38.3

REPORT OF INDUSTRIAL HYGIENE SURVEYS
CONDUCTED DURING FISCAL YEAR 1973 IN
SIX ALUMINUM PLANTS
LOCATED IN THE NORTHWESTERN UNITED STATES

The National Institute for Occupational Safety & Health
Western Area Occupational Health Laboratory
Salt Lake City, Utah 84108

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Worker exposures to coal-tar-pitch (65996932) volatiles and other hazards were surveyed at six aluminum (7429905) factories in the northwestern United States during 1973. Air samples were analyzed for benzene (71432) soluble materials, total dust, carbon-monoxide (630080), sulfur-dioxide (7446095), hydrogen-fluoride (7664393), and total fluoride (7782414). Urine samples from potline workers were analyzed for fluoride. Heat stress and noise measurements also were taken. Use of respirators and engineering controls also was surveyed. Significant exposures to benzene soluble materials were found for anode workers, rammers, and paste area workers. Excessive exposures to carbon-monoxide, hydrogen-fluoride, and total fluoride also were identified at certain work areas. Exposures to all other agents were within acceptable limits. Respirator use and care was inconsistent. Local and roof ventilation systems were used. The author recommends an epidemiologic study of aluminum workers. Better ventilation systems, work practices, and respirator use programs also are suggested.

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Reference Information:

Companies Surveyed:

Aluminum Company of America (ALCOA)
Wenatchee, Washington

Anaconda Aluminum
Columbia Falls, Montana

International Aluminum Company (INTALCO)
Ferndale, Washington

Kaiser Aluminum Company
Tacoma, Washington

Martin-Marietta Company
The Dalles, Oregon

Reynolds Metals Company
Longview, Washington

NIOSH Participants (WAOHL)

Lee B. Larsen, Supervisory Industrial Hygienist
Raymond O. Rivera, Industrial Hygienist
William L. Wagner, Industrial Hygiene Engineer
Bert T. Wisner, Industrial Hygienist

NIOSH Participants (Regional Offices)

Arvin Apol, Regional Industrial Hygienist, Region X
Bobby Gunter, Regional Industrial Hygienist, Region VIII

Data Compiled by:

Raymond O. Rivera
Bert T. Wisner

Report Written by:

Lee B. Larsen

I. INTRODUCTION

A. National Institute for Occupational Safety and Health

The National Institute for Occupational Safety and Health (NIOSH) which was created by Act of Congress in the Occupational Safety and Health Act of 1970 is responsible for conducting occupational safety and health research. The Institute conducts a wide range of research on effects of exposure to toxic substances and harmful physical agents and to combinations of exposures.

Obviously priorities must be established to determine where research may be conducted most effectively. One of the important functions of NIOSH is to conduct research programs directed toward the development or modification of criteria which are used for recommending health or safety standards for promulgation by the U.S. Department of Labor. Research priorities are based upon occupational health and safety risks which are determined by a number of factors including the number of workers exposed to a job hazard, that hazard's potential for causing injury or disease and the number of workers showing effects. Priority lists of needs are developed to guide the research activities of NIOSH.

B. Health Hazards in Coal Tar Industries

A ten-fold risk of lung cancer has been reported for men employed five or more years at full-time top-side coke oven jobs. Dr. Lloyd[1] reports that a review of the literature on cancer mortality of men employed in the coal tar industries show that all of these occupations evidence excess cancer at one or more sites.

C. Use of Coal Tar Pitch in the Aluminum Industry

In the production of aluminum, coal tar pitch is used to prepare anodes and cathodes (a description of the production of aluminum is included in Appendix A). In the form of a carbon paste coal tar pitch is also used to fill between cracks and edges of carbon blocks which are set in place to form the cathode of a cell (often called a "pot"). Once the spaces between the blocks have been filled, a layer of paste is put over the blocks and tamped in place.

Coal tar pitch is also used in the preparation of anodes. The anodes are of two types - pre-baked and Soderberg. As the name implies pre-baked anodes are prepared and baked before use in the cell. In the Soderberg type cell the anode material is added to the top of the cell as a paste or as solid chunks of material called briquettes.

Exposure to coal tar pitch volatiles occurs in the preparation of the carbon paste materials and briquettes, and in the potrooms where fresh anode material is added as the anode is consumed. In the potrooms the greatest exposure appears to be associated with the pin pulling (stud pulling) operation.

D. Purpose of the Industrial Hygiene Survey of Six Northwest Aluminum Plants

As previously stated men employed in the coal tar industries allegedly show evidence of excess cancer at one or more sites. The present survey was therefore conducted to determine exposure levels to coal tar pitch volatiles and other potential health hazards for persons employed in the various types of aluminum plants. The survey was considered a preliminary survey to provide information to the Division of Field Studies and Clinical Investigations to aid in setting priorities for future epidemiological investigations, and to enable NIOSH to evaluate existing guidelines and standards for the air contaminants found in aluminum reduction plants.

II. SURVEY METHODOLOGY

Appendix B lists the aluminum companies in the United States. Many of these are located in the Northwest and from these, six plants were selected for survey. Included were two pre-baked type plants, two horizontal Soderberg, and two vertical Soderberg. Only those areas of the aluminum plant where exposure to coal tar pitch volatiles might occur were surveyed.

This survey was conducted primarily to determine exposure levels of workmen to coal tar pitch volatiles. However, other hazardous chemical or physical agents found in aluminum plants may have a synergistic* action where they occur in the presence of coal tar pitch volatiles. Exposures may be significant. For example Largent[8] states that "the largest single group of industrial workmen potentially exposed to fluorides in the course of their employment are the potmen in aluminum reduction plants." Exposure occurs from inhalation or ingestion of the fluoride materials used in the cell (cryolite, fluorspar, aluminum fluoride) and from inhalation of hydrogen fluoride which may be emitted from the cell.

The following air contaminants were therefore investigated: "benzene soluble material", total dust, carbon monoxide, sulfur dioxide, hydrogen fluoride, and total fluoride. Urinary fluoride was also determined for potline workers at each plant.

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*Synergism-Cooperative action of discrete agencies such that the total effect is greater than the sum of the two effects taken independently.

A complete heat stress evaluation was made at one plant, and measurements were taken at another plant to evaluate equipment developed for NIOSH for determining heat stress. Since most of the industrial hygiene surveys were conducted during the cooler seasons of the year, heat stress studies were not conducted in all plants. The reader is referred to the Physiology and Ergonomics Branch at Cincinnati, Ohio for what information was obtained from the above mentioned surveys.

Asbestos is used in the aluminum industry for thermal insulation. Usage varies from company to company. No environmental samples were taken since the use of asbestos is intermittent. If an epidemiological study is conducted, exposure to asbestos will need to be considered.

Noise measurements were made where considered appropriate.

The present preliminary survey should be viewed as part of a broader study of the potential health hazards of various air contaminants or other health hazards in industry. As shown in Appendix C the aluminum industry is only one of many businesses which use coal tar pitch. It was not the intent of this survey to conduct an extensive survey of the hazards in aluminum plants, but rather to define areas needing further investigation.

III. DISCUSSION OF EXISTING STANDARDS, SAMPLING METHODS USED FOR THIS SURVEY, AND ENVIRONMENTAL DATA

This report is prepared for distribution to two groups - NIOSH and the aluminum companies participating in the survey. General information is included in the main body of the report for distribution to both NIOSH and Industry. Tables previously sent to each plant pertaining to the survey at the plant are included in the Appendix for use of NIOSH personnel.

Each chemical or physical hazard will now be discussed under the appropriate heading.

A. Coal Tar Pitch Volatiles

1. Criteria and Standards

"Polycyclic organic matter can be formed in any combustion process involving fossil fuels or, more generally, compounds containing carbon and hydrogen."[2]

"Coal tar pitch volatiles contain a large quantity of lower molecular weight polycyclic hydrocarbons.[3,4,5] As these hydrocarbons (naphthalene, fluorene, anthracene, acridine, phenanthrene) sublime into the air, there is an increase of benzo(a)pyrene (BaP or 3,4-benzpyrene) and other higher weight polycyclic hydrocarbons in the tar and in the fumes. Polycyclic hydrocarbons known to be carcinogenic are of this large molecular type."[6]

There is no simple analytical procedure available for determining individual polycyclic hydrocarbons, therefore the weight of the benzene soluble fraction of coal tar pitch volatiles is used as an index of the high-molecular weight polycyclic hydrocarbons in the work environment.

"Since no 'safe' limit of exposure can be established for carcinogens and because of instability in the composition of volatiles from coal tar pitch a threshold limit value of 0.2 milligrams of benzene-soluble components of coal tar pitch volatiles per cubic meter of air is recommended. A limit of 0.2 mg/M^3 of the total components present should minimize exposure to these carcinogens."[6]

The U.S. Department of Labor has adopted the Threshold Limit Value of 0.2 mg/M^3. An OSHA Program Directive issued June 2, 1972 states that "any 8-hour time weighted average above 0.2 mg/M^3 (benzene soluble fraction) for an identified worker not wearing proper respiratory protective equipment is considered a serious violation (serious hazard)." It also states that "the terms 'de minimis' and 'nonserious' do not apply to coal tar pitch volatiles exposures above the 8-hour Threshold Limit Value since no 'safe' limit of exposure for all workers can be established for carcinogens."

2. Sampling and Analytical Procedures

a. Sampling

Personal and Hi Volume area samples were taken in the potrooms and the carbon plants. (Hi volume samples were not collected in some plants due to company policy restricting use of plug-in type devices) For personal sampling, battery powered pumps were attached to the belt of each worker. Rubber tubing was run from the pump to a sampling cassette clipped to the workers shirt near his breathing zone. Air was drawn through preweighed 37 mm diameter silver membrane filters having a pore size of 0.8μ. In two plants the silver membrane filter was preceded by a Gelman Type A glass fiber filter. It was noted that if a tight seal were obtained to keep material from going around the edge of the silver membrane filter onto the back-up pad comparable results could be obtained by using silver membrane filters only. The silver membrane filters were extracted with benzene before use in the field. Sampling was conducted with an open face filter since this procedure had been used in the coke oven study and it was thought desirable to be consistent in sampling procedures if data from the two types of industries were to be compared.

The sampling pumps were monitored periodically to verify that consistent flows of two liters per minute were being maintained. The worker wore the sampling equipment throughout the workday where possible to better arrive at an 8-hour time weighted average exposure.

(1) Area Samples versus Personal Samples

Hi volume area samples were generally lower than personal samples. An area sample tells very little about a workers exposure in an aluminum plant. Exposure occurs at the job site for example, when a door which may be part of the ventilation system is opened to permit a worker to perform his job.

(2) Respirable versus Non-respirable Samples

One company indicated they thought the TLV should be based on the respirable portion of an air sample. Some authors have stated that "for assessment of the potential hazards of airborne carcinogens to public health, only the respirable portion of the suspended particulate matter is useful. Samples in the required particle size range should be collected by similar methods of sampling and analysis".[2]*

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*The reference was taken from material which discusses atmospheric pollutants, and refers to suspended particulate matter, the author may not have intended to apply this statement to in-plant environments.

Collecting samples which give the respirable portion of a workers exposure in an aluminum plant may eliminate extraneous material. However, non-respirable material may also be toxic. Present threshold limit values for benzene soluble material are based on gross airborne samples.

A comparison of gross airborne versus respirable samples is presented in Table 1. Few respirable samples were collected and these were not collected simultaneously with non-respirable samples. Also, the benzene soluble concentrations for the respirable samples were determined on very small quantities of material. Therefore, the few samples may be indicative of differences in concentration, but more extensive sampling would be required to reach valid conclusions.

The engineering staff of the Division of Field Studies and Clinical Investigations of NIOSH, Cincinnati, Ohio optically determined the size distribution of dust particles in a potroom atmosphere in an Eastern pre-baked type aluminum plant. The size distribution results of the airborne dust and a bulk sample of alumina by phase-contrast microscopy are shown in Table II.

The above study concluded "These data indicate that the diameter of almost all of the airborne particles were below 10 microns. Generally dust which is greater than 10 microns in diameter is considered to be too large to be respirable. The larger particles which are on the airborne samples appear to be carbon. The majority of the small particles were probably alumina. Apparently then, the mass of the total airborne dust is mostly influenced by the few large carbon particles, but the vast majority of the small alumina particles were potentially respirable. The size distribution of the bulk sample of alumina is completely different. Here most particles ranged from 75-125u. The relatively large particles of the bulk alumina would not stay airborne as long, leaving the dust of smaller diameter particles to most heavily influence the size distribution of the airborne material."

For ten paired personal samples taken in the potroom, during the study mentioned above the weight of the respirable fraction ranged from 7 to 28 percent of the corresponding total airborne dust determination. The average value was approximately 19 percent.

b. Analyses (Refer to Appendix D)

In the benzene soluble determination the particulate material on the pre-weighed filters is extracted by benzene using the continuous cycling process of a Soxhlet extractor. After extraction, the solution is filtered through the original filters and the weight loss of the filters is considered to be the amount of benzene soluble material.

The benzene soluble analysis is based on a method requiring weight determinations. Our experience indicates that the practical accuracy of the weight determination is to the nearest 0.1 milligram. To overcome this source of error (especially at concentrations near the 0.2 mg/M^3 TLV) several samples from the same job type were combined to give greater accuracy.

The chief disadvantage of the benzene soluble method is that it is not specific for the polynuclear aromatic compounds that are potentially carcinogenic. The benzene soluble fraction merely indicates the concentration of organic material present which is soluble in benzene.

On March 29, 1973, seven members of the health committee of the OSH and Loss Prevention Policy Committee of the Aluminum Association, seven chemists from member aluminum companies, three guest experts in the field of PNA analysis, and 12 NIOSH personnel met in Cincinnati, Ohio to discuss the analytical methods available for determining polynuclear aromatic hydrocarbons (PNA's). Industry representatives stated the need for a more accurate and meaningful method for the analysis of coal tar pitch volatiles. Industry expressed concern that benzene soluble material was found in potrooms of prebaked type aluminum plants where industry expected none to occur.* Industry stated that an acceptable analytical method should quantify certain related components as a group.

Samples have been obtained from coke ovens and from two aluminum plants for submission to a private research laboratory for developing methods for coal tar pitch volatiles.

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*Two potential sources of coal tar pitch volatiles in these plants are from the coal tar pitch used in the cathodes of the cells and from exhaust gases blown back into the potrooms. Also no attempt was made to identify those workers who smoked during the sampling period which may have contributed to the benzene soluble concentrations found.

It is thought the values for benzene soluble material included in this report are useful for classifying exposures to various types of job classifications in the aluminum plants surveyed. Samples were analyzed by the Western Area Occupational Health Laboratory at Salt Lake City, Utah. This laboratory has not experienced the difficulty of the total particulate values being less than the benzene soluble concentrations reported by some laboratories, perhaps because of the low humidity in Salt Lake City. The chemist who ran most of the samples states he does not feel that the analytical method is in error by more than a factor of two for those values near the TLV (0.2 mg/M^3). What these values mean is a moot question at the present time.

c. Environmental Data

It is difficult to compare exposures for various job categories for different aluminum plants. Even where similar type processes are used there are differences in work procedures even for the same type of job. Equipment used to perform an operation also varies from one plant to another. For example, crust breaking is performed in all plants, but was done differently in each plant.

A summary of benzene soluble values is presented in Table III. It will be noted that anode workers receive the highest exposures, especially in vertical Soderberg type plants.

Other workers in the potlines in general receive less exposure (generally less than 0.5 mg/M^3). Rammers and paste plant workers work in areas where exposure to volatile material is likely to occur.

Exposures for each job classification in each plant should be evaluated separately for that plant.

B. Total Dust (Nuisance Dust)

1. Criteria and Standards

"In contrast to fibrogenic dusts which cause scar tissue to be formed in lungs when inhaled in excessive amounts, so-called 'nuisance' dusts have a long history of little adverse effect on lungs and do not produce significant organic disease or toxic effect when exposures are kept under reasonable control. The nuisance aerosols have also been called biologically 'inert', but the latter term is inappropriate to the extent that there is no particulate which does not evoke <u>some</u> cellular response in the lung when inhaled in sufficient amounts. However, the lung-tissue reaction caused by inhalation of nuisance aerosols have the following characteristics:

1. The architecture of the air spaces remains intact.
2. Collagen (scar tissue) is not formed to a significant extent.
3. The tissue reaction is potentially reversible.

"Excessive concentrations of nuisance aerosols in the workroom air may seriously reduce visibility, may cause unpleasant deposits in the eyes, ears and nasal passages, or cause injury to the skin or mucous membranes by chemical or mechanical action per se or by the rigorous skin cleansing procedures necessary for their removal.

"A workroom level of 10 mg/M^3 of nuisance aerosol, although 10 to 100 times the level in outdoor community air, should result in appreciable improvement of working conditions in plants where the old A.C.G.I.H. limit of 15 mg/M^3 formerly prevailed.

"Total particulates as described in this A.C.G.I.H. limit includes the air-suspended particles greater than respirable diameter. If particles of respirable diameter only are present or are collected, a limit of 5 mg/M^3 must be used."[6]

The OSHA standards are 15 mg/M^3 for total dust, and 5 mg/M^3 for respirable dust.[17]

A nuisance dust value assumes the dust is biologically inert. This may not be true for the carbonaceous materials used in the carbon plant and potrooms. No standard exists for coke dust or for some of the materials present in potrooms.

2. Sampling and Analytical Procedures

Samples were collected on silver membrane filters as part of the procedure for sampling for benzene soluble material. A few respirable samples were collected with Dorr Oliver 10mm cyclones operated at 1.7 liters per minute. Nuisance dust determinations require no analytical procedures, but are based strictly on a weight and air volume determination.

Comparative gross airborne dust concentrations for the three types of plants are reported in Table IV. Comparison of respirable and non-respirable samples are reported in Table I.

C. Carbon Monoxide

1. Criteria and Standards

Most of the carbon monoxide in the potroom is a result of the oxygen released during the electrolytic reaction combining with the carbon of the anode. The present OSHA standard for carbon monoxide is 50 ppm, determined as a time weighted average (TWA) exposure for an 8-hour work-day. A criteria document has been published by NIOSH,[7] however, which recommends that the U.S. Department of Labor lower this standard to 35ppm.

2. Sampling and Analytical Procedures

A Drager hand pump was used to draw samples of air through direct reading indicator tubes. A color change is produced in the packing of the tube which is read directly from calibrated markings on the tube. The length of stain which is read from the graduated tube is considered an indication of the concentration of the gas.

3. Environmental Data

Measurements for carbon monoxide were below existing standards or proposed standards for carbon monoxide. The few measurements taken that were above 35 ppm were in areas which had not been provided local exhaust ventilation.

D. Sulfur Dioxide

1. Criteria and Standards

The TLV and present OSHA standard for sulfur dioxide is 5 ppm which was set "to prevent respiratory tract irritation in most workers and cause only minimal effects in those workers who are sensitive to irritant gases".[6]

2. Sampling and Analytical Procedures

Drager tubes were used for determining SO_2 exposures as described under the carbon monoxide discussion.

3. Environmental Data

Sulfur dioxide concentrations were below 5 ppm in all plants.

E. Fluorides

1. Airborne Fluoride

a. Criteria and Standards

(1) Hydrogen Fluoride as HF

"Prolonged inhalation of HF in high concentrations would presumably lead to fluorosis, which has been more often observed as a result of the inhalation or ingestion of fluoride salts (q.v.). In view of the greater irritating properties of HF, a slightly lower limit is recommended than for most other inorganic fluorides."[6] The Threshold Limit Value for Hydrogen Fluoride is 3 ppm (approximately 2 mg/M^3). The U.S. Department of Labor has adopted this TLV as a standard for Hydrogen Fluoride.

(2) Fluoride as F

"The toxic effects of fluoride have been placed in three groups by Rohollm: (a) acute systemic intoxication (usually by ingestion); (b) local corrosion of the mucous membranes and skin; and (c) chronic bone changes, ranging from mottling of tooth enamel to crippling skeletal abnormalities."[6]

A Threshold Limit Value of 2.5 mg F/M^3 is sufficiently low to prevent irritative effects and to protect against disabling bone changes. The U.S. Department of Labor has adopted this TLV as a Standard for airborne fluoride.

b. Sampling and Analytical Procedures

Two methods were used to sample for HF and particulate fluoride. In the first surveys the particulates were collected on an 0.8μ vinyl metricel filter. This filter was followed by a midget impinger containing 0.1 N sodium hydroxide to absorb the gaseous fluorides. The second method used the same procedure for determining particulate matter, but the gaseous fluorides were collected on a back-up pad which had been dipped in 6% sodium carbonate solution and air dried before use in the field.

Use of the impregnated filter is not only more convenient to handle for general area sampling but even more important this method facilitates personal sampling.

The filters were analyzed for fluorides by a specific ion electrode method.

c. Environmental Data

Fluoride, both total and hydrogen fluoride, were controlled where local exhaust ventilation had been provided for the individual pots. In pre-baked plant potlines not provided such ventilation about one-third of the analyzed samples exceeded the total fluoride standard of 2.5 mg/M^3 and about one-fourth exceeded the 2.0 mg/M^3 standard for hydrogen fluoride.

2. Urinary Fluoride

a. Biological Threshold Limit Values

Elevation in the level of urinary excretion of fluoride in man is significant because of its relationship to the deposition of fluoride in the bones of the body. The exact amount of fluoride deposited at any particular point in time is not known, but the maximum deposition in the tissues is about 50 per cent, the rest being excreted. It is highly probable that the higher the concentration of fluoride in the urine, the greater the rate of deposition of fluoride in the osseous tissues. Much has been made of the fact that persons drinking water at the level 6 p.p.m. (the concentration present in the communal water supply at Lake Preston, South Dakota) were found to be excreting fluoride in the urine at the level of 6 to 7 mg. per liter. None of the residents there has been shown to have any clear-cut change in osseous radiopacity. A particular point has also been made of the fact that in Bartlett, Texas, the average concentration of fluoride in the drinking water was 8 p.p.m., and the average level of urinary fluoride excretion was 8 mg. per liter, and that a survey revealed changes in osseous radiopacity in 14 to 18 per cent of the persons examined. No other bone changes or ill effects could be attributed to the ingestion of fluoride (mottled enamel in Bartlett was of cosmetic significance only and had no adverse effects on the general health of the residents). Even if those earliest detectable evidences of increased radiopacity have no significance from the standpoint of health, it is highly important to know the level of urinary fluoride excretion at which, or above which, these first changes in osseous radiopacity may be discerned.[8]

Urinary fluoride excretion of 5-8 mg/day was considered safe by Princi[9] and Largent[8]. According to Hodge[10] 5 mg/liter would not result in osteriosclerosis. Derryberry, et al[11] found that 17 workers with increased bone densities had an average urinary fluoride level of 5.18 mg/liter. Agate's group[12] with urinary excretions of 3.6 to 9 mg/day, showed abnormal X-ray findings, but no disability.

Largent[8] has summarized some of the data from the literature pertaining to the relation between urinary fluoride and increased radiopacity in bone. He indicated there was no increase in radiopacity in subjects whose off-the-job urines contained 3.1 to 3.8 mg F/liter, but radiopacity was increased in subjects with higher urinary fluoride levels.

Finally, Irwin[13] has excellent evidence from industrial experience that osteosclerosis does not develop when urinary fluoride concentrations are maintained below 5 mg/liter. The experience of Derryberry, et al[11] with end-of-shift samples and of Rye[14] with pre-shift samples suggest 4 mg/liter and Elkins[15] considers values above 5 mg/liter in pre-shift urines as indicative of excessive exposure.

Largent states that "If fluoride exposures are controlled so well that no workman repeatedly excretes fluoride at a level as high as 8 mg. per liter, there is very little likelihood that any ill effects will result from exposure to fluorides, although a slight increase in osseous radiopacity might in rare instances develop after many years of occupational exposure. Under conditions in which urinary fluoride levels rarely or never exceed 4 mg. per liter, there is very little likelihood that even the slightest increases in osseous radiopacity will occur among workmen, and fluoride-induced disability and/or ill effects will certainly never occur."[8]

No biological threshold limit values for any substance has been adopted by the U.S. Department of Labor. All standards for toxic materials are based on airborne concentrations expressed as parts per million of air or milligrams per cubic meter of air.

The Biochemical Assay Committee of the American Industrial Hygiene Association in 1971 published a Biological Monitoring Guide for fluorides and concluded that "urinary fluoride concentrations not exceeding 5 mg/liter in before-shift spot samples taken after two days off work are not associated with osteosclerosis, and such changes are unlikely at urinary levels of 5 to 8 mg/liter."[16]

Studies need to be conducted to correlate air concentrations of fluoride with urinary fluoride levels.

b. Sampling and Analytical Procedures

In most plants urine samples were collected by the company during routine periodic monitoring of urinary fluoride levels. In two plants spot samples were collected by NIOSH industrial hygienists.

The samples were analyzed by the Western Area Occupational Health Laboratory in Salt Lake City, Utah.

Where fluoride concentrations above 8 mg/liter were determined another sample was obtained and analyzed, since the first sample may have been contaminated.

c. Biological Data

Some 699 fluoride analysis were conducted on the initial samples collected or submitted, and 52 samples or about 7 percent of the samples were found which exceeded 8 mg/liter. Resamples collected by the aluminum companies almost without exception were below 8 mg/liter. However, resamples have not been received from all companies. Table V-1 gives the number and percent of samples exceeding 8 mg/liter, and the mean and standard deviation for <8 mg/liter* for the initial urine samples submitted or collected Table V-2 describes how the samples were collected.

Since company monitoring procedures varied between companies (some collected samples after 6 days work, some pre and post shift samples, etc.) and because samples collected by NIOSH personnel were spot samples obtainable as most practical during the time period of the survey, one should consult the data and

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*Values above 8 mg/liter were discarded as possibly due to contamination. A mean and standard deviation was computed for the remaining values.

the conditions under which the samples were collected for any attempt to evaluate the data for each plant. The findings support the need for consistency in any sampling associated with an epidemiological study. The aluminum companies have conducted urinary fluoride sampling programs for a number of years. Such data would need to be evaluated in terms of the work period in which the samples were obtained.

F. Noise

1. Noise Standard

The current OSHA standard for noise allows an 8-hour exposure to 90 dBA with a ceiling value of 115 dBA. The formula which gives the permitted noise level for a given time of exposure is obtained from:

$$T = 16 \div 2^{(L-85)/5}$$

T = permitted duration in hours

L = effective noise level in dBA-slow meter setting

2. *Noise Measurements*

Due to the variety of equipment used in aluminum plants it is not possible to summarize data for all plants. Table VI presents noise measurements taken in one plant. In general, the crust breaking operation in pot rooms is noisy, but here again this depends upon the type of equipment used to break the crust. Jack hammers are used in pot relining and high noise levels are produced. Ball mills in paste plants also produce high noise levels, but often workers spend little time in the high noise areas.

IV. CONTROL OF EXPOSURE TO AIR CONTAMINANTS

A. Respiratory Protection

Respiratory protection was made available by all companies. A disposable respirator wherein the filter material was coated with activated alumina had been developed for the aluminum industry and was reported to be effective in reducing exposure to fluorides. Cartridge type respirators were also available. Respirators were generally used during short exposures to high concentrations of air contaminants, but it was not uncommon to find two workers performing the same jobs, one wearing a respirator, the other not. The care and cleaning of respirators was an incidental activity in some plants rather than an organized functioning program.

B. Control by Engineering Methods

Respirators should be used only for short term intermittent exposures and should not be considered a substitute for engineering control methods.

The type of ventilation provided at each plant is available in data used to compile the individual plant reports. In general, vertical Soderberg type plants used roof ventilation as a method for controlling exposure to air contaminants. This method of control is ineffective. Pre-baked and horizontal Soderberg type plants used some method of local exhaust ventilation. However, usually when the worker was required to perform his duties around a pot the door to the pot was required to be opened thus exposing the worker to the volatile material from the pot. In spite of this difficulty a workers overall exposure was reduced by the use of local exhaust ventilation as was demonstrated at one plant where one potline had been provided exhaust ventilation and another had not. Personal samples were collected for workers in both potlines. The differences in the concentrations of air contaminants are reported in Table VII. One may question the accuracy of analytical methods for the benzene soluble values, but the fluoride values were also reduced.

V. SUMMARY AND CONCLUSIONS

This preliminary survey has pointed out areas where high exposures of benzene soluble material were found in aluminum plants. Other types of exposures have been defined. In the opinion of the author two areas should be given serious consideration before any further environmental sampling could be justified.

(1) As has been pointed out better methods of identifying and quantifying potential carcinogens in aluminum plants needs to be developed.

(2) An epidemiological study needs to be done in aluminum plants to determine whether illness or deaths in aluminum plants differ from those of similar industries not using coal tar pitch.

Reduction of worker exposure can best be achieved by the elimination of emissions through well maintained engineering controls or operating procedures. Respiratory protective devices will need to be employed until environmental concentrations can be reduced to safe levels.

TABLE 1 - Respirable versus Non-respirable Samples

Job Title	Type of Plant	Type of Sample	mg/M^3 Particulate	mg/M^3 Benzene Soluble Material
Flex Raiser	Soderberg	respirable	0.6	<0.1
" "	"	gross airborne	3.5	0.3
Pot Operator	Soderberg	respirable	1.7	<0.1
" "	"	gross airborne	6.4	0.3
Anode Worker Hanging Channels	Soderberg	respirable	1.1	0.2
" "	"	gross airborne	3.6	0.4
Packer	Pre-baked	respirable	1.4	<0.1
"	"	gross airborne	11.0	0.5
Puller	Pre-baked	respirable	1.5	<0.1
"	"	gross airborne	10.0	0.3

TABLE II

RESULTS OF SIZE DISTRIBUTION DETERMINATIONS IN POTROOMS

LOCATION	PARTICLE SIZE DISTRIBUTION
General Air Sample, by outside wall in potroom	<Particle Diameter 1µ 1.5µ 2.1µ 3.0µ 4.2µ 6.0µ 8.5µ 12.0µ 17µ 24µ Cumulative Percent 67 70 87 89 93 96 97 98 99 100
Personal sample on a craneman	Heavier and difficult to size, has basically the same particle make-up and size distribution as M-1.
Personal sample on the sweeper	Too heavy to size, more carbon particles present. Otherwise the sample particle make-up and size range as M-1.
Bulk sample of alumina	Mostly large particles, approximately 90% of them in the range 75-125µ in diameter

TABLE III- COMPARISON OF BENZENE SOLUBLE VALUES ACCORDING TO PLANT TYPES AND JOB DESCRIPTION

	Number of Samples	Composite Volume M^3	Composite Benzene Solubles mg/M^3	Estimated TWA*** for Job Description Benzene Solubles mg/M^3	
				Per Plant	Per Plant Type
A. Vertical Soderberg Type Plants					
I. Anode Workers					1.1
a. Plant A				1.1	
1. Stud Pullers	15	11.640	1.9		
2. Jack Risers	2	1.420	0.3		
b. Plant B				1.1**	
1. Pinpullers*	18	7.286	2.4		
2. Jack Slippers*	5	1.859	2.0		
II. Pot Operators					0.4
a. Plant A				0.4	
1. Cell Operators	14	13.330	0.4		
b. Plant B				0.3	
1. Potmen	5	3.187	0.3		
III. Tappers					0.3
a. Plant A				0,4	
b. Plant B				0.2	
1. Tapper	1	0.460	0.2		
IV. Rammers					0.7
a. Plant A				0.4	
1. Rammer	11	9.090	0.4		
b. Plant B				1.0	
1. Pot reliners	2	0.508	2.8*		

*These represent 4 hour samples during heaviest work exposures.

**Time weighted average of 1.1 for this plant was figured on the basis that the worker spends part of his time in the lunch room.

***TWA=Time weighted average exposure.

****For two hour ramming period only. Time weighted average would be about 1.0 mg/M^3.

TABLE III (cont'd)

	Number of Samples	Composite Volume M^3	Composite Benzene Solubles mg/M^3	Estimated TWA*** for Job Description Benzene Solubles mg/M^3	
				Per Plant	Per Plant Type
V. Paste Plant Workers					0.7
a. Plant A				0.7	
1. Briquet Drivers	2	1.658	<0.1		
2. Mixer Man	2	1.599	<0.1		
3. Crusherman	1	0.756	2.1		
b. Plant B					
Paste Plant Workers were not sampled.					
B. Horizontal Soderberg Type Plants					
I. Anode Workers					0.5
a. Plant C				0.6	
1. Anode Tenders	5	3.082	0.6		
b. Plant D				0.3	
1. Flex raisers	10	8.295	0.3		
2. Stud Sellers	1	.840	<0.1		
3. Wizzers	2	1.954	0.8		
4. Pin Pullers	4	4.096	0.4		
5. Channel Hangers	4	3.117	0.5		
6. Anode Foreman	3	2.465	0.1		
7. Anode Man	2	1.839	0.3		
II. Pot Operators					0.5
a. Plant C				0.5	
1. Pot Operators	14	13.041	0.5		
b. Plant D				0.3	
1. Pot Operators	28	27.123	0.3		

TABLE III (cont'd)

	Number of Samples	Composite Volume M^3	Composite Benzene Solubles mg/M^3	Estimated TWA*** for Job Description Benzene Solubles mg/M^3	
				Per Plant	Per Plant Type
III. Tappers					0.3
a. Plant C				0.3	
1. Tapper	1	0.909	0.3		
b. Plant D				0.3	
1. Tapper	4	3.973	0.3		
IV. Rammers					0.2
a. Plant C				0.1	
1. Pot Rebuilders	5	4.494	0.1		
b. Plant D				0.3	
1. Rammers	4	1.110	0.9*		
V. PastePlant Workers					0.3
a. Plant C				0.3	
1. Paste Plant M.E.O.	3	2.722	0.3		
2. Pastemen	2	1.209	0.4		
3. Paste Plant Operator	3	2.210	0.2		
b. Plant D				0.2	
1. Anode Liner Pastmen	8	7.891	0.3		
2. Dolly Operator	6	5.835	0.3		
3. Paste Plant Operator	3	3.027	0.1		
C. Pre-Baked Type Plants					
I. Anode Workers					0.3
a. Plant E				0.1	
1. Anode Changer Operator	19	15.670	0.1		
2. Anode Changer Helper	16	14.810	0.1		
b. Plant F				0.5	
1. Carbon Setter	6	3.464	0.5		

*For ramming period only

***Estimated time weighted average exposure.

	Number of Samples	Composite Volume M^3	Benzene Solubles mg/M^3	for Job Description Benzene Solubles mg/M^3	
				Per Plant	Per Plant Type
II. Pot Operator					0.2
a. INTALCO				0.2	
1. Sampling Operators	7	5.819	0.2		
b. ALCOA				0.2	
1. Potmen	13	11.212	0.2		
III. Tappers					0.3
a. INTALCO				0.2	
1. Tapper Operator	9	7.778	0.1		
2. Tapper Helpers	8	6.890	0.2		
b. ALCOA				0.3	
1. Head Tapper	11	10.200	0.3		
IV. Rammers					0.4
a. INTALCO				0.3	
1. Pot Reliners	23	19.992	0.3		
b. ALCOA				0.4	
1. Pot Liners	6	4.958	0.4		
V. Paste Plant Workers					0.4
a. INTALCO				0.3	
1. Pitch Handler	3	2.706	<0.5		
2. Press Operator	3	2.698	0.2		
3. Crusher Operator	6	5.396	0.1		
4. Cathode Lining Paste Plant Op.	2	1.476	0.5		
b. ALCOA				0.5	
1. Mixer Potlining	2	1.555	1.3		
2. Vibrator	3	2.636	0.2		
3. Craneman	4	3.614	0.2		
4. Mixer (Anode area sample not averaged)	3	1.765	0.3		

TABLE IV - DISTRIBUTION OF GROSS AIRBORNE DUST CONCENTRATIONS

Plant	Type of Plant	>15 mg/M^3	10→15 mg/M^3	5→10 mg/M^3	0→5 mg/M^3	Average mg/M^3	Range mg/M^3	Number of Samples
A	Vertical Soderberg					5.9	0.1→21.4	63
No. of Samples		1	3	19	40			
% of Samples		2	5	30	63			
B	Vertical Soderberg					6.5	0.5→49.5	38
No. of Samples		3	4	5	26			
% of Samples		8	11	13	68			
C	Horizontal Soderberg					3.8	0.1→21.7	55
No. of Samples		2		9	44			
% of Samples		4		16	80			
D	Horizontal Soderberg					3.1	0.6→6.4	102
No. of Samples			1	19	82			
% of Samples			1	19	80			
E	Pre-baked					7.3	0.6→46.8	112
No. of Samples		15	8	27	62			
% of Samples		13	7	24	56			
F	Pre-baked					4.2	0.5→12.0	59
No. of Samples			2	16	41			
% of Samples			3	27	70			

TABLE V-1 - Number and Percent of Urine Values Exceeding 8 mg/liter for Initial Samples Submitted or Collected

Plant	Type of Plant	Total Number of Samples Analyzed	Number of Samples >8 mg/liter	% of Samples >8 mg/liter	Mean for Samples <8 mg/liter	Standard Deviation for Samples <8 mg/liter
A	Vertical Soderberg	108	2	2	3.0	1.6
B	Vertical Soderberg	134	0	0	2.1	1.4
C	Horizontal Soderberg	23	Pre 0 Post 4	0 17	2.1 3.7	1.2 1.5
D	Horizontal Soderberg	135	6	4	2.7	1.7
E	Pre-baked	123	21	17	3.7	1.9
F	Pre-baked	176	19	10	3.3	1.8

NOTE: Information concerning the way samples were collected is included on the next page (Table V-2).

TABLE V-2 - SAMPLING INFORMATION FOR URINE SAMPLES

Plant	Sampling Information
A	Samples from Potroom workers. Collected by NIOSH personnel. Samples collected on several shifts. All samples taken after worker showered.
B	Samples from Potroom and Casthouse personnel. Samples collected by NIOSH personnel after worker showered. Random sampling of shifts.
C	Samples were collected for Potroom workers by the Company. Pre and Post shift samples were collected after the worker showered. Several shifts were sampled.
D	Samples were collected as part of physical examination by Company Physician from all types of aluminum plant workers.
E	Urine bottles were sent home by the Company with Potroom worker at the end of the workers 6th shift (day, swing, or graveyard) then brought back on the 7th shift.
F	Samples were collected by the Company at the plant as the Potroom workers were leaving after completing their 6th shift. Samples were obtained after the worker showered.

TABLE VI

NOISE MEASUREMENTS AT ONE ALUMINUM PLANT

MEASUREMENTS:

Location	Sound Level dBA	Comments
Pot rebuild area	102	All hammers operating
Ore truck	90-100	93 most often
Crust breaker	to 112	
Hot metal transfer truck	98 Average	
Cathode rebuild area:	102	8 jackhammers operating
———————————	90	About 50 feet from above area
Anode repair	112	During "buckling up" anode
Paste plant between ball mills	115	
Paste plant general area	108	

TABLE VII - Comparison of a Controlled and Non-Controlled Potlines

BENZENE SOLUBLES:

UNCONTROLLED		CONTROLLED	
Job Description	Benzene Solubles mg/M^3	Job Description	Benzene Solubles mg/M^3
Tapper (Operator)	0.2	Tapper (Operator)	<0.1
Tapper (Helper)	0.5	Tapper (Helper)	0.1
Sampler (Operator)	0.3	Sampler (Operator)	0.1
Sampler (Helper)	0.2	Sampler (Helper)	<0.1
Anode Changer (Operator)	0.2	Anode Changer (Operator)	0.1
Anode Changer (Helper)	0.2	Anode Changer (Helper)	<0.1

FLUORIDE:	Insoluble Fluoride mg/M^3	Soluble Fluoride mg/M^3	HF mg/M^3	Total Fluoride mg/M^3
Uncontrolled (average of 29 samples)	0.77	0.38	1.91	3.1
Controlled (average of 20 samples)	0.32	0.17	0.83	1.3

APPENDIX A

PRODUCTION OF ALUMINUM

Bauxite is the raw material needed to produce primary aluminum. Bauxite is a clay-like material containing at least 40 per cent aluminum oxide (alumina). Calcined alumina, which is nearly free of water is required in the production of aluminum. Alumina can not be smelted like iron ore by heating to a high temperature with coke. If alumina is reacted with carbon, instead of forming carbon dioxide and aluminum metal ($2\ Al_2O_3 + 3\ C \rightarrow 3\ CO_2 + Al_2$) the product formed is aluminum carbide ($2\ Al_2O_3 + 6\ C \rightarrow 3\ CO_2 + Al_4C_3$). The reason for this is that the melting point of the oxide is over 2000°C while the metal melts at only 658°C. So when the oxide melts and dissociates, the metal is a highly reactive vapor which combines immediately to form carbide instead of condensing into the pure metal.

To overcome the great difficulty in reducing the oxide to the metal by the thermal method, electrolysis is employed. Most chemical and thermal processes have been unsuccessful because of higher operating costs or inferior products.

Alumina is reduced in furnaces known as "pots" (cells). A reduction plant consists of a number of pots connected electrically and known as a "potline". The pot assembly is an insulated, carbon lined, steel box, which, when operating contains a mixture of molten fluoride salts in which the alumina is dissolved and wherein electric current disassociates the alumina into molten metal. Electric current is introduced through carbon electrodes suspended in the molten salts. (Metal "pins" are inserted into the anode to facilitate the flow of electric current.) Carbon electrodes are used at the top of the pot (anode) and the bottom of the pot (cathode). However, the aluminum metal in the pot is the true cathode. The passage of current results in the heavier aluminum metal going to the bottom of the pot where the metal is tapped (siphoned off) at intervals and cast into pigs or conveyed to holding furnaces for further treatment.

Two types of processes are used to prepare the anodes for the pots. In one process the anode is prepared in place. Material (a coal tar pitch - coke mixture) is added to the top of the pot as the anode is consumed. This process is called the soderberg process. Another method is to prepare the anodes, pre-bake them, and then place them in the pot. This method is called the pre-bake process.

These two processes will now be discussed in greater detail.

SODERBERG ANODE CELLS

A metal sheet shell is set up over the surface of the bath and packed with a coke and coal tar pitch paste. No further preparation is required since the anode is baked by conductive heat. The lowest zone is always fully baked while fresh carbon paste or briquettes are added at periodic intervals to replace what is consumed.

The operation of these cells is similar to the pre-baked process. The crust on each cell must be broken by the potline worker. Various equipment is used to do this in different aluminum plants. A man must also control the additions of the alumina or other compounds to the pot. There are also crews responsible for pulling pins and raising the bus bar assembly. The metal pins in the anode must be pulled out before they are exposed to the molten bath and a fresh pin is inserted. After cooling and cleaning, the studs can be reused. The entire anode height must be adjusted since the bath depth varies with the production and tapping of the molten aluminum.

Eventually the pot has to be torn down and relined, but fortunately this is infrequent.

PRE-BAKED ANODE CELLS

Finished, cured blocks of carbon with a metal rod inserted into them to provide both support and conduct electricity are put into the molten bath. The electrodes start with soft pitch and coke and are baked before installation in order to make the anodes harder, drive off volatiles, and improve their electrical conductivity. Once in the cell, the anodes are lowered until they are gradually consumed. A new anode must then be inserted to replace the one consumed.

In some plants the operator must lower the anodes, adjust each cell to the proper voltage, break the crust that forms at the top and add alumina and small amounts of fluoride compounds as required. In other plants additions of alumina and fluoride have been computerized and automated.

PRODUCTION OF ANODES AND CATHODES

The materials used in the manufacture of the anodes and cathodes varies in different plants. However, the following description written by Patrick Shuler describes the general processes involved.

To manufacture the carbon materials required, seven basic raw materials are utilized: coal tar pitch of three different softening points, 40°C (liquid), 75°C (liquid), and 110°C (solid), rotary calcined pitch coke, graphite, gilsonite coke, and anthracite coal. The grade and end use of the product determines the proportions of the raw materials needed. The amount of coal tar pitch ranges from 15-28% by weight. A brief description of the methods and materials used in the various carbon products follows.

1. Pre-Baked Anodes: Solid coal tar pitch with a softening point of 110°C and rotary calcined coke are unloaded and conveyed to a storage area. Next they are crushed and sized and put into holding hoppers. The coke and pitch are weighed, dumped into heated mixers, and allowed to agitate. After being dumped, the mixture is conveyed to a hydraulic press which forms the block shape. The anode must then be heated at about 1100°C to drive off the volatiles and form a hard block. Finally the steel studs are sealed into the finished anodes and are ready for installation. (in some plants the anodes are sprayed with aluminum before use in the pots.)

In some plants operations are monitored and controlled from a central control panel.

2. Soderberg Anode Paste: The raw materials are rotary calcined coke, gilsonite coke, 75°C and 110°C softening point pitch. The crushing, sizing, and mixing are very similar to that of the pre-baked anode except that the resulting mixture is in a molten state. The paste mixture is distributed to the Soderberg cells on a regular schedule.

3. Cathode Block: The raw materials graphite, anthracite coal, and the solid coal tar pitch with softening point 110°C are utilized. After unloading, crushing, grinding, and sizing the material is mixed. The cathode blocks are formed near the mixers by a jolt press. After baking in ring furnaces similar to those used for the pre-baked anodes, they are cleaned and metal conductors are inserted.

4. Cathode Lining Mix: One alternative to having several large blocks for the cathode is to have a paste to form one monolithic mass

by filling in the bottom of the cell with paste. Even if several pressed blocks are used, it is still necessary to fill in the cracks with a paste.

The monolithic-type paste is a mixture of anthracite coal and 40°C softening point pitch. The coal tar pitch is handled as a liquid and the coal processed in the carbon plant as described above. After leaving the mixer, this material is ready for use to patch or form new cathodes. A similar mixture is used to produce a paste suitable for filling in among the pressed cathode blocks.

Much of this information was obtained from a report prepared during August, 1972 by Harry M. Donaldson, Patrick J. Shuler, and William Parnes, M.D. - NIOSH, Cincinnati, Ohio.

APPENDIX B

Primary Aluminum Production Capacity in the United States, by Company

Company and Plant	Capacity at yearend (Thousand short tons)
	1971
Aluminum Company of America (Alcoa):	
Alcoa, Tenn	200
Badin, N.C	115
Evansville (Warrick), Ind	275
Massena, N.Y	130
Point Comfort, Tex	185
Rockdale, Tex	280
Vancouver, Wash	115
Wenatchee, Wash	175
Anaconda Aluminum Co.: Columbia Falls, Mont	180
Consolidated Aluminum Corp. (Conalco):	
Lake Charles, La	35
New Johnsonville, Tenn	140
Eastalco Aluminum Co.: Frederick, Md	87
Harvey Aluminum Inc.:	
The Dalles, Oreg	90
Goldendale, Wash	110
Intalco Aluminum Corp.: Ferndale (Bellingham), Wash	260
Kaiser Aluminum & Chemical Corp.:	
Chalmette, La	260
Mead, Wash	206
Ravenswood, W.Va	163
Tacoma, Wash	81

Company and Plant	Capacity at yearend (Thousand short tons) 1971
National-Southwire Aluminum Co.: Hawesville, Ky-	180
Noranda Aluminum Inc.: New Madrid, Mo------------	70
Ormet Corp.: Hannibal, Ohio----------------------	240
Revere Copper & Brass Inc.: Scottsboro, Ala-----	112
Reynolds Metals Co.;	
Arkadelphia, Ark----------------------------	63
Corpus Christi (San Patricio), Tex-----------	111
Jones Mills, Ark----------------------------	122
Listerhill (Sheffield), Ala------------------	221
Longview, Wash------------------------------	200
Massena, N.Y--------------------------------	128
Troutdale, Oreg-----------------------------	130
Total United States--------------------	4,664

FROM: Bureau of Mines Minerals Yearbook - 1971.

APPENDIX C

LIST OF SIC CODE NUMBERS AND DESCRIPTION OF COAL TAR PITCH VOLATILES EXPOSURES
(1967 SIC List)

1621--Heavy Construction, Except Highway and Street Construction (Pipe line wrapping: general contractors)

1761--Roofing and Sheet Metal Work

1771--Concrete Work (Asphalting and Blacktop work)

1799--Special Trade Contractors, Not Elsewhere Classified (Waterproofing and pipe covering)

2661--Building Paper and Building Board Mills (Asphalt)(Tar paper)

2815--Cyclic (Coal Tar) Crudes, and Cyclic Intermediates, Dyes, and Organic Pigments

2821--Plastics Materials, Synthetic Resins, and Nonvulcanizable Elastomers (Coal tar resins)

2851--Paints, Varnishes, Lacquers, Enamels, and Allied Products (Coal tar pitch)

2911--Petroleum Refining (Coke production)

2951--Paving Mixtures and Blocks (Coal tar paving materials)

2952--Asphalt Felts and Coatings

3312--Blast Furnaces (Including Coke Ovens) Steel Works, and Rolling Mills

3321--Gray Iron Foundries (Cast iron pipe and fittings)

3334--Primary Production of Aluminum

3341--Secondary Smelting and Refining of Nonferrous Metals (Aluminum)

3691--Storage Batteries (Sealing compounds)

3692--Primary Batteries, Dry and Wet

3996--Linoleum, Asphalted-felt-base, and Other Hard Surface Floor Coverings, Not Elsewhere Classified

4925--Mixed, Manufactured, or Liquefied Petroleum Gas Production and/or Distribution (Coke oven gas, etc.)

NOTE: This information was taken from a U.S. Department of Labor memo concerning coal tar pitch volatiles.

PARMA STANDARD TEST METHODS

UNION CARBIDE CORPORATION, PARMA TECHNICAL CENTER

PSM- 1013	ANALYSIS Benzene Solubles
RANGE 0.1 mg to > 100 mg	KEY REAGENT Benzene
PRECISION ±0.1 mg @ 1.0 mg range	MATRIX Air Particulates Trapped on Silver and/or Glass Fiber Filters
DATE ISSUED 10-29-71	DATE REVISED 1-14-72

SOXHLET EXTRACTION OF BENZENE SOLUBLE MATERIAL IN AIRBORNE PARTICULATES TRAPPED ON SILVER AND/OR GLASS FIBER FILTERS

1. Purpose and Limitation

1.1. This method was designed for the determination of benzene soluble material in airborne particulates collected on silver and/or glass fiber filters by repeated extraction with hot benzene..

2. Principle of Method

2.1. The particulate material on the filter(s) is extracted by benzene, using the continuous cycling process of a Soxhlet extractor. After extraction the solution is filtered through the original filter(s).

2.2. The weight loss of the filter(s) is considered to be the amount of benzene solubles.

3. Apparatus and Reagents

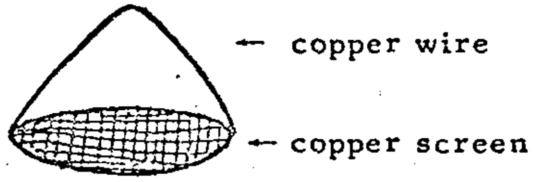
3.1. Apparatus

3.1.1. Soxhlet extractor apparatus - Six 250-ml size, Fisher Scientific, Catalog No. 9-551B or equivalent.

3.1.2. Extraction heater and support - Six positions, Fisher Scientific, Catalog No. 9-678 or equivalent.

3.1.3. Analytical balance - 0.01 mg sensitivity.

3.1.4. Copper basket - A copper basket is fabricated by cutting a copper screen (approximately 40 mesh) into 35-mm diameter circles. Two single strand copper wires are attached to the screen to form handles. This basket is used to support the filter(s) in the Soxhlet extraction chamber (see drawing).



3.1.5. Miscellaneous - Tweezers, 4 inch size and 10 inch size; aluminum tray, 9 x 12 inch; watch glasses, 2 1/2 inch diameter; microspatula; thin cotton gloves; 250-ml graduate; Carborundum boiling chips.

3.1.6. Filtering assembly - 500 or 1000-ml capacity suction flask; a fritted, 40-mm ID, coarse porosity, Pyrex Buchner funnel inserted into a rubber stopper (the appropriate size to fit the suction flask); a 38-mm OD glass ring, approximately 3 mm thick and approximately 12 mm tall. The glass ring is used to hold the filter(s) firmly on the fritted surface. This also prevents the filter from floating.

3.2. Reagents

3.2.1. Benzene - Spectroanalyzed grade.

3.2.2. Alconox and acetone - for preliminary cleaning of apparatus.

4. Procedure

4.1. Preliminary cleaning of Soxhlet extractor glassware.

4.1.1. Using a solution of Alconox in water, wash each part of the Soxhlet extractor. Rinse thoroughly with distilled water. Dry the outside of each part with a lint-free tissue. Dry the inside by rinsing with acetone. Air dry to remove the excess acetone.

4.1.2. Add 180 ml of benzene and 5 to 10 boiling chips to each extraction flask. Assemble the Soxhlet extractor. Place the copper basket in the extractor. Apply heat and continue heating for 2.5 hours after the slowest Soxhlet extractor cycles for the first time.

4.1.3. Turn off the heat and discard the benzene and boiling chips. (Benzene should be discarded in waste solvent can.)

4.2. <u>Sample procedure</u> - Samples are usually analyzed in lots of six.

4.2.1. Check for sample labeling on the bottom portion of the cassettes containing the samples. Relabel if necessary. Remove the tops from the cassettes. Expose the samples to room conditions for 1 hour. This process equilibrates the moisture content of the filter(s).

4.2.2. Using the small tweezers and microspatula, remove all the filters above the bottom support filter. The number and type of filters may vary. A silver filter usually is located next to the filter support. Once removed from the cassette, the silver filter is used both as a sample and as a support for the other filters. If a silver filter is not contained in the cassette, use a silver filter previously extracted in the Soxhlet extractor. Using tweezers, place the filter(s) directly on the balance pan. Weigh and record the filter(s) weight to the nearest 0.01 mg. Remove filter(s) and place on a numbered watch glass. Repeat for each sample.

4.2.3. Place 180 ml of benzene and 5 to 10 boiling chips in each extraction flask.

4.2.4. Carefully transfer the filter(s) to the copper basket. Using the large tweezers, lower the basket into the Soxhlet chamber. Assemble Soxhlet apparatus. Repeat for each sample. This portion of the procedure may be performed the day prior to extraction.

4.2.5. Turn the heaters on maximum setting. Extract for 2.5 hours after the slowest Soxhlet extractor cycles once.

4.2.6. Turn the heaters off. Samples may or may not be filtered immediately.

4.2.7. Assemble the filtering apparatus in well-ventilated hood. Connect the filtering apparatus to suction. Remove the extraction chamber and flask, while still assembled, from the heater. Tilt the entire assembly in order to drain as much benzene as possible from the extraction chamber into the extraction flask. Using the large tweezers, remove the copper basket containing the filter(s) from the Soxhlet chamber. Using the small tweezers, carefully mount the filter(s) on the filtering apparatus. Using the small tweezers, lower the glass ring on to the silver filter. Using a benzene washing bottle, rinse the Soxhlet chamber at least three times. Pour the washings into the filtering funnel. Care should be taken to remove from the Soxhlet chamber all insoluble particles that may have been removed from the filter. Continue filtering the entire contents of the extraction flask (minus the boiling chips) through the filtering funnel. Rinse extraction flask three times with benzene. Add the washings to the filtering funnel.

4.2.8. Using small tweezers, remove the filter(s) and place on a numbered watch glass. Repeat paragraph 4.2.7. for each sample. Air dry all the samples for 1 hour after the last sample is filtered.

4.2.9. Using small tweezers, place the filter(s) directly on the balance pan. Weigh to the nearest 0.01 mg. Record weight.

5. Calculation

$$(A - B)(1000) = C$$

where

A = Weight of filter(s) before extraction, g (Paragraph 4.2.2.)
B = Weight of filter(s) after extraction, g (Paragraph 4.2.9.)
C = Benzene soluble, mg.

Report to the nearest 0.1 mg.

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