Lead Industries Association, Inc.
292 Madison Avenue · New York, N. Y. 10017 · Telephone: (212) 679-6020

January 29, 1974

SUBJECT: DRAFT STANDARD FOR OCCUPATIONAL EXPOSURE TO INORGANIC LEAD

TO THE OFFICIAL MEMBERS OF THE LEAD INDUSTRIES ASSOCIATION, INC.:

Although the attached material is now being received by the members of the LIA Environmental Health Committee, I am sure some of you will wish to have your own file copy of this Department of Labor draft Standard. Comments and suggestions on this draft are solicited by the Department's Office of Standards.

Sincerely,

Jerome F. Smith

JFS:lm
Attachment

Jerome F. Smith
Secretary & General Manager

Lead Industries Association, Inc.
292 Madison Avenue · New York, N. Y. 10017 · Telephone (212) 532 2373

Environmental Health Department

January 18, 1974

TO: LIA Environmental Health Committee

FROM: Donald R. Lynam, Ph.D.

SUBJECT: Department of Labor Standard for Occupational Exposure to Inorganic Lead

Gentlemen:

Enclosed is a draft of the Department of Labor Standard for Occupational Exposure to Inorganic Lead. This draft was obtained from Dr. John O'Neil, Office of Standards, on January 15th when Dr. O'Neil met with the Industrial Health Committee of the Battery Council International. Dr. O'Neil asked that he document be reviewed and comments be submitted to him.

It is emphasized that this is a draft document. Dr. O'Neil indicated that the Department of Labor wanted to evaluate the impact of the proposed standard on the workplace before issuing a final document. He stated that the Department of Labor would like to visit plants in order to evaluate the standard. He stated that the visits could be made without initiating any compliance action regardless of conditions, since such visits would be in conjunction with the writing of standards rather than compliance actions. Dr. O'Neil indicated that the Department of Labor would like to visit a number of lead operations by invitation.

Dr. O'Neil advised that the Department of Labor did not plan to have an Advisory Committee for the lead standards since their experience with Advisory Committees had not been good. It appears that the Department of Labor proposes to use this mechanism of evaluating proposed standards. The Department of Labor hopes to determine by this evaluation:

1. If all provisions of the document are needed or if additional provisions are required?

2. If the standards are applied as written, will the objectives of protecting the worker be met?

3. Are some provisions of the standard stringent but yet ineffective in protecting the worker?

The major provisions of the document are:

1. The standard for airborne concentrations for lead is 0.15 mg/m^3.

2. The employer shall provide or make available at his own cost, biological monitoring to all employees subject to exposure to inorganic lead.

   a. The blood lead limit is 80 ug/100g.
   b. Urine may be used instead of blood. However, if a concentration of lead in urine exceeds 0.20 mg/ml, a blood sample is required within two weeks.

Dr. O'Neil indicated that the employer is required to make available biological monitoring, although the employee is not required to submit to biological monitoring.

Dr. O'Neil indicated that he would like to have a critique of the document. When the field work is completed the final document will be written, published in the Federal Register, public hearings held if requested, comment period provided, and the Department of Labor would then review the total record to come up with a final document.

I think it is most important that the LIA Environmental Health Committee have a meeting to discuss the proposed standard.

We would appreciate any comments that you might have.

Sincerely,

Donald R. Lynam

Donald R. Lynam, Ph.D.
Assistant Director
Environmental Health

jm

DRAFT

DEPARTMENT OF LABOR
Occupational Safety and Health Administration
[29 CFR Part 1910]

Standard for Occupational Exposure
to Inorganic Lead

Notice of Proposed Rulemaking

Pursuant to Section 6(b) of the Williams-Steiger Occupational Safety and Health Act of 1970 (84 Stat. 1593; 29 U.S.C. 655), Secretary of Labor's Order No. 12-71 (36 F.R. 8754) and 29 CFR Part 1911 (36 F.R. 17506), it is hereby proposed to adopt a new standard to protect the health of employees in occupational exposure to inorganic lead.

The National Institute for Occupational Safety and Health (NIOSH), U. S. Department of Health, Education, and Welfare published and submitted to the Secretary of Labor, pursuant to the Williams-Steiger Occupational Safety and Health Act of 1970, criteria for a recommended standard on occupational exposure to inorganic lead. The proposed standard is based for the most part on recommendations in the criteria document of NIOSH. The proposed standard complies with sections 6(b)(5), 6(b)(7) and 8(c)(3) in fulfilling the requirements of the Act for a comprehensive standard.

Written comments concerning the proposal may be mailed to the Office of Standards, Room 509, Railway Labor Building, Washington, D. C. 20210 within 60 days after the publication of this notice in the FEDERAL REGISTER. The data, views, and arguments will be available for public inspection and copying at

DRAFT

DEPARTMENT OF LABOR
Occupational Safety and Health Administration
[29 CFR Part 1910]

Standard for Occupational Exposure
to Inorganic Lead

Notice of Proposed Rulemaking

Pursuant to Section 6(b) of the Williams-Steiger Occupational Safety and Health Act of 1970 (84 Stat. 1593; 29 U.S.C. 655), Secretary of Labor's Order No. 12-71 (36 F.R. 8754) and 29 CFR Part 1911 (36 F.R. 17506), it is hereby proposed to adopt a new standard to protect the health of employees in occupational exposure to inorganic lead.

The National Institute for Occupational Safety and Health (NIOSH), U. S. Department of Health, Education, and Welfare published and submitted to the Secretary of Labor, pursuant to the Williams-Steiger Occupational Safety and Health Act of 1970, criteria for a recommended standard on occupational exposure to inorganic lead. The proposed standard is based for the most part on recommendations in the criteria document of NIOSH. The proposed standard complies with sections 6(b)(5), 6(b)(7) and 8(c)(3) in fulfilling the requirements of the Act for a comprehensive standard.

Written comments concerning the proposal may be mailed to the Office of Standards, Room 509, Railway Labor Building, Washington, D. C. 20210 within 60 days after the publication of this notice in the FEDERAL REGISTER. The data, views, and arguments will be available for public inspection and copying at

the Office of Standards.

Pursuant to 29 CFR 1910.11 (b) and (c), interested persons may, in addition to filing written matter as provided above, file objections to the proposal requesting an informal hearing with respect thereto in accordance with the following conditions:

(1) The objections must include the name and address of the objector;

(2) The objections must be postmarked on or before the 30th day after the date of publication of this notice of proposed rulemaking;

(3) The objections must specify with particularly the provision of the proposed rule to which objection is taken, and must state the grounds therefor;

(4) Each objection must be separately stated and numbered; and

(5) The objections must be accompanied by a summary of the evidence proposed to be adduced at the requested hearing.

Upon consideration of the records of the hearings, if any, together with any other written data, views, or arguments received in response to this notice, the Assistant Secretary may adopt the proposal with or without changes or modify the proposal in light of the comments received.

Accordingly, it is hereby proposed to amend Part 1910 of Title 29 of the Code of Federal Regulations, as set forth below:

§1910.93 [AMENDED]

1. Table G-2 in §1910.93 (F.R. 22142, October 18, 1972) is

proposed to be amended by deleting the following:

* * * * *

Lead and its inorganic . . . 0.2 mg/M^3
compounds (Z37.11-1969).

* * * * *

2. A new section 1910.93 - is proposed to be added to Part 1910, read as follows:

§1910.93 Inorganic Lead.

(a) Scope. This section applies to all places of employment where dusts or fumes of inorganic lead are present or may be present in the air. Where employees are subject to exposure to inorganic lead at or below half the permissible limit specified in paragraph (c) of this section. Compliance with the following paragraphs of this section is not required, except for paragraphs (f)(1)(ii), (f)(2) and (g)(1).

(b) Definitions. For the purpose of this section. (1) "Inorganic lead" includes lead oxides, metallic lead, and lead salts (including organic salts such as lead soaps).

(2) "Exposure to inorganic lead" means exposure above half the permissible limit specified in paragraph (c) of this section.

(c) Permissible exposure to inorganic lead. The airborne concentration of inorganic lead to which any employee may be exposed shall not exceed 0.15 milligram per cubic meter of air (0.15 mg/M^3) determined as a time-weighted-average (TWA) exposure for an 8-hour day.

proposed to be amended by deleting the following:

* * * * *

Lead and its inorganic compounds (737.11-1969).	. . . 0.2 mg/M^3

* * * * *

2. A new section 1910.93 - is proposed to be added to Part 1910, read as follows:

§1910.93 Inorganic Lead.

(a) Scope. This section applies to all places of employment where dusts or fumes of inorganic lead are present or may be present in the air. Where employees are subject to exposure to inorganic lead at or below half the permissible limit specified in paragraph (c) of this section. Compliance with the following paragraphs of this section is not required, except for paragraphs (f)(1)(ii), (f)(2) and (g)(1).

(b) Definitions. For the purpose of this section. (1) "Inorganic lead" includes lead oxides, metallic lead, and lead salts (including organic salts such as lead soaps).

(2) "Exposure to inorganic lead" means exposure above half the permissible limit specified in paragraph (c) of this section.

(c) Permissible exposure to inorganic lead. The airborne concentration of inorganic lead to which any employee may be exposed shall not exceed 0.1% milligram per cubic meter of air (0.1 mg/M^3) determined as a time-weighted-average (TWA) exposure for an 8-hour day.

(d) Methods of sampling and analysis. Methods of sampling and analysis shall be such that inorganic lead at a concentration of 0.15 mg/cu m can be determined with an accuracy of ± 15 per cent in a one hour air sample. (1) Sampling. Lead dust or fumes shall be collected on 0.45 or 0.80 micrometer porosity cellulose membrane filters mounted in either 2 or 3 piece filter cassettes. Air shall be drawn through the filter by means of a pump at a rate of 2 liters per minutes (not less than 1 nor more than 4 liters per minute). A minimum sample of 100 liters shall be collected. Electrostatic precipitators and other collection methods and sampling rates shown to give equivalent results may be used.

(2) Analytical method. The reference dithizone method as specified in Appendix A, or atomic absorption spectrophotometry or any method shown to be equivalent in precision and accuracy to the dithizone method shall be used for the analysis of the lead in air and biological samples.

(e) Environmental monitoring. (1) General requirements. (i) Where exposure levels of employees to lead is not known the employer shall have an industrial hygiene survey done, to determine the employee's exposure to inorganic lead and environmental levels in workroom areas. The program shall be carried out within 6 months of the effective date of this section.

(ii) Workroom areas where it has been determined on the basis of an industrial hygiene survey, that environmental levels of lead do not exceed half the permissible limit specified in

paragraph (c) of this section shall not be considered to have exposure to inorganic lead.

(2) Frequency of sampling. (i) Where there is exposure to inorganic lead the monitoring program shall consist of personal breathing zone samples. Monitoring shall be done on a periodic basis, but at least every six months, or whenever there is a change in exhaust ventilation, process, or operation that may affect the employee's exposure to lead.

(ii) If breathing zone levels are at or above the permissible limit specified in paragraph (c) monitoring shall be done every 3 months. This increased frequency of monitoring shall be continued at least 6 months (i.e. two more quarterly monitoring periods) after the last sampling that demonstrated levels at or above the permissible limit specified in paragraph (c) of this section.

(iii) Periodic air sampling shall be performed to coincide with periodic biologic sampling, i.e., shall be performed within two weeks of biologic sampling.

(3) Breathing zone samples. Breathing zones samples shall be collected to permit construction of an 8-hour time-weighted-average exposure of employees. The following number of samples shall be collected and analyzed, as a minimum, based on the maximum number of employees in any given work area:

Number of Employees Exposed		Number of Samples
(i)	1 - 20	50% of the number of employees.
(ii)	20 - 100	10 samples plus 25% of the

	excess over 20 employees.
(iii) over 100	30 samples plus 5% of the excess over 100 employees.

(4) Employee observation of monitoring. Affected employees or their representatives, shall be given opportunity to observe any monitoring required by this paragraph and shall have access to the records thereof.

(f) Method of control. (1) Engineering control. Engineering controls shall be used to maintain the airborne lead concentration, where feasible, below the permissible limit specified in paragraph (c) of this section. (i) Exhaust systems. Where a local exhaust ventilation and dust collection system is used it shall be designed and maintained to prevent the accumulation of lead dust and fume.

(ii) Recirculation of air. Air from the exhaust ventilation systems shall not be recirculated into the workroom, and shall not be discharged outside the plant in such a manner as to create an air pollution problem.

(2) Housekeeping. (i) All external surfaces shall be maintained free of accumulation of inorganic lead dust, if with their dispersion into the air there would be an excessive concentration. Leaks and spills shall be cleaned up as soon as possible to prevent dispersion of lead into the air.

(ii) Vacuuming, wet sweeping or other methods which do not generate airborne lead shall be used for cleaning the workplace. No dry sweeping or blowing shall be permitted.

(iii) Materials which may contaminate the work area with

inorganic lead dust shall be properly stored and disposed of to prevent such occurrence.

(g) Sanitation practices. (1) Food facilities. Food preparation, dispensing (including vending machines), and eating shall be prohibited in lead work areas in compliance with §1910.141(g).

(2) Locker facilities. Work and street clothing shall not be stored in the same locker in compliance with §1910.141(e).

(3) Shower facilities shall be provided in accordance with §1910.141(d)(3) and used by employees who are exposed to airborne concentrations of lead above the permissible limit specified in paragraph (c) of this section, or when work clothing or exposed body surfaces become contaminated with inorganic lead dust.

(h) Personal protective equipment. (1) Respirators. Compliance with the exposure limit specified in paragraph (c) of this section may not be achieved by the use of respirators or shift rotation of employees, except: (i) During the time period necessary to install the engineering controls required by paragraph (f) of this section.

(ii) In work situations in which the methods prescribed in paragraph (f) of this section are either technically not feasible or feasible to an extent insufficient to reduce the airborne concentrations of inorganic lead below the limit specified in paragraph (c) of this section.

(iii) In emergencies; or

(iv) Occasional brief exposures of a nonroutine nature above the limit specified in paragraph (c) of this section.

(v) Where both respirators and personnel rotation are allowed by subdivisions (i), (ii) or (iii) of this subparagraph and both are practicable, personnel rotation shall be preferred and used.

(2) Where a respirator is permitted by subparagraph (1) of this paragraph, it shall be selected from among those approved by the National Institute for Occupational Safety and Health, Department of Health, Education, and Welfare, and the Mining Enforcement and Safety Administration, Department of the Interior under the provisions of 30 CFR Part 11 (37 F.R. 6244, March 25, 1972) and shall be used in accordance with subparagraph (3) of this paragraph.

(3) The employer shall provide respirators when required by this section, and shall assure that employees use the respirators provided. Table I shall be used for the selection of respirators at concentrations of airborne inorganic lead above the limit specified in paragraph (c).

TABLE I

Requirements for Respirator Usage at
Concentrations Above the Permissible Exposure Limit

Exposure	8 Hr TWA mg/m^3	*Respirator Type
Inorganic lead dust	less than 1.5	A, B
	less than 15.0	C
	greater than 15.0	D
Inorganic lead fume	less than 1.5	F
	less than 15.0	F
	greater than 15.0	D

*A - Reusable filter-type air-purifying dust respirator

B - Single-use dust respirator

C - Powered air-purifying positive-pressure dust respirator

D - Type C positive-pressure supplied air respirator

E - Reusable filter-type air-purifying fume respirator

F - Powered air-purifying positive-pressure fume respirator

(4) Employees experiencing breathing difficulty while using respirators shall be referred to a physician for evaluation. This evaluation shall investigate if the employee had adequate ventilatory capacity and any evidence of obstructive lung disease. Employees with inadequate ventilatory capacity or evidence of obstructive lung disease shall not wear types A, B, and E respirators.

(5) The employer shall establish a respirator program in accordance with the requirements of subparagraphs (b)(1) through (b)(10) of §1910.134 of this Part.

(6) If both fumes and dust are present the recommended usage respirator is that for fume.

(7) Usage of a respirator specified for use in higher concentrations of lead is permitted in atmospheres of lower concentration.

(8) Employees shall be given instructions on the use of respirators assigned to them, cleaning of the respirators, and how to test for leakage.

(9) Protective clothing. (i) Each employee subject to contamination by contact of clothing or exposed body surfaces with inorganic lead, or to airborne concentrations of inorganic lead above the limit specified in paragraph (c) of this section shall wear coveralls or similar full body work clothing and head covering during working hours in these areas. Employees not subject to contamination by contact of clothing or body surfaces with lead but subject to "exposure to inorganic lead" at or below the limit specified in paragraph (c) of this section shall change into suitable work clothing before starting work, and shall remove work clothing before leaving work. This work clothing need not afford full body coverage.

(ii) Work clothing contaminated with lead dust shall not be cleaned by blowing or shaking. When practicable, work clothing shall be vacuumed before removal.

(iii) When work clothing becomes contaminated with inorganic lead it shall be changed for clean work clothing on the next shift or next day's work.

(i) Apprisal of employees of hazards from lead. (1) Each employee exposed to lead shall be apprised at the beginning of his employment or assignment to a lead work area of all hazards, relevant symptoms, appropriate emergency procedures, proper conditions and precautions for safe use or exposure. Employees shall be advised as to availability of such information which shall be kept on file and shall be accessible to employees at each place of employment where lead is used.

(j) Medical. (1) Biological monitoring. (i) The employer shall provide or make available at his cost biological monitoring to all employees subject to "exposure to inorganic lead." It consists of sampling and analysis of whole blood, or alternatively, or urine for lead content. Such monitoring shall be performed to ensure that no employee absorbs an unacceptable amount of lead. Unacceptable absorption of lead posing a risk of lead poisoning is demonstrated at levels of 0.08 milligrams of lead per liter of urine (with urine specific gravity corrected to 1.024) or greater. Procedures for sampling and analysis of blood or urine shall be as described in Appendix A and subparagraph (d)(2).

(ii) Blood sample. Half of all employees subject to "exposure to inorganic lead" shall have biological monitoring made available to them every 6 months so that each employee shall have blood sampling and analysis made available to him yearly. A second blood sample shall be taken within two weeks if the blood level is found to be 0.08 milligrams per 100 grams of whole blood or

greater. If this second blood sample confirms an excessive blood lead of 0.08 milligrams of lead per 100 grams of whole blood, or greater, steps to reduce the employee's absorption of lead shall be taken. Steps to be considered include improvement of environmental controls, improvement of personal protection or personal hygiene, and use of administrative controls. A medical examination for possible lead poisoning shall be made available.

(iii) Urine sample. If urine sampling and analysis are chosen instead of blood sampling and analysis to satisfy the biological monitoring requirement, each employee shall have urine sampling and analysis made available at 6 months intervals. Spot urine specimens of about 100 ml. shall be collected during a workday, and urine specimens with a specific gravity less than 1.010 shall be discarded and another sample obtained. If an employee's urine lead level is found to be 0.20 mg/liter or greater, calculated to specific gravity of 1.024, a blood sample shall be obtained and analyzed within 2 weeks.

(iv) Abnormal levels of environmental or biological samples. If the concentration of airborne inorganic lead exceeds the limit prescribed in paragraph (c) of this section, the interval of biological monitoring shall be halved (i.e., blood analysis shall be conducted quarterly, with each employee sampled semi-annually, or urinalysis shall be conducted quarterly on each employee. This increased frequency shall be continued for at least 6 months after the high environmental level has been shown.

(v) Biologic monitoring shall also be made available where there is reason to believe that operations produce unusual exposure excursions or that environmental samples do not adequately describe the employee's exposure to inorganic lead.

(2) Medical examinations. (i) General requirements. The employer shall provide or make medical examinations available at his cost to employees under any of the following conditions:

(a) When the airborne concentrations of inorganic lead exceed the limit prescribed in paragraph (c) of this section.

(b) For employees with an unacceptable absorption of lead as indicated by biological monitoring.

(c) When administrative controls involving rotation of personnel or respiratory protection are used.

(ii) These medical examinations shall be provided or made available prior to employee placement in areas where the airborne concentration of inorganic lead exceeds the limit specified in paragraph (c) of this section, and annually thereafter. Current employees who meet the requirements for a medical examination in subdivisions (j)(2)(a), (b), or (c), and who have not received such examination within one year of the effective date of this standard shall have such medical examinations conducted within 6 months of the effective date of this section and annually thereafter.

(iii) The medical examinations shall include a physical examination, complete blood counts, blood lead determinations, routine urinalysis (specific gravity, sugar and protein determinations,

and microscopic examinations), and record of any signs or symptoms of plumbism, if present.

(iv) Where urine is selected instead of blood for biologic monitoring, the preplacement examination shall also include a urinary lead determination. Each employee who absorbs unacceptable amounts of lead as indicated by biologic monitoring shall be examined as soon as practicable after such absorption is demonstrated and confirmed, and at least every 3 months thereafter until his blood or urine lead levels have returned to normal, i.e. below 0.080 mg/100 g of blood or 0.20 mg/liter or urine. If clinical evidence of plumbism is developed from these medical examinations, the worker shall be kept under a physicians care, in accordance with applicable Workman's Compensation provisions, until the worker has completely recovered or maximal improvement has occurred.

(k) Recordkeeping. (1) Environmental records. Records shall be maintained for all sampling schedules to include the sampling and analytical methods, type of respiratory protection in use (if applicable), and the concentration of inorganic lead in personal breathing zone samples, and work area samples. Records shall be maintained so that they can be classified by employee. Each employee shall be able to obtain information on his own environmental exposure. The records shall be kept for at least 3 years.

(2) Medical records. Medical records shall include information on all biological monitoring and medical examinations.

These records shall be kept for at least 5 years following the last occupational exposure to inorganic lead.

(3) The medical records shall be available to the medical representatives of the employer, of the Assistant Secretary of Labor for Occupational Safety and Health, of the Director of NIOSH, Department of Health, Education, and Welfare, and, at the employee's request, to the employee's physician.

(l) Caution signs. (i) Posting. Caution signs shall be provided and displayed at each location where airborne inorganic lead concentrations are likely to occur which exceed one-half the limit specified in paragraph (c) of this section.

(2) Sign specifications. (i) The caution sign required shall display the following legend with letter sizes, styles, and contrasting colors of a visibility to permit comprehension of the warning at a distance of no less than 10 feet. Signs shall be replaced when they are not readable at a distance of 10 feet.

LEAD AREA
CAUTION

Follow Supervisors Instructions

On Precautions To Observe

(ii) When the concentration of airborne inorganic lead exceeds the limit specified in paragraph (c) of this section, all requirements of subdivision (2)(i) of this paragraph shall be complied with, except the sign shall display the following legend:

LEAD

DANGER

High Concentration of Fume or Dust

Wear Proper Respirator

APPENDIX A

REFERENCE DITHIZONE METHOD FOR ANALYSIS OF LEAD IN AIR AND BIOLOGICAL SAMPLES

The following directions for analysis of lead are taken from the first part of the report, "The 'USPHS' Method for Determining Lead in Air and in Biological Materials" by Keenan, Byers, Saltzman, and Hyslop.[1] Additional information on the reproducibility and accuracy of the method is given in other portions of the report.

1. REAGENTS

1.1 Analytical grade reagents are used. Purification is essential when analyzing biological tissues and fluids because of the very low levels of lead in these materials; purification of reagents may not be required for air samples containing quantities of lead sufficiently greater than that present in the reagent blank. A reagent blank sample is carried through the entire procedure with each set of unknown samples (air, biological, or other type) and its analyzed lead content is subtracted from each analytical result to calculate the net quantity of lead in each unknown sample.

1.2 A boiling rod is used or prevent bumping in the flasks when distilling reagents. This is prepared by cutting 3 or 4 mm O.D glass tubing to a length which is one cm greater than the height of the flask. The tubing is sealed at a spot about one cm above the bottom end which is fire-polished but left open. Before each use, the liquid is shaken out of the bottom section

[1] Keenan, R.G., Byers, D., Saltzman, B.E., Hyslop, F.L: The "USPHS" Method of Determining Lead in Air And in Biological Materials. Am. Ind. Hyg. Assoc J 24:481-91, 1963.

and the rod inserted in the flask. As the flask is heated a steady stream of air and vapor bubbles issues from the open space, thus providing nuclei for smooth boiling.

1.3 Double-distilled water - To distilled water in an all borosilicate-glass still add a crystal each of potassium permanganate and barium hydroxide and redistill. Use for reagent and biological sample solutions unless tests indicate that single-distilled water is satisfactory; single-distilled water is usually adequate for determinations on air sample.

1.4 Nitric Acid, Concentrated - Redistill in an all borosilicate-glass still the ACS reagent grade acid, 69.0% minimum, specific gravity 1.42. Use an electric heating jacket on the boiling flask to minimize danger of its breakage, and a boiling rod to prevent bumping, which otherwise would be severe. Discard the first 50 ml of distillate; this may be combined with the acid allowed to remain in the flask at the end of the distillation and used for washing glassware. The reagent is conveniently dispensed from a small automatic burette. No grease should be used on the stopcock.

1.5 Nitric Acid, 1:99 - Dilute 10 ml of the redistilled, concentrated acid to one liter with doubled-distilled water.

1.6 Ammonium Hydroxide, Concentrated - Distill in an all borosilicate-glass still 3 liters of the ACS reagent grade, 28.9% minimum specific gravity 0.8957 at 60°F, into 1.5 liters of double distilled water, contained in a 2-liter reagent bottle which is chilled in an ice bath. Continue the distillation until the bottle

is filled to the previously marked 2 liter level. Submerge the condenser tube deeply in the water in the receiver, but withdraw it before discontinuing the heat to avoid siphoning back the distillate. This reagent may be prepared more conveniently by tank ammonia, using a wash bottle to scrub the gas and a sintered glass delivery tube which extends to the bottom of the reagent bottle. The ammonia gas is absorbed in double-distilled water until the solution reaches the desired specific gravity.

1.7 Chloroform - Use a brand with a statement on the label that the chloroform passes the American Chemical Society test for suitability for use in dithizone gas column. In addition, each batch of chloroform should be purchased in glass containers only and should be tested as follows in the laboratory to make sure that it is satisfactory for preparing the dithizone solutions: add a minute quantity of dithizone to a portion of the chloroform in a test tube, shake gently, then stopper with a cork. The faint green color should be stable for one day. Our experience has indicated that the procedures for reclaiming used chloroform are tedious, time-consuming, sometimes unsuccessful, and no longer warranted in view of the commercial availability of acceptable reagent grades.

1.8 Extraction Dithizone - Dissolve 16 mg of diphenylthiocarbazone (dithizone), Eastman Kodak Co. No. 807, or equivalent, in one liter of chloroform. Store in a brown bottle in the refrigerator.

1.9 Standard Dithizone - Dissolve 8 mg of diphenythiocarbazone in one liter of chloroform. Store in a brown bottle in the refrigerator but allow to warm to room temperature before using. Age for at least one day, then standardize as described in the procedure. Restandardize every few months.

1.10 Sodium Citrate - Dissolve 125 g of the 2 $Na_3C_6H_5O_7.11\ H_2O$ salt in sufficient distilled water to provide a solution nearly 500 ml in volume. Adjust the pH to 9-10, using a very small quantity of phenol red indicator solution (strong red color) and fresh, pHydrion test paper to check the pH. Extract in a large separatory funnel with a 100 mg per liter solution of dithizone and finally with the extraction dithizone reagent until a green extract is obtained with the latter reagent. Add a small volume of lead-free citric acid until an orange color (pH 7) appears. Extract the excess dithizone repeatedly with chloroform until a colorless extract is obtained. Remove the last traces of chloroform.

1.11 Hydroxylamine Hydrochloride - Dissolve 20 g of the salt in distilled water to provide a volume of 65 ml. Add a few drops of m-cresol purple indicator, then add ammonia until the indicator turns yellow (pH 3). Add a sufficient quantity of a 4% solution of sodium diethyldithiocarbamate to combine with metallic impurities, then mix. After a few minutes extract repeatedly with chloroform until the excess carbamate reagent has been removed, as indicated by the absence of a yellow color in the final chloroform extract tested with a dilute copper solution. To the aqueous solution of the hydroxylamine hydrochloride add redistilled, 6N hydrochloric

acid until the indicator turns pink, and adjust the volume to 100 ml with double-distilled water.

1.12. Potassium Cyanide - (Danger! Highly poisonous!!) To 50 g of potassium cyanide in a beaker, add sufficient distilled water to make a sludge. Transfer the sludge to a separatory funnel previously marked to show 100 ml volume. Add a small amount of distilled water to the beaker and warm. (Potassium cyanide cools the solution as it dissolves, thus retarding the solution process.) Add this warm water to the separatory funnel but do not permit contents to exceed the 100-ml mark. Shake, then let stand until the contents come to room temperature. A practically saturated solution results.

1.12.1 Extract the lead by shaking repeatedly with portions of the extraction dithizone solution until the lead has been removed. Part of the dithizone dissolves in the aqueous phase but enough remains in the chloroform to color it. A green extract indicates that all the lead has been completely extracted. Most of the dithizone in the aqueous phase is then removed by repeated extractions with pure chloroform. Dilute the concentrated solution of potassium cyanide with double-distilled water to 500 ml. It should not be necessary to filter the solution, if the directions are followed precisely. Extraction is carried out before dilution because the higher pH of the dilute solution is less favorable.

1.12.2 (NOTE: A colorless solution usually results if above directions are followed. Occasionally aging results in a brown color or precipitate due to polymerization of hydrogen cyanide.

This does not interfere with use of the reagent if it is carefully decanted. Old potassium cyanide reagent may lose enough strength to cause insufficient complexing of large amounts of zinc.)

1.13 Ammonia-cyanide Mixture - Mix 200 ml of the purified 10% potassium cyanide reagent with 150 ml of distilled ammonium hydroxide (specific gravity 0.9, corresponding to 28.4% NH_3) and dilute to one liter with double-distilled water. If the measured specific gravity of the ammonia is not 0.9, use the equivalent volume as calculated from a table of specific gravity vs. percentage ammonia.

1.14 Standard Lead Solution - Dissolve 1.5984 g of pure lead nitrate in one liter of 1:99 nitric acid to provide a strong stock solution containing one mg Pb per ml. Pipet exactly 20 ml into a 500-ml volumetric flask and make to mark with 1:99 nitric acid to give a dilute stock solution containing 40 µg Pb per ml. (A standard lead solution, 10 µg Pb/ml, was stable in 1:99 nitric acid for three years.) Prepare a working solution, containing 2 µg Pb per ml, just before it is needed by pipetting 5 ml of the dilute stock solution into a 100-ml volumetric flask and making to mark with 1:99 nitric acid.

1.15 Phenol Red - 0.1% aqueous solution.

1.16 Ashing Aid Acid - Dissolve 25 g potassium sulfate in sufficient redistilled concentrated nitric acid to make 100 ml.

1.17 White Petrolatum - Supplied in a glass jar, for greasing stopcocks. To check on the purity, put a pinch of this petrolatum in a beaker, add a few milliliters of the standard

dithizone and swirl. If the dithizone is no longer green after a few minutes, the material is unsatisfactory for preparing stopcock

2. APPARATUS

2.1 A Beckman Model DU Spectrophotometer has been used in this laboratory since this instrument became available in the 1940's. However, the Beckman Model B and the Bausch and Lomb Spectronic 20 have been shown to give comparable results for blood lead determinations, provided that appropriate standardizations are conducted with each instrument. Other laboratories, whose results are reported in this paper, have presumably used a diversity of available photometers and spectrophotometers. In our laboratory, 22 x 175 mm matched test tubes are used in most spectrophotometric procedures employing the Model DU, which is fitted with a tube holder which does not interfere with the use of the instrument with regular cells. These same tubes are used in the Model B fitted with a test tube adaptor. A 3/4-inch tube, supplied by the manufacturer, is used in the Bausch and Lomb Spectronic 20.

2.2 Borosilicate glassware is used thoughout the procedures (except for vacutainers used for blood sampling). Ashing is performed in 125- or 250-ml Phillips beakers. Automatic burettes are used for the addition of most reagents. The extractions are conducted in the Squibb-type, 125-ml separatory funnels supported in electrically operated shakers provided with timer switches. The stopcocks of the separatory funnels are greased with white

petrolatum (purchased in a glass jar rather than in a metal can or tube) unless Teflon stopcocks, which require no grease, are used. All glassware should be reserved for trace analysis only to avoid possible gross contamination.

2.3 Soak all ashing beakers in a detergent solution (Alconox or Duponol is suitable) immediately after each usage to prevent any material from drying on the surfaces. Rinse 8-10 times with hot water and store in a dust-proof drawer or cabinet until needed. Use the following acid cleaning, lead-freeing techniques immediately before the next use of the glassware: Rinse the ashing beakers with a saturated solution of sodium dichromate in concentrated sulfuric acid. Leave a 1-2 ml portion in the beaker or flask (proportionally less in a small volumetric flask!). Add about 5-10 ml of warm tap water and allow the hot solution to flow over all inner surfaces to remove the last traces of grease. Rinse with three or four portions of cold tap water. Rinse with one portion of either concentrated or 1:1 nitric acid, as preferred. (This wash nitric acid may be used repeatedly until it loses its strength) Then rinse successively with three or four portions each of tap water, distilled and double-distilled water. Set the beakers upright on the bench and cover with a clean dust-case or a large piece of filter paper (or otherwise protect from dust). Under no circumstances is glassware turned upside down to drain on a towel or cheesecloth placed on a laboratory bench. Use an oven operating at 105 C if dry glassware is required.

2.4 Separatory funnels are rinsed with tap water immediately after use. If a high lead sample was present or if a visible precipitate remains on the inside, it is rinsed with a small portion of 1:1 wash nitric acid (which is discarded), followed by tap water. The stoppered funnels are stored in double-deck racks. Immediately before use, stopcocks are regreased if necessary. Then the funnels are rinsed with wash acid, four times with tap water, and four times with distilled water. Each rinse is accomplished by shaking with the stopper, then draining through the stopcock with two or three turns.

2.5 Spectrophotometer tubes are rinsed four times each with tap and distilled water immediately after use. They are placed upright in a large beaker and dried in an oven at 105 C, then stored under a dust-cover. Occasionally they are cleaned with dichromate-sulfuric acid and nitric acid as described above.

2.5.1 (NOTE: With this method of cleaning glassware we have never encountered cross-contamination from chromium, lead, or from any other trace element being determined routinely in this laboratory.)

3. ANALYTICAL PROCEDURE

3.1 Warm the sample ash (prepared as described in the following sections) with 2 ml of concentrated nitric acid for a few minutes, then add 25 ml of distilled water, heating on the hotplate until a clear solution is obtained.

3.2 Cool to room temperature. Add to the solution in the

beaker one ml of hydroxylamine hydrochloride, 4 ml of sodium citrate (10 ml is required for a urine sample), one drop of phenol red indicator, and titrate to a strong red color with concentrated ammonia reagent. Add a few drops excess of ammonia to make sure that the pH is between 9 and 10, using fresh pHydrion test paper to check the pH.

3.2.1 (NOTE: Phenol red has a weak orange-red color in strong acid, yellow in weak acid, and a red color in alkaline solution. Do not mistake the first color for that produced in alkaline medium!)

3.3 Transfer the sample quantitatively with double-distilled water rinsings to a 125-ml Squibb separatory funnel containing 5 ml of the potassium cyanide reagent.

3.4 Add 5 ml of the extraction dithizone and shake two minutes, after releasing the initial pressure by momentarily opening the stopcock of the inverted separatory funnel. Allow the chloroform layer to settle.

3.5 Draw off most of the extraction dithizone into a second funnel containing exactly 30 ml of 1:99 nitric acid.

3.6 Add a second 5-ml portion of extraction dithizone to the first funnel and shake as before. Allow the layers to separate and combine the extracts in the second funnel. Continue this process with fresh portions of extraction dithizone until the reagent remains green. A rough estimate of the lead present in the sample may be made on the basis of 20 µg for each cherry-red 5-ml extract portion.

3.7 Shake the second funnel for two minutes to transfer the lead to the 1:99 nitric acid layer. Allow the layers to separate. Discard the chloroform layer.

3.8 Shake the nitric acid solution with approximately 5 ml of reagent chloroform and let settle. Drain the settled chloroform through the stopcock bore as completely as possible without loss of the aqueous layer. Evaporate the last drop of chloroform clinging to the upper surface of the liquid.

3.8.1 (NOTE 1: Start a zero lead standard at the beginning of this step by placing 30 ml of 1:99 nitric acid in a separatory funnel. This zero lead standard will be used to set the spectrophotometer at zero absorbance for each series of samples being analyzed.)

3.8.2 (NOTE 2: If the quantity of lead estimated for any sample exceeds the 25 ug range of the colorimetric determination, pipet an appropriate aliquot of the nitric acid solution at the end of step 7 into a clean separatory funnel containing 5 ml 1:99 nitric acid to minimize errors caused by possible leakage of the stopcock, add sufficient additional 1:99 nitric acid to make 30 ml total volume, and continue with step 8.)

3.8.3 (NOTE 3: Start lead standards at this point if required. Add 5-ml portions of 1:99 nitric acid to each of four separatory funnels, then 2.5, 5.0, 7.5, and 12.5 ml of dilute standard lead solution (2 ug Pb/ml) from a burette, respectively to the separatory funnels, finally add the proper quantity of 1:99 nitric acid to make total volume 30 ml in each. Continue

with step 8.)

3.9 Add 6.0 ml of the ammonia-cyanide mixture, exactly 15.0 ml of the standard dithizone, and shake two minutes. Allow the layers to separate. Drain the chloroform layer containing the lead dithizonate into a clean, dry test tube, and cork the tube immediately.

3.10 Decant this solution carefully into a dry photometer tube leaving the water behind. If any water spots are visible in the optical light path, transfer again to another photometer tube.

3.11 Set the spectrophotometer at a wavelength of 510 nm.

3.12 Set the instrument at zero absorbance using the zero lead standard solution.

3.13 Read the absorbances of the samples and of the reagent blank.

3.14 Calculate the lead content of each by multiplying its absorbance by the standardization factor (which is the slope of the standardization plot in micrograms of lead per unit of absorbance.) Subtract the blank value from the gross lead content of each sample to obtain the net amount of lead expressed in micrograms.

4. SPECIAL MATERIALS FOR BLOOD SAMPLING

4.1 Vacutainers, Becton-Dickinson, No. 3208, 20-ml or 10-ml, complete with stoppers are used for blood sampling. The vacutainers are used repeatedly and are lead freed by the technique described previously. Blood is removed from the vacutainers and

the stoppers, after each use, by soaking in cold tap water. When no further visible trace of blood remains on these items, they are soaked overnight in the detergent solution. They are then rinsed repeatedly with hot tap water to remove alkaline materials. The vacutainers are then subjected to the chromic and nitric acid cleaning procedures. The stoppers are soaked for 20- to 30-minute periods, three times, with single distilled water and finally three times with double distilled water. The lead-freed vacutainers are dried at 105°C, fitted with clean stoppers, and stored in a drawer reserved for them. Layers of cheese-cloth are placed between the separate layers of vacutainers and the drawer is sealed with masking tape to prevent the admittance of any dust. They are evacuated just before shipment to the field. A vacuum tester is used both in the laboratory and field to test for loss of vacuum, which usually will not occur until stoppers have been used several times.

4.2 Vacuum Tester, High Frequency, Fisher Cat. No. 1-179, or equivalent.

4.3 Needles, Becton-Dickinson, Gauge 20, one and one-half inches in length, stainless steel, B-D No. 3200 N. As these needles are used repeatedly, check the tips for burrs by drawing them across the thumb nail. When burrs develop either discard the needles or file off the burrs. After filing, they must be re-cleaned. Vacutainer needles are soaked in a dilute detergent solution. A Becton-Dickinson Needle Cleaner, No. 3200 C is used to force detergent solution and subsequent rinse water through

the needles. Needles are subjected to thorough rinsing with distilled water. They are then placed in sterilubes and either autoclaved or heated for two hours in a drying oven operating at 180°C. The sterilubes are then fitted with rubber caps.

4.4 Sterilubes, Becton-Dickinson, No. 3260 L, with rubber caps.

4.5 Stillets for No. 3200 N needles, 20 Gauge, two and seven-eights inches long.

4.5.1 (These BD items are available from the Becton-Dickinson Company, Rutherford, New Jersey.)

5. COLLECTING AND ASHING BLOOD SAMPLES

5.1 Collect a 10-ml sample of whole blood using a lead-free vacutainer and a sterilized, stainless steel needle. In the laboratory, transfer the sample to a weighed, lead-free, 125-ml borosilicate Phillips beaker. No aliquoting of the blood is permissible, as most of the lead is present in the clot. Determine the weight of the blood sample to the nearest 0.01 gram, weighing rapidly to minimize evaporation. Add 2-ml of ashing aid acid reagent. Add 7 ml of concentrated nitric acid. (This ashing system permits the analyst to handle a large number of samples at a time as the blood clot breaks up readily and smoothly without bumping and without requiring the constant attention of the analyst.) Place the samples on a hotplate operating about 130 C and evaporate just to dryness. After the water is driven off in the initial evaporation to dryness, keep

the beaker covered with a lead-free watchglass to increase the reflux action of the concentrated acid. This serves to wash solids down from the sides to the hotter zone at the bottom, and also reduces the amount of acid needed. Cool the beaker briefly and then add successive portions of the nitric acid ranging from 2 ml down to 0.5 ml as the ashing proceeds. Do not remove the watchglass at any time but merely slide it back sufficiently to facilitate each new addition of the acid. Each time, as soon as the residue becomes light colored, heat on a 400 C hotplate just long enough to blacken the residue, then remove and cool the sample Throughout the remainder of the ashing procedure, alternately heat the sample with a few drops of nitric acid on the 130 C hotplate and bake the residue for the few minutes required to darken it on the 400 C hotplate. Finally, the residue will remain pale yellow or light brown (due to iron content) after heating for 5-10 minutes at the high temperature. Avoid excess baking at this stage, as the ash will become decomposed to a difficulty soluble form. It is now ready for solution and analysis. Report results as milligrams of lead per 100 grams of whole blood.

6. COLLECTING AND ASHING URINE SAMPLES

6.1 Use lead-free, narrow-mouthed, reagent-type, borosilicate, 250-ml bottles provided with standard taper glass stoppers to collect grab samples of urine. Add 2.0 ml of a 37% formalin solution as a preservative, shaking the bottle 10-12 times after the contribution of the urine to mix the specimen with the

formalin thoroughly.

6.1.1 Alternatively, urine specimens may be collected in 125-ml polyethylene bottles containing as a preservative 100-200 mg of EDTA (acid form) per bottle. This is convenient and economical for shipping samples considerable distances.

6.2 If the urine sample is clear and only one or two days old, measure a 50 ml portion into a graduated cylinder. However, if the sample is older, much of the lead may be in a sediment or on the walls of the bottle and must be dissolved before aliquoting. Transfer the entire specimen to a glass-stoppered graduated cylinder, record the volume, rinse the sample bottle with three small portions of concentrated nitric acid and add these rinsings to the cylinder. Mix thoroughly (Caution! Old samples may foam over.) Note the total volume and remove an aliquot equivalent to 50 ml of urine for analysis. Transfer the aliquot portion to a lead-free, 250-ml borosilicate Phillips beaker and add 5 ml of redistilled concentrated nitric acid. Evaporate just to dryness on a hotplate operating at about 130 C. Cool, add sufficient nitric acid to moisten the residue and cover the beaker with a lead-free watchglass. Heat on the 130 C hotplate and then alternately bake for a few minutes and digest with minimal amounts of nitric acid (as described in the ashing method for blood) until a white residue remains after the final heating for 5-ml minutes at the high temperature. The sample is now ready for solution and analysis. Report results as milligrams of lead per liter of urine.

7. PROCEDURE FOR AIR SAMPLES

7.1 It is convenient to wash out samples in electrostatic precipitator tubes with redistilled ethanol, using a special policeman made with a rubber disc cut to fit the tube like a piston, and transferring the sample through a short stem funnel into a 250-ml Phillips beaker; gently evaporate just do dryness. (Ethanol is helpful in removing greasy deposits on the walls of the precipitator tube. Some chemists may prefer hot 1 to 5% nitric acid to transfer the sample.) Transfer impinger samples or membrane filter samples to Phillips beakers. If little ash is expected (usually for impinger or membrane filter samples), add 2 ml of ashing aid acid reagent. (The presence of this salt will prevent loss of lead by glazing onto the surface of the beaker during ashing.) Otherwise add 1-2 ml nitric acid. Evaporate to dryness. Continue ashing with nitric acid at a moderate heat until organics are destroyed.

7.2 Dissolve the ash in 2 ml of concentrated nitric acid and distilled water and then transfer quantitatively to a 100-ml volumetric flask and make to mark. Pipet a suitable aliquot into a separatory funnel, containing about 5 ml of double-distilled water, add sufficient additional double-distilled water to make the total volume about 25 ml, and apply the Analytical Procedure, starting with step 2. In step 3, as the sample is already in a separatory funnel, merely add the cyanide. The amount of lead present in the aliquot may be estimated as described in Step 6. If it is less than a few micrograms, an additional aliquot may be

added to the same funnel, and the pH readjusted with ammonia. The extraction is then continued, and extracts combined with those collected previously in the second funnel. If the estimated amount of lead exceeds the range of the method (25 micrograms), take an aliquot as described in Note 2, step 8.

7.3 When calculating the results, make allowance for the total number of aliquots. If convenient, aliquot the reagent blank in the same manner so that the correction represents the same amounts of ashing and extraction reagents as are present in the sample. However, the blank correction is usually small for air samples. Report results as milligrams of lead per cubic meter of air.