	12.		3	31111	17.	.182	1.0	9.2	406.5	3
2	14	1	40	1.	20.		1	31111	17.	.182	1.0	9.2	406.5	3
2	15	1	41	1.	19.		1	31111	17.	.182	1.0	9.2	406.5	3
2	15	2	42	.5	12.		2	31111	17.	.182	1.0	9.2	406.5	3
2	15	3	43	.25	8.		2	31111	17.	.182	1.0	9.2	406.5	3
2	15	4	44	.25	3.		3	31111	17.	.182	1.0	9.2	406.5	3
2	16	1	45	.5	5.		2	31111	17.	.182	1.0	9.2	406.5	3
2	16	2	46	.2	3.		3	31111	17.	.182	1.0	9.2	406.5	3
2	17	1	47	1.	25.	2	1	31111	17.	.182	1.0	9.2	406.5	3
2	17	2	48	1.	20.	2	1	31111	17.	.182	1.0	9.2	406.5	3
2	17	3	49	.5	6.	2	1	31111	17.	.182	1.0	9.2	406.5	3
2	17	4	50	.75	8.		2	31111	17.	.182	1.0	9.2	406.5	3
2	17	5	51	.1	12.		3	31111	17.	.182	1.0	9.2	406.5	3
2	18	1	52	.5	30.		1	31111	17.	.182	1.0	9.2	406.5	3
2	18	2	53	1.5	8.		1	31111	17.	.182	1.0	9.2	406.5	3
2	18	3	54	.2	8.		2	31111	17.	.182	1.0	9.2	406.5	3
2	18	4	55	1.	10.	2	1	31111	17.	.182	1.0	9.2	406.5	3

* See page [illegible] for detailed explanation of the column headings.

Table D-2

ILLUSTRATION OF FORTRAN CODING FORM SCHEME

1	1	1	1	1.	20.		1	31111	17.	.182	1.0	9.2	406.5	
1	1	2	2	.25	7.		2							
1	2	1	3	.5	17.		2							
1	2	2	4	1.	10.		1							
1	2	3	5	1.	18.		1							
1	2	4	6	.75	22.		1							
1	2	5	7	1.	12.		1							
1	2	6	8	.5	10.		3							
1	3	1	9	.25	24.		1							
1	3	2	10	.75	18.		2							
1	3	3	11	1.	10.		1							
1	3	4	12	1.	8.		1							
1	3	5	13	.25	10.		3							
1	4	1	14	.25	6.		1							
1	4	2	15	.25	20.		2							
1	4	3	16	.5	5.		3							
1	5	1	17	2.	65.	2	1							
1	5	2	18	1.	10.		2							
1	5	3	19	.5	4.		3							
1	6	1	20	1.	30.		1							
1	6	2	21	2.	32.		1							
1	7	1	22	1.	25.		1							
1	8	1	23	.5	5.		2							
1	9	1	24	.25	6.		2							
1	9	2	25	1.	30.	2	1							

Table D-3 (continued)

1*	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
2	19	1	56	.5	13.			1	31111	17.	.182	1.0	0.2	406.5	3
2	19	2	57	.25	6.			4	31111	17.	.182	1.0	0.2	406.5	3
2	19	3	58	.25	12.			3	31111	17.	.182	1.0	0.2	406.5	3
2	20	1	59	.1	8.			2	31111	17.	.182	1.0	0.2	406.5	3
2	20	2	60	1.5	25.			1	31111	17.	.182	1.0	0.2	406.5	3
2	20	3	61	.5	27.	2		2	31111	17.	.182	1.0	0.2	406.5	3
2	20	4	62	.25	10.			2	31111	17.	.182	1.0	0.2	406.5	3
3	21	1	63	.75	15.			1	31211	17.	.182	1.0	0.2	406.5	3
3	21	2	64	.25	6.			2	31211	17.	.182	1.0	0.2	406.5	3
3	21	3	65	.5	15.			2	31211	17.	.182	1.0	0.2	406.5	3
3	21	4	66	.25	3.			3	31211	17.	.182	1.0	0.2	406.5	3
3	22	1	67	.5	6.	2		1	31211	17.	.182	1.0	0.2	406.5	3
3	22	2	68	.5	10.			5	31211	17.	.182	1.0	0.2	406.5	3
3	22	3	69	.25	5.			3	31211	17.	.182	1.0	0.2	406.5	3
3	23	1	70	.5	7.			1	31211	17.	.182	1.0	0.2	406.5	3
3	23	2	71	.25	12.			2	31211	17.	.182	1.0	0.2	406.5	3
3	23	3	72	.2	3.			3	31211	17.	.182	1.0	0.2	406.5	3
3	24	1	73	1.	24.			1	31211	17.	.182	1.0	0.2	406.5	3
3	24	2	74	1.	30.			1	31211	17.	.182	1.0	0.2	406.5	3
3	25	1	75	1.5	6.			1	31211	17.	.182	1.0	0.2	406.5	3
3	25	2	76	.25	8.			3	31211	17.	.182	1.0	0.2	406.5	3
3	26	1	77	.75	13.			1	31211	17.	.182	1.0	0.2	406.5	3
3	26	2	78	.5	10.			2	31211	17.	.182	1.0	0.2	406.5	3
3	26	3	79	.25	5.			3	31211	17.	.182	1.0	0.2	406.5	3
3	27	1	A0	.5	26.			1	31211	17.	.182	1.0	0.2	406.5	3
3	28	1	A1	.5	15.			2	31211	17.	.182	1.0	0.2	406.5	3
3	29	1	A2	2.	17.			1	31211	17.	.182	1.0	0.2	406.5	3
3	29	2	A3	.25	3.			3	31211	17.	.182	1.0	0.2	406.5	3
3	30	1	A4	1.	3.	2		1	31211	17.	.182	1.0	0.2	406.5	3
3	30	2	A5	.5	4.			2	31211	17.	.182	1.0	0.2	406.5	3
3	30	3	A6	.25	4.			3	31211	17.	.182	1.0	0.2	406.5	3
4	31	1	A7	3.	18.			1	31211	17.	.182	1.0	0.2	406.5	3
4	31	2	A8	.5	7.			4	31211	17.	.182	1.0	0.2	406.5	3
4	31	3	A9	.5	15.			4	31211	17.	.182	1.0	0.2	406.5	3
4	32	1	B0	1.5	25.			1	31211	17.	.182	1.0	0.2	406.5	3
4	32	2	B1	1.	15.	2		1	31211	17.	.182	1.0	0.2	406.5	3
4	32	3	B2	1.	10.			4	31211	17.	.182	1.0	0.2	406.5	3
4	33	1	B3	1.	35.	2		1	31211	17.	.182	1.0	0.2	406.5	3
4	33	2	B4	.25	5.			3	31211	17.	.182	1.0	0.2	406.5	3
4	34	1	B5	2.	10.	2		1	31211	17.	.182	1.0	0.2	406.5	3
4	34	2	B6	1.	15.	2		1	31211	17.	.182	1.0	0.2	406.5	3
4	34	3	B7	1.	12.			4	31211	17.	.182	1.0	0.2	406.5	3
4	35	1	B8	2.	24.	2		1	31211	17.	.182	1.0	0.2	406.5	3
4	35	2	B9	2.	12.			1	31211	17.	.182	1.0	0.2	406.5	3
4	35	3	100	1.	11.			4	31211	17.	.182	1.0	0.2	406.5	3
4	35	4	101	1.	6.			4	31211	17.	.182	1.0	0.2	406.5	3
4	35	5	102	.5	14.			3	31211	17.	.182	1.0	0.2	406.5	3
4	36	1	103	.5	13.	2		1	31211	17.	.182	1.0	0.2	406.5	3
4	36	2	104	.5	4.			4	31211	17.	.182	1.0	0.2	406.5	3
4	36	3	105	.5	10.			3	31211	17.	.182	1.0	0.2	406.5	3
4	37	1	106	.5	9.			1	31211	17.	.182	1.0	0.2	406.5	3
4	37	2	107	.5	5.			4	31211	17.	.182	1.0	0.2	406.5	3
4	37	3	108	.25	8.			3	31211	17.	.182	1.0	0.2	406.5	3
4	38	1	109	1.	45.	2		1	31211	17.	.182	1.0	0.2	406.5	3
4	39	1	110	1.	25.			1	31211	17.	.182	1.0	0.2	406.5	3
4	39	2	111	.25	5.			3	31211	17.	.182	1.0	0.2	406.5	3
4	40	1	112	.5	17.			1	31211	17.	.182	1.0	0.2	406.5	3
4	40	2	113	2.	12.			1	31211	17.	.182	1.0	0.2	406.5	3
4	40	3	114	.75	5.	2		1	31211	17.	.182	1.0	0.2	406.5	3

* See page 44 for detailed explanation of the column headings.

EXPLANATION OF THE COLUMNS IN TABLE D-3

Column 1 -- EM grid opening identification number

Column 2 -- Identification number for the field of view

Column 3 -- Sequence number of a fiber within a given field of view

Column 4 -- Cumulative number of fibers counted

Column 5 -- Fiber width in mm

Column 6 -- Fiber length in mm

Column 7 -- A '2' indicates the fiber crossing the perimeter and, hence, one that is counted as a half-fiber

Column 8 -- A '1' indicates a bundle

Column 9 -- Fiber type identification code
1 → chrysotile
2 → ambiguous
3 → no SAED pattern, etc.

Column 10 -- Case identification. Laboratory code, sample code, TEM grid index, type of TEM instrument code, the operator code, etc.

Column 11 -- Magnification at the TEM fluorescent screen in multiples of 1000

Column 12 -- Area of one field of view in multiples of 10^{-6} cm^2

Column 13 -- Ashing factor, to account for the dilution or concentration resulting in the ashing step. In the procedure without the ashing step, the ashing factor is taken as 1.0.

Column 14 -- Volume of air sampled in m^3

Column 15 -- Effective area of the original air filter in cm^2

Column 16 -- Index for the data set

Table D-4

PRINTOUT FROM PROGRAM CONLAB CHARACTERIZING PARAMETERS PER TEM GRID

FIBER AND MASS CONCENTRATION SUMMARY — LAB 3 SAMPLE 1 GRID 1 CASE 3

TOTAL AREA SCANNED = .4004-05 SQ CM
TOTAL AREA FILTER = 906.5 SQ CM
TOTAL FIBER COUNT = 56.5 FIBERS
TOTAL VOLUME AIR = 9.2 CUBIC METERS

		CHRYSOTILE	AMPHIBOLE	AMBIGUOUS	NO PATTERN	NON-ASBESTOS	ALL FIBERS
FIBER COUNT (FIBERS)		26.5	.0	19.0	10.0	1.0	56.5
FIBER CONCENTRATION (FIBERS PER SQ CM OF FILTER)		.6618+07	.0000	.4745+07	.2498+07	.2498+06	.1411+08
(FIBERS PER CUB METER OF AIR)		.2924+09	.0000	.2097+09	.1104+09	.1104+08	.6235+09
MASS CONCENTRATION (GRAMS PER SQ CM OF FILTER)		.1241-06	.0000	PERCENT TOTAL FIBERS 33.63 %	17.70 %	1.77 %	
(GRAMS PER CUB METER OF AIR)		.5482-05	.0000				
LENGTH (MICRONS)	MEAN	1.A5-2	.0000	.7152	.4471	.3529	1.1036
	STD DEV	1.3292	.0000	.6267	.2188	.0000	1.1182
	MEAN LOG	.0696	.0000	-.6538	-.9470	-1.0415	-.3733
	GEOM MN	1.0726	.0000	.5201	.3879	.3529	.6885
	COEF VAR	1.2066	.0000	.8473	.7397	.0000	1.2524
DIAMETER (MICRONS)	MEAN	.0691	.0000	.0279	.0162	.0147	.0445
	STD DEV	.0099	.0000	.0140	.0071	.0000	.0233
	MEAN LOG	-3.0254	.0000	-3.9964	-4.2171	-4.2195	-3.7716
	GEOM MN	.0325	.0000	.0184	.0147	.0147	.0230
	COEF VAR	.1513	.0000	.9282	.5463	.0000	1.2885
VOLUME (CUB CM)	MEAN	.7218-14	.0000	.5595-15	.1054-15	.5995-16	.3590-14
	STD DEV	.1554-13	.0000	.0882-15	.1116-15	.0000	.1118-13
	MEAN LOG	-30.3488	.0000	-37.9861	-37.2538	-37.3531	-38.5023
	GEOM MN	.7844-17	.0000	.3183-16	.4620-16	.5995-16	.1900-16
	COEF VAR	.3178+07	.0000	.4293+04	.1586+01	.0000	.7941+05

Table D-5

PRINTOUT FROM PROGRAM COMLAB CHARACTERIZING PARAMETERS PER TEM GRID

FIBER AND MASS CONCENTRATION SUMMARY — LAB 3 SAMPLE 1 GRID 2 CASE 3

TOTAL AREA SCANNED = .3640-05 SQ CM
TOTAL AREA FILTER = 4905.5 SQ CM
TOTAL FIBER COUNT = 47.0 FIBERS
TOTAL VOLUME AIR = 9.2 CUBIC METERS

		CHRYSOTILE	AMPHIBOLE	AMBIGUOUS	NO PATTERN	NON-ASBESTOS	ALL FIBERS
FIBER COUNT (FIBERS)		20.0	1.0	6.0	12.0	8.0	47.0
FIBER CONCENTRATION (FIBERS PER SQ CM OF FILTER)		.5495+07	.2747+06	.1648+07	.3297+07	.2198+07	.1291+08
(FIBERS PER CUBIC METER OF AIR)		.2428+09	.1214+08	.7283+08	.1457+09	.9711+08	.5705+09
MASS CONCENTRATION (GRAMS PER SQ CM OF FILTER)		.1208-08	.3296-09	12.77 %	25.53 %	17.02 %	
(GRAMS PER CUBIC METER OF AIR)		.5320-05	.1455-07	PERCENT TOTAL FIBERS			
LENGTH (MICRONS)	MEAN	1.7981	.5882	.6078	.3284	.5147	1.0250
	STD DEV	1.4226	.0000	.2465	.1410	.2116	.9549
	MEAN LOG	.1371	-.5306	-.6029	-1.2002	-.7569	-.4648
	GEOM MN	1.1470	.5882	.5472	.3011	.4701	.6282
	COEF VAR	1.1574	.0000	.6297	.5105	.5447	1.4627
DIAMETER (MICRONS)	MEAN	.0840	.0294	.0285	.0169	.0441	.0522
	STD DEV	.0182	.0000	.0069	.0056	.0147	.0334
	MEAN LOG	-3.5238	-3.5264	-3.7574	-4.1226	-3.1198	-3.6480
	GEOM MN	.0295	.0294	.0233	.0162	.0416	.0260
	COEF VAR	1.3040	.0000	.3865	.3146	.4182	1.3776
VOLUME (CUBIC CM)	MEAN	.6429-14	.3097-15	.3231-15	.1048-15	.9342-15	.3822-14
	STD DEV	.8552-14	.0000	.2220-15	.1327-15	.8864-15	.8055-14
	MEAN LOG	-41.7513	-35.8559	-35.9903	-37.3179	-34.9870	-38.5986
	GEOM MN	.7373-18	.3097-15	.2342-15	.6209-16	.8387-15	.1725-16
	COEF VAR	.1219+09	.0000	.1378+01	.1471+01	.1582+01	.1319+08

Table D-6

SUMMARY OF TEST RESULTS ON ONE AIR SAMPLE (SEE TABLES D-4 AND D-5)

1	2	3	4	5	6	7	8	9	10	11
		Size Distribution of All Fibers					Size Distribution of Chrysotile			
Data Set Code	Number Conc. of All Fibers, $10^6/m^3$	Mean Length, μm	Mean Dia., μm	Mean Volume, 10^{-15} cm^3	Volume Conc. of all Fibers, 10^{-15} cm^3/m^3	Number Conc. of Chrysotile, $10^6/m^3$	Mean Length, μm	Mean Dia., μm	Mean Volume, 10^{-15} cm^3	Chrysotile Mass Conc. in Air, ng/m^3
3-1	623.5	1.104	0.044	3.590	2238.4	292.4	1.658	0.068	7.210	5.482
3-2	570.5	1.025	0.032	3.822	2180.5	242.8	1.794	0.086	8.428	5.320
Mean	597.0				2209.4	267.6				5.401
Std. Dev.	37.48				40.94	35.07				0.115
Std. Error (SEm)	26.50				28.95	24.80				0.081
t	12.706									
t · SEm	336.71				367.84	315.11				1.029
95% Conf. Interval										
Upper	933.71				2577.24	582.71				6.430
Lower	260.29				1841.56	(negative)*				4.372

* Negative values are truncated to zero. Such situations are due to limited replication. It is recommended that at least 3 or 4 TEM grids be examined to substantially improve the precision. t-value decreases sharply to 4.30 for n = 3 and to 2.77 for n = 5. Also the standard error decreases with greater replication.

Appendix I

Methods of Sectioning and Digestion of TSP Filters

METHODS OF AIR ANALYSIS, 3rd edition
Lodge, James P. 1989

See section 7.2 for filter sectioning

303A.

General Method for the Preparation of Non-Tissue Environmental Samples for Trace Metal Analysis

1. Principle of the Method

1.1 Trace elements in environmental samples, including collected particulate matter, sludge and soils, are solubilized by ultrasonication in a heated nitric/hydrochloric acid matrix. The resulting material is centrifuged, decanted and analyzed by the method of choice (1).

2. Range, Sensitivity, and Detection Limit

2.1 The range, sensitivity, and detection limits are characteristic of the element sought and the analytical method used.

3. Interferences

3.1 Analytical interferences are those of the analytical method used.

3.2 This method is not applicable to mineral samples or other non-tissue samples in which the target elements are incorporated in a silicaceous matrix unless the dried samples are reduced mechanically to -600 mesh prior to ultrasonication/extraction.

3.3 Scrupulous attention to housekeeping is a must. Glassware must be segregated for use with blanks, low level samples and spiked samples.

4. Precision and Accuracy

4.1 The precision and accuracy are to be found in the procedures describing an instrumental approach or in the procedure for the element of interest.

5. Apparatus

5.1 *Sampling equipment.* The samples are assumed to be obtained by standard or special techniques appropriate to the medium sampled.

5.2 *Analysis.* The equipment necessary is listed under the individual analytical procedures.

5.3 *Preparative.*

5.3.1 *Equipment.*

a. Centrifuge (IEC Model K or equivalent), equipped with 12-place rotor and 30.2 × 100 mm shields.

b. Desiccator for cooling oven-dried chemicals.

c. Gravity convection type oven for drying glassware and chemicals.

d. Ultrasonic bath (Blackstone Ultrasonics, Inc. Model HT 11.2 with Model SU-8W/pc Controller or equivalent); cleaning power of at least 450 W and an operating temperature of 100°C are necessary.

e. Balance accurate to 0.1 mg or less.

f. Template to aid in sectioning glass fiber filters. See figures 303A:1 and 303A:2.

g. Pizza cutter, thin wheel, thickness less than 1 mm.

h. Rack, wire (Fisher 14-793-1, or equivalent), or polypropylene (Fisher 14-8090 or equivalent) for holding centrifuge tubes during ultrasonication.

5.3.2 *Labware.*

a. Centrifuge tubes. 50-mL linear polypropylene tubes with polypropylene screw tops. (Nalgene 3119-0050 or equivalent).

b. Bottles, linear polyethylene or polypropylene with leakproof caps.

c. Pipettes (Class A borosilicate glass).

d. Cleaning. Wash all labware with (or ultrasonicate for 30 min) in laboratory detergent, rinse, soak for a minimum of 4 h in 20 percent HNO_3, rinse 3 times with distilled-deionized water, and dry in a dust-free manner.

6. Reagents

6.1 ANALYSIS.

6.1.1 Water—all references to water are to ASTM Reagent water, Type II.

6.1.2 Concentrated (12.3M) hydrochloric acid—ACS Reagent grade.

6.1.3 Concentrated (16.0M) nitric acid, redistilled spectrographic grade for preparing samples.

6.1.4 Concentrated (15.0M) nitric acid, ACS Reagent grade, for the 20% labware cleanser only. The ACS Reagent grade nitric acid has metallic contaminants at too high a level for environmental analyses.

6.1.5 Extracting acid (1.03M HNO_3 and 2.23M HCl) is prepared with a 1000 mL volumetric flask with 500 mL of water to which 64.6 mL of concentrated distilled nitric acid (6.1.3) and 182 mL of concentrated HCl (6.1.2) are added. Shake well, cool to room temperature and dilute to volume with water. *Caution*: Acid fumes are toxic. Prepare in a well-ventilated hood.

6.1.6 Filter blanks. For batches of filters over 500, randomly select 25–30 filters per batch. For smaller batches, use a lesser number but not less than 5%. Section each filter to obtain the same fraction obtained from a sample composed of a single strip.

7. Procedure.

7.1 SAMPLING. Airborne particulate matter collection and storage is described in Method 501.

7.1.2 Other types of samples are placed in non-linear polyethylene screw cap vials or jars and stored under refrigeration until they are analyzed.

7.2 SAMPLE PREPARATION.

7.2.1 Hi-vol samples. Cut a 2 × 20 cm or 2.5 × 20 cm strip of the exposed filter using a template and a pizza cutter as shown in Figures 303A:1 and 303A:2 or use an alternate procedure after checking reproducibility of sectioning.

7.2.2 Filters other than glass-fiber may be used (providing they contain no interferences and afford quantitative capture of the desired element). Using historical data for the locale, season and conditions (or estimating from historical data for the site) take a large enough section to afford enough of the element(s) sought to give an estimated instrumental reading 3 times the standard deviation of the background. Polymeric filters may be sectioned readily using a scalpel and paper backing. The section should be weighed with uniform particulate matter distribution assumed.

7.2.3 Sludge samples are prepared by drying prior to reweighing (to establish loss on drying) and analysis.

7.2.4 Soil and mineralogical samples containing material in a non-silicaceous matrix are dried, weighed, and prepared as described. Materials with a siliceaceous matrix require reduction to -600 mesh size prior to processing.

7.3 EXTRACTION. See 303A.

7.3.1 For glass fiber filters, accordion fold or tightly roll the filter strip and place on its edge in a 50-mL polypropylene centrifuge tube, using vinyl gloves or plastic forceps. Sections of other filters should be similarly rolled or folded to fit into the centrifuge tubes.

7.3.2 For other samples, introduce a weighed quantity (1.0 g or enough material to yield a sample containing a sufficient quantity of the material sought).

7.3.3 Pipette 12.0 mL of the extraction acid (6.1.5), which should completely cover the sample, into the centrifuge tube. Cap the tube loosely (finger tight) with the polypropylene screw top. *Caution*: Centrifuge tubes must be loosely capped to prevent elevated pressures during ultrasonication at elevated temperatures. They *will not* withstand repeated cycling to elevated pressures.

7.3.4 Label the centrifuge tube, place in a sample rack, and place upright in the preheated (100°C) ultrasonic water bath (in fume hood) so that the water level is slightly above the acid level in the centrifuge tubes but well below the centrifuge tube caps.

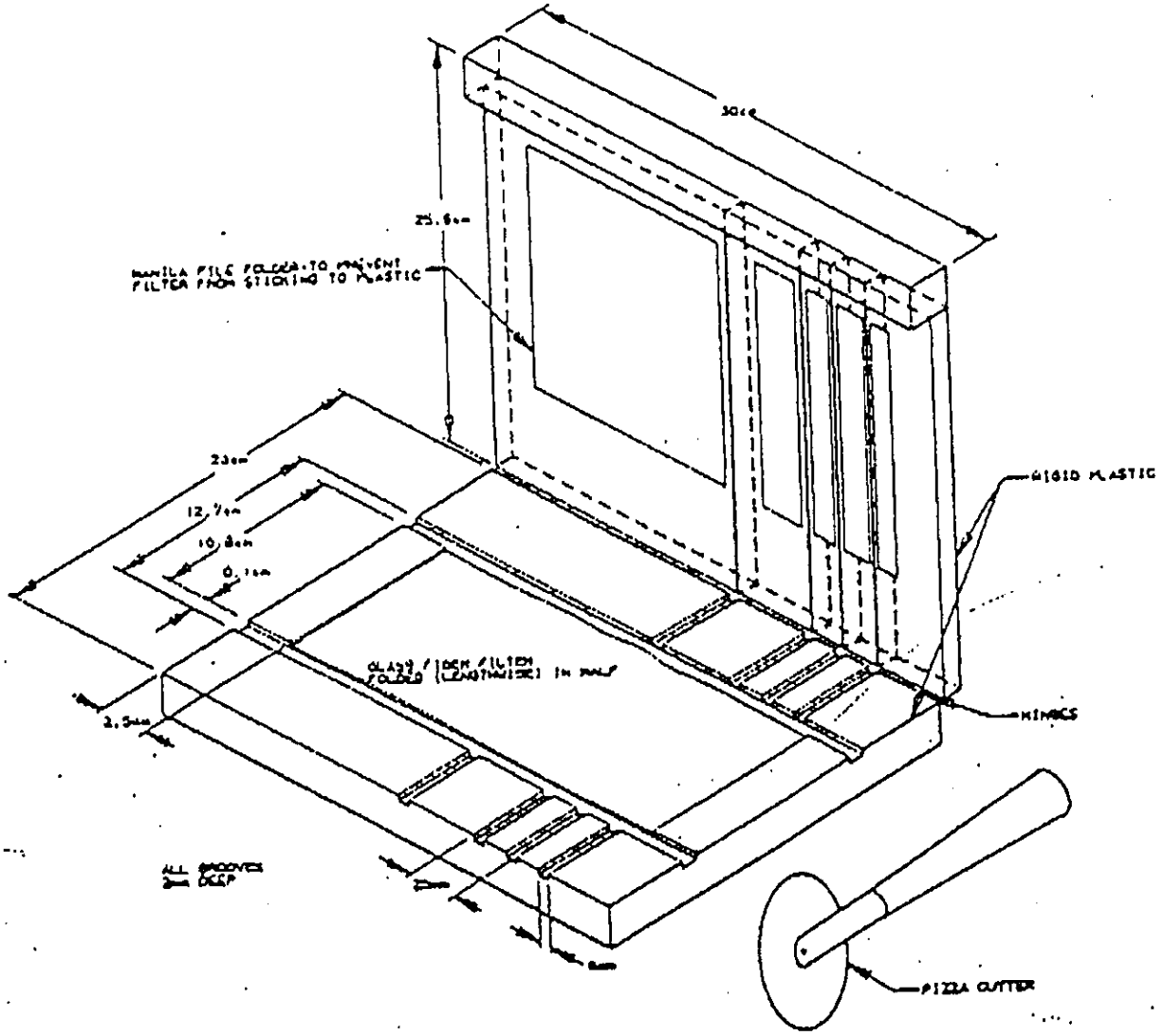

Figure 303A:1 — Template for reproducible sectioning of 20 × 25 cm filters.

This will prevent contamination of the samples during ultrasonication. Ultrasonicate the sample at 100°C for 50 min at a power setting ≥ 450 watts.

7.3.5 Remove the centrifuge tube from the ultrasonic bath and allow to cool.

7.3.6 Uncap the centrifuge tube in the fume hood and add 28.0 mL of water with pipettes or the automatic dispensing pipette. Recap the tube tightly, shake well, and centrifuge for 20 min at 2500 RPM.

7.3.7 Decant the extract into a clean polyethylene storage bottle bearing the sample I.D. Be careful not to disturb any solids in the bottom of the tube. Cap the bottle tightly and store until analysis. The final extract is now in 0.31M HNO_3 + 0.67 M HCl.

8. Analysis.

8.1 Proceed with the analysis of the sample by the appropriate method.

to ~~ICAP~~ CLP ~~GFAA~~ methods

9. Calibration.

9.1 See the appropriate method chosen in 8.1. Obtain the concentration in terms of micrograms of element sought per milliliter of final solution.

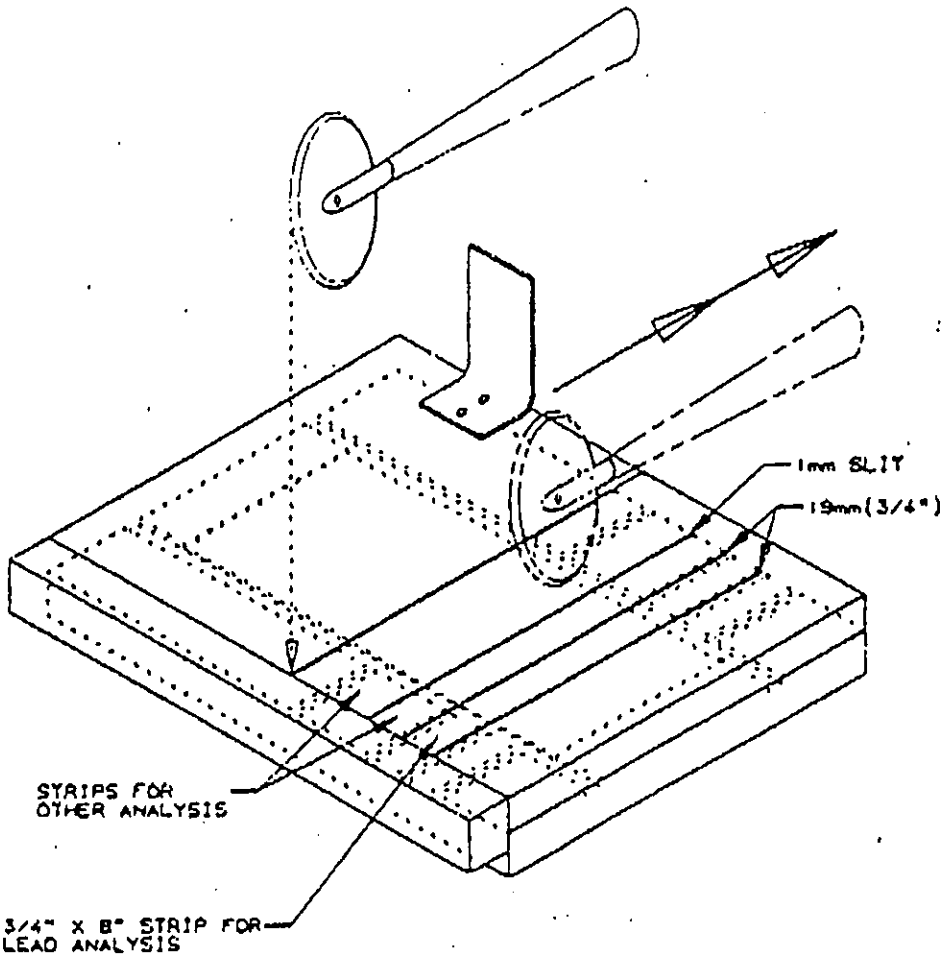

Figure 303A:2—Template closed for sectioning.

10. Calculation

10.1 CONCENTRATION OF CHOSEN ELEMENTS.

10.1.1 *Air Samples.*

$$C = \frac{C_s \times 1/n - \overline{F}_b}{V}$$

where C = concentration of element E in the air sample, $\mu g/m^3$.
E = element determined.
C_s = concentration of E in solution, $\mu g/mL$.
n = fraction of sample per section/portion.
V = volume of air sampled, at STP or otherwise as required, m^3.
$\overline{F}_b$ = mean concentration of E in blank filter section, figure from 6.1.6, μg/filter.

10.2.2 Soil and sludge samples I4

$$C = \frac{C_s \times 40}{M}$$

where C = concentration of element E in the sample, $\mu g/g$ or ppm.
m = mass of sample taken, in grams.

10.2.3 Calculate the mean, $\overline{F}_b$, the values for C and the relative standard deviation. If the value of $\overline{F}_b$ is high enough to result in a significant error in C, the filter batch should be rejected (for $\overline{F}_b \geq 10\%$ C). Below lower limit of detection (3 σ response above background) a correction is not warranted.

11. Quality Control

11.1 For particulate matter samples, controls of knowns (filter strips spiked with salts of E approximating 1/4, 1/2, 3/4 and 100% of the maximum expected value, blanks, and spiked sample replicates) should be used as every n^{th} sample. (For robust quality control, 20% of the samples should be q.c. samples; usually 5–10% is

822.

General Atomic Absorption Procedure for Trace Metals in Airborne Material Collected on Filters

1. Principle of Method

1.1 This procedure describes a general method for the collection, dissolution and determination of trace metals in industrial and ambient airborne material. The samples are collected on filters and treated with nitric acid to oxidize the organic matrix and to dissolve the metals present in the sample. The analysis is subsequently made by flame atomic absorption spectrophotometry (AAS).

1.2 Samples and standards are aspirated into the appropriate AAS flame. A hollow cathode lamp for the metal being measured provides a source of characteristic radiation energy for that particular metal. The absorption of this characteristic energy by the atoms of interest in the flame is related to the concentration of the metal in the aspirated sample. The flames and operating conditions for each element are listed in Table 822:I.

1.3 This method can also be applied to non-flame electrothermal atomization atomic absorption spectrophotometry (ETA). ETA can be extremely valuable for measuring low solution concentration levels, in the range of 0.001 to 0.5 μg/mL if matrix interferences and high blank levels are not a problem. To overcome these problems, several different strategies have been developed by the various instrument manufacturers. Detailed discussion of these strategies is beyond the scope of this method.

2. Range and Sensitivity

2.1 The sensitivity, detection limit and optimum working range for each metal are given in Table 822:II. The sensitivity is defined as that concentration of a given element which will absorb 1% of the incident radiation (0.0044 absorbance units) when aspirated into the flame. The detection limit is defined as that concentration of a given element which produces a signal equivalent to three times the standard deviation of the blank signal (Note: The blank signal is defined as that signal that results from all added reagents and a clean filter which has been ashed exactly as the samples.) The working range for an analytical precision better than 3% is generally defined as those sample concentrations that will absorb 10% to 70% of the incident radiation (0.05 to 0.52 absorbance units). The values for the sensitivity and detection limits are instrument-dependent and may vary from instrument to instrument. Higher blank levels and, hence, worsened sensitivities may be found for other filter matrices. The values in Table 822:II should be taken only as a guide.

3. Interferences

3.1 In atomic absorption spectrophotometry the occurrence of interferences is less common than in many other analytical determination methods. Interferences can occur, however, and when encountered are corrected for as indicated in the following sections. The known interferences and correction methods for each metal are indicated in Table 822:I. The methods of standard additions and background monitoring and correction (1–4) are used to identify the presence of an interference problem. Insofar as possible the matrix of the samples and standards are matched to minimize the possible interference problems.

3.1.1 Background or non-specific absorption can be caused by particles produced in the flame that can scatter the incident radiation, causing an apparent

Table 822:I Flame and Operating Condition for Metals

Element	Type of Flame	Analytical Wavelength nm	Interferences†	Remedy†	References
Ag	Air-C_2H_2 (oxidizing)	328.1	IO_3^-, WO_4^{-2}, MnO_4^{-2}	‡	(5)
Al*	N_2O-C_2H_2 (reducing)	309.3	Ionization, SO_4^{-2}, V	‡,§,‖	(4)
Ba	N_2O-C_2H_2 (reducing)	553.6	Ionization, large conc. of Ca	§, #	(1, 4)
Be*	N_2O-C_2H_2 (reducing)	234.9	Al, Si, Mn	‡	(4)
Bi	Air-C_2H_2 (oxidizing)	223.1	None known		
Ca	Air-C_2H_2 (reducing) N_2O-C_2H_2	422.7	Ionization & chemical	§, ‖	(1, 4)
Cd	Air-C_2H_2 (oxidizing)	228.8	None known		
Co*	Air-C_2H_2 (oxidizing)	240.7	None known		
Cr*	Air-C_2H_2 (oxidizing)	357.9	Fe, Ni	‡	(4)
Cu	Air-C_2H_2 (oxidizing)	324.8	None known		
Fe	Air-C_2H_2 (oxidizing)	248.3	High Ni conc., Si	‡	(1, 4)
In	Air-C_2H_2 (oxidizing)	303.9	Al, Mg, Cu, Zn, $H_xPO_4^{x-3}$	‡	(10)
K	Air-C_2H_2 (oxidizing)	766.5	Ionization	§	(1, 4)
Li	Air-C_2H_2 (oxidizing)	670.8	Ionization	§	(10)
Mg	Air-C_2H_2 (oxidizing) N_2O-C_2H_2 (oxidizing)	285.2	Ionization & chemical	§, **	(1, 4)
Mn	Air-C_2H_2 (oxidizing)	279.5	None known		
Na	Air-C_2H_2 (oxidizing)	589.6	Ionization	**	(1, 4)
Ni	Air-C_2H_2 (oxidizing)	232.0	None known		
Pb	Air-C_2H_2 (oxidizing)	217.0 283.3	Ca, high conc. SO_4^{-2}	‡	(7)
Rb	Air-C_2H_2 (oxidizing)	780.0	Ionization	§	(1, 8)
Sr	Air-C_2H_2 (reducing) N_2O-C_2H_2 (reducing)	460.7	Ionization & chemical	§, **	(1, 8)
Tl	Air-C_2H_2 (oxidizing)	276.8	None known		
V*	N_2O-C_2H_2 (reducing)	318.4	None known in N_2O-C_2H_2 flame		
Zn	Air-C_2H_2 (oxidizing)	213.9	None known		

*Some compounds of these elements will not be dissolved by the procedure described here. When determining these elements one should verify that the types of compounds suspected in the sample will dissolve using this procedure. (See Section 3.2)

†High concentrations of Si in the sample can cause an interference for many of the elements in this table and may cause aspiration problems. No matter what elements are being measured, if large amounts of silica are extracted from the samples, the samples should be allowed to stand for several hours and centrifuged or filtered to remove the silica.

‡Samples are periodically analyzed by the method of additions to check for chemical interferences. If interferences are encountered, determinations must be made by the standard additions method or, if the interferent is identified, it may be added to the standards.

§Ionization interferences are controlled by bringing all solutions to 1000 ppm Cs (samples and standards).

**1000 ppm solution of La as a releasing agent is added to all samples and standards.

#In the presence of very large Ca concentrations (greater than 0.1%) a molecular absorption from $Ca(OH)_2$ may be observed. This interference may be overcome by using background correction when analyzing for Ba.

absorption signal. Light scattering problems may be encountered when solutions of high salt content are being analyzed. Light scattering problems are most severe when measurements are made at the lower wavelengths (i.e., below about 250 nm). Background absorption may also occur as the result of the formation of various molecular species that can absorb light. The background absorption can be accounted for by the use of background correction techniques (1).

3.1.2 Spectral interferences are those interferences that occur as the result of an atom different from that being measured absorbing a portion of the incident radia-

Table 822:II Sensitivity Detection Limit, and Optimum Working Range of Metals

Element	Sensitivity* µg/mL	Range µg/mL	Detection Limits* µg/mL	Detection Limits* µg/m³	Minimum† TLV µg/m³
Ag	0.04	0.5-5.0	.003	0.1	10 (metal and soluble compounds)
Al	0.40	5-50	.04	2	1,000 (metal and oxides)
Ba	0.20	1-10	.01	0.4	500 (soluble compounds)
Be	0.01	0.1-1.0	.002	0.08	2
Bi	0.20	1-10	.07	3	10,000 (as bismuth telluride)
Ca	0.02	0.1-1.0	.002	0.03	2,000 (CaO)
Cd	0.01	0.1-1.0	.002	0.03	50 (metal dust & soluble salts)
Co	0.96	0.5-5.0	.005	0.3	50 (metal fume and dust)
Cr	0.05	0.5-5.0	.003	0.2	50 (water soluble Cr (VI) compounds)
Cu	0.03	0.5-5.0	.004	0.1	200 (fume) 1,000 (dusts and mists)
Fe	0.05	0.5-5.0	.003	0.2	10,000 (iron oxide fume, as iron oxide) 1,000 (soluble compounds)
K	0.02	0.1-1.0	.003	0.1	2,000 (as potassium hydroxide)
Li	0.02	0.1-1.0	.002	0.08	24 (as lithium hydride)
Mg	0.004	.05-.50	.0002	0.01	10,000 (as magnesium oxide fume)
Mn	0.026	0.5-5.0	.003	0.1	5,000 (metal and compounds)
Na	0.005	.05-.05	.0002	0.01	2,000 (as sodium hydroxide)
Ni	0.05	0.5-5.0	.007	0.3	100 (soluble compounds)
Pb	0.10	1-10	.01	0.8	159 (inorganic compounds, fumes & dusts)
Rb	0.02	0.5-5.0	.003	0.1	NL§
Sr	0.06	0.5-5.0	.00	0.2	NL§
Tl	0.23	5-50	.03	0.8	100 (soluble compounds)
V	0.96	10-100	0.5	4	50 (V_2O_5 dust and fume)
Zn	0.007	0.1-1.0	.002	0.08	1,000 ($ZnCl_2$ fume) 5,000 (ZnO fume)

*Sensitivity and solution detection limits are taken from Reference 10. The atmospheric concentrations were calculated assuming a collection volume of 0.24 m^3 (2 L/min for 2 h) and an analyte volume of 10 mL for the entire sample. (NOTE: These detection limits represent the ultimate values since the blanks resulting from the reagents and the filter material have not been taken into account.)

†Threshold limit values of airborne contaminants and physical agents with intended changes adopted by ACGIH for 1987-1988. All values listed are expressed as elemental concentrations except as noted.

§NL signifies No Limit expressed for this element or its compounds.

tion. Such interferences are extremely rare in atomic absorption. In some cases multi-element hollow cathode lamps may cause a spectral interference by having closely adjacent radiation lines from two different elements. In such instances multi-element hollow cathode lamps should not be used.

3.1.3 Ionization interferences can occur when easily ionized atoms are being measured. The degree to which such atoms are ionized is dependent upon the atomic concentration and presence of other easily ionized atoms in the sample. Ionization interferences can be controlled by the addition to the sample of a high concentration of another easily ionized element that will buffer the electron concentration in the flame.

3.1.4 Chemical interferences occur in atomic absorption spectrophotometry when species present in the sample cause variations in the degree to which atoms are formed in the flame. Such interferences may be corrected for by controlling the sample matrix or by using the method of standard additions (2).

3.1.5 Physical interferences may result if the physical properties of the samples vary significantly. Changes in viscosity and surface tension can affect the sample aspiration rate and thus cause erroneous results. Sample dilution and/or the method of standard additions are used to correct

such interferences. High concentrations of Si in the sample can cause an interference for many of the elements and may cause aspiration problems. No matter what elements are being measured, if large amounts of Si are extracted from the samples, the samples should be allowed to stand for several hours and centrifuged or filtered to remove the Si.

3.2 This procedure describes a generalized method for sample preparation which is applicable to the majority of samples of interest. There are, however, some relatively rare chemical forms of a few of the elements listed in Table 822:I that will not be dissolved by this procedure. If such chemical forms are suspected, results obtained using this procedure should be compared with those obtained using an appropriately altered dissolution procedure. Alternatively, the results may be compared with values obtained utilizing a nondestructive technique that does not require sample dissolution (e.g., x-ray fluorescence, activation analysis).

4. Precision and Accuracy

4.1 The relative standard deviation of the analytical measurement is approximately 3% when measurements are made in the ranges listed in Table 822:II. The overall relative standard deviation will be somewhat larger than this value due to errors associated with the sample collection and preparation steps.

4.2 No data are presently available on the accuracy of this method for actual air samples.

5. Advantages and Disadvantages of the Method

5.1 The sensitivity is adequate for all metals in air samples but only for certain metals in biological matrices. The sensitivity of this direct aspiration method is not adequate for Be, Cd, Ca, Cr, Mn, Mo, Ni, and Sn in biological samples.

5.2 A disadvantage of the method is that at least 1 to 2 mL of solution is necessary for each metal determination. For small samples, the necessary dilution would decrease sensitivity.

5.3 To a great extent, these difficulties can be overcome using non-flame ETA methods. Adequate sensitivity for all of the above samples can be obtained and typical analyses require from 15 μL to 75 μL per element. (Assuming 3 atomizations per analysis; 5 μL to 25 μL per atomization.)

5.4 Disadvantages to ETA include the relatively high cost of instrumentation, reliance on sophisticated background correction schemes, and decreased atomization-to-atomization precision, unless an automated sample injector is used (at additional cost).

6. Apparatus

6.1 SAMPLING EQUIPMENT.

6.1.1 Membrane filters with a pore size of 0.8 μm appropriately sized for the sampling holder are satisfactory for air sampling. Quartz and glass fiber filters, fluorocarbon filters and cellulose filters can also be used. The selection will depend on the specific application.

6.1.2 Sampling pump must be of sufficient capacity to maintain a face velocity of 7 cm/s (5). A personal sampling pump must be calibrated with a representative filter unit in the line.

6.1.3 Flow measurement device such as a calibrated rotameter is required to monitor, or a critical flow orifice is used to control the sampling rate.

6.1.4 Typical personal sampling configurations might include a two-piece open-face cassette holder or a filter holder preceded by an impaction or cyclone stage to sample size-segregated aerosols. Other devices such as multi-stage cascade impactors may be used, and area samples may be taken with devices ranging in dimension from 47 mm diameter to 20 × 25 cm rectangular high volume units. Air volumes sampled might range from a few hundred cubic centimeters to thousands of cubic meters (over 7 orders of magnitude).

6.2 GLASSWARE, BOROSILICATE. Before use all glassware must be cleaned in 1:1 diluted nitric acid and rinsed several times with distilled water.

6.2.1 125-mL Phillips or Griffin beakers with watch glass covers.

6.2.2 15-mL graduated centrifuge tubes.

6.2.3 10-mL volumetric flasks.
6.2.4 100-mL volumetric flasks.
6.2.5 1-L volumetric flasks.
6.2.6 125-mL polyethylene bottles.
6.2.7 Additional auxiliary glassware such as pipettes and different size volumetric glassware will be required depending on the elements being determined and dilutions required to have sample concentrations above the detection limit and in the linear response range (i.e., see Table 822:I). All pipettes and volumetric flasks required in this procedure should be calibrated class A volumetric glassware.

6.3 EQUIPMENT.

6.3.1 Atomic absorption spectrophotometer, with burner heads for air-acetylene and nitrous oxide-acetylene flames.
6.3.2 Hollow cathode lamps for each metal, and a continuum lamp.
6.3.3 Hotplate, suitable for operation at 140°C and 250°C.
6.3.4 Two-stage regulators, for air, acetylene and nitrous oxide.
6.3.5 Heating tape and rheostat, for nitrous oxide regulator (second regulator stage may need to be heated to approximately 60°C to prevent freeze-up).

6.4 SUPPLIES.

6.4.1 Acetylene gas (cylinder). A grade specified by the manufacturer of the instrument. (Replace cylinder when pressure decreases below 100 psi or 700 kPa.)
6.4.2 Nitrous oxide gas (cylinder).
6.4.3 Air supply, with a minimum pressure of 40 psi (275 pKa), filtered to remove oil and water.

7. Reagents

7.1 PURITY. ACS reagent grade chemicals or equivalent shall be used in all tests. References to water shall be understood to mean ASTM reagent water Type II. Care in selection of reagents and in following the listed precautions is essential if low blank values are to be obtained.

7.2 CONC NITRIC ACID (68 to 71%). Redistilled, sp.gr. 1.42

7.3 STANDARD STOCK SOLUTIONS (1000 μg/mL) for each metal in Table 822:I. Commercially prepared or prepared from the following:

7.3.1 *Silver nitrate ($AgNO_3$).*
7.3.2 *Aluminum wire.*
7.3.3 *Barium chloride ($BaCl_2 \cdot 2H_2O$).**
7.3.4 *Beryllium metal.*
7.3.5 *Bismuth metal.*
7.3.6 *Calcium carbonate ($CaCO_3$).**
7.3.7 *Cadmium metal.*
7.3.8 *Cobalt metal.*
7.3.9 *Copper metal.*
7.3.10 *Potassium chromate (K_2CrO_4).*
7.3.11 *Iron wire.*
7.3.12 *Indium metal.*
7.3.13 *Potassium chloride (KCl).**
7.3.14 *Lithium carbonate (Li_2CO_3).**
7.3.15 *Magnesium ribbon.*
7.3.16 *Manganese metal.*
7.3.17 *Sodium chloride (NaCl).**
7.3.18 *Nickel metal.*
7.3.19 *Lead nitrate [$Pb(NO_3)_2$].**
7.3.20 *Rubidium chloride (RbCl).**
7.3.21 *Strontium nitrate [$Sr(NO_3)_2$].**
7.3.22 *Thallium nitrate ($TlNO_3$).*
7.3.23 *Vanadium metal.*
7.3.24 *Zinc metal.*

7.4 LANTHANUM NITRATE [$La(NO_3)_3 \cdot 6H_2O$].

7.5 CESIUM NITRATE ($CsNO_3$).

8. Procedure

8.1 CLEANING OF EQUIPMENT.

8.1.1 Before initial use, glassware is cleaned with a saturated solution of sodium dichromate in concentrated sulfuric acid (Note: Do not use for chromium analysis) and then rinsed thoroughly with warm tap water, conc nitric acid, tap water and reagent water, in that order, and then dried.
8.1.2 All glassware is soaked in a mild detergent solution immediately after use to remove any residual grease or chemicals.

8.2 COLLECTION AND SHIPPING OF SAMPLES.

8.2.1 Ambient atmospheric particulate matter and industrial dusts and fumes are sampled with cellulose ester membrane filters of 0.8 μm average pore size (Millipore Type AA or equivalent). The pump used with any membrane filter must be sufficient to maintain a face velocity of at least 7 cm/s throughout the sampling period.

*These salts must be stored in a desiccator to avoid pick-up of water from the atmosphere.

Sample flow rate is monitored with a calibrated rotameter (5) or the equivalent. The flow rate, ambient temperature and barometric pressure are recorded at the beginning and the end of the sample collection period.

8.2.2 For personal sampling, 37-mm diam filters in holders (Millipore Filter Type AA or equivalent) are used. The personal sampler pumps for this application are operated at 1.5 L/min. In general, a 2-h sample at 1.5 L/min will provide enough sample to detect the elements sought at air concentrations of 0.2 × TLV.

8.2.3 After sample collection is complete the exposed filter surface should be covered with a clean filter. Losses of sample due to overloading of the filter must be avoided.

8.3 SHIPMENT OF SAMPLES.

8.3.1 Filter samples (with clean filter covers) should be sealed in individual plastic filter holders for storage and shipment.

8.4 PREPARATION OF SAMPLES. Most workplace or environmental air samples collected on membrane filters or cellulose-based filters can be prepared by the total dissolution method described in sections 8.4.1 through 8.4.3. Filters of quartz or glass fiber or fluorocarbon-based media are treated via the extraction method which begins at Section 8.4.4.

8.4.1 Samples suitable for total dissolution including the clean filter covers and blanks (minimum of 1 filter and cover blank for every 10 filter samples) are transferred to clean 125-mL Phillips or Griffin beakers and sufficient concentrated HNO_3 is added to cover the sample. Each beaker is covered with a watch glass and heated on a hot plate (140°C) in a fume hood until the sample dissolves and a slightly yellow solution is produced. Approximately 30 min of heating will be sufficient for most air samples. However, subsequent additions of HNO_3 may be needed to completely ash and destroy high concentrations of organic material, and under these conditions longer ashing times will be needed. Once the ashing is complete as indicated by a clear solution in the beaker, the watch glass is removed; and the samples are allowed to evaporate to near dryness.

8.4.2 Place the sample beaker on a hot plate controlled at 250°C for several minutes. If evidence of charring is observed, remove from hot plate, cool and repeat the procedure in 8.4.1. If the residue in the beaker is a light whitish material the beaker is cooled and 1 mL of HNO_3 and 2 to 3 mL of distilled H_2O are added. The beaker is replaced on the hot plate and swirled occasionally until the residue is dissolved (as indicated by a light clear solution). The beaker is then removed and the solution is quantitatively transferred with distilled water to a 10-mL volumetric flask. If any elements are being determined that require the ionization buffer, 0.2 mL of 50 mg/mL Cs (9.1.2) is added to the volumetric flask (see Table 822:1, footnote §). If any elements requiring the releasing agent are being determined, 0.2 mL of 50 mg/mL La (9.1.1) is added to each volumetric flask (see Table 822.1, footnote **). The samples are then diluted to volume with water.

8.4.3 The 10 mL solution may be analyzed directly for any element of very low concentration in the sample. Aliquots of this solution may then be diluted to an appropriate volume for the other elements of interest present at high concentrations (Note: Approximately 2 mL of solution are required for each element being analyzed.) The dilution factor will depend upon the concentration of elements in the sample and the number of elements being determined by this procedure.

8.4.4 Samples on non-ashable filter media (e.g., glass or quartz fiber, or fluorocarbon filters), including blanks and appropriate quality assurance samples, are placed into clean, 125 mL Phillips or Griffin beakers. Samples should lie face-up on the bottom of the beaker; they may be cut if necessary. Add 15 mL of hot (85°C), mixed acid extractant (65 mL HNO_3 and 182 m HCl diluted to 1 L with water and cover the beakers with parafilm. Agitate the samples in a heated (85°C) ultrasonic bath at 100 W power for 60 min. Remove the beakers from the bath and allow them to cool to room temperature.

8.4.5 Assemble the vacuum filtration unit (Figure 822:1) with a 25 mm glass filter and prerinse the apparatus with 10 mL of clean, hot mixed acid extractant, carefully rinsing the walls of the funnel, and discard the filtrate. Place a clean 25-mL volumetric flask in the bell jar and express the sample

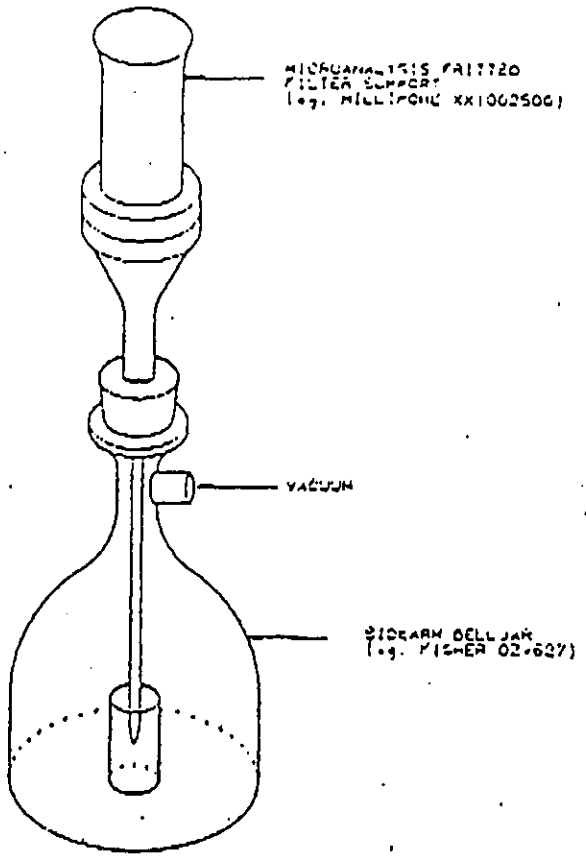

Figure 822:1 – Vacuum filtration apparatus.

through the filter using vacuum, retaining the insoluble sampling medium in the beaker. Rinse the beaker and insoluble materials 3 times with 3 mL portions of water and express the rinse liquid through the filter. Use a clean glass stirring rod to agitate the insoluble material, to ensure complete recovery of trapped liquid. If any of the metals being detected require the use of ionic buffer (see Table 822:I), add 0.5 mL of 50 mg/mL Cs (9.1.2) to the volumetric flask. If releasing agent is required add 0.5 mL of 50 mg/mL La (9.1.1). Dilute to volume with water and proceed with analysis in Section 8.5. Note: Samples small enough to be adequately treated in 25 mL beakers can be extracted with 5 mL of hot extractant, washed with 1.5 mL portions and collected in 10 mL volumetric flasks. Reduce additions of releasing agent and ionization buffer to 0.2 mL.

8.5 ANALYSIS.

8.5.1 Set the instrument operating conditions as recommended by the manufacturer. The instrument should be set at the radiation intensity maximum for the wavelength listed in Table 822:I for the element being determined.

8.5.2 Standard solutions should match the sample matrix as closely as possible and should be run in duplicate. Working standard solutions, prepared fresh daily, are aspirated into the flame and the absorbance recorded. Prepare a calibration graph as described in Section 9.2.4 (Note: All combustion products from the AA flame must be removed by direct exhaustion through use of a good separate flame ventilation system.)

8.5.3 Aspirate the appropriately diluted samples directly into the instrument and record the absorbance for comparison with standards. Should the absorbance be above the calibration range, dilute an appropriate aliquot to 10 mL. Aspirate water between samples. A mid-range standard must be aspirated with sufficient frequency (i.e., once every 10 samples) to assure the accuracy of the sample determinations. To the extent possible, all determinations are to be based on replicate analysis.

9. Calibration and Standards

9.1 IONIZATION AND CHEMICAL INTERFERENCE SUPPRESSANTS.

9.1.1 *Lanthanum solution (50 mg/mL).* Dissolve 156.32 g of lanthanum nitrate [$La(NO_3)_3 \cdot 6H_2O$] in 2% (v/v)HNO_3. Dilute to volume in a 1-L volumetric flask with 2% (v/v)HNO_3. When stored in a polyethelene bottle this solution is stable for at least one year.

9.1.2 *Cesium solution (50 mg/mL).* Dissolve 73.40 g of cesium nitrate ($CsNO_3$) in distilled water. Dilute to volume in a 1-L volumetric flask with distilled water. When stored in a polyethylene bottle this solution is stable for at least one year.

9.2 STANDARD METAL SOLUTIONS.

9.2.1 *Standard stock solutions.* All standard stock solutions are made to a concentration of 1.0 mg of metal per mL. Except as noted these standard stock solutions are stable for at least one year when stored in polyethylene bottles.

a. Master silver standard. Dissolve 1.574 g silver nitrate ($AgNO_3$) in 100 mL distilled water. Dilute to volume in a 1-L volumetric flask with 2% (v/v) HNO_3. The silver nitrate solution will decompose in light and must be stored in an amber bottle away from direct light. New master silver standards should be prepared every few months.

b. Master aluminum standard. Dissolve 1.000 g of Al wire in a minimum volume of 1:1 HCl. Dilute to volume in a 1-L flask with 10% v/v HNO_3.

c. Master barium standard. Dissolve 1.779 g of barium chloride ($BaCl_2 \cdot 2H_2O$) in water. Dilute to volume in a 1-L volumetric flask with distilled water.

d. Master beryllium standard. Dissolve 1.000 g of Be metal in a minimum volume of 1:1 HCl. Dilute to volume in a 1-L flask with 2% (v/v) HNO_3.

e. Master bismuth standard. Dissolve 1.000 g of bismuth metal in a minimum volume of 6 N HNO_3. Dilute to volume in a 1-L volumetric flask with 2% (v/v) HNO_3.

f. Master calcium standard. To 2.498 g of primary standard calcium carbonate ($CaCO_3$) add 50 mL of deionized water. Add dropwise a minimum volume of HCl (approximately 10 mL) to dissolve the $CaCO_3$. Dilute to volume in a 1-L volumetric flask with distilled water.

g. Master cadmium standard. Dissolve 1.000 g of cadmium metal in a minimum volume of 6 N HCl. Dilute to volume in a 1-L volumetric flask with 2% (v/v) HNO_3.

h. Master cobalt standard. Dissolve 1.000 g of Co metal in a minimum volume of 1:1 HCl. Dilute to volume in a 1-L flask with 2% (v/v) HNO_3.

i. Master copper standard. Dissolve 1.000 g of copper metal in a minimum volume of 6 N HNO_3. Dilute to volume in a 1-L volumetric flask with 2% (v/v) HNO_3.

j. Master chromium standard. Dissolve 3.735 g of potassium chromate (K_2CrO_4) in distilled water. Dilute to volume in a 1-L flask with distilled water.

k. Master iron standard. Dissolve 1.000 g of iron wire in 50 mL of 6 N HNO_3. Dilute to volume in a 1-L volumetric flask with distilled water.

l. Master indium standard. Dissolve 1.000 g of indium metal in a minimum volume of 6 N HCl. Addition of a few drops of HNO_3 and mild heating will aid in dissolving the metal. Dilute to volume in a 1-L volumetric flask with 10% (v/v) HNO_3.

m. Master potassium standard. Dissolve 1.907 g of potassium chloride (KCl) in distilled water. Dilute to volume in a 1-L volumetric flask with distilled water.

n. Master lithium standard. Dissolve 5.324 g of Li_2CO_3 in a minimum volume of 6 N HCl. Dilute to volume in a 1-L volumetric flask with distilled water.

o. Master magnesium standard. Dissolve 1.000 g of magnesium ribbon in a minimum volume of 6 N HCl. Dilute to volume in a 1-L volumetric flask with 2% (v/v) HNO_3.

p. Master manganese standard. Dissolve 1.000 g of manganese metal in a minimum volume of 6 N HNO_3. Dilute to volume in a 1-L volumetric flask with 2% (v/v) HNO_3.

q. Master sodium standard. Dissolve 2.542 g of sodium chloride (NaCl) in distilled water. Dilute to volume in a 1-L volumetric flask with distilled water.

r. Master nickel standard. Dissolve 1.000 g of nickel metal in a minimum volume of 6 N HNO_3. Dilute to volume in a 1-L volumetric flask with 2% (v/v) HNO_3.

s. Master lead standard. Dissolve 1.598 g of lead nitrate [$Pb(NO_3)_2$] in 2% (v/v) HNO_3. Dilute to volume in a 1-L volumetric flask with 2% (v/v) HNO_3.

t. Master rubidium standard. Dissolve 1.415 g of rubidium chloride (RbCl) in distilled water. Dilute to volume in a 1-L volumetric flask with distilled water.

u. Master strontium standard. Dissolve 2.415 g of strontium nitrate [$Sr(NO_3)_2$ in distilled water. Dilute to volume in a 1-L volumetric flask with distilled water.

v. Master thallium standard. Dissolve 1.303 g of thallium nitrate ($TlNO_3$) in 10% (v/v) HNO_3. Dilute to volume in a 1-L volumetric flask with 10% HNO_3.

w. Master vanadium standard: Dissolve 1.000 g of vanadium metal in minimum volume of 6 N HNO_3. Dilute to volume in a 1-L volumetric flask with 10% (v/v) HNO_3.

x. Master zinc standard. Dissolve 1.000 g of zinc metal in a minimum volume of 6 N HNO_3. Dilute to volume in a 1-L volumetric flask with 2% (v/v) HNO_3.

9.2.2 *Dilute standards.* Diluted standard mixtures of the elements listed in 9.2.1 are prepared according to the directions in the following sections a to c. The mixed dilute standards are prepared such that the accuracy of the working standard preparation (section 9.2.3) is maximized. Only those elements being determined in the samples need to be prepared as dilute and working standards.

a. Mixed calcium, cadmium, potassium, lithium, magnesium, sodium and zinc standard (0.010 mg/mL for each metal). Pipet 10 mL of the master standards for calcium, cadmium, potassium, lithium, magnesium, sodium, and zinc into a 1-L flask, add 100 mL of conc HNO_3, and dilute to volume with distilled water. Prepare fresh monthly.

b. Mixed barium, bismuth, cobalt, chromium, copper, iron, manganese, nickel, lead, rubidium and strontium standard (0.100 mg/mL for each metal). Pipet 10 mL of the master standards for barium, bismuth, cobalt, chromium, copper, iron, manganese, nickel, lead, rubidium and strontium into a 100-mL volumetric flask, add 10 mL of conc HNO_3 and dilute to volume with distilled water. Prepare fresh monthly (Note: Due to volume considerations, if more than 8 elements are to be prepared one must prepare 2 dilute standards.)

c. Dilute silver standard (1.100 mg of silver per mL). Pipet 10 mL of the master silver standard and 10 mL conc HNO_3 into a 100-mL volumetric flask, and dilute to volume with distilled water. Store in an amber bottle away from direct light. Prepare fresh weekly.

9.2.3 *Working standards.*

a. Mixed working standards. Working standards are prepared by pipetting appropriate amounts of the dilute standards from 9.2.2.a, 9.2.2.b and the master standards for Al, In, Tl and V. Pipet 1 mL of the dilute standard from section 9.2.2.a and 1 mL from the dilute standard from 9.2.2.b into a 100-mL volumetric flask. Pipet into this same volumetric flask, 1 mL from each of the master standards for Al, In, Tl and V. Add 2 mL of 50 mg/mL Cs solution, 2 mL of 50 mg/mL La solution and 10 mL of HNO_3 to the volumetric flask and dilute to volume with distilled water.* This solution contains the following metals at the indicated concentrations: Ca, Cd, K, Li, Mg, Na and Zn—0.1 ppm; Rb, Ba, Bi, Co, Cr, Cu, Fe, Mn, Ni, Pb, & Sr—1.0 ppm; Al, In, Tl, and V—10.0 ppm. (Note: dilute and working standards need to be prepared only for the elements being determined in the sample. If Cr and K are being determined in the sample, separate working solutions must be prepared since the chromium standard contains K. Using the above described preparation procedures a standard containing 1.0 ppm Cr will also contain 1.5 ppm K). This procedure is repeated using 2, 3, 4, and 5 mL of the same standard metal solutions indicated above. These standards must be prepared fresh daily.

b. Working silver standard. Pipet 1 mL of the dilute silver standard (from section 9.2.2.c) into a 100-mL volumetric flask and dilute to volume with distilled water. This solution contains 1.0 ppm silver ion. Repeat this procedure using 2, 3, 4, and 5 mL of the dilute silver standard. The working silver standards must be prepared fresh daily.

9.2.4 The standard solutions are aspirated into the flame and the absorbance recorded. If the instrument used displays transmittance, these values must be converted to absorbance. A calibration curve is prepared by plotting absorbance versus metal concentration. The best fit curve (calculated by linear least squares regression analysis) is fitted to the data points. This line or the equation describing the line is used to obtain the metal concentration in the samples being analyzed.

9.2.5 To ensure that the preparation is being properly followed, clean membrane filters are spiked with known amounts of the elements being determined by adding appropriate amounts of the previously described standards and carried through the entire procedure. The amount of metal is

*The procedure as described has been designed to match the nitric acid concentration of samples and standards (i.e., 10% v/v HNO_3). If the sample solution from section 8.4.3 is to be diluted prior to analysis the amount of acid added to the standards must be reduced by an amount equal to the sample dilution factor.

determined and the percent recovery calculated. These tests will provide recovery and precision data for the procedure as it is carried out in the laboratory for the soluble compounds of the elements being determined.

9.2.6 Analysis by the method of standard additions. In order to check for interferences, samples are initially and periodically analyzed by the method of standard additions and the results compared to those obtained by the conventional analytical determination. For this method the sample is divided into three 2-mL aliquots. To one of the aliquots an amount of metal approximately equal to that in the sample is added. To another aliquot twice this amount of metal is added. (Note: Additions should be made by micropipetting techniques such that the added volume does not exceed 1% of the original aliquot volume—i.e., 10 μL and 20μL additions to a 2-mL aliquot.) The solutions are then analyzed and the absorbance readings (ordinate) are plotted against metal added to the original sample (abscissa). The line obtained from such a plot is extrapolated to 0 absorbance and the intercept on the concentration axis is taken as the amount of metal in the original sample (2). If the result of this determination does not agree to within 20% of the values obtained with the procedure described in section 9.2.4, an interference is indicated and standard addition techniques should be utilized for sample analysis.

9.3 BLANK. Blank filters must be carried through the entire procedure each time samples are analyzed.

10. Calculations

10.1 The uncorrected air volume sampled by the filter is calculated by averaging the beginning and ending sample flow rates, converting to cubic meters and multiplying by the sample collection time.

$$V = \frac{F_B + F_E}{2 \times 1000} t$$

where V = uncorrected sample volume (m^3)
F_B = sample flow rate at beginning of sample collection (L/min)
F_E = sample flow rate at end of sample collection (L/min)
t = sample collection time (minutes)

10.2 If required, the volume is corrected to 25°C and 101.3 kPa by using the formula

$$V_{corr} = \frac{(298)\,(P)\,(V)}{(101.3)\,(T)}$$

where V_{corr} = corrected sample volume (m^3)
P = average barometric pressure during sample collection period (kPa)
T = average temperature during the sample collection period (K)
(Note: K = °C + 273.)
V = uncorrected volume calculated from 10.1 (m^3).

10.3 After any necessary correction for the blank has been made, metal concentrations are calculated by multiplying the μg of metal per mL in the sample aliquot by the aliquot volume and dividing by the fraction which the aliquot represents of the total sample and the volume of air collected by the filter.

$$\mu g \text{ metal}/m^3 = \frac{(C \times V) - B}{V_{corr} \times F}$$

where C = concentration (μg metal/mL) in the aliquot
V = volume of aliquot (mL)
B = total μg of metal in the blank
F = fraction of total sample in the aliquot used for measurement (dimensionless)
V_{corr} = corrected volume of air sample and calculated from 10.2.

10.4 Untreated filter samples may be stored indefinitely.

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Subcommittee 6

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Appendix J

Revised Mining Permit Quality Assurance/Quality Control Document for Asbestiform Sampling, February 1993

Foth & Van Dyke

REPORT

Revised Mining Permit Quality Assurance/ Quality Control Document for Asbestiform Sampling

Flambeau Mining Company

February 1993

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Revised Mining Permit Quality Assurance/ Quality Control Document for Asbestiform Sampling

Scope ID: 91F6

Prepared for:

Flambeau Mining Company
Ladysmith, Wisconsin

Prepared by:

Foth & Van Dyke and Associates
St. Louis, Missouri

February 1993

Flambeau Mining Company
Revised QA/QC Document

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Appendices

1 Introduction

A monitoring and quality assurance plan has been developed for the Flambeau Mining Company (Flambeau) project for the construction and operation phase in response to NR 132.06(3)(d), NR 182.08(2)(e)8, and NR 182.09(2)(a)7, and the project's long-term care and maintenance phase in response to NR 132.08, NR 182.09, NR 182.16, and NR 182.19 as written in April, 1991 and revised in August 1991. That document will be referred to as the August 1991 Quality Assurance/Quality Control (QA/QC) document.

Operation phase monitoring includes a program to monitor asbestiform fibers for the period May through September for the first three years or throughout the operating life of the mine, if found necessary. Pursuant to the approved Mining Permit, Part 4, Condition 8, this addendum to the Mining Permit Quality Assurance/Quality Control Document, which addresses the asbestiform monitoring program, is submitted to the Wisconsin Department of Natural Resource (WDNR). The QA/QC documents are required to be submitted to WDNR at least 90 days prior to implementation of this element of the monitoring plan. Contained herein are methodologies for asbestiform fiber sample collection and analyses and descriptions of sampling equipment. The sampling schedule, locations, and equipment calibration and preventative maintenance procedures are also presented. QA/QC procedures for other monitoring requirements are described in the April and August QA/QC 1991 documents.

This addendum to the QA/QC plan is structured to meet the intent of the Department's requirement for QA/QC documents and the USEPA's guidelines and specifications for preparing QA/QC project plans.

2 Organization and Responsibility

2.1 Field Operations

Asbestiform sample collection activities will be performed by personnel from Foth & Van Dyke and from Flambeau. Additional descriptions of the organization and responsibilities for field operations can be found in Section 4.0 of the August 1991 QA/QC document.

2.2 Laboratory Operations

Laboratory analytical activities were also described in the QA/QC document as revised in August 1991. Asbestiform analysis will be performed by Wisconsin Occupational Health Lab (WOHL). This lab is a WDNR-certified laboratory. A copy of their quality assurance plan is included in Appendix A.

3 Quality Assurance Targets for Precision, Accuracy, and Method Detection Limits

The purpose of quality assurance objectives is to define the precision and accuracy targets as well as the method detection limits which will be used for both laboratory and field measurement data.

All measurements must be made such that results are representative of the media and conditions being measured. Data quality objectives for accuracy and precision for each measurement parameter will be based on the measurement system employed and the requirements of this plan. Quality assurance objectives for laboratory data are found in Table 3-1.

Table 3-1

Quality Assurance Objectives for Laboratory Measurement Data

Parameter	Matrix	Analytical	Precision	Accuracy	Method Det. Limit	Sample Volume
Asbestos Fibers	Mixed Cellulose Ester	NIOSH 7400	0.10 to 0.12	80 to 100 fibers	0.25 um	50-150 ft^3 of air
Asbestos Fibers	Mixed Cellulose Ester	NIOSH 7402	0.28[1] 0.20[2]	80 to 100 fibers	0.25 um	50-150 ft^3 of air

1. When 65% of fibers are asbestos.

2. When adjusted fiber count is applied to PCM count.

4 Sampling Procedures

4.1 Sampling Locations and Schedule

Asbestiform samples will be collected at three of the sites where total suspended particulate (TSP) samples will also be collected. These are the northeast, northwest and southeast sites as shown on Figure 4-1. Site selections for TSP monitoring were based on USEPA siting criteria as described in the Ambient Monitoring Guidelines for Prevention of Significant Deterioration, EPA 450/4-87-007.

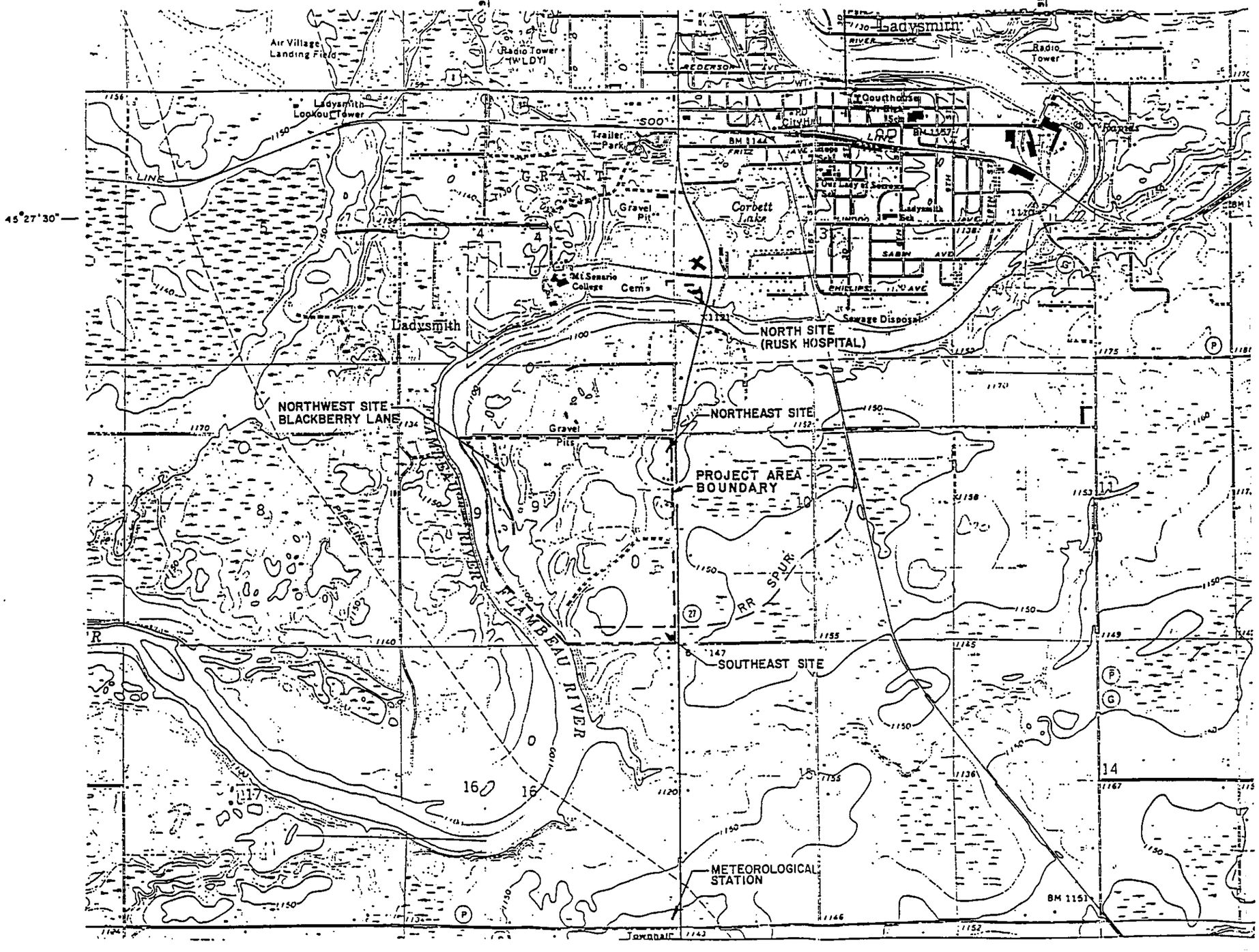
Samples will be collected one day a month during the period May through September for a total of five sample sets of two per site per year. One sample will be coordinated with a blasting day at the mine or during another significant material handling procedure. This monitoring will be conducted only once if no asbestiform fibers are detected. The remaining samples will be collected according to the commonly employed national ambient air sampling schedule.

Each monitoring event will be conducted over an eight-hour duration coincident with the normal daily operating schedule of the mine. Two samples will be collected at each site, one at a low flow rate and the other at a high flow rate. Two flow rates will be used in order to prevent voiding a sampling event due to overloaded or underloaded samples.

Monitoring shall begin when the mining phase begins and shall be repeated annually. If monitoring during the first three years of active mining does not detect asbestiform fibers from the mining operations, monitoring will be discontinued per Part 4, Condition 5 of the Mining Permit.

4.2 Sampling Equipment

In the sampling process, air is drawn through a filter at a known rate by a flow-controlled pump. The sampling components are described below.



NOTE: BASE MAP PREPARED FROM U.S.G.S. MAPS 7.5 MINUTE SERIES, LADYSMITH AND THORNAPPLE WISCONSIN QUADRANGLES

FIGURE 4-1

Asbestiform Sampling Sites

Flambeau Mining Company

Ladysmith, Wisconsin

Scale: N/A	Date: 01/93
Prepared by: Foth & Van Dyke	By:

4.2.1 Filter Media and Cassettes

Commercially available filters comprised of the filter media and cassettes will be used for sample collection. The cassette shall be loaded with a 25 mm diameter mixed cellulose ester (MCE) filter of pore size 0.8 um. The filter shall be backed with a 5.0 mm pore size MCE filter followed by a cellulose support pad. The support pad is provided so that distortion of the filter caused by differential pressure across it does not occur during sampling. The cassettes shall be purchased with the required filters in position. The cassettes will be sealed by the manufacturer to prevent air leakage.

The movement of air through the filter may cause a significant buildup of static charge on the cassettes. The static charge, in turn, is likely to affect the distribution of fibers on the filter and may cause fibers to collect on the cassette walls rather than on the filter. To guard against static buildup, a metal cowl or electrically conductive cassette shall be used in conjunction with the sampling train.

4.2.2 Sampling Pump

The sampling pump shall be capable of achieving flow rates of 2-12 liters per minute (lpm) and of pumping over an eight hour duration. A typical pump and sampling train is shown in Figure 4-2. Flexible tubing shall be used to connect the filter cassette to the sampling pump. The sampling pump shall provide a non-fluctuating air-flow through the filter, and shall maintain the initial flow rate to within $\pm 10\%$ throughout the sampling period. A critical orifice will be used to meet this requirement. Because slight changes in size and shape of the orifice (due to wear or accumulation of particles) will change the orifice characteristics, orifices shall be inspected during each sampling event.

4.2.3 Rotameter

A high quality rotameter with arbitrary unit graduations shall be used to monitor the sample flow rate through the sampling apparatus. The flow measuring device shall be inserted downstream of the filter and the pump assembly. The rotameter shall be accurate to $\pm 5\%$

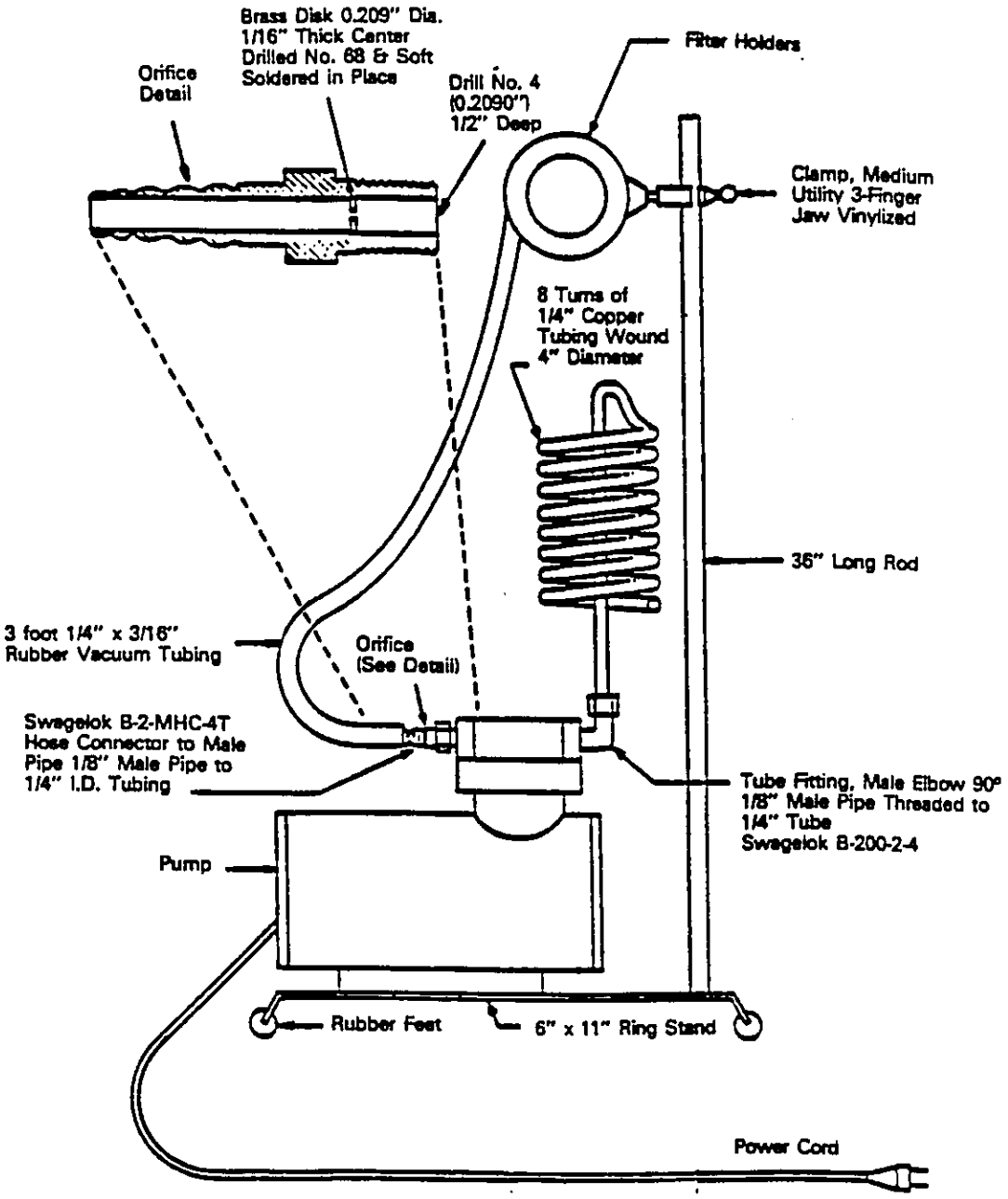


FIGURE 4-2	
Asbestiform Sampling Train Flambeau Mining Company Ladysmith, Wisconsin	
Scale: N/A	Date: 01/93
Prepared by: **Foth & Van Dyke**	By: CDA

of the expected sampling flow rate. The rotameter shall be calibrated before and after each sampling event against a National Bureau of Standards (NBS) traceable primary flow standard with an accuracy of $\pm 1\%$.

4.3 Sampling Procedures

4.3.1 Air Volume

The sampling rate and the period of sampling shall be selected to yield as high a sampled volume as possible. Two samples will be collected over an eight hour period; one at 3-4 lpm and the other at 6-8 lpm in order to collect an optimum volume of air per unit area of filter. This will minimize the potential that filters will have to be rejected for analysis due to overloading or underloading.

4.3.2 Sampling Operation

Air samples shall be collected using the cassettes described in Section 4.2.1. Each cassette assembly will be visually checked for leaks both before and after each sampling event.

Sampling shall be conducted with the cassette open-face. During sampling, the filter cassette shall be supported on a stand so that it is isolated from the vibrations of the pump. The cassette shall be held facing vertically downward at a height of approximately 2.1 meters above ground level and connected to the pump with a flexible tube. It may be sufficient to collect samples with a standard cassette configuration. If conditions dictate the need for additional protection, however, an extension cowl may be affixed to the front of the cassette.

The sampling pumps will be calibrated with a loaded cassette in line. A rotameter, which has been calibrated against a primary standard, will be inserted downstream of the filter and the pump assembly. Once the sampling equipment is in place, as shown in Figure 4-2, and has been calibrated, the sampling site location, start time, filter number, pump number and other pertinent information will be recorded. The pump will be started and the flow rate recorded. Flow will be verified after 15-30 minutes of sampling. The critical orifice should maintain the set flow rate. The rate will be verified at least every two hours. If at any time the

measurement indicates that the flow rate has decreased by more than 30%, the sampling will be terminated. The mean value of these flow rate measurements will be used to calculate the total air volume sampled.

At the end of each sampling event, the final flow rate and the stop time will be recorded. A cap will be placed over the open end of the cassette, and the cassette will be packed in a clean plastic bag for return to the laboratory. Field blank filters will also be included in the shipment to the laboratory, as described in Section 7.1.2, and will be processed through the remaining analytical procedures along with the samples.

5 Sample Custody

5.1 Sample Transport and Chain-of-Custody Procedures

After collecting each sample, precaution must be taken to ensure its integrity and prevent contamination until it is analyzed. The plastic top cover and small end caps will be replaced on the monitor immediately after sampling. Collected samples will be shipped in a rigid container with sufficient packing material to prevent damage. Each step in the transfer of the samples from the field to the laboratory will be recorded on a Chain of Custody form. Each time the custody of the samples is relinquished to another individual (or to the laboratory), the date, time, and items transferred are noted on the form. Upon receipt of samples in the laboratory, the Chain of Custody Record will be checked and signed. A copy of the form will be retained by the laboratory and the remaining copy returned to the sampling team. Detailed Chain of Custody procedures can be found in Section 7.0 of the August 1991 QA/QC document. An example of the Chain of Custody Record is shown as Figure 5-1.

5.2 Laboratory Arrangements

Foth & Van Dyke or Flambeau will send all samples for asbestiform analysis to the Wisconsin Occupational Health Lab.

Procedures for the receipt and logging of samples by the laboratory are addressed in the lab's quality assurance plan found in Appendix A.

5.3 Sample Disposal

These procedures are found in Sections 7.3 of the August 1991 QA/QC document.

CHAIN OF CUSTODY

Client: _____ Scope I.D.: _____
Project: _____ Page: _____
Prepared by: _____ Date: _____
Sampler(s): _____ Date: _____
(Signature)

Sta. No.	Date	Time	Comp	Grab	Station Location	Serial Tag Number	No. of Con-tain-ers	Lab Numbers	Analysis Required							Remarks

Signature	Company	Date	Time	Carrier
Relinquished By:				
Received By:				
Relinquished By:				
Received By:				
Relinquished By:				
Received by Lab:				

Foth & Van Dyke

Remarks:

FORM EES005 (1/91)

FIGURE 5-1
Chain of Custody
Flambeau Mining Company
Ladysmith, Wisconsin

Scale: N/A	Date: 01/93
Prepared by: Foth & Van Dyke	By: CDA

5.4 Documentation

Asbestiform sampling activities will be documented by keeping a written record of sampling activities and implementing the Chain of Custody procedures described above. This will provide for the integrity of data by tracking and documenting samples from the time they are collected by the sampling team through receipt at the laboratory.

5.4.1 Sample Numbering System

A sample numbering system will be used to identify each sample. This numbering system will provide a tracking procedure to allow retrieval of information about a particular sample and assure that each sample is uniquely numbered. The numbers will identify the project and the site at which the sample was collected using the site I.D. number used for TSP samples. Site No. 0003 will be used for the southeast site, No. 0004 for the northeast site, and No. 0005 for the northwest site. For example, FA-0003-001 will be used for asbestos sample number one at the southeast site.

5.4.2 Sample Collection Data

Sample collection data will be collected and documented in the field notebook for each sample acquired. The following data will be recorded:

- Sample identification numbers, and time/date of collection, location (site I.D. number), and description.
- Calibrations performed in the field.
- Statements pertaining to any problems encountered.
- Weather and site conditions.
- Individuals collecting the samples and field supervisor's signature.

5.4.3 Sample Labelling

Sample labels must contain sufficient information to uniquely identify the sample in the absence of other documentation. This will include at a minimum:

- Project number
- Unique sample number
- Sample location
- Sampling date and time
- Individual collecting the sample

6 Analytical Procedure

The MCE filters will first be analyzed by phase contrast microscopy (PCM) in order to screen out samples with small amounts of asbestiform fiber on them. Samples will be analyzed for fibers which have parallel sides with aspect ratios which are greater than 3:1. Laboratory results will be reported as:

- Total number of fibers - length, width and aspect ratio.
- Fiber density on the filter (fibers/mm^2).
- Concentration of asbestos fibers per milliliter of air sampled.

Transmission electron microscopy (TEM) will be used to analyze filters with a concentration of greater than or equal to 0.01 fibers per cubic centimeter (f/cc) as analyzed by PCM. This analysis will be performed because PCM does not differentiate between asbestos and other fibers. When the concentration of all filters is less than 0.01 f/cc, only the filter from the downwind site with the highest fiber concentration will be analyzed by TEM.

A concentration of 0.01 f/cc was selected as the level at which TEM will be performed because it is the limit for reliable quantification by PCM. It was also selected because this is the level at which asbestos removal contractors are commonly released following an abatement action as specified by the Quality Assurance Division of the USEPA.

The PCM analytical method will be based on NIOSH Method 7400. A copy of this method is presented in Appendix B. The equipment used, and the sample preparation, calibration, quality control and measurement procedures and calculations are described within the method.

The TEM method will be based on NIOSH method 7402. A copy of this method is presented in Appendix C.

7 Calibration Procedures and Frequency

Standardized calibration of the equipment used is necessary to obtain valid data. Monitoring equipment will be calibrated prior to and after each use.

7.1 Field Instruments

The sampling pumps will be calibrated with a loaded cassette in line. A rotameter will be inserted downstream of the filter and the pump assembly. The rotameter shall be accurate to ±5% of the expected sampling flow rate. The rotameter shall be calibrated before and after each sampling event against a NBS traceable primary flow standard with an accuracy of ±10%. If the calibrations do not agree, the samples will be discarded and resampling shall be conducted.

7.2 Laboratory Instruments

Calibration procedures for the Walton-Beckett graticule and the microscope are described in Appendices A and B. See pages A-13, number B-4 for WOHL's procedures and 7400-4, number 11 for the NIOSH procedure.

8 Quality Control Checks

8.1 Field QC Checks

8.1.1 Internal Quality Control Checks

Prior to actual sampling on site, all of the applicable sampling equipment will be thoroughly checked to ensure that the components are clean and operable. In addition, the cassette assembly and sampling train should be checked for leaks before use. A flow measuring device, such as a rotameter, will be inserted downstream of the filter and the pump assembly. The flow measuring device shall be accurate to $\pm 5\%$ of the expected sampling flow rate. All flow measurement equipment shall be calibrated against a NBS traceable primary flow standard with an accuracy of $\pm 1\%$.

8.1.2 Field Blanks

To ensure that contamination by extraneous asbestos structures during specimen preparation is insignificant compared with the results reported on samples, it is essential that a continuous program of blank measurements be established. The number of field blanks incorporated into the program will be at least 10% of the total number of samples collected. All of these field blanks will be analyzed. The caps from the field blank cassettes will be removed and then the caps and cassettes will be stored in a clean area (bag or box) during each sampling event. The caps on the blank cassettes will be replaced when the sampling event is completed.

8.2 Laboratory QC Checks

8.2.1 Training

Everyone involved with measuring airborne asbestos (field technicians, microscopists, etc.) will be properly trained in applicable procedures. Only trained analytical laboratories will be

hired. It is currently planned to use WOHL which participates in NIOSH's Proficiency Analytical Testing Program. WOHL will provide information on:

- The laboratory's quality control program;
- The lowest fiber counts in f/cc that are routinely reported;
- The thinnest fibers that are routinely detected.

The Wisconsin Occupational Health Laboratory's training procedures are described in Appendix A, page A-16.

8.2.2 Laboratory Blanks

Blank filters shall be analyzed to determine the mean background asbestos structure count for the analytical procedure. Before air samples are collected, a minimum of two unused MCE filters from each lot of 100 filters shall be sectioned and analyzed by PCM to determine the mean background asbestos structure concentration. If the mean concentration for all types of asbestos structures, expressed as the concentration per unit area of the sample collection filter, is found to be more than five fibers per 100 fields, the reasons for the high blank values will be determined and the situation corrected before scheduled air samples are collected.

Laboratory blanks shall be collected intermittently at all critical phases of the laboratory program. The mean of the field blank counts and laboratory blank counts will be calculated and these values will be subtracted from each sample count before reporting the results.

8.2.3 Analytical Checks

Since there is a subjective component in the structure counting procedure, it is necessary that recounts of some specimens be made by different microscopists in order to minimize the subjective effects. Such recounts provide a means of maintaining comparability between counts made by different microscopists. Variability between microscopists will be characterized. These quality assurance measurements will be made for a minimum of approximately 10% of all scheduled analyses. Upon completion of the recounts, the results

are compared and the formula given on page A-18 is used to determine if a pair of counts should be rejected. If a pair of counts are rejected, then the rest of the filters in the submitted set are recounted.

In addition, WOHL participates in two round robin programs; the first with the Salt Lake OSHA Lab and the NIOSH Lab and the second with seven other private laboratories listed in Appendix A.

8.2.4 Quality Control Check Samples

A rather comprehensive intra-laboratory program is being utilized at WOHL. For each study undertaken, a request for QC control samples is initiated. The samples are prepared and assigned and entered into the computer. Two QC samples plus a blank are prepared for each set of samples.

Wisconsin Occupational Health Laboratory's quality assurance procedures can be found in Appendix A starting on page A-17.

Additional routine procedures to assess precision and accuracy can be found in section 11 of the revised QA/QC document dated August 1991.

9 Miscellaneous Items

Preventative maintenance, data reduction, validation and reporting procedures, required corrective actions, a description of performance and system audits, and maintenance of quality assurance records are described in Sections 10, 12, 13, 14, and 15 of the August 1991 QA/QC document. Additional preventative measures can be found in Appendices B & C, in the NIOSH methods.

Appendix A
Wisconsin Occupational Health Laboratory
Quality Assurance Manual

WISCONSIN OCCUPATIONAL HEALTH LABORATORY

ASBESTOS FIBER COUNTING

QUALITY ASSURANCE MANUAL

January 1989

PROCEDURE FOR REVIEWING AND MAKING CHANGES IN THIS MANUAL

This manual shall be submitted on an annual basis to the appropriate supervisor, Lab Director and Section Chief for review. In addition, any changes that are made in this manual must also be made in the supervisor's, Lab Director's and Section Chief's copies and must be signed by both the supervisor and Lab Director.

No pages may be added or deleted from this manual without making the same changes in all the other copies. Again, signatures of the supervisor and Lab Director are required.

SUPERVISOR	DATE	LAB DIRECTOR	DATE	SECTION CHIEF	DATE
Steve Stahl	7-16-90	Terry L Bush	7-17-90	[signature]	7/17/90
Steve Stahl	3-10-92				

INDEX

PART IV
SECTION E
QUALITY ASSURANCE

All analysts must adhere to a written quality assurance program.
Attach a copy of the written quality assurance manual used for asbestos fiber counting. The following items must be addressed:

How is internal quality control established (*i.e.*, repetitive counts on the same filter, blank counts, blind repeats, control charts, *etc.*)?
In which interlaboratory quality control programs have you actively pursued participation?
Who has overall responsibility for quality assurance and what criteria are used for measuring acceptable performance?

Attach examples of **COMPLETED** report sheets, work sheets and log-in documentation. In addition, attach examples of control charts, tables or other written documentation of routine proficiency review.
With which laboratories do you participate in interlaboratory round-robin fiber counting programs and with what frequency?

1. See Round Robin Participants Sheet
2. These Round Robins are perfomred biannually

(Optional) Would you be willing to include other participants? Y (N)

Group is too large

QUALITY CONTROL PERSONNEL

QC Officer - Derek Popp

Responsible for overall quality assurance of airborne asbestos analysis.

Asbestos Section Supervisor - Steve Strebel

Responsible for day to day running of Asbestos Section and its quality control program.

1. Mr. Tom Stavros
Wausau Insurance Company
2000 West Wood Drive
Wausau, WI 54401

2. Mr. Robert Voborsky
Northland Environmental Services, Inc.
15 Park Ridge Drive
Stevens Point, WI 54481

3. Ms. Sandy Von Holdt
Sentry Parker Services
1800 North Point Drive
Stevens Point, WI 54481

4. Dr. Hector MacDonald
MacDonald Research Group, Inc
1441 North Mayfair Rd
Milwaukee, WI 53226

5. Mr. Robert Weisberg
Analytical Testing Services
25 Thurber Blvd
Smithfield, RI 02917

6. Mr. Phillip A. Peterson
Fibertec, Inc.
700 Abbott Road
East Lansing, MI 48823

7. Mr. Keith Trombley
Sierra Technical Service, Inc.
Suite A
237 Dino Drive
Ann Arbor, MI 48103

8. Daniel C Walker Jr.
Mechanical Insulation Systems Inc.
304 S. Niagra Street
Saganaw, MI 48602

9. Ms. Carol Gannon
CG Technologies
535 Science Drive Suite B
Madison, WI 53711

10. Mr. Doug Dube
Wisconsin Occupational Health Lab
979 Jonathon Drive
Madison, WI 53713

ROUND ROBIN PARTICIPANTS - GROUP 2

1. NIOSH

2. OSHA Salt Lake City Lab

PART IV
SECTION A
ANALYSTS

Training

Analyst's Name	Formal Program (for example, NIOSH 582)	In-House YES	In-House NO
Dick Kittel	NIOSH 582 March 1991	X	
Steve Strebel		X	
John Knight		X	
Cheri Johnson		X	
Derek Popp	NIOSH 582 December 1989	X	

PART IV
SECTION B
EQUIPMENT

Complete the following table to describe microscope(s) used by the laboratory:

Manufacturer	Model	Ser. No.	** Magnification ** Eyepiece	Objective	Filter Type	Walton-Beckett Graticule Yes	No
ZEISS		4752136	lox Model 464042-9903 464042-9902	Ph2 Plan 40 #4464146	Green	X	
Zeiss	473011-9901	467065-9914	lox Model 464042-9903 46 4042-9902	Ph2 Plan 40 #460711-9902	Green	X	

Describe any additional instruments or equipment that enhance the laboratory's ability to count asbestos fiber:

Quick Fix, Counters

AO Micrometer Slide for calibration of reticule

Phase Contrast Test Slide

Optometric Slide for Calibration

Porton Reticule

JEOL 1200 EX Scanning Transmission Electron Microscope

SECTION C
PROCEDURES

Provide copies of all procedures used by the laboratory for fiber counting.

See attached procedures titled "Airborne Asbestos Fiber Counting," 7400 Method & P&CAM 239 Method

PART IV
SECTION D
TRAINING

Provide a copy of any in-house training program(s) or a description sufficient to determine the scope of training and the number of hours required for completion.

See attached page titled "Training for Phase Contrast Microscope Fiber Counting."

Wisconsin Occupational Health Lab

Receiving and Logging Procedures for Air Asbestos Samples

1. Samples are received in office.

2. The following sample rejection criteria is followed:
   A. Bulk samples included with air samples.
   B. Filters not uniquely identified.
   C. Tampering with cassettes is evident.
   D. A filter is rejected if cassette is open or top plug is missing.

3. Samples are given sequential lab numbers. A sticker with this lab number is placed on the filters, and a copy of the corresponding number is placed on the paperwork.

4. Samples are brought into the asbestos section and logged into section for double check of field and lab numbers.

5. Sample paperwork is logged into Labs LIMS system.

6. Computer generated worksheets and original paperwork brought to asbestos section.

AIRBORNE ASBESTOS FIBER COUNTING

A. Filter Preparation (mixed cellulose ester filters)

1. Quick Fix Method (preferred)
   a. Clean slides, plug in unit and wait until red light comes on.
   b. Using scalpel, cut wedge from filter and position.
   c. Place slide on stage and position wedge under nozzle at bottom of unit.
   d. Draw approximately 0.2 ml of acetone into syringe or pipette. Inject acetone into fitting at top of unit. The acetone should be injected very slowly to avoid blowing fibers off the filter.
   e. Wait 5-8 seconds and withdraw slide. Filter is now "fixed."
   f. Mark slide on bottom to show outline of wedge.
   g. Apply just enough triacetin (about one small drop) to cover filter wedge to insure a minimum of flowing over the edge when cover slip is applied.
   h. Apply cover slip within 30 seconds of application of triacetin.
   i. Filter should clear immediately. If not, wait 10 minutes or until filter completely clears.

2. Dimethyl phthalate-diethyl oxalate procedure (alternate)

   a. Clean slide.
   b. Place drop of mounting media on slide and spread to wedge piece.
   c. Using scalpel, cut about 1 cm x 2 cm wedge shaped piece.
   d. With forceps, place wedge (dust side up) on mounting media.
   e. Place a clean cover slip (#1) over filter wedge, being careful to avoid air bubbles. Take felt tipped pen and outline filter on bottom of slide.
   f. Filter should clear in 15 to 30 minutes.
   g. Filters should be counted as soon as possible but may be counted up to 48 hours after mounting. Beyond this time, crystals start to form making counting difficult.

B. Microscope Preparation

1. Should include
   a. Binocular head.
   b. 10x Huygenian or wide field eyepieces.
   d. Walton-Beckett Graticule.
   e. Mechanical stage.
   f. Phase contrast condenser with numerical aperture (N.A.) equal or greater than the N.A. of the objective.
   g. 40x phase contrast achromatic objective (N.A.) 0.65 - 0.75).
   h. Phase-ring centering telescope.
   i. Green filter.
   j. Stage micrometer with 0.01 mm subdivisions.

2. Daily check phase ring alignment.

3. Adjust microscope to manufacturer's recommendations daily.
   a. Light source must be in focus and centered on the condenser iris or annular diaphragm.
   b. Particulate matter to be examined must be in focus.
   c. The illuminator field iris must be in focus, centered on the sample and only opened to the point where the field of view is illuminated.
   d. Phase rings must be concentric.

4. Calibrating Walton-Beckett reticle.
   a. Using the micrometer slide measure the diameter of the reticle circle in mm.
   b. Calculate the area of the circular field using the formula:

$$\text{AREA} - \frac{\text{diameter}}{2}^2$$

C. Counting fibers
   1. Place slide on mechanical stage and position under objective.
   2. Count fibers using counting rules A.
   3. Count only fibers 5 microns or greater.
   4. Count only fibers with a length to width ratio of 3:1 or greater
   5. Bundles of fibers are counted as one fiber unless both ends of the fiber are clearly resolved.
   6. When a mass of material covers more than 25% of the field of view, reject the field and select another. Do not include in number of fields counted.
   7. Count as many fields as necessary to get 100 fibers but count at least 20 fields even if you have more than 100 fibers. Stop at 100 fields even with no fibers.
   8. Count fibers that cross out of the count area on the top half of the counting field with both ends visible, and reject fibers crossing the half or more than one boundry.

D. Calculations

$$F/cc = \frac{(AFC_s - AFC_b)\ \text{Filter area}}{MFA \times V \times 1000}$$

Where:

AFC_s = Average Fiber Count of sample
AFC_b = Average Fiber Count of blank
Filter area = sampling area of filter (for 37mm filter 855mm^2)
MFA = Microscope field area in mm^2
V = Air volume in L

E. References

NIOSH 7400

Time Weighted Average for Airborne Asbestos

Since exposure may vary because of many factors, a total exposure weighted by time and level of exposure is frequently requested. The "Time Weighted Average" (TWA) is the method used to determine the exposure which best reflects the time and concentration interaction.

The calculation for obtaining TWA is as follows when two or more filters have been used:

$$TWA = \frac{C_1T_1 + C_2T_2 \ldots + C_nT_n}{(T_1 + T_2 \ldots T_n)}$$

where C_1 = F/ml of filter 1
T_1 = Time filter 1 was exposed in minutes
C_2 = F/ml of filter 2
T_2 = Time filter 2 was exposed in minutes
C_n = F/ml of last filter in series
T_n = Time last filter in series was exposed in minutes

TRAINING FOR PHASE CONTRAST MICROSCOPE FIBER COUNTING

The following listed items shall be included in training any individual who will report phase contrast fiber counts.

1. This individual will be required to read the NIOSH method 7400 and be familiar with the techniques involved.

2. The individual will be familiarized with a microscope, including cleaning, alignment, Kohler illumination, checking phase ring and how to correct any of these that are not at the expected condition.

3. This training shall consist of at least 40 hours, of which at least 8 hours are spent with an experienced fiber counter in drawing out fibers in the field, so that the individual can recognize and find all fibers that should be counted.

4. At least 32 hours of samples should be counted by the new counter and an experienced counter and the results should be compared.

5. At least 10 QC samples should be counted for proficiency and the results should be within the expected limits prior to the analyst being allowed to count on his own.

6. Two QC samples should be run with each batch of samples counted and the individual shall pass these quality control samples prior to any results being reported by this analyst.

7. The analyst must run each round of NIOSH PATS and pass each round successfully or go back through comparison counting with a proficient experienced counter.

This training program shall be reviewed annually by the Program Director in order to see that analysts are proficient and that this provides adequate training for the individuals involved.

QUALITY ASSURANCE

Quality Assurance is designed to provide, within known error levels, all results reported from this laboratory. It is our objective that the levels of precision and accuracy should be the best possible with the given equipment, manpower, and Time constraints.

To accomplish this objective, the program consists of testing both inter and intra-laboratory unknowns, thorough record keeping, routine checking and calibration of equipment, a complete up-to-date procedure manual, and routing evaluation of results.

This laboratory has participated in the PAT program since round seven. The asbestos section has consistently had satisfactory ratings for the asbestos counting. Each person trained for doing fiber counting is required to count the samples provided and to give the supervisor a copy of his results. These are then compared to the results returned by the program provider.

The second inter-laboratory program is a round robin program between the Salt Lake OSHA Lab, the NIOSH Lab, and the Wisconsin Occupational Health Lab. Again, all personnel who are qualified to count, must count the slides provided. The results are forwarded to the Salt Lake OSHA Lab, which scores the results and sends a copy to each lab for posting.

A third program in which the Wisconsin Occupational Health Lab (WOHL) participates and (and acts as coordinator) involves seven other private or commercial laboratories. Each lab, in rotation, provides a set of slides which is forwarded from lab to lab. The results are sent to the W.O.H.L. where the scoring is done and results sent to the participating labs.

A rather comprehensive intra-laboratory program is being utilized. For each study received, a request for QC control samples is initiated. The samples are prepared and assigned and entered into the computer. In general, two QC or two QC plus a blank are prepared for each set of samples.

Details on sample preparation are shown in the QC procedure manual. Each set of controls or controls and blank are prepared so the type of matrix and constituents match the unknown samples. As a rule, this follows whether the samples are run-of-the-mill or non-routine.

Each day randomly selected slides are chosen by the supervisor and re-marked. The re-marked slides are then given to an analyst for recounting. At least 10% of all slides are recounted.

Upon completion of recounts, the results are compared and the following formula is used to determine if a pair of counts should be rejected:

$$F2 - F1 > 2.77\ (F)(CV_F)$$

where:

F1 = lower airborne fiber concentration
F2 = higher airborne fiber concentration
F = average of the two fiber concentration
CV_F = CV for the average fiber concentration

If a pair of counts are rejected by this criterion then recount the rest of the filters in the submitted set. Apply the test and reject any other pairs failing the test. Rejection shall include a memo the the industrial hygienist or client that the sample failed a statistical test for homogeneity and the true air concentration may be significantly different than the reported value.

Each analyst will count a minimum of 2 coefficient of variation samples daily. These samples will be taken from our CV pool of samples. All results will be entered into the computer to provide updated CV values for various loadings.

After the computer has been fed data regarding the identification number, matrix or method of collection, units to be measured, identification code for the constituent, and the actual value of the constituent, the samples are given to the analyst.

Upon completion of the analysis, the chemist logs into the computer and gives his initials, date, and values as prompted. Various messages may be returned if errors are detected or sample results are unacceptable. An acceptable set of values generates a request for the next set of numbers. This acceptable report must be attached to the values to be reported out as evidence of a satisfactory run. Values will be not be reported out unless a satisfactory hard copy is printed out by the computer. If unsatisfactory results are obtained, the samples must be re-run. The computer will not accept more than two tries. Should the second set also be out of the acceptable range, the analyst must contact the supervisor or QC person.

The present ranges for acceptability are based upon criteria derived from the X-R charts (as discussed in the HSMHA-NIOSH Industrial Hygiene Service Laboratory Quality Control Manual, Technical Report no. 78) and based upon accumulated data from this laboratory's past assays. Three areas of competency are recognized - an inner central area where samples are considered accurate, a second or warning area in which the values may be of an undesirable accuracy although still not out of control,

and a third area considered out of control. The computer will flag an "unacceptable" if one or both controls are outside the outer limits and it will flag an unacceptable if both controls are in the warning area. Consultation with the QC person or supervisor is necessary to determine the real reason for the flag.

Maintenance records are kept within each section and room. It remains the responsibility of the operator and his supervisor to see that these are kept up. These records make provisions for both routine (daily, weekly, etc.) and non-routine or "as needed" items. Most major equipment is on service contract with routine maintenance kept up by the laboratory staff. The records are scrutinized by the QC person on an unannounced basis.

Each section maintains its own procedure manual. This is inspected by a supervisor or the director on a regular basis. All changes of or modifications to established procedures must be approved by the Director or Supervisor. New procedures likewise must be approved by him before insertion.

The procedure manual is readily available to the analyst at the work bench and he is expected to follow it.

This laboratory is equipped to do fiber counts using either P & CAM 239 or 7400. Both Porton and Walton-Beckett graticules are available for use and the analysts can count using A or B counting rules. Unless specifically directed otherwise, the 7400 method with the Walton-Beckett graticule will be used with counting rules A as of July 1987.

The 7400 method simplifies filter preparation by collapsing the filter using acetone vapor, 1 to 2 drops of triacetin is placed on the filter, and the filter area is covered with a glass cover slip. If a permanent mount is desired, the edges can be sealed with a lacquer or nail polish.

The P & CAM 239 and 7400 methods are included in this procedure manual and carry the complete methodology and instructions.

APPENDIX

Mounting Fluid for Asbestos Counting

1 volume dimethyl phthalate
1 volume diethyl oxalate

Mix in beaker and stir. A magnetic stirrer is preferred. One at a time, add 0.05g of filter material per milliliter of solution until proper viscosity is reached. This will generally require a minimum of 18-19 filters per 20 ml solution. If properly refrigerated in a covered bottle, this material will have a long useful shelf life.

Appendix B
NIOSH Method 7400 - Fibers

FORMULA: various

M.W.: various

FIBERS

METHOD: 7400

ISSUED: 2/15/84

REVISION #3: 5/15/89

PROPERTIES: solid, fibrous

OSHA: 0.2 asbestos fiber (≥5 µm long)/cc;
1 asbestos fiber/cc/30 minute excursion [1]

MSHA: 2 asbestos fibers (>5 µm long)/cc [2]

NIOSH: carcinogen; control to lowest level possible [3]; 3 glass fibers (>10 µm x <3.5 µm)/cc [4]

ACGIH: 0.2 crocidolite; 0.5 amosite; 2 chrysotile and other asbestos, fibers/cc [5]

SYNONYMS: actinolite [CAS #13768-00-8] or ferroactinolite; cummingtonite-grunerite (amosite) [CAS #12172-73-5]; anthophyllite [CAS #17068-78-9]; chrysotile [CAS #12001-29-5] or serpentine; crocidolite [CAS #12001-28-4] or riebeckite; tremolite [CAS #14567-73-8]; amphibole asbestos; fibrous glass.

SAMPLING

SAMPLER: FILTER
(0.45- to 1.2-µm cellulose ester membrane, 25-mm diameter; conductive cowl on cassette)

FLOW RATE*: 0.5 to 16 L/min

VOL-MIN*: 400 L @ 0.1 fiber/cc
-MAX*: (step 4, sampling)
*Adjust to give 100 to 1300 fibers/mm^2

SHIPMENT: routine (pack to reduce shock)

SAMPLE STABILITY: stable

FIELD BLANKS: 10% of samples

ACCURACY

RANGE STUDIED: 80 to 100 fibers counted

BIAS: see EVALUATION OF METHOD

OVERALL PRECISION (s_r): 0.115 to 0.13 [7]

MEASUREMENT

!TECHNIQUE: LIGHT MICROSCOPY, PHASE CONTRAST
!
!ANALYTE: fibers (manual count)
!
!SAMPLE PREPARATION: acetone/triacetin "hot block" method [6]
!
!COUNTING RULES: Described in previous version of this method as A rules [1,7]
!
!EQUIPMENT: 1. Positive phase-contrast microscope
! 2. Walton-Beckett graticule (100-µm field of view) Type G-22
! 3. phase-shift test slide (HSE/NPL)
!
!CALIBRATION: HSE/NPL test slide
!
!RANGE: 100 to 1300 fibers/mm^2 filter area
!
!ESTIMATED LOD: 7 fibers/mm^2 filter area
!
!PRECISION: 0.10 to 0.12 [7]; see EVALUATION OF METHOD
!

APPLICABILITY: The quantitative working range is 0.04 to 0.5 fiber/cc for a 1000-L air sample. The LOD depends on sample volume and quantity of interfering dust, and is <0.01 fiber/cc for atmospheres free of interferences. The method gives an index of airborne fibers. It is primarily used for estimating asbestos concentrations, though PCM does not differentiate between asbestos and other fibers. Use this method in conjuction with electron microscopy (e.g., Method 7402) for assistance in identification of fibers. Fiber <ca. 0.25 µm diameter will not be detected by this method [8]. This method may be used for other materials such as fibrous glass by using alternate counting rules (see Appendix C).

INTERFERENCES: Any other airborne fiber may interfere since all particles meeting the counting criteria are counted. Chain-like particles may appear fibrous. High levels of non-fibrous dust particles may obscure fibers in the field of view and increase the detection limit.

OTHER METHODS: This method introduces changes for improved sensitivity and reproducibility. It replaces P&CAM 239 [7,9] and NIOSH Method 7400, Revision #2 (dated 8/15/87).

REAGENTS:

1. Acetone.*
2. Triacetin (glycerol triacetate), reagent grade.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: field monitor, 25-mm, three-piece cassette with ca. 50-mm electrically-conductive extension cowl and cellulose ester filter, 0.45- to 1.2-µm pore size, and backup pad.
   NOTE 1: Analyze representative filters for fiber background before use. Discard the filter lot if mean is ≥5 fibers per 100 graticule fields. These are defined as laboratory blanks. Manufacturer-provided quality assurance checks on filter blanks are normally adequate as long as field blanks are analyzed as described below.
   NOTE 2: The electrically-conductive extension cowl reduces electrostatic effects. Ground the cowl when possible during sampling [10].
   NOTE 3: Use 0.8-µm pore size filters for personal sampling. The 0.45-µm filters are recommended for sampling when performing TEM analysis on the same samples. However, their higher pressure drop precludes their use with personal sampling pumps.
2. Sampling pump, 0.5 to 16 L/min (see step 4 for flow rate), with flexible connecting tubing.
3. Microscope, positive phase (dark) contrast, with green or blue filter, adjustable field iris, 8 to 10X eye-piece, and 40 to 45X phase objective (total magnification ca. 400X); numerical aperture = 0.65 to 0.75.
4. Slides, glass, frosted-end, pre-cleaned, 25- x 75-mm.
5. Cover slips, 22- x 22-mm, No. 1-1/2, unless otherwise specified by microscope manufacturer.
6. Lacquer or nail polish.
7. Knife, #10 surgical steel, curved blade.
8. Tweezers.
9. Heated aluminum block for clearing filters on glass slides (see ref. [6] for specifications or see manufacturer's instructions for equivalent devices).
10. Micropipets, 5-µL and 100- to 500-µL.
11. Graticule, Walton-Beckett type, 100-µm diameter circular field (area = 0.00785 mm^2) at specimen plane (Type G-22). Available from PTR Optics Ltd., 145 Newton Street, Waltham, MA 02154 [phone (617) 891-6000] and McCrone Accessories and Components, 850 Pasquinelli Drive, Westmont, IL 60559 [phone (312) 887-7100].
    NOTE: The graticule is custom-made for each microscope. (See Appendix A for the custom-ordering procedure).
12. HSE/NPL phase contrast test slide, Mark II. Available from PTR Optics Ltd. (address above).
13. Telescope, ocular phase-ring centering.
14. Stage micrometer (0.01-mm divisions).
15. Wire, multi-stranded, 22-gauge.
16. Tape, shrink- or adhesive-.

SPECIAL PRECAUTIONS: Acetone is extremely flammable. Take precautions not to ignite it. Heating of acetone in volumes greater than 1 mL must be done in a ventilated laboratory fume hood using a flameless, spark-free heat source.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. For personal sampling, fasten sampler to the worker's lapel near the worker's mouth. Remove top cover from cowl extension ("open-face") and orient face down. Wrap joint between cowl and monitor body with tape to help hold the cassette together, keep the joint free of dust, and provide a marking surface to identify the cassette.

NOTE: If possible, ground the cassette to remove any surface charge, using a wire held in contact (e.g., with a hose clamp) with the conductive cowl and an earth ground such as a cold-water pipe.

3. Submit at least two field blanks (or 10% of the total samples, whichever is greater) for each set of samples. Handle field blanks in the same fashion as other samplers. Open field blank cassettes at the same time as other cassettes just prior to sampling. Store top covers and cassettes in a clean area with the top covers from the sampling cassettes during the sampling period.
4. Sample at 0.5 L/min or greater [11]. Adjust sampling flow rate, Q (L/min), and time, t(min), to produce a fiber density, E, of 100 to 1300 fibers/mm^2 ($3.85 \cdot 10^4$ to $5 \cdot 10^5$ fibers per 25-mm filter with effective collection area A_c= 385 mm^2) for optimum accuracy. These variables are related to the action level (one-half the current standard), L (fibers/cc), of the fibrous aerosol being sampled by:

$$t = \frac{A_c \cdot E}{Q \cdot L \cdot 10^3}, \text{ min.}$$

NOTE 1: The purpose of adjusting sampling times is to obtain optimum fiber loading on the filter. A sampling rate of 1 to 4 L/min for 8 hrs is appropriate in atmospheres containing ca. 0.1 fiber/cc in the absense of significant amounts of non-asbestos dust. Dusty atmospheres require smaller sample volumes ($\leq$400 L) to obtain countable samples. In such cases take short, consecutive samples and average the results over the total collection time. For documenting episodic exposures, use high flow rates (7 to 16 L/min) over shorter sampling times. In relatively clean atmospheres, where targeted fiber concentrations are much less than 0.1 fiber/cc, use larger sample volumes (3000 to 10000 L) to achieve quantifiable loadings. Take care, however, not to overload the filter with background dust. If $\geq$ 50% of the filter surface is covered with particles, the filter may be too overloaded to count and will bias the measured fiber concentration.

NOTE 2: OSHA regulations specify a maximum sampling rate of 2.5 L/min [1].

NOTE 3: OSHA regulations specify a minimum sampling volume of 48 L for an excursion measurement [1].

5. At the end of sampling, replace top cover and end plugs.
6. Ship samples with conductive cowl attached in a rigid container with packing material to prevent jostling or damage.

NOTE: Do not use untreated polystyrene foam in shipping container because electrostatic forces may cause fiber loss from sample filter.

SAMPLE PREPARATION:

NOTE 1: The object is to produce samples with a smooth (non-grainy) background in a medium with refractive index of $\leq$1.46. This method collapses the filter for easier focusing and produces relatively permanent mounts which are useful for quality control and interlaboratory comparison. The aluminum "hot block" or similar flash vaporization techniques may be used outside the laboratory [6]. Other mounting techniques meeting the above criteria may also be used (e.g., the laboratory fume hood procedure for generating acetone vapor as described in Method 7400 - revision of 5/15/85, or the non-permanent field mounting technique used in P&CAM 239 [3,7,9,12]). A videotape of the mounting procedure is available from the NIOSH Publication Office [13].

NOTE 2: Excessive water in the acetone may slow the clearing of the filters, causing material to be washed off the surface of the filter. Also, filters that have been exposed to high humidities prior to clearing may have a grainy background.

7. Ensure that the glass slides and cover slips are free of dust and fibers.
8. Adjust the rheostat to heat the "hot block" to ca. 70 °C [6].
   NOTE: If the "hot block" is not used in a fume hood, it must rest on a ceramic plate and be isolated from any surface susceptible to heat damage.
9. Mount a wedge cut from the sample filter on a clean glass slide.
   a. Cut wedges of ca. 25% of the filter area with a curved-blade knife using a rocking motion to prevent tearing. Place wedge, dust side up, on slide.
      NOTE: Static electricity will usually keep the wedge on the slide.
   b. Insert slide with wedge into the receiving slot at the base of "hot block". Immediately place tip of a micropipet containing ca. 250 µL acetone (use the minimum volume needed to consistently clear the filter sections) into the inlet port of the PTFE cap on top of the "hot block" and inject the acetone into the vaporization chamber with a slow, steady pressure on the plunger button while holding pipet firmly in place. After waiting 3 to 5 sec for the filter to clear, remove pipet and slide from their ports.
      CAUTION: Although the volume of acetone used is small, use safety precautions. Work in a well-ventilated area (e.g., laboratory fume hood). Take care not to ignite the acetone. Continuous, frequent use of this device in an unventilated space may produce explosive acetone vapor concentrations.
   c. Using the 5-µL micropipet, immediately place 3.0 to 3.5 µL triacetin on the wedge. Gently lower a clean cover slip onto the wedge at a slight angle to reduce bubble formation. Avoid excess pressure and movement of the cover glass.
      NOTE: If too many bubbles form or the amount of triacetin is insufficient, the cover slip may become detached within a few hours. If excessive triacetin remains at the edge of the filter under the cover slip, fiber migration may occur.
   d. Glue the edges of the cover slip to the slide using lacquer or nail polish [14] Counting may proceed immediately after clearing and mounting are completed.
      NOTE: If clearing is slow, warm the slide on a hotplate (surface temperature 50 °C) for up to 15 min to hasten clearing. Heat carefully to prevent gas bubble formation.

CALIBRATION AND QUALITY CONTROL:

10. Microscope adjustments. Follow the manufacturer's instructions. At least once daily use the telescope ocular (or Bertrand lens, for some microscopes) supplied by the manufacturer to ensure that the phase rings (annular diaphragm and phase-shifting elements) are concentric. With each microscope, keep a logbook in which to record the dates of calibrations and major servicings.
    a. Each time a sample is examined, do the following:
       (1) Adjust the light source for even illumination across the field of view at the condenser iris. Use Kohler illumination, if available. With some microscopes, the illumination may have to be set up with bright field optics rather than phase contrast optics.
       (2) Focus on the particulate material to be examined.
       (3) Make sure that the field iris is in focus, centered on the sample, and open only enough to fully illuminate the field of view.
    b. Check the phase-shift detection limit of the microscope periodically for each analyst/microscope combination:
       (1) Center the HSE/NPL phase-contrast test slide under the phase objective.
       (2) Bring the blocks of grooved lines into focus in the graticule area.
           NOTE: The slide contains seven blocks of grooves (ca. 20 grooves per block) in descending order of visibility. For asbestos counting the microscope optics must completely resolve the grooved lines in block 3 although they may appear somewhat faint, and the grooved lines in blocks 6 and 7 must be invisible

when centered in the graticule area. Blocks 4 or 5 must be at least partially visible but may vary slightly in visibility between microscopes. A microscope which fails to meet these requirements has resolution either too low or too high for fiber counting.

(3) If image quality deteriorates, clean the microscope optics. If the problem persists, consult the microscope manufacturer.

11. Document the laboratory's precision for each counter for replicate fiber counts.
    a. Maintain as part of the laboratory quality assurance program a set of reference slides to be used on a daily basis [15]. These slides should consist of filter preparations including a range of loadings and background dust levels from a variety of sources including both field and PAT samples. The Quality Assurance Officer should maintain custody of the reference slides and should supply each counter with a minimum of one reference slide per workday. Change the labels on the reference slides periodically so that the counter does not become familiar with the samples.
    b. From blind repeat counts on reference slides, estimate the laboratory intra- and intercounter s_r (step 21). Obtain separate values of relative standard deviation for each sample matrix analyzed in each of the following ranges: 5 to 20 fibers in 100 graticule fields, >20 to 50 fibers in 100 graticule fields, >50 to 100 fibers in 100 graticule fields, and 100 fibers in less than 100 graticule fields. Maintain control charts for each of these data files.
    NOTE: Certain sample matrices (e.g., asbestos cement) have been shown to give poor precision [16]
12. Prepare and count field blanks along with the field samples. Report counts on each field blank.
    NOTE 1: The identity of blank filters should be unknown to the counter until all counts have been completed.
    NOTE 2: If a field blank yields greater than 7 fibers per 100 graticule fields, report possible contamination of the samples.
13. Perform blind recounts by the same counter on 10% of filters counted (slides relabeled by a person other than the counter). Use the following test to determine whether a pair of counts by the same counter on the same filter should be rejected because of possible bias: Discard the sample if the absolute value of the difference between the square roots of the two counts (in fiber/mm^2) exceeds 2.8 (X) s_r, where X = the average of the square roots of the two fiber counts (in fiber/mm^2) and s_r = one-half the intracounter relative standard deviation for the appropriate count range (in fibers) determined from step 11. For more complete discussions see reference [15].
    NOTE 1: Since fiber counting is the measurement of randomly placed fibers which may be described by a Poisson distribution, a square root transformation of the fiber count data will result in approximately normally distributed data [15].
    NOTE 2: If a pair of counts is rejected by this test, recount the remaining samples in the set and test the new counts against the first counts. Discard all rejected paired counts. It is not necessary to use this statistic on blank counts.
14. The analyst is a critical part of this analytical procedure. Care must be taken to provide a non-stressful and comfortable environment for fiber counting. An ergonomically designed chair should be used, with the microscope eyepiece situated at a comfortable height for viewing. External lighting should be set at a level similar to the illumination level in the microscope to reduce eye fatigue. In addition, counters should take 10 to 20 minute breaks from the microscope every one or two hours to limit fatigue [17]. During these breaks, both eye and upper back/neck exercises should be performed to relieve strain.
15. All laboratories engaged in asbestos counting should participate in a proficiency testing program such as the AIHA-NIOSH Proficiency Analytical Testing (PAT) Program or the AIHA Asbestos Analyst Registry and routinely exchange field samples with other laboratories to compare performance of counters.
    NOTE: OSHA requires that each analyst performing this method take the NIOSH direct training course #582 or equivalent [1]. Instructors of equivalent courses should have attended the NIOSH #582 course at NIOSH within three years of presenting an equivalent course.

MEASUREMENT:

16. Center the slide on the stage of the calibrated microscope under the objective lens. Focus the microscope on the plane of the filter.
17. Adjust the microscope (Step 10).
    NOTE: Calibration with the HSE/NPL test slide determines the minimum detectable fiber diameter (ca. 0.25 µm) [8].
18. Counting rules: (same as P&CAM 239 rules [3,7,9]; see APPENDIX B).
    a. Count only fibers longer than 5 µm. Measure length of curved fibers along the curve.
    b. Count only fibers with a length-to-width ratio equal to or greater than 3:1.
    c. For fibers which cross the boundary of the graticule field:
       (1) Count any fiber longer than 5 µm which lies entirely within the graticule area.
       (2) Count as 1/2 fiber any fiber with only one end lying within the graticule area, provided that the fiber meets the criteria of rules a and b above.
       (3) Do not count any fiber which crosses the graticule boundary more than once.
       (4) Reject and do not count all other fibers.
    d. Count bundles of fibers as one fiber unless individual fibers can be identified by observing both ends of a fiber.
    e. Count enough graticule fields to yield 100 fibers. Count a minimum of 20 fields. Stop at 100 graticule fields regardless of count.
19. Start counting from the tip of the filter wedge and progress along a radial line to the outer edge. Shift up or down on the filter, and continue in the reverse direction. Select graticule fields randomly by looking away from the eyepiece briefly while advancing the mechanical stage. Ensure that, as a minimum, each analysis covers one radial line from the filter center to the outer edge of the filter. When an agglomerate covers ca. 1/6 or more of the graticule field, reject the graticule field and select another. Do not report rejected graticule fields in the total number counted.

    NOTE 1: When counting a graticule field, continuously scan a range of focal planes by moving the fine focus knob to detect very fine fibers which have become embedded in the filter. The small-diameter fibers will be very faint but are an important contribution to the total count. A minimum counting time of 15 seconds per field is appropriate for accurate counting.

    NOTE 2: This method does not allow for differentiation of fibers based on morphology. Although some experienced counters are capable of selectively counting only fibers which appear to be asbestiform, there is presently no accepted method for ensuring uniformity of judgment between laboratories. It is, therefore, incumbent upon all laboratories using this method to report <u>total</u> fiber counts. If serious contamination from non-asbestos fibers occurs in samples, other techniques such as transmission electron microscopy must be used to identify the asbestos fiber fraction present in the sample (see NIOSH Method 7402). In some cases (i.e., for fibers with diameters >1 µm), polarized light microscopy techniques may be used to identify and eliminate interfering non-crystalline fibers [18].

    NOTE 3: Under certain conditions, electrostatic charge may affect the sampling of fibers. These electrostatic effects are most likely to occur when the relative humidity is low (below 20%), and when sampling is performed near the source of aerosol. The result is that deposition of fibers on the filter is reduced, especially near the edge of the filter. If such a pattern is noted during fiber counting, choose fields as close to the center of the filter as possible [10].

CALCULATIONS AND REPORTING OF RESULTS:

20. Calculate and report fiber density on the filter, E (fibers/mm^2), by dividing the average fiber count per graticule field, F/n_f, minus the mean field blank count per graticule field, B/n_b, by the graticule field area, A_f (approx. 0.00785 mm^2):

$$E = \frac{\left(\frac{F}{n_f} - \frac{B}{n_b}\right)}{A_f}, \text{ fibers/mm}^2.$$

NOTE: Fiber counts above 1300 fibers/mm^2 and fiber counts from samples with >50% of filter area covered with particulate should be reported as "uncountable" or "probably biased."

21. Calculate and report the concentration, C (fibers/cc), of fibers in the air volume sampled, V (L), using the effective collection area of the filter, A_c (approx. 385 mm^2 for a 25-mm filter):

$$C = \frac{(E)(A_c)}{V \cdot 10^3}.$$

NOTE: Periodically check and adjust the value of A_c, if necessary.

22. Report intralaboratory and interlaboratory relative standard deviations (Step 11) with each set of results.

NOTE: Precision depends on the total number of fibers counted [7,19]. Relative standard deviation is documented in references [7,18,19,20] for fiber counts up to 100 fibers in 100 graticule fields. Comparability of interlaboratory results is discussed below. As a first approximation, use 213% above and 49% below the count as the upper and lower confidence limits for fiber counts greater than 20 (Fig. 1).

EVALUATION OF METHOD:

A. This method is a revision of P&CAM 239 [3,7,9]. A summary of the revisions is as follows:

1. Sampling:
   The change from a 37-mm to a 25-mm filter improves sensitivity for similar air volumes. The change in flow rates allows for 2-m^3 full-shift samples to be taken, providing that the filter is not overloaded with non-fibrous particulates. The collection efficiency of the sampler is not a function of flow rate in the range 0.5 to 16 L/min [11].
2. Sample Preparation Technique:
   The acetone vapor-triacetin preparation technique is a faster, more permanent mounting technique than the dimethyl phthalate/diethyl oxalate method of P&CAM 239 [6,8,9]. The aluminum "hot block" technique minimizes the amount of acetone needed to prepare each sample.
3. Measurement:
   a. The Walton-Beckett graticule standardizes the area observed [21,22,23].
   b. The HSE/NPL test slide standardizes microscope optics for sensitivity to fiber diameter [8,21].
   c. Because of past inaccuracies associated with low fiber counts, the minimum recommended loading has been increased to 100 fibers/mm^2 filter area (80 fibers total count). Lower levels generally result in an overestimate of the fiber count when compared to results in the recommended analytical range [25]. The recommended loadings should yield intracounter s_r in the range of 0.10 to 0.17 [7,24,26].

B. Interlaboratory comparability:
An international collaborative study involved 16 laboratories using prepared slides from the asbestos cement, milling, mining, textile, and friction material industries [16]. The relative standard deviations (s_r) varied with sample type and laboratory. The ranges were:

	s_r		
	Intralaboratory	Interlaboratory	Overall
AIA (NIOSH Rules)*	0.12 to 0.40	0.27 to 0.85	0.46

*Under AIA rules, only fibers having a diameter less than 3 µm are counted and fibers attached to particles larger than 3 µm are not counted. NIOSH Rules are otherwise similar to the AIA rules.

A NIOSH study was conducted using field samples of asbestos [24]. This study indicated intralaboratory s_r in the range 0.17 to 0.25 and an interlaboratory s_r of 0.45. This agrees well with other recent studies [16,19,21].

At this time, there is no independent means for assessing the overall accuracy of this method. One measure of reliability is to estimate how well the count for a single sample agrees with the mean count from a large number of laboratories. The following discussion indicates how this estimation can be carried out based on measurements of the interlaboratory variability, as well as showing how the results of this method relate to the theoretically attainable counting precision and to measured intra- and interlaboratory s_r. (NOTE: The following discussion does not include bias estimates and should not be taken to indicated that lightly loaded samples are as accurate as properly loaded ones).

Theoretically, the process of counting randomly-distributed (Poisson) fibers on a filter surface will give an s_r that depends on the number, N, of fibers counted:

$$s_r = 1/(N)^{1/2} \qquad (1)$$

Thus s_r is 0.1 for 100 fibers and 0.32 for 10 fibers counted. The actual s_r found in a number of studies is greater than these theoretical numbers [16,19,20,21].

An additional component of variability comes primarily from subjective interlaboratory differences. In a study of ten counters in a continuing sample exchange program, Ogden [18] found this subjective component of intralaboratory s_r to be approximately 0.2 and estimated the overall s_r by the term:

$$\frac{(N + (0.2 \cdot N)^2)^{1/2}}{N} \qquad (2)$$

Ogden found that the 90% confidence interval of the individual intralaboratory counts in relation to the means were +2 s_r and - 1.5 s_r. In this program, one sample out of ten was a quality control sample. For laboratories not engaged in an intensive quality assurance program, the subjective component of variability can be higher.

In a study of field sample results in 46 laboratories, the Asbestos Information Association also found that the variability had both a constant component and one that depended on the fiber count [21]. These results gave a subjective interlaboratory component of s_r (on the same basis as Ogden's) for field samples of ca. 0.45. A similar value was obtained for 12 laboratories analyzing a set of 24 field samples [24]. This value falls slightly above the range of s_r (0.25 to 0.42 for 1984-85) found for 80 reference laboratories in the NIOSH Proficiency Analytical Testing (PAT) program for laboratory-generated samples [20].

A number of factors influence s_r for a given laboratory, such as that laboratory's actual counting performance and the type of samples being analyzed. In the absence of other information, such as from an interlaboratory quality assurance program using field samples, the value for the subjective component of variability is estimated as 0.45. It is hoped that laboratories will carry out the recommended interlaboratory quality assurance programs to improve their performance and thus reduce the s_r.

The above relative standard deviations apply when the population mean has been determined. It is more useful, however, for laboratories to estimate the 90% confidence interval on the mean count from a single sample fiber count (Figure 1). These curves assume similar shapes of the count distribution for interlaboratory and intralaboratory results [19].

For example, if a sample yields a count of 24 fibers, Figure 1 indicates that the mean inter-laboratory count will fall within the range of 227% above and 52% below that value 90% of the time. We can apply these percentages directly to the air concentrations as well. If, for instance, this sample (24 fibers counted) represented a 500-L volume, then the measured concentration is 0.02 fibers/mL (assuming 100 fields counted, 25-mm filter, 0.00785 mm^2 field counting area). If this same sample were counted by a group of laboratories, there is a 90% probability that the mean would fall between 0.01 and 0.08 fiber/mL. These limits should be reported in any comparison of results between laboratories.

Note that the s_r of 0.45 used to derive Figure 1 is used as an estimate for a random group of laboratories. If several laboratories belonging to a quality assurance group can show that their interlaboratory s_r is smaller, then it is more correct to use that smaller s_r. However, the estimated s_r of 0.45 is to be used in the absence of such information. Note also that it has been found that s_r can be higher for certain types of samples, such as asbestos cement [16].

Quite often the estimated airborne concentration from an asbestos analysis is used to compare to a regulatory standard. For instance, if one is trying to show compliance with an 0.5 fiber/mL standard using a single sample on which 100 fibers have been counted, then Figure 1 indicates that the 0.5 fiber/mL standard must be 213% higher than the measured air concentration. This indicates that if one measures a fiber concentration of 0.16 fiber/mL (100 fibers counted), then the mean fiber count by a group of laboratories (of which the compliance laboratory might be one) has a 95% chance of being less than 0.5 fibers/mL; i.e., 0.16 + 2.13 x 0.16 = 0.5.

It can be seen from Figure 1 that the Poisson component of the variability is not very important unless the number of fibers counted is small. Therefore, a further approximation is to simply use +213% and -49% as the upper and lower confidence values of the mean for a 100-fiber count.

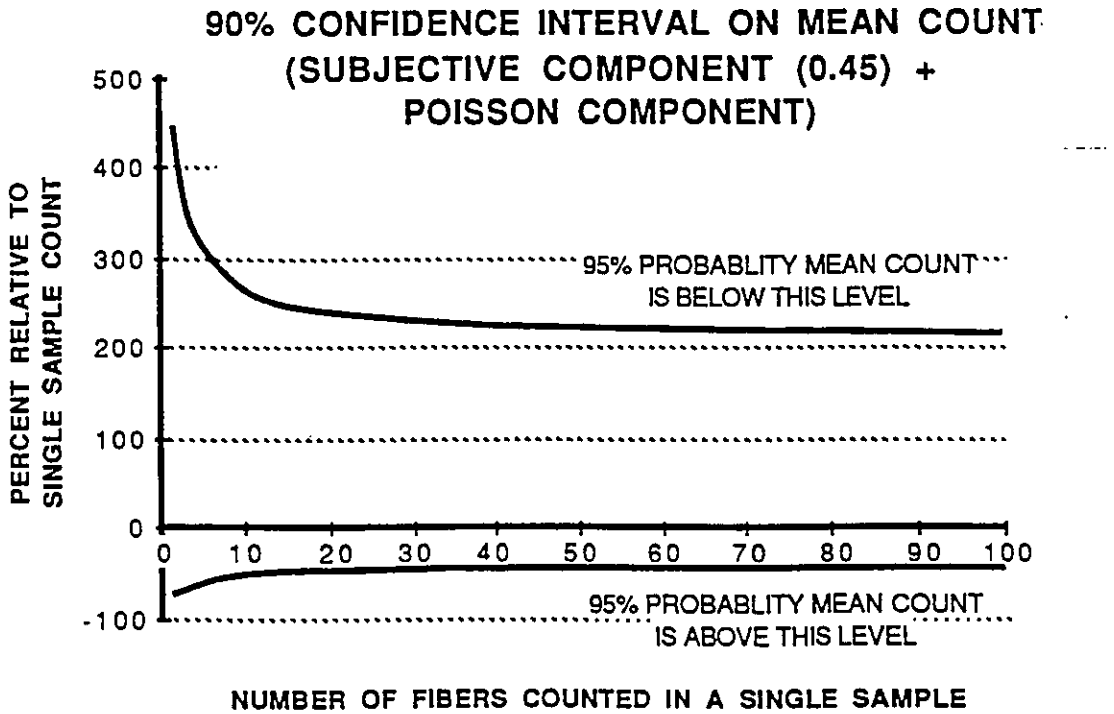


Figure 1. Inter-laboratory Precision of Fiber Counts

The curves in Figure 1 are defined by the following equations

$$UCL = \frac{2x + 2.25 + \sqrt{(2.25 + 2x)^2 - 4(1 - 2.25 s_r^2) x^2}}{2(1 - 2.25 s_r^2)} \quad (3)$$

$$LCL = \frac{2x + 4 - \sqrt{(4 + 2x)^2 - 4(1 - 4 s_r^2) x^2}}{2(1 - 4 s_r^2)} \quad (4)$$

where s_r = subjective inter-laboratory relative standard deviation, which is close to the total inter-laboratory s_r when approximately 100 fibers are counted.

x = total fibers counted on sample

LCL = lower 95% confidence limit

UCL = upper 95% confidence limit.

Note that the range between these two limits represents 90% of the total range.

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APPENDIX A: CALIBRATION OF THE WALTON-BECKETT GRATICULE

Before ordering the Walton-Beckett graticule, the following calibration must be done to obtain a counting area (D) 100 µm in diameter at the image plane. The diameter, d_c (mm), of the circular counting area and the disc diameter must be specified when ordering the graticule.

1. Insert any available graticule into the eyepiece and focus so that the graticule lines are sharp and clear.
2. Set the appropriate interpupillary distance and, if applicable, reset the binocular head adjustment so that the magnification remains constant.
3. Install the 40 to 45X phase objective.
4. Place a stage micrometer on the microscope object stage and focus the microscope on the graduated lines.
5. Measure the magnified grid length of the graticule, L_o (µm), using the stage micrometer.
6. Remove the graticule from the microscope and measure its actual grid length, L_a (mm). This can best be accomplished by using a stage fitted with verniers.
7. Calculate the circle diameter, d_c (mm), for the Walton-Beckett graticule:

$$d_c = \frac{L_a}{L_o} \times D.$$

Example: If L_o = 112 µm, L_a = 4.5 mm and D = 100 µm, then d_c = 4.02 mm.

8. Check the field diameter, D (acceptable range 100 µm ± 2 µm) with a stage micrometer upon receipt of the graticule from the manufacturer. Determine field area (acceptable range 0.00754 to 0.00817 mm^2).

APPENDIX B: EXAMPLES OF COUNTING RULES

Figure 2 shows a Walton-Beckett graticule as seen through the microscope. The rules will be discussed as they apply to the labeled objects in the figure.

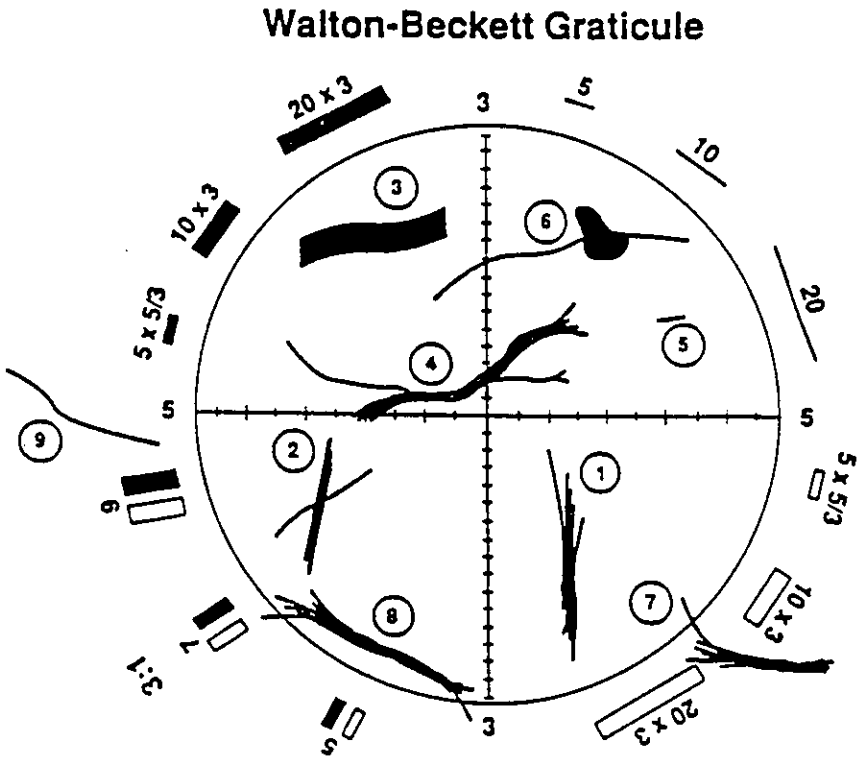

Figure 2. Walton-Beckett graticule with fibers.

FIBER COUNT		
Object	Count	DISCUSSION
1	1 fiber	Optically observable asbestos fibers are actually bundles of fine fibrils. If the fibrils seem to be from the same bundle the object is counted as a single fiber. Note, however, that all objects meeting length and aspect ratio criteria are counted whether or not they appear to be asbestos.
2	2 fiber	If fibers meeting the length and aspect ratio criteria (length >5 μm and length-to-width ratio >3 to 1) overlap, but do not seem to be part of the same bundle, they are counted as separate fibers.
3	1 fiber	Although the object has a relatively large diameter (>3 μm), it is counted as fiber under the rules. There is no upper limit on the fiber diameter in the counting rules. Note that fiber width is measured at the widest compact section of the object.
4	1 fiber	Although long fine fibrils may extend from the body of a fiber, these fibrils are considered part of the fiber if they seem to have originally been part of the bundle.
5	Do not count	If the object is ≤5 μm long, it is not counted.
6	1 fiber	A fiber partially obscured by a particle is counted as one fiber. If the fiber ends emanating from a particle do not seem to be from the same fiber and each end meets the length and aspect ratio criteria, they are counted as separate fibers.
7	1/2 fiber	A fiber which crosses into the graticule area one time is counted as 1/2 fiber.
8	Do not count	Ignore fibers that cross the graticule boundary more than once.
9	Do not count	Ignore fibers that lie outside the graticule boundary.

Appendix C. ALTERNATE COUNTING RULES

Other counting rules may be more appropriate for measurement of specific non-asbestos fiber types, such as fibrous glass. These include the "B" rules (from NIOSH Method 7400, Revision #2, dated 8/15/87), the World Health Organization reference method for man-made mineral fiber [27], and the NIOSH fibrous glass criteria document method [4]. The upper diameter limit in these methods prevents measurements of non-respirable fibers. It is important to note that the aspect ratio limits included in these methods vary. NIOSH recommends the use of the 3:1 aspect ratio in counting fibers.

It is emphasized that hybridization of different sets of counting rules is not permitted. Report specifically which set of counting rules are used with the analytical results.

"B" Counting Rules:

1. Count only ends of fibers. Each fiber must be longer than 5 µm and less than 3 µm diameter.
2. Count only ends of fibers with a length-to-width ratio equal to or greater than 5:1.
3. Count each fiber end which falls within the graticule area as one end, provided that the fiber meets rules b.1 and b.2. Add split ends to the count as appropriate if the split fiber segment also meets the criteria of rules 1 and 2 above.
4. Count visibly free ends which meet rules 1 and 2 above when the fiber appears to be attached to another particle, regardless of the size of the other particle. Count the end of a fiber obscured by another particle if the particle covering the fiber end is less than 3 µm in diameter.
5. Count free ends of fibers emanating from large clumps and bundles up to a maximum of 10 ends (5 fibers), provided that each segment meets rules 1 and 2 above.
6. Count enough graticule fields to yield 200 ends. Count a minimum of 20 graticule fields. Stop at 100 gradicule fields, regardless of count.
7. Divide total end count by 2 to yield fiber count.

Appendix C
NIOSH Method 7402 - Asbestos Fibers

FORMULA: various

M.W.: various

ASBESTOS FIBERS
METHOD: 7402
ISSUED: 8/15/87
REVISION #1: 5/15/89

PROPERTIES: solid, fibrous

OSHA: 0.2 asbestos fiber (>5 μm long)/cc
1 asbestos fiber/cc/30 minute excursion [1]
MSHA: 2 asbestos fibers (>5 μm long)/cc [2]
NIOSH: carcinogen; control to lowest level possible [3]
ACGIH: 0.2 crocidolite; 0.5 amosite; 2 chrysotile and other asbestos, fibers/cc [4]

SYNONYMS: actinolite [CAS #13768-00-8] or ferroactinolite; cummingtonite-grunerite (amosite) [CAS #12172-73-5]; anthophyllite [CAS #17068-78-9]; chrysotile [CAS #12001-29-5] or serpentine; crocidolite [CAS #12001-28-4] or riebeckite; tremolite [CAS #14567-73-8]; amphibole asbestos.

SAMPLING

SAMPLER: FILTER
(0.45-to 1.2-μm cellulose ester membrane, 25-mm diameter; conductive cassette)

FLOW RATE*: 0.5 to 16 L/min

VOL-MIN*: 400 L @ 0.1 fiber/cc
-MAX*: (step 4, sampling)
*Adjust for 100 to 1300 fibers/mm^2

SHIPMENT: routine (pack to reduce shock)

SAMPLE STABILITY: stable

FIELD BLANKS: 10% of samples

ACCURACY

RANGE STUDIED: 80 to 100 fibers counted [1000-L samples]

BIAS: not determined

OVERALL PRECISION (s_r): EVALUATION OF METHOD

MEASUREMENT

!TECHNIQUE: MICROSCOPY, TRANSMISSION ELECTRON (TEM)
!
!ANALYTE: asbestos fibers
!
!SAMPLE PREPARATION: modified Jaffe wick
!
!EQUIPMENT: transmission electron microscope; energy dispersive X-ray system (EDX) analyzer
!
!CALIBRATION: qualitative electron diffraction; calibration of TEM magnification and EDX system
!
!RANGE: 100 to 1300 fibers/mm^2 filter area [5]
!
!ESTIMATED LOD: 1 confirmed asbestos fiber above 95% of expected mean blank value
!
!PRECISION: 0.28 when 65% of fibers are asbestos; 0.20 when adjusted fiber count is applied to PCM count [6].

APPLICABILITY: The quantitative working range is 0.04 to 0.5 fiber/cc for a 1000-L air sample. The LOD depends on sample volume and quantity of interfering dust, and is <0.01 fiber/cc for atmospheres free of interferences. This method is used to determine asbestos fibers in the optically visible range and is intended to complement the results obtained by phase contrast microscopy (Method 7400).

INTERFERENCES: Other amphibole particles that have aspect ratios greater than 3:1 and elemental compositions similar to the asbestos minerals may interfere in the TEM analysis. Some non-amphibole minerals may give electron diffraction patterns similar to amphiboles. High concentrations of background dust interfere with fiber identification.

OTHER METHODS: This revises Method 7402 (8/15/87). This method is designed for use with Method 7400 (phase contrast microscopy).

REAGENTS:

1. Acetone. See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: field monitor, 25-mm, three-piece cassette with ca. 50-mm electrically-conductive extension cowl, cellulose ester membrane filter, 0.45- to 1.2-µm pore size, and backup pad.
   NOTE 1: Analyze representative filters for fiber background before use. Discard the filter lot if mean count is >5 fibers/100 fields. These are defined as laboratory blanks.
   NOTE 2: Use an electrically-conductive extension cowl to reduce electrostatic effects on fiber sampling and during sample shipment. Ground the cowl when possible during sampling.
   NOTE 3: 0.8-µm pore size filters are recommended for personal sampling. 0.45-µm filters are recommended for sampling when performing TEM analysis on the samples because the particles deposit closer to the filter surface. However, the higher pressure drop through these filters normally preclude their use with personal sampling pumps.
2. Personal sampling pump, 0.5 to 16 L/min, with flexible connecting tubing.
3. Microscope, transmission electron, operated at ca. 100 kV, with electron diffraction and energy-dispersive X-ray capabilities, and having a fluorescent screen with inscribed or overlaid calibrated scale (Step 15).
   NOTE: The scale is most efficient if it consists of a series of lines inscribed on the screen or partial circles every 2 cm distant from the center.
4. Diffraction grating replica with known number of lines/mm.
5. Slides, glass, pre-cleaned, 25- x 75-mm.
6. Knife, #10 surgical steel, curved-blade.
7. Tweezers.
8. Grids, 200-mesh TEM copper, (optional: carbon-coated).
9. Petri dishes, 15-mm depth. The top and bottom of the petri dish must fit snugly together. To assure a tight fit, grind the top and bottom pieces together with an abrasive such as carborundum to produce a ground-glass contact surface.
10. Foam, clean polyurethane, spongy, 12-mm thick.
11. Filters, Whatman No. 1 qualitative paper or equivalent, or lens paper.
12. Vacuum evaporator.
13. Cork borer, No. 5 (8-mm).
14. Pen, waterproof, marking.
15. Reinforcement, page, gummed.
16. Asbestos standard bulk materials for reference; e.g. SRM #1866, available from the National Institute of Standards and Technology.
17. Carbon rods, sharpened to 1 mm x 8 mm.
18. Microscope, light, phase contrast (PCM), with Walton-Beckett graticule (see method 7400).
19. Grounding wire, 22-gauge, multi-strand.
20. Tape, shrink- or adhesive-.

SPECIAL PRECAUTIONS: Acetone is extremely flammable (flash point = 0 °F). Take precautions not to ignite it. Heating of acetone must be done in a fume hood using a flameless, spark-free heat source.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line [7].
2. For personal sampling, fasten sampler to worker's lapel near worker's mouth. Remove the top cover from cowl extension ("open-face") and orient sampler face down. Wrap joint between extender and monitor body with tape to help hold the cassette together and provide a marking surface to identify the cassette. Where possible, especially at low %RH, attach sampler to electrical ground to reduce electrostatic effects during sampling.

3. Submit at least two field blanks (or 10% of the total samples, whichever is greater) for each set of samples. Remove top covers from the field blank cassettes and store top covers and cassettes in a clean area (e.g., closed bag or box) during sampling. Replace top covers when sampling is completed.
4. Sample at 0.5 to 16 L/min [8]. Adjust sampling rate, Q (L/min), and time, t (min), to produce fiber density, E, of 100 to 1300 fibers/mm^2 [$3.85 \cdot 10^4$ to $5 \cdot 10^5$ fibers per 25-mm filter with effective collection area (A_c= 385 mm^2)] for optimum accuracy. Do not exceed ca. 0.5 mg total dust loading on the filter. These variables are related to the action level (one-half the current standard), L (fibers/cc), of the fibrous aerosol being sampled by:

$$t = \frac{A_c \cdot E}{Q \cdot L \cdot 10^3}, \text{ min.}$$

   NOTE: The purpose of adjusting sampling times is to obtain optimum fiber loading on the filter. A sampling rate of 1 to 4 L/min for 8 hrs (700 to 2800 L) is appropriate in atmospheres containing ca. 0.1 fiber/cc in the absence of significant amounts of non-asbestos dust. Dusty atmospheres require smaller sample volumes ($\leq$400 L) to obtain countable samples. In such cases take short, consecutive samples and average the results over the total collection time. For documenting episodic exposures, use high rates (7 to 16 L/min) over shorter sampling times. In relatively clean atmospheres, where targeted fiber concentrations are much less than 0.1 fiber/cc, use larger sample volumes (3000 to 10000 L) to achieve quantifiable loadings. Take care, however, not to overload the filter with background dust [8].
5. At the end of sampling, replace top cover and small end caps.
6. Ship samples upright with conductive cowl attached in a rigid container with packing material to prevent jostling or damage.
   NOTE: Do not use untreated polystyrene foam in the shipping container because electrostatic forces may cause fiber loss from sample filter.

SAMPLE PREPARATION:

7. Remove three circular sections from any quadrant of each sample and blank filter using a cork borer [9]. The use of three grid preparations reduces the effect of local variations in dust deposit on the filter.
8. Affix the circular filter sections to a clean glass slide with a gummed page reinforcement. Label the slide with a waterproof marking pen.
   NOTE: Up to eight filter sections may be attached to the same slide.
9. Place the slide in a petri dish which contains several paper filters soaked with 2 to 3 mL acetone. Cover the dish. Wait 2 to 4 min for the sample filter(s) to fuse and clear.
   NOTE: The "hot block" clearing technique [10] of Method 7400 or the DMF clearing technique [11] may be used instead of steps 8 and 9.
10. Transfer the slide to a rotating stage inside the bell jar of a vacuum evaporator. Evaporate a 1- by 5-mm section of a graphite rod onto the cleared filter(s). Remove the slide to a clean, dry, covered petri dish [9].
11. Prepare a second petri dish as a Jaffe wick washer with the wicking substrate prepared from filter or lens paper placed on top of a 12-mm thick disk of clean, spongy polyurethane foam [12]. Cut a V-notch on the edge of the foam and filter paper. Use the V-notch as a reservoir for adding solvent.
    NOTE: The wicking substrate should be thin enough to fit into the petri dish without touching the lid.
12. Place the TEM grids face up on the filter or lens paper. Label the grids by marking with a pencil on the filter paper or by putting registration marks on the petri dish halves and marking with a waterproof marker on the dish lid. In a fume hood, fill the dish with acetone until the wicking substrate is saturated.
    NOTE: The level of acetone should be just high enough to saturate the filter paper without creating puddles.

13. Remove about a quarter section of the carbon-coated filter from the glass slide using a surgical knife and tweezers. Carefully place the excised filter, carbon side down, on the appropriately-labeled grid in the acetone-saturated petri dish. When all filter sections have been transferred, slowly add more solvent to the wedge-shaped trough to raise the acetone level as high as possible without disturbing the sample preparations. Cover the petri dish. Elevate one side of the petri dish by placing a slide under it (allowing drops of condensed acetone to form near the edge rather than in the center where they would drip onto the grid preparation).

CALIBRATION AND QUALITY CONTROL:

14. Determine the TEM magnification on the fluorescent screen:
    a. Define a field of view on the fluorescent screen either by markings or physical boundaries.
       NOTE: The field of view must be measurable or previously inscribed with a scale or concentric circles (all scales should be metric) [12].
    b. Insert a diffraction grating replica into the specimen holder and place into the microscope. Orient the replica so that the grating lines fall perpendicular to the scale on the TEM fluorescent screen. Ensure that goniometer stage tilt is zero.
    c. Adjust microscope magnification to 10,000X. Measure the distance (mm) between the same relative positions (e.g., between left edges) of two widely-separated lines on the grating replica. Count the number of spaces between the lines.
       NOTE: On most microscopes the magnification is substantially constant only within the central 8- to 10-cm diameter region of the fluorescent screen.
    d. Calculate the true magnification (M) on the fluorescent screen:

$$M = \frac{X \cdot G}{Y}$$

       where: X = total distance (mm) between the two grating lines;
              G = calibration constant of the grating replica (lines/mm);
              Y = number of grating replica spaces counted
    e. After calibration, note the apparent sizes of 0.25 and 5.0 µm on the fluorescent screen. (These dimensions are the boundary limits for counting asbestos fibers by phase contrast microscopy.)
15. Measure 20 grid openings at random on a 200-mesh copper grid by placing a grid on a glass slide and examining it under the PCM. Use the Walton-Beckett graticule to measure the grid opening dimensions. Calculate an average graticule field dimension from the data and use this number to calculate the graticule field area for an average grid opening.
    NOTE: A grid opening is considered as one graticule field.
16. Obtain reference selected area electron diffraction (SAED) or microdiffraction patterns from standard asbestos materials prepared for TEM analysis.
    NOTE: This is a visual reference technique. No quantitative SAED analysis is required [12]. Microdiffraction may produce clearer patterns on very small fibers or fibers partially obscured by other material.
    a. Set the specimen holder at zero tilt.
    b. Center a fiber, focus, and center the smallest field-limiting aperture on the fiber. Use a 20-cm camera length and 10X binocular head. Obtain a diffraction pattern. Photograph each distinctive pattern and keep the photo for comparison to unknowns.
       NOTE: Not all fibers will present diffraction patterns. The objective lens current may need adjustment to give optimum pattern visibility. There are many more amphiboles which give diffraction patterns similar to the analytes named on p.7402-1. Some, but not all, of these can be eliminated by chemical separations. Also, some non-amphiboles (e.g., pyroxenes, some talc fibers) may interfere.

17. Acquire energy-dispersive X-ray (EDX) spectra on approximately 5 fibers having diameters between 0.25 and 0.5 µm of each asbestos variety obtained from standard reference materials [12].
    NOTE: The sample may require tilting to obtain adequate signal. Use same tilt angle for all spectra.
    a. Prepare TEM grids of all asbestos varieties.
    b. Use acquisition times (at least 100 sec) sufficient to show a silicon peak at least 75% of the monitor screen height at a vertical scale of ≥500 counts per channel.
    c. Estimate the elemental peak heights visually as follows:
        (1) Normalize all peaks to silicon (assigned an arbitrary value of 10).
        (2) Visually interpret all other peaks present and assign values relative to the silicon peak.
        (3) Determine an elemental profile for the fiber using the elements Na, Mg, Si, Ca, and Fe. Example: 0-4-10-3-<1 [12].
        NOTE: In fibers other than asbestos, determination of Al, K, Ti, S, P, and F may also be required for fiber characterization.
        (4) Determine a typical range of profiles for each asbestos variety and record the profiles for comparison to unknowns.

MEASUREMENT:

18. Perform a diffraction pattern inspection on all sample fibers counted under the TEM, using the procedures given in step 17. Assign the diffraction pattern to one of the following structures:
    a. chrysotile;
    b. amphibole;
    c. ambiguous;
    d. none.
    NOTE: There are some crystalline substances which exhibit diffraction patterns similar to those of asbestos fibers. Many of these, (brucite, halloysite, etc.) can be eliminated from consideration by chemistry. There are, however, several minerals (e.g., pyroxenes, massive amphiboles, and talc fibers) which are chemically similar to asbestos and can be considered interferences. The presence of these substances may warrant the use of more powerful diffraction pattern analysis before positive identification can be made. If interferences are suspected, morphology can play an important role in making positive identification.
19. Obtain EDX spectra in either the TEM or STEM modes from fibers on field samples using the procedure of step 18. Using the diffraction pattern and EDX spectrum, classify the fiber:
    a. For a chrysotile structure, obtain EDX spectra on the first five fibers and one out of ten thereafter. Label the range profiles from 0-5-10-0-0 to 0-10-10-0-0 as "chrysotile."
    b. For an amphibole structure, obtain EDX spectra on the first 10 fibers and one out of ten thereafter. Label profiles ca. 0-2-10-0-7 as "possible amosite"; profiles ca. 1-1-10-0-6 as "possible crocidolite"; profiles ca. 0-4-10-3-<1 as "possible tremolite"; and profiles ca. 0-3-10-0-1 as "possible anthophyllite."
        NOTE: The range of profiles for the amphiboles will vary up to ±1 unit for each of the elements present according to the relative detector efficiency of the spectrometer.
    c. For an ambiguous structure, obtain EDX spectra on all fibers. Label profiles similar to the chrysotile profile as "possible chrysotile." Label profiles similar to the various amphiboles as "possible amphiboles." Label all others as "unknown" or "non-asbestos."
20. Counting and Sizing:
    a. Insert the sample grid into the specimen grid holder and scan the grid at zero tilt at low magnification (ca. 300 to 500X). Ensure that the carbon film is intact and unbroken over ca. 75% of the grid openings.

b. In order to determine how the grids should be sampled, estimate the number of fibers per grid opening during a low-magnification scan (500 to 1000X). This will allow the analyst to cover most of the area of the grids during the fiber count and analysis. Use the following rules when picking grid openings to count [12,13]:
   (1) Light loading (<5 fibers per grid opening): count total of 40 grid openings.
   (2) Moderate loading (5 to 25 fibers per grid opening): count minimum of 40 grid openings or 100 fibers.
   (3) Heavy loading (>25 fibers per opening): count a minimum of 100 fibers and at least 6 grid openings.

   Note that these grid openings should be selected approximately equally among the three grid preparations and as randomly as possible from each grid.

c. Count only grid openings that have the carbon film intact. At 500 to 1000X magnification, begin counting at one end of the grid and systematically traverse the grid by rows, reversing direction at row ends. Select the number of fields per traverse based on the loading indicated in the initial scan. Count at least 2 field blanks per sample set to document possible contamination of the samples. Count fibers using the following rules:
   (1) Count all particles with diameter greater than 0.25 µm that meet the definition of a fiber (aspect ratio ≥3:1, longer than 5 µm). Use the guideline of counting all fibers that would have been counted under phase contrast light microscopy (Method 7400). Use higher magnification (10000X) to determine fiber dimensions and countability under the acceptance criteria. Analyze a minimum of 10% of the fibers, and at least 3 asbestos fibers, by EDX and SAED to confirm the presence of asbestos. Fibers of similar morphology under high magnification can be identified as asbestos without SAED. Particles which are of questionable morphology should be analyzed by SAED and EDX to aid in identification.
   (2) Count fibers which are partially obscured by the grid as half fibers.
   NOTE: If a fiber is partially obscured by the grid bar at the edge of the field of view, count it as a half fiber only if more than 2.5 µm of fiber is visible.
   (3) Size each fiber as it is counted and record the diameter and length:
      (a) Move the fiber to the center of the screen. Read the length of the fiber directly from the scale on the screen.
      NOTE 1: Data can be recorded directly off the screen in mm and later converted to µm by computer.
      NOTE 2: For fibers which extend beyond the field of view, the fiber must be moved and superimposed upon the scale until its entire length has been measured.
      (b) When a fiber has been sized, return to the lower magnification and continue the traverse of the grid area to the next fiber.

d. Record the following fiber counts:
   (1) f_s, f_b = number of asbestos fibers in the grid openings analyzed on the sample filter and corresponding field blank, respectively.
   (2) F_s, F_b = number of fibers, regardless of indentification, in the grid openings analyzed on the sample filter and corresponding field blank, respectively.

CALCULATIONS:

21. Calculate and report the fraction of optically visible asbestos fibers on the filter, $(f_s - f_b)/(F_s - F_b)$. Apply this fraction to fiber counts obtained by PCM on the same filter or on other filters for which the TEM sample is representative. The final result is an asbestos fiber count. The type of asbestos present should also be reported.
22. As an integral part of the report, give the model and manufacturer of the TEM as well as the model and manufacturer of the EDX system.

EVALUATION OF METHOD:

The TEM method, using the direct count of asbestos fibers, has been shown to have a precision of 0.275 (s_r) in an evaluation of mixed amosite and wollastonite fibers. The estimate of the asbestos fraction, however, had a precision of 0.11 (s_r). When this fraction was applied to the PCM count, the overall precision of the combined analysis was 0.20 [6].

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