

TEST PLAN FOR AN IN-DEPTH STUDY
OF THE SB BATTERY SMELTING FURNACE IN
GLOSTRUP, DENMARK

RADIAN
CORPORATION

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GLOSTRUP, DENMARK

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SECTION 1

INTRODUCTION

Radian Corporation of Austin, Texas is currently under contract to the National Institute for Occupational Safety and Health to determine the most effective controls used by the secondary nonferrous metals industry to protect workers from hazardous chemical and physical agents. As part of a preliminary survey of the Secondary Lead Industry, Radian has identified the SB battery smelting furnace and the flash dust agglomeration furnace operated by Paul Bergsøe and Sons as two new processes possibly offering the best control of secondary lead smelting process emissions. The purpose of this study plan is to quantify, to some degree, the amount of worker protection afforded by these processes in reducing the fugitive emission of fumes and dust to the workplace.

A second objective of this test plan is to quantify the extent and nature of emissions to the atmosphere. This portion of the program is sponsored by the U.S. Environmental Protection Agency under an interagency grant. The gathering of information for both government organizations simultaneously is proposed for efficiency of time and money and in order to generate more complete results. The basic philosophy of this test plan is to quantify workplace and atmosphere emissions during a time period in which the operating parameters and material flows of the process are also well defined. This process knowledge will be useful in estimating the potential change in emissions due to process changes (such as different feedstocks) should this technology be applied in the U.S.

SECTION 2

PROGRAM OBJECTIVES AND APPROACH

The objective of both the Control Technology Research Branch of NIOSH and the Metals and Inorganic Chemicals Branch of EPA in pursuing this program is to provide technical support for the current or proposed regulations regarding lead and the other toxic elements processed by the secondary lead industry. Both agencies are interested in identifying the best technology available for controlling lead emissions.

The SB smelting system and the flue dust flash agglomeration furnace used at the Glostrup, Denmark smelter have been identified as two processes which potentially represent best available control technology (BACT) for the secondary lead industry. This program will provide some of the answers needed to judge the effectiveness of these furnaces in meeting both workroom exposure and atmospheric emission standards.

The interests of these two agencies are different in that NIOSH is concerned with controlling the workroom environment while EPA focuses on stack or over-the-fence emissions. Some overlap in interests occurs because EPA is interested in the effect of fugitive process emissions on the ambient environment. Fugitive emissions are essentially the same as the workroom contamination studied by NIOSH except that the effects of the emissions outside the workplace rather than inside are of concern to EPA.

The general objectives of this program are to:

- Quantify the stack emission rates for lead, antimony, arsenic, chlorine, fluorine, and sulfur dioxide,

- Quantify the exposure to lead and other agents received by the workers at the smelter,
- Complete a material balance around the SB smelting furnace for lead, arsenic, antimony, chlorine, and fluorine,
- Document the process operating conditions under which the above measurements were taken, and
- Identify the potential limitations of the process which may limit or prevent its applicability to the U.S. smelting industry.

In addition, the operation of several other small furnaces will be studied by NIOSH. The following discussion describes the specific approach to information gathering and evaluation used by both agencies in performing this study.

TECHNICAL APPROACH - NIOSH

Integrated Process Description

An appreciation for materials flow, energy consumption, transformation of raw materials, etc., must be obtained to completely evaluate process controls. The observations made and data collected on each of these topics during this study will be added to the plant description given in Section 3 to give a complete description of how the SB smelting furnace operates. The three factors needed to complete this type of process description are:

- Chemical Agent/Physical Agent Control
- Process/Control Illustration
- Equipment Description

Each of these are described below.

Chemical Agent/Physical Agent Control --

Each control within a process has been designed to eliminate problems with chemical or physical agents. An important part of the description of existing controls will be an analysis of which hazards are influenced by the presence of the control. In some situations a control may be an effective means of reducing exposure to a chemical agent while offering little or no relief from exposure to various physical agents. Similarly, a particular control may afford reduced exposure to particular types of chemical agents while being virtually ineffective against others. Examples would be different physical forms of contaminant materials, gases, vapors, particulates, fibers, etc. The presence of occupational hazards associated with a particular operation and the effects of the control being studied on these hazards will be documented by collecting personal, area, and grab samples. This sampling data will be supplemented with visual observations by a trained industrial hygienist.

Process/Control Illustration --

Description of existing controls would not be complete without the pictorial representations of control configurations. Pictorial or graphic information may take the form of engineering drawings similar to those found in the ACGIH Ventilation Manual; heating and ventilating engineering drawings; or photographic prints taken of actual control installations. The purpose of these drawings or photographs is to clarify the physical shape of the control and its relationship to the operation or process. In some situations where lighting and contaminant visibility permit it may be possible to use photographs to visually record the effectiveness of a particular control during certain portions of an operating cycle. Sole reliance will not be placed on photographs for documentation of engineering design parameters.

Equipment Description --

The equipment involved in a particular operation will be documented. Where appropriate, equipment will be described in detail to include model numbers,

horsepower, age, associated attachments, state of repair, etc. A variety of measurements will be made to describe the control being studied. These measurements will include physical dimensions of the control structure itself and its relationship to the operation or process. Materials of construction will be noted, and if possible, historical capital and operating costs of control equipment will be obtained. An effort will be made to obtain information regarding the expected service life of control equipment, the amount of downtime associated with this equipment, and specific precautions or problems associated with making routine repairs to the control. Measurements of this type will be of crucial importance to the evaluation of a control.

Documentation of Control Operating Parameters

Essential to this project effort will be the quantification of operating parameters for controls studied. A variety of techniques will be utilized in the field for this purpose. In some situations, physical measurements may adequately describe operating parameters. These measurements may include capture velocity, hood static pressure, duct transport velocity, etc. In other situations, it may be necessary to perform certain types of air sampling. This air sampling may involve a point emission source, sampling within a duct or stack, or work area/personnel monitoring. Sampling will only be performed where it will aid the analysis of operating parameters associated with a particular control.

Documentation of operating parameters will also be approached using visual observation techniques, for example, the use of ventilation smoke tubes. In some cases, comparison of observed control efficiencies to theoretical design relationships obtained from engineering manuals and other sources will be conducted.

Relationships Between Employees, Hazards, Operations, Processes and Controls

In some situations, the actions of the employee may significantly affect the relative protection afforded by a control device. The subjective area concerning work practices will be examined by observing the interrelationship between employee actions and control effectiveness. In a similar fashion,

the use of personal protective clothing and equipment will be noted to determine what additional protection is potentially afforded by these items. These observations will help determine whether the employees' interaction with the engineering controls limit its effectiveness.

Maintenance activities often involve employee exposure to levels of contaminants or energy produced by a process which are atypical to the normal working exposure. Often, engineering controls are not in operation during maintenance periods. For these reasons, each control will be examined to determine how maintenance is performed, how often it is performed and what procedures are utilized in performing routine and emergency maintenance.

A similar analysis or evaluation will be performed concerning process upsets or particularly energetic cycles in a production process. It is possible that some controls studied during these in-depth evaluations will offer complete or nearly complete control during major portions of operating cycles. However, there may be certain periods during an operating cycle where a rapid emission of contaminants or burst of physical energy is liberated for which the control is not capable of handling. The importance of these momentary upsets will depend on their frequency, duration, and the relative intensity of energy release or toxicity of contaminant emitted. Where these conditions are observed, an attempt to evaluate the importance of such conditions will be made. Realistically, however, this evaluation will have to be qualitative in nature.

Critique of Control Application

Possibly the most important product to be derived from these in-depth surveys is the evaluation of the control with emphasis on how it may be improved, what other forms of control may be equally effective, and what potential exists for transferring the particular control technology to other operations. A discussion of possible improvements will be included with each control evaluation. The possible improvements are expected to cover a wide range. In some cases, it may be necessary to offer more

enclosure or to change the shape or structure of a particular exhaust hood. Potential improvements will not be limited to the physical construction of the control. In some circumstances, it may be possible to improve employee work practices, use of personal protective equipment, or management of the process or operation to minimize the impact of upsets or energetic process cycles.

A discussion of alternative controls will be approached with caution. It will be difficult and demanding for the survey team to gain complete understanding of the trade-offs offered by various means of control and how they impact the working environment in the production of product in a particular smelter. Heavy reliance will be placed on the experience of smelting operators to critique any alternative approach which may be forwarded. The intent of this project is to suggest and document reasonable and effective controls for specific operations in secondary smelting.

TECHNICAL APPROACH - EPA

The approach used by EPA in this study is designed to quantify the environmental emissions generated by the SB smelting furnace and relate those emissions to a specific set of process operating conditions. This will establish a basis for comparing emissions from this process to other lead smelting processes. To do this, two sets of experiments will be performed. First, the standard EPA stack sampling will be performed (EPA Method 5) to quantify the atmospheric emissions. Second, material balances for six of the important toxic elements processed, lead, antimony, arsenic, fluorine, chlorine, and sulfur will be completed in order to define the flow of material through the smelter. These measurements will be examined along with the data generated by NIOSH in order to establish a baseline for the total emissions which can be expected from this process. Section 4 presents a detailed list of each measurement to be made for the experiments described above.

The preparation of a detailed process description will also be a part of the EPA scope of work. It is of prime interest to relate atmospheric emissions

from the SB smelting furnace to the furnace design and operation. An integral process description similar to that described under the NIOSH TECHNICAL APPROACH will be prepared.

SECTION 3

PLANT DESCRIPTION

Secondary lead smelting involves three major operations: scrap pretreatment, smelting, and refining. Figure 1 outlines the material flow in a secondary lead smelter and lists the major processes, raw materials, and products. Whole battery smelting is an important process in the smelting operation because it eliminates the battery breaking step. In addition, since flue dust agglomeration is an integral part of the whole battery smelter, a major part of the smelter fugitive dust emissions are eliminated.

The concept of whole battery smelting includes both environmental emissions and occupational health as key design parameters. Plant layout, raw material storage and handling, process and hygiene ventilation, housekeeping, process control, flue dust agglomeration, particulate collection, and the smelting parameters are all included in the smelter design. This concept has been implemented in Europe where strict environmental and occupational health regulations have forced lead smelters to modernize their processes.

The SB shaft furnace has an oblong cross section unlike most cylindrical secondary lead blast furnaces used in the United States. Figure 2 is a diagram of the furnace and associated gas treatment system. There are two rows of tuyeres, one on either side of the furnace, designed to use air preheated to 500°C. The construction is similar to a primary lead blast furnace. The tuyeres have special covers which minimize fugitive emissions during punching.

The furnace is constructed so as to isolate the charging floor from the bottom of the furnace. Thus, only the front end loader operator works in a "dirty" area. However, the front end loader does have a filtered air

Figure 1. General process flowsheet for the secondary lead smelting industry.

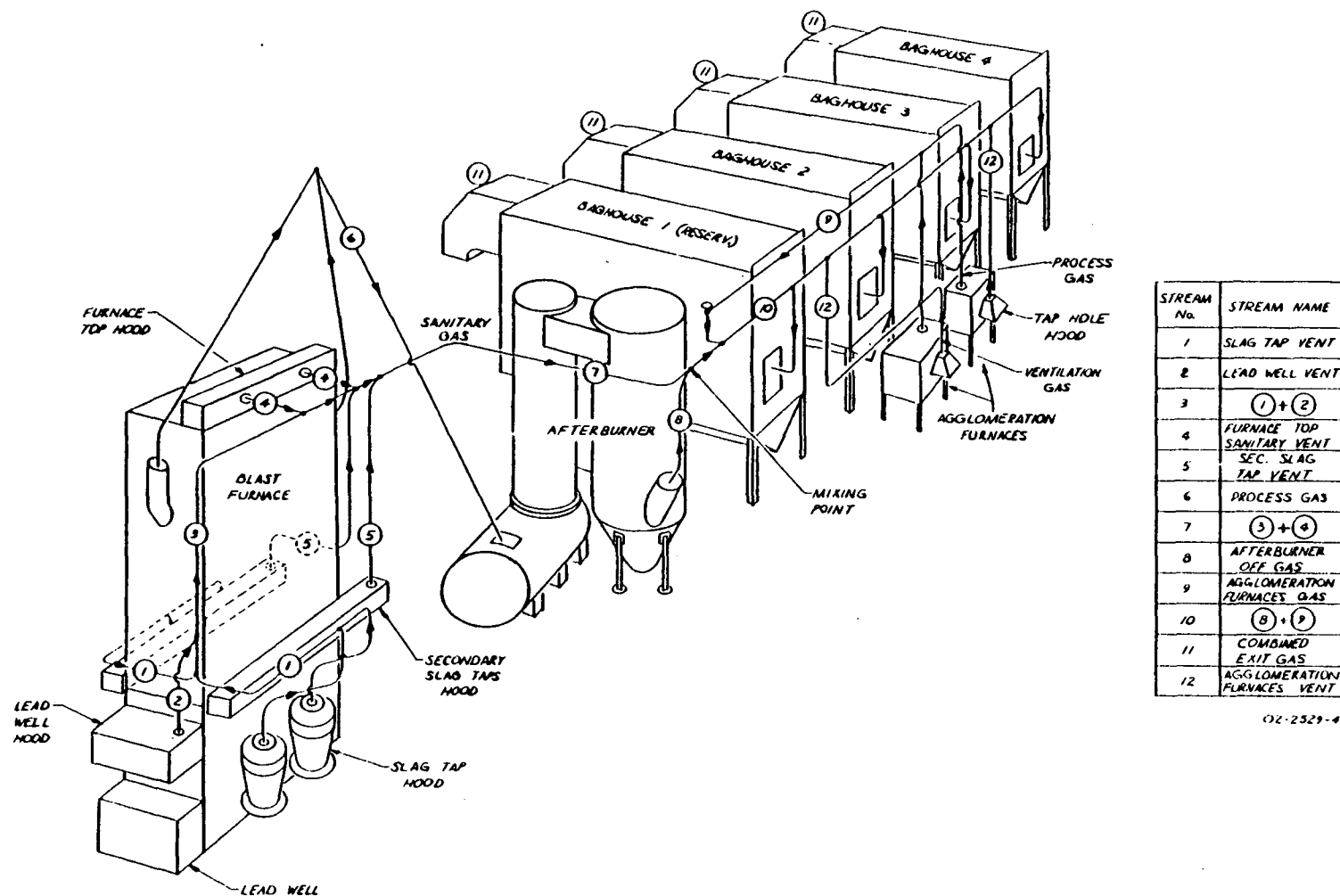


Figure 2. Whole battery smelter furnace and flue gas treatment system.

supply. In addition, the top of the blast furnace is well hooded so as to minimize fugitive emissions.

At the bottom of the furnace, the four slag taps and one lead well are hooded. The strong draft on these hoods virutally eliminates any fugitive emissions. In addition, a special clay/wood plug minimizes the time required for slag tapping.

The sanitary ventilation and process gases are mixed and all gases pass to a single baghouse (at 100-125°C). The baghouse is a Swedish design using felted polyester cloth. The dust is collected on the outside of the bag and only a mild cleaning air jet is required to dislodge the dust. This gives the bags an exceptionally long life.

The collected dust is conveyed in an enclosed system to one of two small flash agglomeration furnaces. In this patented process, the dust is melted and greatly reduced in volume. The agglomerated dust represents only 2 or 3 percent by weight of the furnace charge rather than the normal 8 to 10 percent. This reduces the dust load circulating in the gas cleaning system, increases production per square foot of furnace cross section, and lowers energy consumption. The flash agglomerator furnace is oil fired and consumes 24.6 liters of oil per hour.

The entire smelter area is paved and is wetted and swept periodically. This practice minimizes fugitive emissions normally caused by the wind blowing dry load dust in the yard. This rinse water is collected and combined with the acid drainage from cracked batteries stored in the yard and is finally treated using a soda ash precipitation process. The treated effluent is discharged to the municipal wastewater treatment facility and the sludge is withdrawn periodically, approximately once every two weeks, and charged back to the furnace for additional recovery of metals. The use of soda ash in lieu of lime as the precipitation agent allows the disposal of sludge in the furnace. A lime process sludge would increase the scaling potential in the furnace.

This smelter is serviced with two additional sewer collection systems including one for rainfall and one for sanitary sewage. The rainfall collected is of sufficient quality to be used directly as makeup cooling water for the furnace. Additional makeup cooling water is obtained from the municipal water supply. This water is first softened in an ion exchange unit before use. Sanitary sewage is discharged directly to the municipal collection system.

SECTION 4

SCOPE OF WORK

Separate sampling efforts are required for the NIOSH and EPA portions of the study at the Glostrup, Denmark smelter. Both efforts use a similar strategy with the following subtasks:

- Test Plan
- Trip Preparation
- Sampling at Glostrup
- Sample Analysis
- Data Evaluation
- Reporting
- Presentation of Results
- Program Management

The following discussion describes the specific test plans for both the NIOSH and EPA efforts. The other subtasks are described in a general fashion.

TEST PLAN - NIOSH

A combination of personal breathing zone, work area, and grab sampling techniques will be utilized to help characterize the effectiveness of the hooding over the copper induction furnaces, the rotary furnaces, and the SB battery smelting furnace. An attempt will be made to evaluate control during various phases of the smelting operations. Accordingly, samples will be taken during specific time intervals to describe variations related to operating phases. The following paragraphs describe the sampling to be performed.

Personal Monitoring

Copper Induction Furnaces--

Personal breathing zone samples will be obtained for the two furnacemen normally assigned to the copper induction furnace. Sampling will commence with the initial charging of the furnace and continue through the complete furnace operating cycle. Sampling will terminate when pouring of the furnace has been concluded. Two complete furnace cycles occurring during the day shift of two separate working days will be monitored.

Each employee selected to participate in personal sampling will be asked to wear a small battery powered pump with plastic hose and filter cassette during his workshift. Filters will be changed at the completion of each major phase in furnace operation (i.e. charging, refining, pouring).

Samples will be analyzed for metal particulates according to the methods described in the appendix. Specifically, samples will be analyzed for copper, lead, zinc and arsenic.

Rotary Furnaces--

Personal breathing zone samples will be obtained for the two furnacemen normally assigned to charge preparation and the two or three furnacemen assigned to tapping and pouring the rotary furnaces. Sampling will be conducted for the entire furnace cycle with filters being changed at the completion of each major furnace operating phase. Two complete furnace cycles occurring on two separate working days will be monitored.

The same type of sampling equipment as described for the copper induction furnace will be used. Samples will be analyzed for lead, antimony, and arsenic. A few selected samples will also be analyzed for copper, chlorine, and fluorine.

SB Battery Smelting Furnace--

Personal breathing zone samples will be obtained for the furnace charge mixer/charger on the upper level of the furnace building, the approximately five furnacemen who are assigned to slagging, tapping, and pouring on the lower level. In addition, any other employees working in the whole battery furnace area will be monitored. Sampling will be conducted for the entire furnace cycle with filters being changed at the completion of each major furnace operating phase. At least two complete furnace cycles occurring on separate working days will be monitored.

The same type of sampling equipment as described for the copper induction furnace. Samples will be analyzed for lead, arsenic, antimony, chlorine and fluorine.

Area Sampling

Copper Induction Furnaces--

Work area samples will be obtained at two locations around the copper induction furnaces. These locations will be selected upon arrival at the smelter.

Area samples will be collected using similar equipment as described for personal monitoring, located in stationary positions around the process of interest. Area sampling will extend over the same work periods during the same days as personal sampling. Filters will be changed at each station at the conclusion of each major phase of furnace operation. Area samples will be analyzed using the methods described in the appendix. Samples will be analyzed for copper, lead, zinc and arsenic.

Rotary Furnaces--

Work area samples will be obtained at approximately two locations around the rotary furnaces. These locations will be selected upon arrival at the smelting site.

The technique used for area sampling is similar to the personal monitoring described for the copper induction furnaces. The samples collected will be analyzed for lead, antimony, and arsenic. A few selected samples will be analyzed for copper, chlorine, and fluorine.

SB Battery Smelting Furnace--

Work area samples will be obtained at a minimum of four locations around the whole battery furnace. These locations include the upper charging level, around the slag tapping area and around the bullion tapping area. Filters will be changed at each station at the conclusion of each major phase of furnace operation. In addition to the area samples taken around the whole battery furnace, area samples may be taken around the flash agglomeration furnace located adjacent to the baghouse.

These samples will be collected using similar equipment as described for personal monitoring. Methods for chemical analysis of these samples are described in the appendix. These samples will be analyzed for lead, arsenic, antimony, chlorine and fluorine.

Grab Sampling

During the personal and area sampling periods described in the previous sections, grab samples will be taken to determine the presence of gaseous contaminants. These gaseous contaminants include carbon monoxide and oxides of nitrogen. These contaminant concentrations will be measured using NIOSH certified gas detector tubes.

TEST PLAN - EPA

The EPA portion of this program will focus only on the SB smelting furnace and the agglomeration furnace. Table 1 is a schedule describing the order and number of measurements which will be made for this characterization. Four types of samples will be collected: stack gases and particulates, solid inlet and outlet streams, area gas particulates, and personal exposure.

TABLE 1. SAMPLING SCHEDULE

MEASUREMENT	STREAM NUMBER**		
	Day 1	Day 2	Day 3
Temperature Profiles	11	11	11
Velocity Profiles	11	11	11
Grain Loadings		11	11
• in-stack filter			
• impingers			
Material Balance Samples (WEP)		Yes	Yes
Ambient Air Area Samples	Yes	Yes	Yes
Personal Monitoring		Yes	Yes
Agglomeration Hood Ventilation Measurements		Yes	Yes
Slag Tap Hood Measurements		Yes	Yes
Lead Well Hood Measurements		Yes	Yes
Composite Solid Samples			
Coke	Yes		
Iron	Yes		
Lime	Yes		
Drosses	Yes	Yes	Yes
Batteries*			
Plates	Yes		
Mud	Yes		
Acid	Yes		
Case	Yes		
Bullion	Yes	Yes	Yes
Slag	Yes	Yes	Yes
Speiss	Yes	Yes	Yes
Flue Dust	Yes	Yes	Yes

* Battery component composition data will also be obtained from the manufacturers.

** Stream numbers refer to those indicated in Figure 2.

particulates. Some of these samples will be those taken by NIOSH. In addition, process stream temperature and flow rate measurements will be made to determine how the process is performing.

The stack samples will allow controlled process emission factors to be calculated. The solid stream samples will allow material balances to be completed for six key elements: lead, antimony, arsenic, fluorine, chlorine, and sulfur. The combined data will provide the information necessary to determine the fate of these toxic materials as they pass through the smelting process.

~~Fugitive emissions are expected to be minimal at the whole battery smelter.~~ However, both the area and personal samples taken by NIOSH will be used to estimate over-the-fence lead levels which can be compared to similar measurements made at smelters using different control technology.

The analysis of the samples taken should provide the data needed to calculate emission factors, close material balances, and identify other potentially toxic emissions not currently known. Table 2 lists the types of survey and detailed techniques needed to complete these analyses for the furnace feed. Particulate and gas samples taken at the stack will be analyzed using the same techniques.

Grain Loadings - EPA Method 5

The standard EPA Method 5 pictured in Figure 3 will be used to measure total stack particulate emissions. Each filter will be weighed for total particulate mass and then analyzed for Pb, As, Sb, F, and Cl. An on-line SO₂ monitor will be used to measure SO₂ emissions.

Material Balance

Integral solid samples of each of the feed and discharge streams will be collected during the sample period. The stack gas will be sampled using a special sampling train which employs a wet electrostatic precipitator as the major collection device.

TABLE 2. ANALYTICAL SCHEDULE FOR COMPOSITE SOLID STREAM SAMPLES

Stream	Survey	Analytical Techniques			
		X-Ray Diffraction	Detailed		
			AA*	SIE**	ICED†
Furnace Feed					
Coke	SSMS***				S
Iron	SSMS				
Lime	SSMS				
Drosses	SSMS				
Batteries					
Plates	SSMS		Pb,Sb,As	F,CL	S
Mud	SSMS		Pb,Sb,As	F,C1	S
Acid	SSMS			F,C1	S (GBP)††
Case				F,CL	S
Bullion	SSMS		Pb,Sb,As	F,C1	S
Slag	SSMS		Pb,Sb,As		S
Speiss	SSMS		Pb,Sb,As		S
Flue Dust	SSMS	Yes	Pb,Sb,As	F,C1	S

* Atomic Absorption

** Na₂CO₃ fusion, H₂O leach, specific ion electrode

*** Spark source mass spectrometry

† Ion chromatography of an Eschka digestion

†† Gravimetric barium precipitation

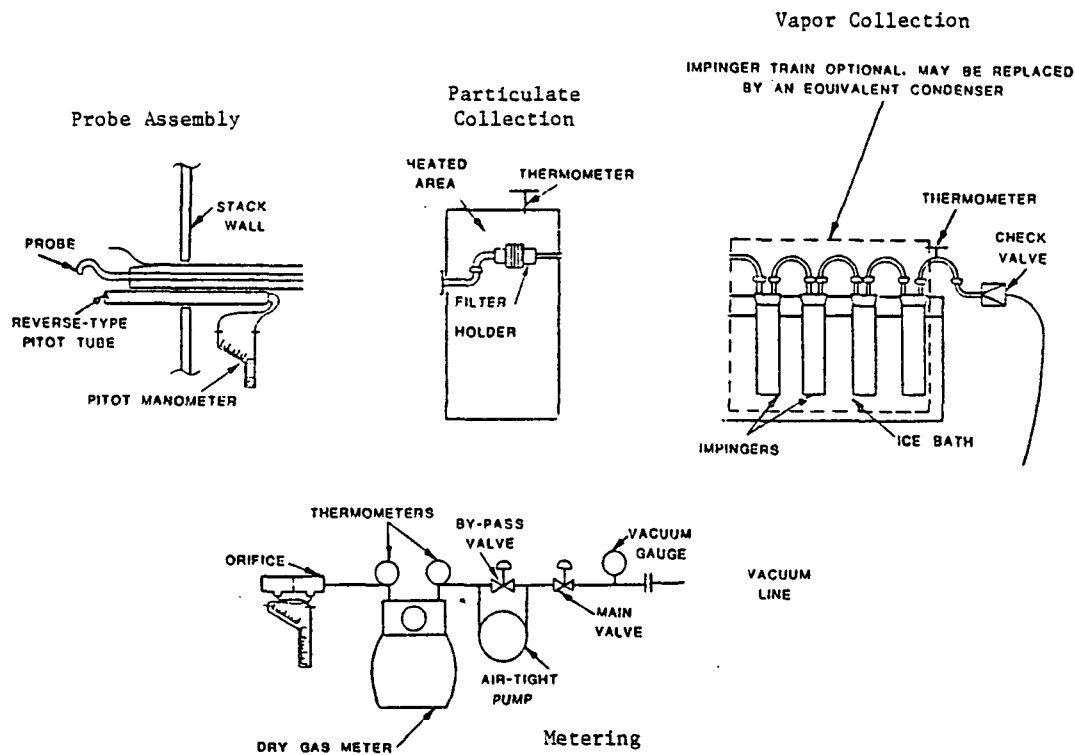


Figure 3. EPA 5 sampling train.

The wet electrostatic precipitator (WEP) is used to collect particulates and acid mist. It is part of the Integral WEP Sampling Train designed to collect solids, mist, and gaseous components from a gas stream and is shown in Figure 4. An electrolyte is circulated through a round bottom flask and a vertical glass cylinder by a peristaltic pump. The walls of the cylinder are wetted by the falling film of electrolyte. A thin platinum wire is suspended in the center of the glass cylinder. A high voltage of 12-15 KV-DC causes a corona discharge at the center electrode.

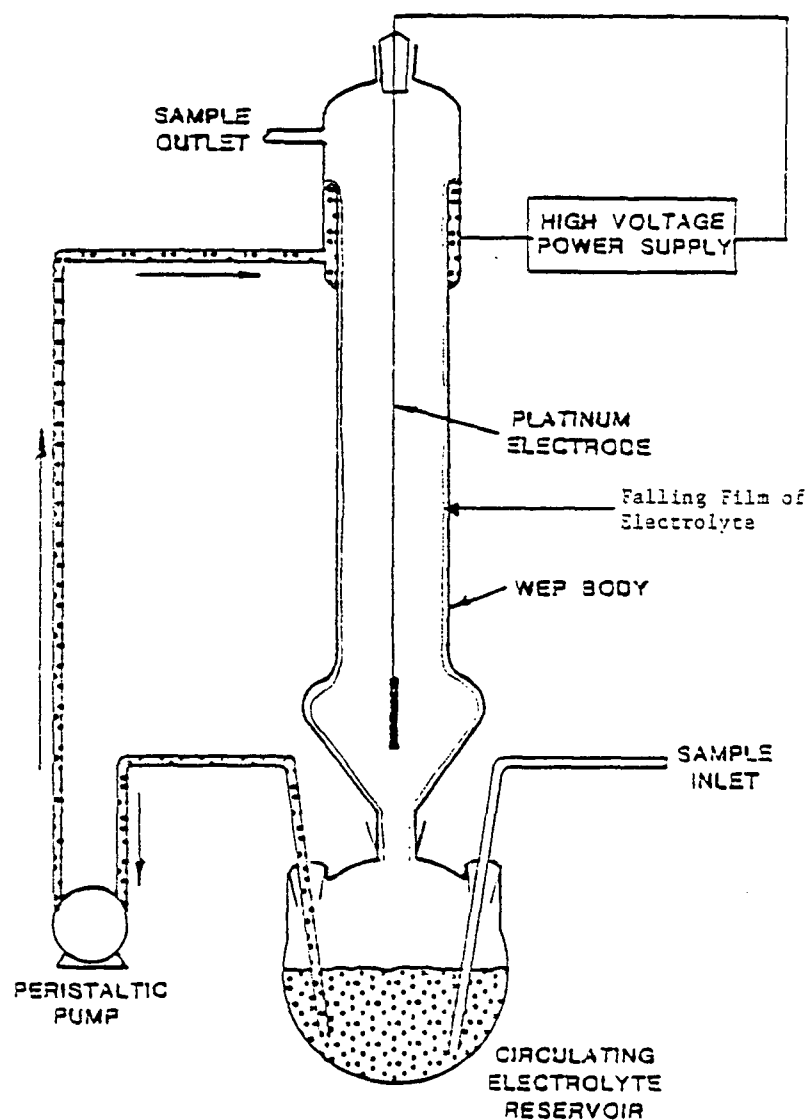


Figure 4. Wet electrostatic precipitator.

The gas entering the WEP is first scrubbed and cooled in the round bottom flask. Particulates and mist not retained here are electrically charged in the glass cylinder, collected in the falling film and washed into the electrolyte reservoir. This sampling device does not clog like a filter or a thimble, and no analytical background corrections are necessary since no extraneous material is introduced as is the case with filters.

The wet electrostatic precipitator was integrated into the sampling device shown in Figure 5. The probe consists of a pyrex nozzle and is pyrex lined. Teflon tubing is used to connect it with the WEP. All the lines are rinsed after sampling. The WEP is followed with eight impingers in an ice bath. The charge of the impingers is summarized in Table 3. A pump and a dry gas meter complete the assembly.

PREPARATION OF SAMPLING TRIP

Radian will supply all the equipment to perform the sampling at the Glostrup smelter. The gear will be assembled, checked, packed and shipped to Glostrup. Changes will be made and any special equipment necessary will be purchased or built during this program phase.

SAMPLING AT GLOSTRUP

Sampling at Glostrup is expected to take approximately seven days, with two days for equipment set-up, check-out and take down. The main sampling effort will take four days.

SAMPLE ANALYSES

A spark source mass spectrometry survey analysis will be performed on the feed material. Level of concentration and toxicity will be used as guidelines for selecting those elements to be included in the material balance calculations. At present, six substances are thought to be of interest. These are: lead, arsenic, antimony, fluorine, chlorine, and sulfur.

Radian recommends the analytical procedures discussed in Appendix B. These methods proved to be successful in a balance attempt around the electrostatic precipitator servicing a reverberatory furnace. Selected samples will be subjected to spark source mass spectrometry analysis. Scanning electron microscopy and X-ray diffraction will be used to further characterize the samples if warranted.

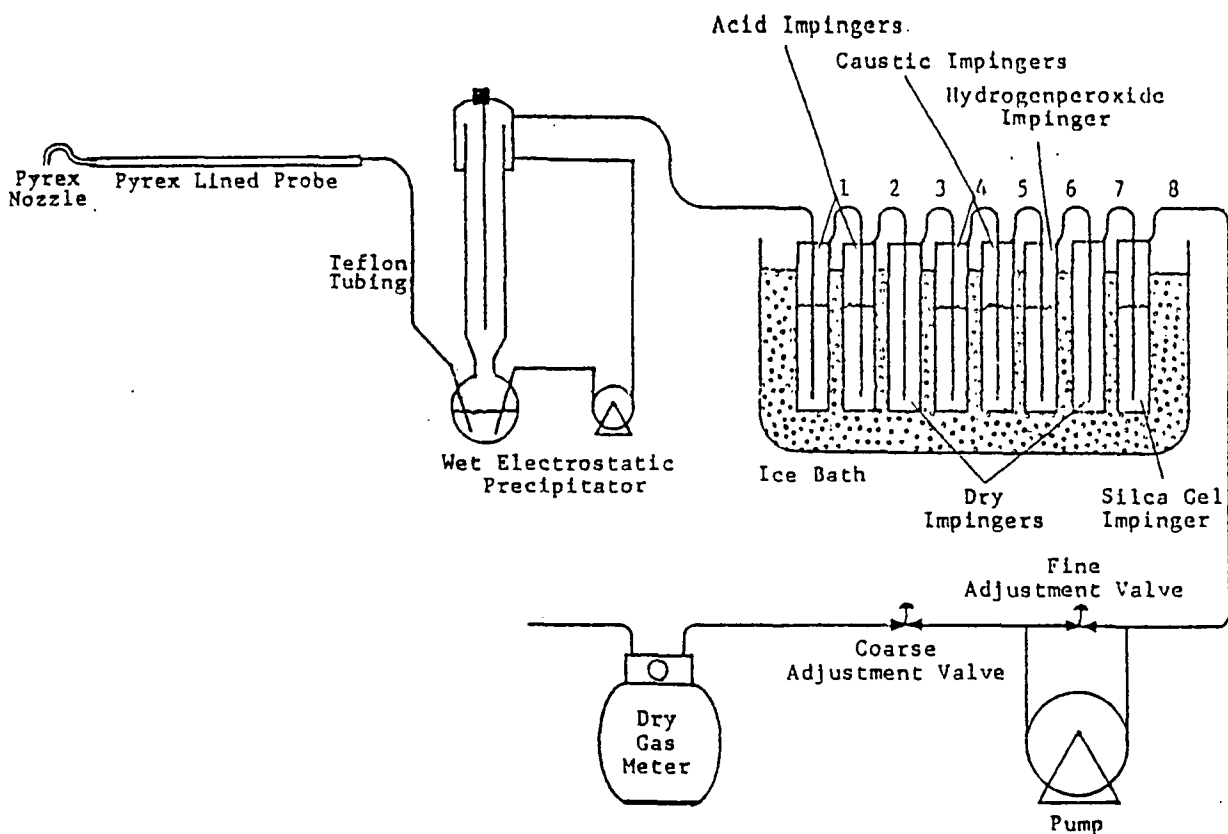


Figure 5. Schematic of the integral WEP sampling train.

TABLE 3. IMPINGER SOLUTIONS COMPOSITIONS

Impinger Number	Solutions
1, 2	1:1:1 sulfuric acid, nitric acid, deionized water in a Smith-Greenburg impinger
3, 7	dry modified Smith-Greenburg impingers
4, 5	20% potassium hydroxide in a Smith-Greenburg impinger
6	hydrogen peroxide in a Smith-Greenburg impinger
8	preweighed silica gel in a modified Smith-Greenburg impinger

DATA EVALUATION

The analytical results and the flow rates will be used to establish the material balances. Error propagation calculations will bracket the confidence limits of the results generated for the EPA measurements.

The EPA data evaluation part of the study includes the selection of elements present in minor concentrations in the smelter feed for detailed analysis. Lead, the major element important in the smelting process, will be used in the analytical scheme in order to check the accuracy of flow rate data.

Spark source mass spectrometry will be used as the technique to analyze the element combination in the smelter feed. This technique provides semi-quantitative results. It has the advantage of covering 73 elements of the periodic chart. From these data, elements will be selected for quantitative determination.

Atomic absorption, x-ray fluorescence, ion specific electrodes, fluorometry, spectrophotometry as well as wet chemical methods will be used for quantitative elemental analysis. Detailed analytical methods employed by Radian are described in Appendix B.

Errors are inherent to both the chemical analysis results and the flow rates of the streams sampled. Both errors propagate if the chemical concentration of an element is multiplied by the flow rate of the stream to give the flow rate of an element. Similarly, the errors propagate if a mass balance is established for a minor element.

The error propagation analysis used to establish error limits for the calculated total inlet and outlet mass rates of each element is described below. The values indicate the degree of variance to be expected due to random errors and should not be interpreted as variance over a set of data points.

A 95 percent confidence interval of $2S(Q)$ is calculated for a given value of Q according to the following standard definition:

$$S^2(Q) = \sum_i^n \frac{\partial Q}{\partial q_i} S^2(q_i)$$

where, $S(Q)$ = the variance in Q ,

Q = the mass flow rate of a given element into or out
of the system,

q_i = the i^{th} independent measured value
(stream flow or elemental concentration),

and

$S(q_i)$ = the variance of q_i .

The analytical results from the air samples taken, the engineering data gathered, and the visual observations made will be used to qualitatively evaluate the engineering controls for NIOSH at the smelter. Quantitative results expected will be the actual employee exposure to hazardous agents at various workplaces and the general workroom concentrations measured during different phases of operations. Comparisons of actual engineering data to design specifications will determine if the controls are operating as expected. Documentation of maintenance procedures as well as observations of employee interaction with the equipment will also contribute to the overall control equipment evaluation.

REPORTING

A final report will be produced conforming to the format and instructions provided by the NIOSH and EPA project officers. A copy of the draft report will be reviewed by the Bergsøe smelter management prior to release to insure the technical accuracy of all process descriptions and to avoid disclosing any proprietary information. The report will contain both the NIOSH and EPA sampling results. A final copy of the report will be issued after all technical and editorial comments are received.

PRESENTATION OF RESULTS

Radian's project technical director will present the results of the sampling effort to both EPA and NIOSH after submittal of the draft final report. The reason for this meeting is to clarify all questions concerning the draft final report.

PROGRAM MANAGEMENT

Effort devoted in this task is aimed to keep close liaison to the NIOSH and EPA program officers, to the Bergsøe smelter management and also to coordinate Radian's in-house effort.

SECTION 5

SCHEDULE AND MILESTONES

Timely completion of this study will depend heavily on the operation of the plant during the sampling period. Plant upsets or delays caused by customs or sample analysis could cause delays. At present, the plan calls for the schedule shown in Figure 6. The milestones and expected completion dates are shown in Table 4.

TABLE 4. MILESTONES AND COMPLETION DATE

Milestone	Description	Completion Date
M-1	Preliminary Test Plan	July 17, 1978
M-2	Final Test Plan	July 31, 1978
M-3	Trip Preparation	August 31, 1978
M-4	Field Sampling	September 22, 1978
M-5	Sample Analysis	October 30, 1978
M-6	Data Analysis	November 30, 1978
M-7	Draft Final Report	December 15, 1978
M-8	Final Report	January 31, 1978
M-9	Presentation of Results	February 9, 1978

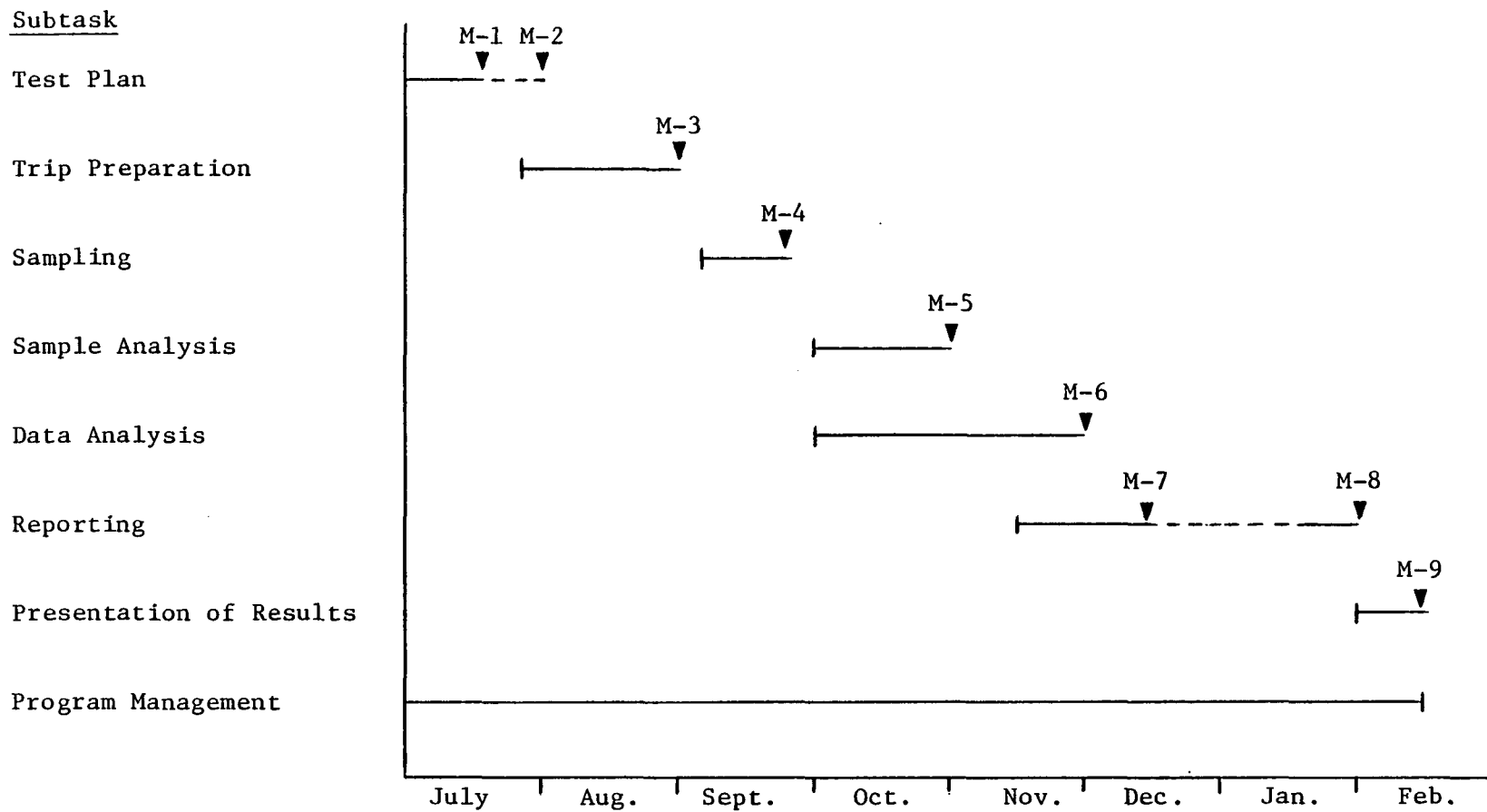


Figure 6. Test program schedule.

APPENDIX A

NIOSH SAMPLING AND ANALYTICAL TECHNIQUES

SAMPLING TECHNIQUES AND EQUIPMENT

Personal and Area Monitoring

Personal and area monitoring is performed using small battery powered pumps fitted with filters to collect any metal fume which is present in the work-room atmosphere. For personal monitoring, the pump is worn by the employee and the filter worn in the vicinity of the breathing zone. For area sampling, the pump and attached filter are located in a stationary position. The sampling techniques for the elements of interest in this study, *i.e.*, copper, lead, arsenic, zinc, antimony, tin are described in the NIOSH Manual of Sampling Data Sheets as follows:

General Procedure for Metals --

Method - A known volume of air is drawn through a cellulose membrane filter to trap the metal fume present. The filter is digested with an acidic solution to destroy the filters and any organic material. The analyte is then solubilized in a suitable acid solution (see Analytical Methods), and aspirated into an atomic absorption spectrophotometer for determination of concentration.

Sampling Equipment.- A calibrated personal sampling pump whose flow can be determined to an accuracy of $\pm 5\%$ over the range of 1.0 to 2.0 liters per minute; a 37-mm three-piece cassette filter holder and a 37-mm diameter 0.8-micrometer pore size mixed cellulose ester membrane filter (MCEF) supported by a cellulose backup pad.

Sample Size - A sample size of 250 liters is recommended. Sample at a flow rate of 1.5 liters per minute.

Sampling Procedure - Assemble the filter and three-piece filter cassette and close firmly to insure that the center ring seals the edge of the filter. Examine the holder for a good filter seal. If the cassette will not seal tightly, it should be discarded. Secure the cassette holder together with tape or shrinkable band.

Remove the cassette plugs and attach to the personal sampling pump tubing. Clip the cassette to the worker's lapel.

Air being sampled should not be passed through any hose or tubing before entering the filter cassette.

Set the flow rate as accurately as possible using the manufacturer's directions. Record the temperature and pressure of the atmosphere being sampled. If the pressure reading is not available, record the elevation. Position the middle of the rotameter ball of the personal sampling pump to the 1.5-liter per minute calibration mark as accurately as possible. Since it is possible for the filter to become plugged by heavy particulate loading or by the presence of oil mists or other liquids in the air, the pump rotameter should be observed frequently, and readjusted as needed. If the rotameter cannot be adjusted to correct a problem, terminate the sampling.

Cassettes containing collected samples should be firmly sealed with the plugs in both the inlets and outlets.

Carefully record sample identity and all relevant sample data.

Blank. With each batch of ten samples, submit one filter from the same lot of filters which was used for sample collection and which is subjected to exactly the same handling as the samples except that no air is drawn through it. Label this as a blank.

Procedure for Hydrogen Fluoride --

Method - A known volume of air is drawn through a midget bubbler containing 10 ml of 0.1 N sodium hydroxide to trap hydrogen fluoride. The resulting solution is diluted to 25 ml with 0.1 N sodium hydroxide and buffered with an equal volume of total ionic strength activity buffer (TISAB). The sample is analyzed using a fluoride ion specific electrode and an expanded scale millivolt/pH meter. The method has been validated over the range of 1.33-4.50 mg/cu m for a 45-liter sample at an atmospheric temperature and pressure of 22°C and 761 mm Hg.

Sampling Equipment - A calibrated personal sampling pump whose flow can be determined accurately, $\pm 5\%$, at 1.5 liters per minute, plus midget bubbler with 1/8-in O.D. Teflon inlet tube, containing 10 ml of 0.1 N sodium hydroxide. A prefilter unit, consisting of a 37-mm/0.8-micrometer mixed cellulose ester membrane filter and a polystyrene cassette filter holder, is connected in front of the bubbler to collect fluoride particulate that may be present. A backup pad should not be used. Care must be taken to insure that the filter is sealed tightly to avoid air leaks during sampling. The sampling pump is protected from splashover by a 5-cm long by 6-mm I.D. glass adsorption tube loosely packed with a plug of glass wool and inserted between the exit arm of the bubbler and the pump. (An additional 100 ml of collection medium should accompany each set of bubblers for use in rinsing the bubbler stems after sampling).

Sample Size - A sample size of 45 liters, taken at a flow of 1.5 liters per minute for 30 minutes, is recommended.

Sampling Procedure - Connect the midget bubbler (containing 10 ml of the collection medium) with a 5-cm glass adsorption tube containing the glass wool plug to the prefilter unit and the personal sampling pump using short pieces of flexible tubing. The minimum amount of tubing necessary to make the joint between the prefilter and bubbler should be used.

The bubbler must be maintained in a vertical position during sampling.

Air being sampled should not be passed through any hose or tubing before entering the bubbler.

Set the flow rate as accurately as possible using the manufacturer's directions. Position the middle of the rotameter ball of the personal sampling pump to the 1.5 liter per minute calibration mark as accurately as possible. Record the temperature and pressure of the atmosphere being sampled. If the pressure reading is not available, record the elevation.

After sampling, the bubbler stems may be removed and cleaned. Tap the stems gently against the inside walls of the bubbler bottles to recover as much of the sampling solution as possible. Wash the stem with 1 ml of 0.1 N sodium hydroxide, adding the wash to the bubbler. Transfer the contents of the bubbler to a 50-ml polyethylene bottle. Rinse the bubbler vessel with 2-3 ml of 0.1 N sodium hydroxide and add the wash to the bottle. Seal tightly for shipment.

Care should be taken to minimize spillage or loss by evaporation.

A "blank" bubbler should be handled in the same manner as the bubblers containing the samples (fill, seal, and transport) except that no air is sampled through this bubbler.

The filter may be discarded since the method is designed to measure gaseous hydrogen fluoride only.

Procedure for Hydrogen Chloride --

Method - A known volume of air is drawn through a midget bubbler containing 10 ml of 0.5 M sodium acetate to trap hydrogen chloride. The resulting solution is diluted to 25 ml with distilled water. The sample is analyzed using a chloride ion specific electrode and an expanded scale millivolt/pH meter.

The method has been validated over the range of 3.5-14 mg/cu m for a 15-liter sample at an atmospheric temperature and pressure of 22°C and 764 mm Hg.

Sampling Equipment - A calibrated personal sampling pump whose flow can be determined accurately, $\pm 5\%$, at 1.0 liter per minute, plus midget bubbler, containing 10 ml of 0.5 M sodium acetate. The sampling pump is protected from splashover by a 5-cm long by 6-mm I.D. glass splashover tube loosely packed with a plug of glass wool and inserted between the exit arm of the bubbler and the pump. (An additional 100 ml of collection medium should accompany each set of bubblers for use in rinsing the bubbler and bubbler stems after sampling.) Samples are shipped in polyethylene containers.

Sample Size - A sample size of 15 liters, taken at a flow of 1.0 liter per minute for 15 minutes, is recommended.

Sampling Procedure - Connect the midget bubbler (containing 10 ml of the collection medium) with a 5-cm glass splashover tube containing the glass wool plug to the personal sampling pump using short pieces of flexible tubing.

The bubbler must be maintained in a vertical position during sampling.

Air being sampled should not be passed through any hose or tubing before entering the bubbler.

Set the flow rate as accurately as possible using the manufacturer's directions. Position the middle of the rotameter ball of the personal sampling pump to the 1.0 liter per minute calibration mark as accurately as possible. Record the temperature and pressure of the atmosphere being sampled. If the pressure reading is not available, record the elevation.

After sampling remove the bubbler stem and transfer the contents of the bubbler to a polyethylene container. Rinse the bubbler and bubbler stem

with 3-5 ml of collection medium, adding the rinse to a polyethylene container. Seal the polyethylene container with the associated caps just prior to shipment.

Care should be taken to minimize spillage or loss by evaporation.

A "blank" bubbler should be handled in the same manner as the bubblers containing the samples (fill, seal, and transport) except that no air is sampled through this bubbler.

Grab Sampling

Grab sampling for gaseous contaminants such as carbon monoxide will be done using NIOSH approved detector tubes attached to a hand operated pump. This method is described in the NIOSH Manual of Sampling Data Sheets as follows:

Sampling Equipment --

Certified or NIOSH approved detector tubes and a hand operated pump (not rubber bulb type) may be used for compliance purposes. (Secondary Method)

Analytical Procedure --

Detector tubes are read for length of stain, strokes of pump are noted, and appropriate corrections are made for pressure (or altitude above 5,000 feet (1,500 m). The tubes are not to be used when below 0 degrees F (-18°C) or above 125 degrees F (52°C).

Sampling Period --

Depends on portable instrument used.

Detector tubes: direct reading, length-of-stain detector tubes (certified or NIOSH approved) may be used for compliance purposes, if at least one sample per hour is taken per exposed worker or close group of workers. In an 8-hour day more frequent sampling per hour is preferred, especially for

exposures over 50 ppm. Eight different samplings, one per hour, is considered the minimum acceptable number.

ANALYTICAL METHODS

The following paragraphs describe the chemical analysis methods which will be used to analyze the filter samples taken during both personal and area monitoring. These methods are taken from the NIOSH Manual of Analytical Methods with modifications to the methods as noted. For specific information for each element of interest, see Table A-1.

General Procedure for Metals

Principle of the Method --

Samples are ashed using nitric acid to destroy the organic matrix and the metals are solubilized in an acidic solution maintaining a pH of 1.

Samples and standards are aspirated into the appropriate AA flame. A hollow cathode lamp for each metal of interest provides the characteristic line for that particular metal. The absorption of this line by the ground state atoms in the flame is proportional to the metal concentration in the aspirated sample.

Range and Sensitivity --

The optimum working range for each metal is given in the Table. This value can be extended to higher concentrations by dilution of the sample.

The sensitivity of this method for each metal in aqueous solution is also given in the Table. This value will vary somewhat depending upon the instrument used.

Table A-1. DATA TABLE FOR METAL ANALYSIS

Element	Sensitivity ($\mu\text{g/ml}$)	Range of Method ($\mu\text{g/ml}$)	Method No.	Analytical Wavelength (\AA)	Modifications to Method
Be	0.03	0.03-8	P & CAM 173	2349	
Ca	0.07	0.07-10	P & CAM 173	4227	
Cd	0.04	0.04-5	P & CAM 173	2288	perchloric acid used to aid digestion
Co	0.15	0.15-8	P & CAM 173	2407	
Cr	0.2	0.2-10	P & CAM 173	3579	
Cu	0.1	0.1-10	P & CAM 173	3247	perchloric acid used to aid digestion
Fe	0.1	0.1-10	P & CAM 173	2483	
K	0.1	0.1-10	P & CAM 173	7665	
Mg	0.007	0.007-0.7	P & CAM 173	2852	
Mn	0.05	0.05-4	P & CAM 173	2795	
Mo	1.0	1.0-60	P & CAM 173	3133	
Na	0.02	0.02-5	P & CAM 173	5890	
Ni	0.2	0.2-20	P & CAM 173	2320	
Pb	0.5	0.5-30	P & CAM 173	2170, 2833	perchloric acid used to aid digestion
Sn	5.0	5.0-300	P & CAM 173	2246, 2354	terniary acid used to aid digestion: 4:4:1 of H_2SO_4 , HNO_3 , HClO_4
Sn (alt)			5183	5183	
Sb			P & CAM 173		
Zn	0.025	0.025-27	P & CAM 173	2139	perchloric acid used to aid digestion
As			P & CAM 173		
As (alt)	Hydride Generation Method				
F			P & CAM 117		
Cl			5246		

Interferences --

Known interferences may occur when analyzing for metals listed in the table. Therefore, procedures for eliminating or overcoming these interferences are listed. Whenever additions are made to the samples to overcome or eliminate interferences, similar additions must be made to the standards.

Chemical interferences in the flame prevent conversion of the metal being determined to the atomic state. Higher flame temperatures ($\text{N}_2\text{O}-\text{C}_2\text{H}_2$) can overcome this problem in some cases.

Precision and Accuracy --

In general, this method will provide a coefficient of variation for the analysis of approximately 2% depending upon the instrument used and the absorbance of the samples. (If absorbance is less than 0.1, the coefficient of variation is higher.)

No data on accuracy is available at this time.

Advantages and Disadvantages of the Method --

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.

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.

Apparatus --

Sampling Equipment - The sampling unit for the collection of personal air samples for the determination of metal content has the following components:

- The filter unit, consisting of the filter media (Section 6.2) and appropriate cassette filter holder, either a 2- or 3-piece filter cassette (Millipore Filter Corporation, Bedford, Massachusetts).
- A vacuum-pump such as a personal sampling pump. This pump must be properly calibrated so the volume of air sampled can be measured as accurately as possible. The pump must be calibrated with a representative filter unit in the line. Flow rate, times, and/or volume must be known.
- Thermometer.
- Manometer.
- Stopwatch.
- Various clips, tubing, spring connectors, and belt for connecting sampling apparatus to worker being sampled.

0.8 μ cellulose membrane filter (or equivalent), 37 mm.

Hollow cathode lamps for each metal.

Atomic absorption spectrophotometer, having a monochromator with a reciprocal linear dispersion of about 6.5 Å/mm in the ultraviolet region. The instrument must have the necessary burner heads for air-acetylene and nitrous oxide-acetylene flames.

Oxidant:

- Air, which has been filtered to remove water, oil, and other foreign substances is the usual oxidant.
- Nitrous oxide is required as an oxidant when higher temperatures are required in the analysis of refractory-type metals.

Fuel - Acetylene, commercially available for atomic absorption use.

Pressure-reducing valves - A 2-gauge, 2-stage pressure reducing valve and appropriate hose connections are needed for each compressed gas tank used. When using nitrous oxide, heating tape, with the temperature controlled by a rheostat, is wound around the second stage of the regulator and connecting hose to prevent freeze-up of the line.

Glassware, borosilicate:

- 125 mL Phillips beakers with watchglass covers
- 15 mL graduated centrifuge tubes
- 10 and 100 mL volumetric flasks
- 125 mL polyethylene bottles

Three-switch hot plates capable of reaching 400°C.

Reagents --

All reagents used must be ACS Reagent Grade or better.

Double Distilled or deionized water

Redistilled concentrated nitric acid

Distilled 1:1 hydrochloric acid

Commercially prepared *aqueous stock standards* (1000 µg/mL) for each metal listed in the Table.

Lanthanum stock solution (for Ca determination) - 5% La in 25% HCl (v/v). Wet 29.33 g La₂O₃ with double distilled water. Add 125 mL concentrated HCl. Dilute to 500 mL.

Aluminum solution (for Mo determination) - commercially prepared aqueous aluminum stock containing 1000 $\mu\text{g Al/ml}$.

Procedure --

Cleaning of Equipment:

- 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, concentrated nitric acid, tap water and deionized water, in that order, and then dried.
- All glassware is soaked in a mild detergent solution immediately after use to remove any residual grease or chemicals.
- For glassware which has previously been subjected to the entire cleaning procedure, it is not necessary to use the chromic acid cleaning solution.

Collection and Shipping of Samples:

- Dusts and fumes containing metal can be sampled with a 0.8 μ cellulose membrane filter. The filters must not be loaded to the point where portions of the sample might be dislodged from the collecting medium during handling. Personal filter samples should be sealed in individual plastic filter holders during shipment. A two-hour sampling period at 1.5 liters per minute will provide enough sample for air concentrations of 0.2 x TLV. Beryllium requires a full eight-hour sample at 0.2 x TLV.
- Blood samples - 10 ml should be collected in chemically clean, heparinized vacutainers. If the vacutainers have not been pretreated, 1-2 ml of a heparin sodium solution should be injected into the vacutainer. Refrigerate for shipment if possible.

- Urine samples - 50 mL should be collected in chemically clean, borosilicate or polyethylene bottles. The urine samples should be preserved by the addition of approximately 2.5 mg of thymol and refrigerated for shipment if possible.
- Tissue samples should be collected in chemically clean jars and preserved in dry ice. Tissue samples must be shipped back to the laboratory immediately.

Analysis of Samples:

- Samples are transferred to clean 125 mL Phillips beakers and several mL of concentrated HNO_3 is added to each. Each beaker is covered with a watchglass and heated on a hot plate (140°C) in a fume hood until the sample chars or until a slightly yellow solution remains. Several additions of HNO_3 may be needed to completely ash and destroy the organic material. Completion of the digestion procedure is indicated by a white residue in the beaker.
- For samples containing arsenic (a fairly volatile element), the residue is dissolved in 2 mL of 6N HCl using the low temperature hot plate (140°C) and quantitatively transferred to a graduated centrifuge tube with deionized water.
- For samples not containing arsenic, the residue is heated several minutes on the high temperature hot plate (400°C) and converted to a salt by three successive evaporations with 1:1 HCl or concentrated HNO_3 . The ash is then dissolved with 1:1 HCl or concentrated HNO_3 and deionized water and quantitatively transferred to a graduated centrifuge tube. Aliquots of this can be diluted if necessary or the volume can be reduced by evaporation to get the metal concentration within the working range of the method.

- The sample solution is then aspirated into the appropriate flame for each metal as indicated in the Table. The analytical wavelength is also listed in the Table. The other operating parameters are set according to the instrument manufacturer's conditions for each metal being determined. The absorbance of each sample is recorded. When very low metal concentrations are found in the sample, scale expansion can be used to increase instrument response.

Calibration and Standards --

From each of the 1000 $\mu\text{g}/\text{ml}$ stock metal standard solutions, prepare working standards to cover the range for each metal as indicated in the Table. All standard solutions are made 0.3 N in HCl and are stored in polyethylene bottles. The low concentration standards may deteriorate and should be remade each day.

When analyzing for any of the metals where interferences are known to occur, as is indicated in the Table, standards should be prepared according to the "Remedy" listed in the Table.

Aspirate the series of standards and record the percent absorption.

Prepare a calibration curve by plotting on linear graph paper the absorbance versus the concentration of each standard in $\mu\text{g}/\text{ml}$. It is advisable to run a set of standards both before and after a sample run to insure that conditions have not changed.

Calculations --

From the calibration curve, read the concentration ($\mu\text{g}/\text{ml}$) in the analysis sample.

Blank values, if any, are subtracted from each sample.

The concentration of the metal in the original sample is:

$$\mu\text{g metal/ml sample} = \mu\text{g/ml} \times \text{dilution factor}$$

where:

$$\mu\text{g/ml} = \text{metal concentration determined from the appropriate calibration curve (Section 10.1).}$$

Fluorides and Hydrogen Fluoride in Air

Principle of the Method --

Atmospheric samples are taken using midget impingers containint 10 ml of 0.1M NaOH.

Samples are diluted 1:1 with Total Ionic Strength Activity Buffer (TISAB).

The diluted samples are analyzed using the fluoride ion specific electrode.

Range and Sensitivity --

The range and sensitivity have not been established at this time. The recommended range of the method is 0.009-95 mg/m³ air.

Interferences --

Hydroxide ion is the only significant electrode interference; however, addition of the TISAB eliminates this problem. Very large amounts of complexing metals such as aluminum may result in low readings even in the presence of TISAB.

Precision and Accuracy --

The accuracy and precision of this method have not been completely determined at this time. No collaborative tests have been performed on this method.

Advantages and Disadvantages of the Method --

Advantages over previous methods include simplicity, accuracy, speed, specificity and elimination of distillation, diffusion and ashing of the samples.

No significant disadvantages are known at present.

Apparatus --

Sampling Equipment - The sampling unit for the impinger collection method consists of the following components:

- A prefilter unit (if needed) which consists of the filter media and cassette filter holder.
- A midget impinger containing the absorbing solution or reagent.
- A pump suitable for delivering desired flow rates. The sampling pump is protected from splashover or water condensation by an adsorption tube loosely packed with a plug of glass wool and inserted between the exit arm of the impinger and the pump.
- An integrating volume meter such as a dry gas or wet test meter.
- Thermometer.
- Manometer.
- Stopwatch.

Orion Model 94-09 Fluoride Specific Ion Electrode, or equivalent.

Reference Electrode, Orion 90-01 single junction, or equivalent calomel or silver/silver chloride electrode.

Expanded Scale Millivolt-pH Meter, capable of measuring to within 0.5 millivolt.

Polyethylene Beakers, 50-ml capacity.

Laboratory Glassware.

Magnetic Stirrer and Stirring bars for 50-ml Beakers.

Reagents --

All chemicals must be ACS reagent grade or equivalent. Polyethylene beakers and bottles should be used for holding and storing all fluoride-containing solution.

Double Distilled Water.

Glacial Acetic Acid.

Absorbing Solution: 0.1M Sodium Hydroxide Solution. Dissolve 4 g sodium hydroxide pellets in 1 liter distilled water.

Sodium Hydroxide, 5M Solution, Dissolve 20 g sodium hydroxide pellets in sufficient distilled water to give 100 ml of solution.

Sodium Chloride.

Sodium Citrate.

Total Ionic Strength Activity Buffer (TISAB). Place 500 ml of double distilled water in a 1-liter beaker. Add 57 ml of glacial acetic acid, 58 g of sodium chloride and 0.30 g of sodium citrate. Stir to dissolve. Place beaker in a water bath (for cooling) and slowly add 5M sodium hydroxide until the pH is between 5.0 and 5.5. Cool to room temperature and pour into a 1-liter volumetric flask and add double distilled water to the mark.

Sodium Fluoride, for preparation of standards.

Standard Fluoride Solution

- Dissolve 4.2 g of sodium fluoride in double distilled water and dilute to 1 liter. This solution contains 10^{-1} M[F⁻] (1900 µgF⁻/ml). The 0.1M fluoride solution may also be purchased from Orion Research, Inc., Cambridge, Mass.
- Prepare 10^{-2} M[F⁻] by diluting 10 ml of 10^{-1} M[F⁻] to 100 ml with double distilled water (190 µgF⁻/ml).
- Prepare 10^{-3} M[F⁻] by diluting 10 ml of 10^{-2} M[F⁻] to 100 ml with double distilled water (19 µgF⁻/ml).
- Prepare 10^{-4} M[F⁻] by diluting 10 ml of 10^{-3} M[F⁻] to 100 ml with double distilled water (1.9 µgF⁻/ml).
- Prepare 10^{-5} M[F⁻] by diluting 10 ml of 10^{-4} M[F⁻] to 100 ml with double distilled water (0.19 µgF⁻/ml).

Procedure --

Cleaning of Equipment. All glassware and plastic ware are washed in detergent solution, rinsed in tap water, and then rinsed with double distilled water.

Collection and Shipping of Samples:

- Pour 10 ml of the absorbing solution (section 7) into the midget impinger, using a graduated cylinder to measure the volume.
- Connect the impinger (via the adsorption tube) to the vacuum pump and the prefilter assembly (if needed) with a short piece of flexible tubing. The minimum amount of tubing necessary to make the joint between the prefilter and impinger should be used. The air being sampled should not be passed through any other tubing or other equipment before entering the impinger.

- Turn on pump to begin sample collection. Care should be taken to measure the flow rate, time and/or volume as accurately as possible. The sample should be taken at a flow rate of 2.5 lpm. A sample size of not more than 200 liters and no less than 10 liters should be collected. The minimum volume of air sampled will allow the measurement at least 1/10 times the TLV, 0.2 mg/m^3 (760 mm Hg, 25°C).
- After sampling, the impinger stem can be removed and cleaned. Tap the stem gently against the inside wall of the impinger bottle to recover as much of the sampling solution as possible. Wash the stem with a small amount (1-2 m) of unused absorbing solution and add the wash to the impinger. Then the impinger is sealed with a hard, non-reactive stopper (preferably Teflon). Do not seal with rubber. The stoppers on the impingers should be tightly sealed to prevent leakage during shipping. If it is preferred to ship the impingers with the stems in, the outlets of the stem should be sealed with Parafilm or other non-rubber covers, and the ground glass joints should be sealed (i.e., taped) to secure the top tightly.
- Care should be taken to minimize spillage or loss by evaporation at all times. Refrigerate samples if analysis cannot be done within the day.
- Whenever possible, hand delivery of the samples is recommended. Otherwise, special impinger shipping cases designed by NIOSH should be used to ship the samples.
- A "blank" impinger should be handled as the other samples (fill, seal and transport) except that no air is sampled through this impinger.
- Where a prefilter has been used, the filter cassettes are capped and placed in an appropriate cassette shipping container. One filter disc should be handled as the other samples (seal and transport) except that no air is sampled through, and this is labeled as a blank.

Analysis of Samples:

- The sample is transferred from the impinger to a 50-cc plastic beaker; an equal volume of TISAB is added and the solution is stirred.
- The fluoride ion electrode and the reference electrode are lowered into the stirred solution and the resulting millivolt reading recorded (to the nearest 0.5 millivolt) after it has stabilized (drift less than 0.5 millivolt per minute).

Calibration and Standards --

Prepare a series of fluoride standard solutions by diluting equal volumes of each fluoride standard (7.9) and TISAB in a clear polyethylene beaker. Insert the fluoride ion electrode and the reference electrode into each of the stirred calibration solutions starting with the most dilute solution and record the resulting millivolt reading to the nearest 0.5 millivolt. Plot the millivolt readings vs the fluoride ion concentration of the standard of semi-log paper. The fluoride ion concentration in $\mu\text{g}/\text{ml}$ is plotted on the log axis. The calibration points should be repeated twice daily.

Calculations --

The concentration ($\mu\text{g}/\text{ml}$) of fluoride in the sample solution is obtained from the calibration curve.

Total $\mu\text{g F}^-$ in the sample = sample concentration ($\mu\text{g}/\text{ml}$) x sample solution volume (ml).

The total μgF^- is divided by the volume in liters, of air sampled to obtain concentration in $\mu\text{gF}^-/\text{liter}$ or $\text{mg}^3\text{F}^-/\text{ml}$.

$$\text{mgF}^-/\text{m}^3 = \mu\text{gF}^-/\text{liter}$$

$$\text{mgF}^-/\text{m}^3 = \frac{\text{total } \mu\text{gF}^-}{V_s} \quad (\text{Section 10.4})$$

Convert the volume of air sampled to standard conditions of 25°C and 760 mm Hg.

$$= V \times \frac{P}{760} \times \frac{298}{T + 273}$$

where:

V_s = volume of air in liters at 25°C and 760 mm Hg

V = volume of air in liters as measured

P = barometric pressure in mm Hg

T = temperature of air in degree centigrade

The concentration can also be expressed in ppm, defined as $\mu\ell$ of component per liter of air.

$$\begin{aligned} \text{ppmF}^- &= \mu\ell\text{F}^-/V_s = \frac{24.45}{\text{MW}} \times \mu\text{gF}^-/V_s \\ &= 1.29 \text{ gF}^-V_s \end{aligned}$$

Where:

24.45 = molar volume at 25°C and 760 mm Hg

MW = 19, weight of fluoride ion,

(i.e., $19 \mu\text{gF}^- = 24.45 \mu\ell$ at 25°C, 760 mm Hg)

To calculate the concentration of hydrogen fluoride as $\text{mg HF}/\text{m}^3$ or ppm HF, simply multiply the corresponding concentration of F^- (from 10.3 or 10.4) by 1.05.

APPENDIX B

METHODS FOR CHEMICAL ANALYSIS

This Appendix presents the methods and techniques used for chemical characterization and analysis of the smelter sampling data.

ELEMENTAL METHODS

Quantitative analysis consists of two major steps:

- sample dissolution, and
- chemical analysis.

Sample dissolution techniques include acid reflux digestion, perchloric acid digestion and lithium borate fusion.

The techniques used for the quantitative determinations of trace elements in samples collected from the copper smelter are based are:

- atomic absorption,
- ion selective electrode, and
- fluorometry.

Figures 1 through 3 summarize the dissolution and analytical procedures used for the trace element determinations. The various dissolution and analytical procedures are described in the remainder of this section.

Sample Preparation --

The dissolution techniques applied to the samples are:

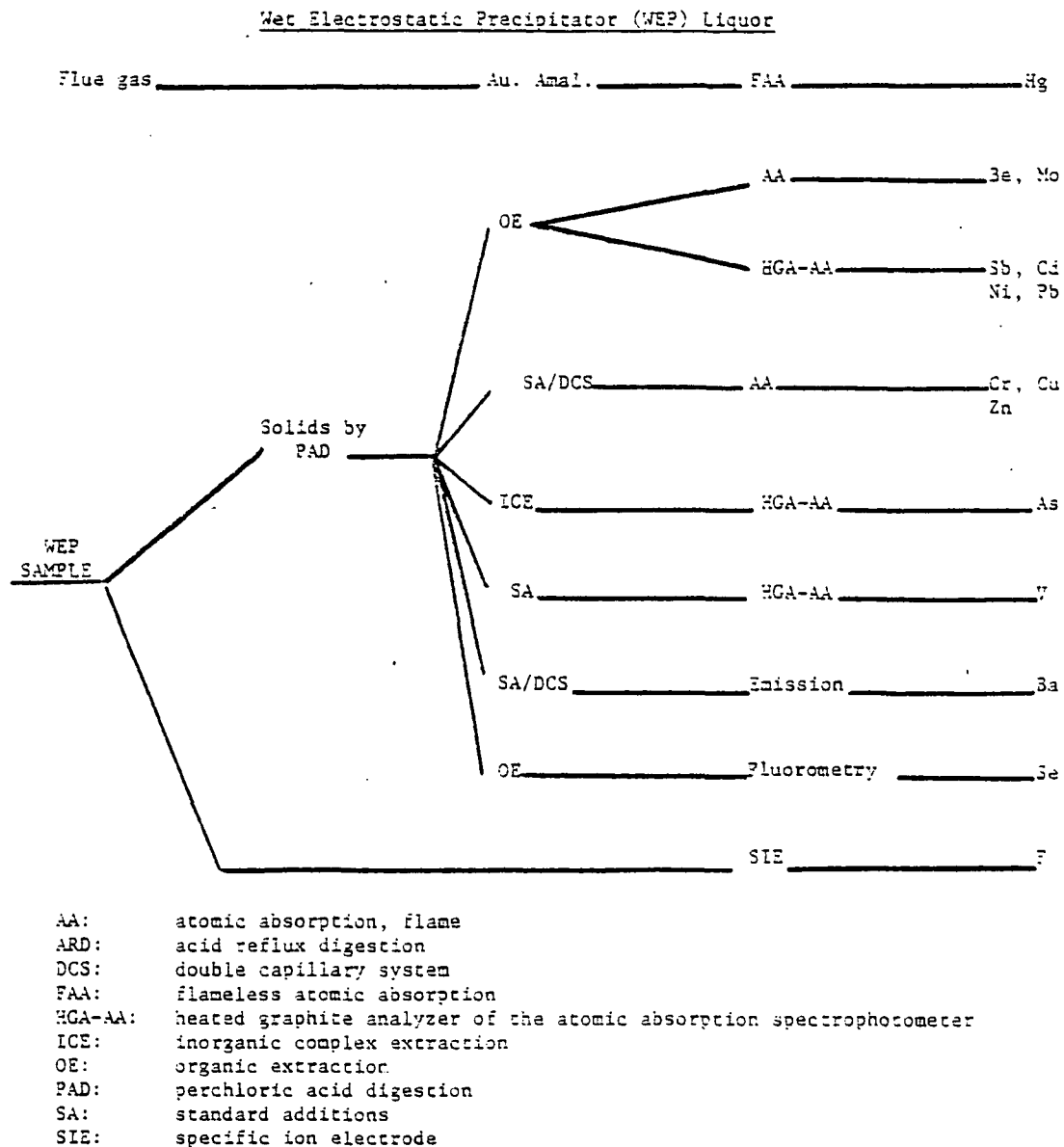


Figure B-1. Dissolution and analytical scheme of a WEP slurry.

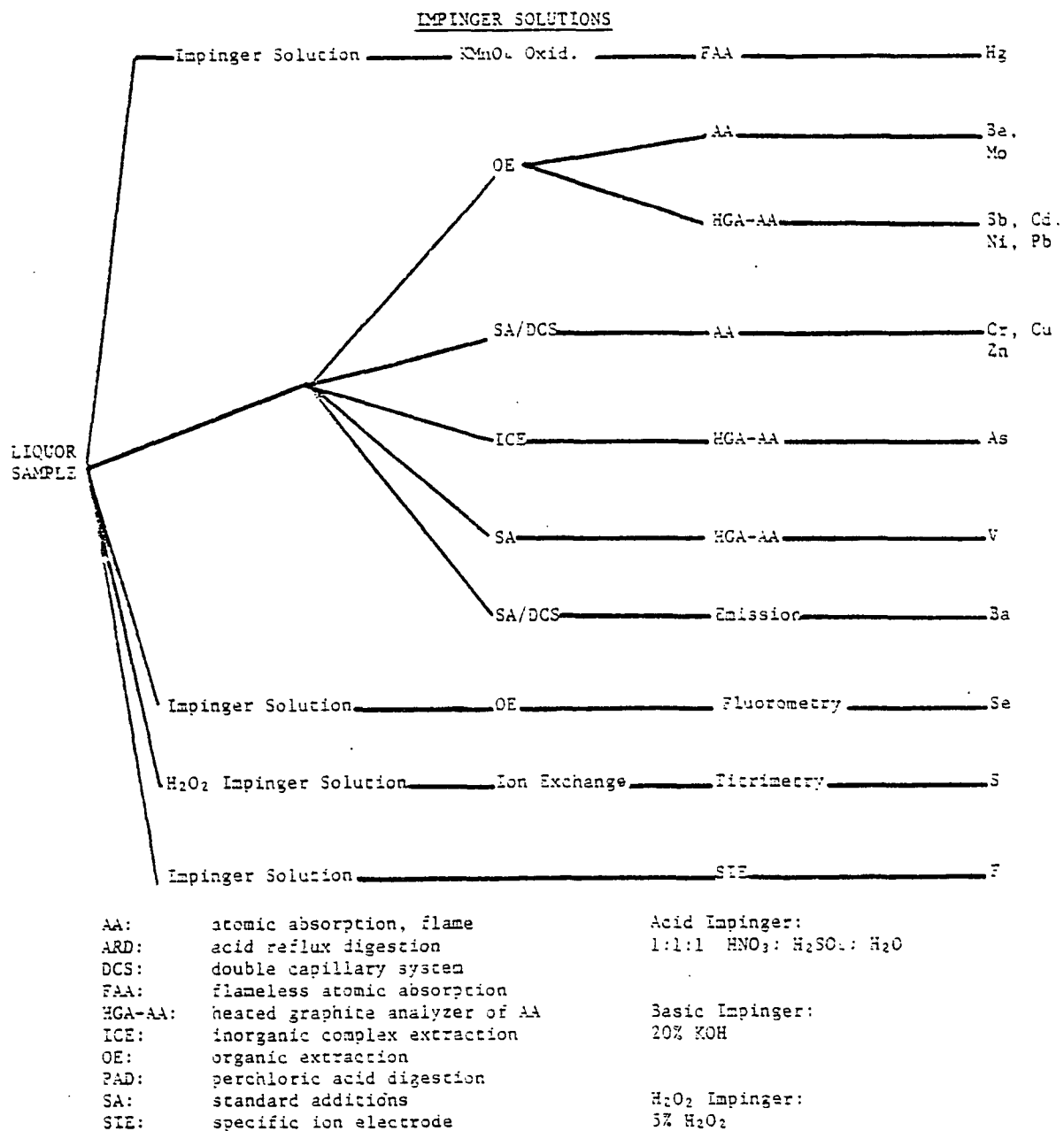
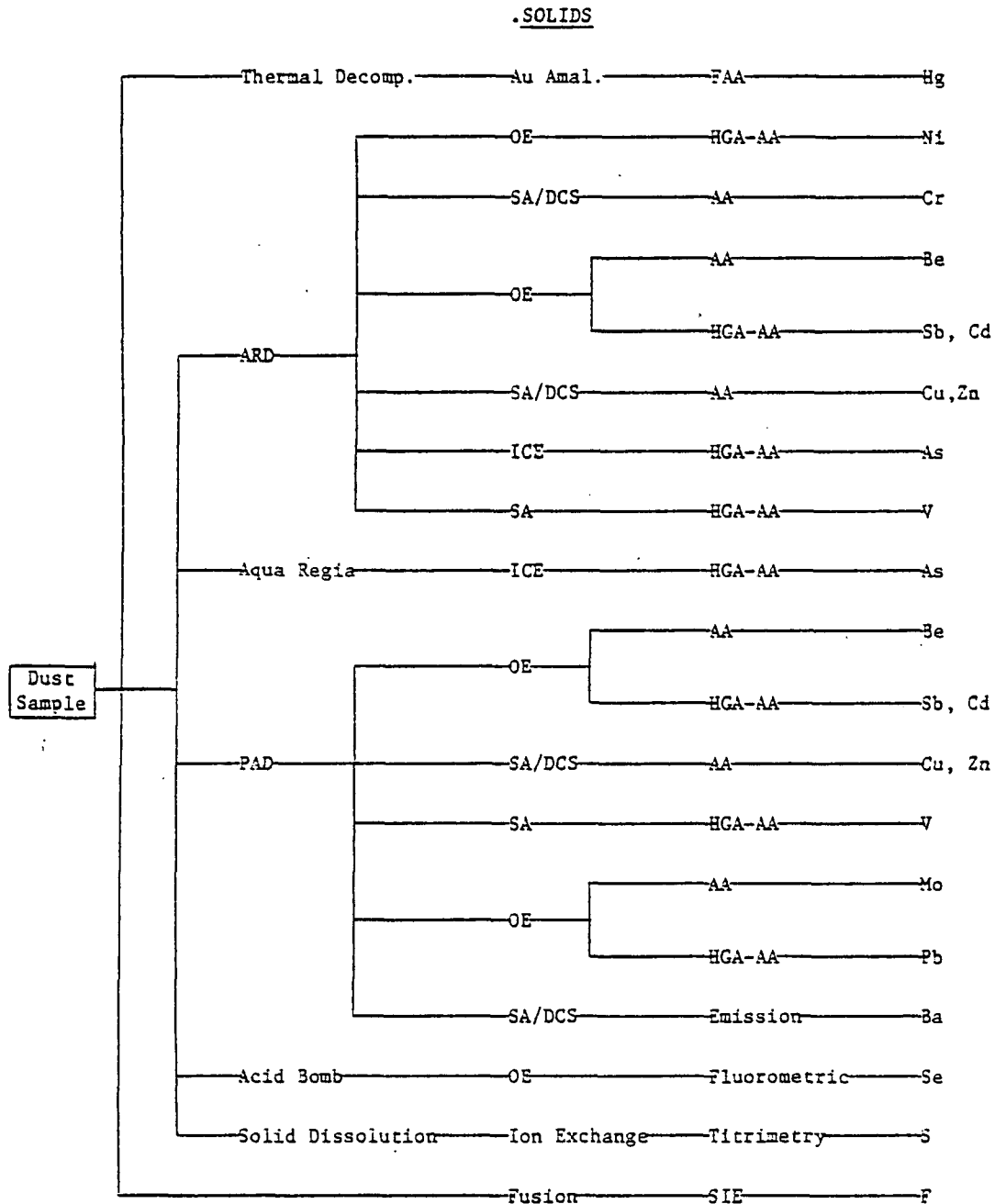


Figure B-2. Analytical scheme of an impinger liquor sample.



AA: atomic absorption, flame
 ARD: acid reflux digestion
 DCS: double capillary system
 HGA-AA: heated graphite analyzer of the atomic absorption spectrophotometer
 HGA: heated graphite analyzer
 ICE: inorganic complex extraction
 OE: organic extraction
 PAD: perchloric acid digestion
 SA: standard additions
 SIE: specific ion electrode

Figure B-3. Dissolution and analytical scheme of solid samples.

- Acid Reflux Digestion - Solid samples are dissolved by refluxing with a mixture of nitric acid, sulfuric acid, and perchloric acid. Silicates are not attacked by this procedure.
- Perchloric Acid Digestion - The first step is a treatment using nitric and hydrofluoric acid. Perchloric acid is added for final oxidation of the sample. A small amount of hydrochloric is added to insure complete dissolution.
- Lithium Borate Fusion - A small amount of sample is fused with lithium borate. The cooled melt is dissolved in hydrochloric acid and hot water. Most elements present in higher concentrations are analyzed from this digestion. Elements present in trace concentrations are, in general, determined from solutions derived from the acid reflux or the perchloric acid digestion.

ANALYTICAL PROCEDURES

The analytical procedures used were originally developed for the determination of trace elements in coal, coal ashes, sludges and plant and animal tissues. The drastic change in the matrix observed in samples collected at a copper smelter necessitate screening of the procedures for accuracy and reliability. This task is accomplished using the method of standard addition and interference studies.

Gas samples are drawn through a plug of gold wool. Deamalgamation is accomplished by heating the gold wool. The released mercury is purged through the absorption cell of an atomic absorption spectrophotometer (AA).

Solid samples are analyzed for mercury by weighing a sample into a platinum boat and heating the sample slowly in a chamber. The off-gases containing elemental mercury are purged through a gold plug. Deamalgamation and determination by AA follow the same procedure as described above.

Liquid samples are acidified and then the mercury is oxidized with potassium permanganate. Hydroxylamine hydrochlorid and stannous chloride are used to reduce the mercury to the metallic state. Air is bubbled through the solution. The mercury entrained in air is passed through the absorption cell of an AA.

Lead and Cadmium - Lead and cadmium are extracted simultaneously with MIBK from the WEP liquor, impinger solutions, and the perchloric acid digestion of the hopper dust. The double complexing agent of ammonium pyrrolidine dithiocarbamate and diethylammonium diethyldithiocarbamate chelates lead and cadmium. The extracted sample is injected into the graphite furnace attachment to the AA.

Antimony - Antimony is extracted as the iodide into a mixture of tributylphosphate and MIBK. Extraction is performed on the WEP liquor, impinger solutions are boiled to decompose the H_2O_2 . The extracted solution is injected into a graphite tube of the AA which has been coated with ammonium molybdate.

Arsenic - The WEP liquor, impinger solutions and the perchloric acid digestion of the solids are used for the arsenic determination. Arsenic is complexed, in acidic medium, as the heteropoly acid of molybdenum. The aqueous complex is injected into the heated graphite analyzer (HGA) attachment to the atomic absorption spectrophotometer. A charring temperature of $1200^{\circ}C$ is used to remove any interferences in the HGA.

Fluorine - Solid samples are fused with sodium carbonate and the melt dissolved in deionized water. WEP and impinger solutions are run direct. Final determination is done with a fluoride specific ion electrode utilizing the method of known additions to remove the effects of any interfering ions.

Sulfur - Solid samples are dissolved in a solution of hydrochloric acid and hydrogen peroxide. Solutions from the solid dissolution and the H_2O_2

impingers are boiled to remove excess peroxide. The solutions are then eluted through a cation exchange resin to convert the sulfate to sulfuric acid. Volatile acids are removed by heating and the sulfuric acid is titrated with a standard base.