NATIONAL BUREAU OF STANDARDS REPORT

10 674

EXPERIMENTAL EVALUATION OF ANALYTICAL METHODS FOR DETERMINING LEAD IN PAINT AND BUILDING MATERIALS



U.S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

NATIONAL BUREAU OF STANDARDS

The National Bureau of Standards ' was established by an act of Congress March 3, 1901. Today, in addition to serving as the Nation's central measurement laboratory, the Bureau is a principal focal point in the Federal Government for assuring maximum application of the physical and engineering sciences to the advancement of technology in industry and commerce. To this end the Bureau conducts research and provides central national services in four broad program areas. These are: (1) basic measurements and standards, (2) materials measurements and standards, (3) technological measurements and standards, and (4) transfer of technology.

The Bureau comprises the Institute for Basic Standards, the Institute for Materials Research, the Institute for Applied Technology, the Center for Radiation Research, the Center for Computer Sciences and Technology, and the Office for Information Programs.

THE INSTITUTE FOR BASIC STANDARDS provides the central basis within the United States of a complete and consistent system of physical measurement; coordinates that system with measurement systems of other nations; and furnishes essential services leading to accurate and uniform physical measurements throughout the Nation's scientific community, industry, and commerce. The Institute consists of an Office of Measurement Services and the following technical divisions:

Applied Mathematics—Electricity—Metrology—Mechanics—Heat—Atomic and Molecular Physics—Radio Physics ²—Radio Engineering ²—Time and Frequency ²—Astrophysics ²—Cryogenics.²

THE INSTITUTE FOR MATERIALS RESEARCH conducts materials research leading to improved methods of measurement standards, and data on the properties of well-characterized materials needed by industry, commerce, educational institutions, and Government; develops, produces, and distributes standard reference materials; relates the physical and chemical properties of materials to their behavior and their interaction with their environments; and provides advisory and research services to other Government agencies. The Institute consists of an Office of Standard Reference Materials and the following divisions:

Analytical Chemistry—Polymers—Metallurgy—Inorganic Materials—Physical Chemistry. **THE INSTITUTE FOR APPLIED TECHNOLOGY** provides technical services to promote the use of available technology and to facilitate technological innovation in industry and Government; cooperates with public and private organizations in the development of technological standards, and test methodologies; and provides advisory and research services for Federal, state, and local government agencies. The Institute consists of the following technical divisions and offices:

Engineering Standards—Weights and Measures — Invention and Innovation — Vehicle Systems Research—Product Evaluation—Building Research—Instrument Shops—Measurement Engineering—Electronic Technology—Technical Analysis.

THE CENTER FOR RADIATION RESEARCH engages in research, measurement, and application of radiation to the solution of Bureau mission problems and the problems of other agencies and institutions. The Center consists of the following divisions:

Reactor Radiation-Linac Radiation-Nuclear Radiation-Applied Radiation.

THE CENTER FOR COMPUTER SCIENCES AND TECHNOLOGY conducts research and provides technical services designed to aid Government agencies in the selection, acquisition, and effective use of automatic data processing equipment; and serves as the principal focus for the development of Federal standards for automatic data processing equipment, techniques, and computer languages. The Center consists of the following offices and divisions:

Information Processing Standards—Computer Information — Computer Services — Systems Development—Information Processing Technology.

THE OFFICE FOR INFORMATION PROGRAMS promotes optimum dissemination and accessibility of scientific information generated within NBS and other agencies of the Federal government; promotes the development of the National Standard Reference Data System and a system of information analysis centers dealing with the broader aspects of the National Measurement System, and provides appropriate services to ensure that the NBS staff has optimum accessibility to the scientific information of the world. The Office consists of the following organizational units:

Office of Standard Reference Data—Clearinghouse for Federal Scientific and Technical Information "—Office of Technical Information and Publications—Library—Office of Public Information—Office of International Relations.

¹ Headquarters and Laboratories at Gaithersburg, Maryland, unless otherwise noted; mailing address Washington, D.C. 20234. ² Located at Boulder, Colorado 80302.

³ Located at 5285 Port Royal Road, Springfield, Virginia 22151.

NATIONAL BUREAU OF STANDARDS REPORT

NBS PROJECT

NBS REPORT

3105452

January 6, 1972

10 674

EXPERIMENTAL EVALUATION OF ANALYTICAL METHODS FOR DETERMINING LEAD IN PAINT AND BUILDING MATERIALS

Milestone 2a

INTERIM REPORT OF PROGRESS October 1 - November 15, 1971

by

Bernard Greifer with contributions from Kurt Heinrich, Richard Durst, Oscar Menis and their staffs Analytical Chemistry Division Institute for Materials Research

> Lead Paint Poisoning Project Building Research Division Institute for Applied Technology National Bureau of Standards Washington, D. C. 20234

Sponsored by Department of Housing and Urban Development

NATIONAL BUREAU OF STAN for use within the Government. Be and review. For this reason, the p whole or in part, is not authorize Bureau of Standards, Washington, the Report has been specifically pr IMPORTANT NOTICE

Approved for public release by the director of the National Institute of Standards and Technology (NIST) on October 9, 2015 accounting documents intended bjected to additional evaluation sting of this Report, either in)ffice of the Director, National he Government agency for which es for its own use.



U.S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

LINE DISTURBANCE AND ADDRESS OF ADDRESS OF ADDRESS ADDRESS ADDRESS ADDRESS ADDRESS ADDRESS ADDRESS ADDRESS ADDR

ABSTRACT

This report describes the progress on Task 2, the experimental evaluation of analytical procedures for determining lead in paint, during the reporting period. Ten analytical procedures are being examined experimentally to evaluate their suitability for determining lead in paint and building materials at the one per cent level. The methods are (1) Polarography; (2) Potentiometry using a lead electrode; (3) Atomic absorption spectrometry using conventional solution aspiration of the sample; (4) Atomic absorption using a spiral coil sample atomizer; (5) Atomic absorption using a carbon rod atomizer; (6) X-ray fluorescence laboratory instrument; (7) X-ray fluorescence portable instruments; (8) Spectrophotometry using the dithizone procedure; (9) Emission spectroscopy laboratory instrument; and (10) Chemical spot tests.

Preliminary results indicate that field methods for determining lead in paint, such as X-ray fluorescence and chemical spot tests are qualitative and cannot distinguish reliably between less than one per cent or more than one per cent lead; however, both methods can indicate the presence of appreciable lead concentrations.

Favored laboratory methods for routine determinations are solutionaspirated atomic absorption spectrometry and X-ray fluorescence, using a sample dissolution procedure developed for dried paint chips. The dithizone spectrophotometric procedure continues to be favored as a referee method for reference use in determining lead in paint and building materials.

i

TABLE OF CONTENTS

1	TNEEDO		Page
1.	INTRO.	DUCTION .	·····
2.	PROGR	AM OUTLI	NE • • • • • • • • • • • • • • • • • • •
	2.1.	Objectiv	ve••••••
	2.2.	Program	Organization
		2.2.1.	Electrochemical Section • • • • • • • • • • • 3
		2.2.2.	Spectrographic Section
		2.2.3.	Coordination Chemistry Section 3
		2.2.4.	Microchemical Analysis Section · · · · · · 3
3.	ANAL Y	TICAL ME	THODOLOGY. 4
	3.1.	Paint Sa	amples
	3.2.	Electro	chemical Methods 4
		3.2.1.	Polarography
		3.2.2.	Results of Polarographic Analyses 6
		3.2.3.	Potentiometry (Ion-Selective Electrode) 8
			A. User Attributes of Potentiometry 8
			B. Equipment for Potentiometric Measurement 8
			C. Characterization of Electrode 9
			D. Measurement of Lead Concentration 10
		3.2.4.	Results of Potentiometric Analyses
		3.2.5.	Summary and Conclusions, Electrochemical Analysis
	3.3.	X-ray F	luorescence Methods
		3.3.1.	Laboratory Procedure
			A. Preparation of Samples
			B. Instrumentation and Procedure 13
			C. Results and Testing of Laboratory Method. 15
		3.3.2.	Portable X-Ray Analyzers
			A. Results of In Situ Experiments
			B. Comments on Wall Inspection
		3 3 3	User Attributes of X-Ray Eluorescence
		3 3 /	Summary and Conclusions X-Ray Fluorescence 23
		J.J. J.	Builling and Constability A Ray Figurescence 25

TABLE OF CONTENTS (Continued)

				Page
	3.4.	Atomic	Absorption Spectrometry	25
		3.4.1.	Solution Aspiration into Flame	25
			A. Dry Ashing of Sample	26
			B. Wet Digestion of Sample	26
			C. Results of Solution Aspirated A.A.S. • •	26
			D. Summary and Conclusions for Solution Aspirated A.A.S	28
		3.4.2.	Wire Coil Sample Holder	28
			A. General	28
			B. Instrumentation	29
			C. Operation and Results	31
			D. User Attributes	35
			E. Summary and Conclusions for Wire Coil Holder	36
		3.4.3.	Carbon Rod Flameless Sample Holder	36
			A. Results of Carbon Rod Determinations	36
	3.5.	Spectro	ophotometry (Dithizone Method)	37
		3.5.1.	Experimental	37
		3.5.2.	Results of Dithizone Determinations • • • •	37
		3.5.3.	Performance Attributes of Spectrophotometric Method	37
		3.5.4.	Summary and Conclusions, Spectrophotometry	39
	3.6.	Spot Te	ests for Qualitative Lead Detection \cdot \circ \cdot \cdot \cdot	39
		3.6.1.	Procedures	40
		3.6.2.	Results of Spot Tests • • • • • • • • • • • •	40
		3.6.3.	Summary and Conclusions of Spot Tests • • •	41
•	SUMMA	RY AND C	CONCLUSIONS • • • • • • • • • • • • • • • • • • •	42
	BIBLI	OGRAPHY.	• • • • • • • • • • • • • • • • • • • •	47
	APPEN	DIX Ato Lea	omic Absorption Spectrometric Determination of ad in Paint • • • • • • • • • • • • • • • • • • •	A-1

TABLE OF CONTENTS (Continued)

	Page	Ð
Figures	. X.R.F. Calibration with Addition of Absorbers 16	
	2. Portable X-Ray Analyzer Test, L-line Instrument 18	
	3. Portable X-Ray Analyzer Test, K-line Instrument • • 19	
	4. X.R.F. Signal vs. Lead Concentration in Per Cent and in mg/cm ²	
	5. X.R.F. Signal vs. Lead Concentration, Field Samples vs. Test Panels	
	6. General View, Wire Coil Sample Holder	
	7. Schematic Diagram, Wire Coil Sample Holder 32	
	8. Wire Coil Holder, A.A.S. Calibration for Lead 34	
Tables I.	Polarographic Analysis of Paints • • • • • • • • • • • • 7	
II.	X.R.F. Instrument Parameters	
III.	User Attributes of X-Ray Fluorescence	
IV.	A.A.S. Analysis of Dried Paint Chips	
V.	Comparison of A.A.S. and Dithizone Methods 27	
VI.	Spectrophotometric Determination of Lead (Dithizone) . 38	
VTT.	Summary of Status of Analytical Methods for Lead 43	

iv

EXPERIMENTAL EVALUATION OF ANALYTICAL METHODS

FOR

DETERMINING LEAD IN PAINT AND BUILDING MATERIALS

1. INTRODUCTION

It is generally accepted that the primary cause of lead poisoning of children is the ingestion of lead-bearing paint, putty, or other non-food items in their environment. The National Bureau of Standards program under the sponsorship of the Department of Housing and Urban Development is concerned with determining the nature and extent of the lead paint poisoning hazard, and with recommending steps for its elimination.

Potentially hazardous environments may be recognized through an analysis of the circumstances which favor lead poisoning, namely the presence of lead paint and the condition of the environment that makes it available to children who may eat it. The chemical determination of lead in paint and building materials is the final confirmation in the overall process for detection of lead paint hazards.

There are many procedures for the determination of lead, including standard methods for paint analysis used by paint and pigment manufacturers. Some of these methods may be suitable for the analysis of dried, aged paints which have different properties from fresh paints. They have been reviewed in a previous report on this program.^{1/} No information has been available up to now on the relative merits of these various analytical procedures as applied to the determination of lead in aged, crumbling, peeling, inhomogeneous paint chips or painted panels.

Because lead paint screening activities may involve the collection of analytical data on hundreds of thousands of samples by non-technical people in coordinated programs in many cities, the criteria for judging the merits of analytical procedures include consideration of attributes that pertain to the suitability of analytical procedures in the hands of non-technical people. These user attributes derive

from the involvement of building inspectors, health personnel, homeowners, and volunteers who may be called upon to carry out large numbers of lead paint determinations. They call attention to the human factors to be considered along with the accepted scientific principles of precision, accuracy, and sensitivity. The user attributes include cost, speed of analysis, sample requirements, sample treatment, skills required, instrument portability, safety, and aesthetics. They are discussed in a separate report.^{2/}

The performance attributes were used to make a tentative choice of analytical procedures worthy of further experimental evaluation and testing. This preliminary selection was based on the subjective judgment of personnel with extensive experience in related analyses, and is summarized in another report of this program. $\frac{3}{}$ The methods of choice include colorimetry (dithizone method), atomic absorption spectroscopy, X-ray fluorescence, polarography, potentiometry, and chemical spot tests.

This report summarizes the results of the first six weeks of experimental evaluation and testing of these methods.

2. PROGRAM OUTLINE

2.1. Objective

The experimental portion of the Analytical Chemistry Division's program has as its objective the testing and evaluation of analytical procedures for determining lead in paint, chosen from a consideration of their desirable performance characteristics. $\frac{3}{}$ The procedures under consideration have been listed above. At the completion of the experimental program it will be possible to recommend suitable methodologies for the determination of lead in paint.

2.2. Program Organization

The experimental responsibilities have been assigned to analytical chemistry specialists in a pairing of their skills with the chemical disciplines required for the proper investigation of the analytical

procedures. Experimental determinations include sensitivity, precision, accuracy, interferences, sample pre-treatment, possible modifications to standard procedures, and other parameters required for a thorough evaluation of the methods under test.

2.2.1. Electrochemical Section

This section is carrying out two electrochemical studies concerned with (1) determining lead using the solid state lead ion-selective electrode and a portable meter to read the total lead concentration, directly and (2) studying polarographic analysis with a view to its application as a portable system for field use. Both studies involve evaluation of interferences, dissolution procedures, and matrix effects.

2.2.2 Spectrographic Section

This section is investigating (1) theoretical and practical limitations of in situ analysis of wall paints by means of X-ray fluorescence techniques; (2) the usefulness and economic aspects of screening unprepared collected specimens from wall paints by means of X-ray fluorescence and emission spectrometry; and (3) the limitations of quantitative analysis of such specimens by spectrochemical means, particularly X-ray fluorescence analysis. The studies are being carried out on prepared paint samples, supported by actual specimens collected in the field.

2.2.3. Coordination Chemistry Section

This section is studying (1) the dithizone procedure as a possible referee method for backup of the instrumental methods; (2) rapid sampling procedures for atomic absorption spectroscopy; (3) anodic deposition as an electrogravimetric procedure for leadin-paint determination. The studies also involve evaluation of interferences, dissolution procedures, and matrix effects.

2.2.4. Microchemical Analysis Section

This section is studying the suitability of chemical spot tests for qualitative and semi-quantitative determination of lead in paints. The studies involve an evaluation of masking reactions,

color-forming reactions, and considerations of safety and aesthetics.

3. ANALYTICAL METHODOLOGY

3.1. Paint Samples

Lead determinations were carried out on three types of paint samples: (1) paint scraped off a living room window sash of a Philadelphia home which was being renovated; (2) liquid paints formulated to contain 1% lead, 20% lead, and no lead pigments, with titanium pigments making up the balance; and (3) painted panels containing one or more layers of 1% lead paint, with and without non-lead overcoat layers.

The liquid paints and painted panels were prepared by the Building Research Division. A dried, scraped paint sample from Philadelphia slum housing was removed from the polyethylene bag in which it had been sent, crushed with a mortar and pestle, and shaken for 30 seconds on #40 and #100 mesh sieves. Material retained on the #100 mesh sieve (-40, 100) and material passing the #100 mesh sieve (-100) were denoted "coarse" and "fine" fractions and placed in 2 oz. bottles for distribution to the cooperating Sections. 3.2. Electrochemical Methods

Two electrochemical methods of analysis were applied to the determination of lead in paint. One of the methods of previously proven success, polarography (with some supporting measurements by anodic stripping voltammetry) was studied with consideration toward simplification of the sample pretreatment steps and evaluation of interferences. The second method, potentiometry, using the lead ion-selective electrode, was evaluated as a possible sensor for the direct readout of lead in solution.

Both of these techniques require dissolution of the paint sample in order to free the lead for analysis. The dissolution procedure was therefore of major concern and received considerable attention.

3.2.1. Polarography

Polarography was examined as a possible procedure for determing lead in various paint samples. Two types of sample

dissolution processes were examined, wet ashing in various acids, and dry ashing plus wet ashing in acids. Lead determinations were made in aged dry paint; wet paint; and dry paint pigments.

<u>Perchloric acid - Nitric acid Digestion</u>: Immediately it must be pointed out that this procedure is potentially hazardous and should be used only by a trained chemist. Our purpose for using this technique was to obtain a reference value for lead in those samples where the lead levels were not known.

Aged paint samples from Philadelphia housing, No. 10504D (coarse) and No.10507D (fine) weighing 500 mg were wet ashed to dryness with 50 ml of 3:1 HNO_3 -HClO₄. The residue was taken up in 0.1M HNO_3 , filtered, and the resulting filtrate was analyzed polarographically. The remaining residue was analyzed for trace amounts of lead by first dissolving it in H_2SO_4 (apparently the residue was mostly titanium oxides), evaporating to dryness, extracting with 0.1M HCl, and using the technique of anodic stripping voltammetry (ASV) for analysis.

<u>Hydrochloric Acid Digestion</u>: Coarse 10504D and fine 10507D paint samples (500 mg) were wet ashed (boiled down to dryness) with 50 ml of conc. HCl and taken up with dilute (0.1M) HCl. The solutions were analyzed polarographically.

<u>Nitric Acid Digestion</u>: Coarse 10504D and fine 10507D paint samples (500 mg) were wet ashed (boiled down to dryness) with 50 ml of conc. HNO₃, then taken up with 0.1M HNO₃. The solutions were analyzed polarographically.

<u>Nitric Acid Digestion with HCl Uptake</u>: Paint samples coarse 10504D and fine 10507D (500 mg) were wet ashed with 50 ml conc. HNO_3 and taken up with 50 ml 0.1M HCl. The solutions were analyzed polarographically, and the insoluble residues were dissolved in H_2SO_4 and analyzed by anodic stripping voltammetry to determine whether any lead had not been extracted into solution.

Dry Ashing with Nitric Digestion and HCl Uptake: A sample of coarse 10504D paint was dry ashed in a muffle furnace at 500°C for 10 min., then wet ashed in HNO₃ and taken up with 0.1M HCl. The

solution was analyzed polarographically.

The dry ash, wet digestion dissolution procedure was used to dissolve samples of wet paints and white pigments, before determining lead polarographically. Liquid paints No. 1A containing 1% lead (nominal) and 4C containing 20% lead (nominal) were analyzed, as were two white pigments, No. S30 containing 2% lead (nominal), and S31 containing no lead.

3.2.2. Results of Polarographic Analyses:

Polarography was found to be suitable for determining lead in dried paint chips and pigments, and in liquid paint samples. The polarogram waves were reproducible in HCl supporting electrolyte, and no serious interferences were encountered. The results of some paint analyses are described in Table I.

<u>Results of HCl Digestion</u>: The chloride supporting electrolyte produced well defined, reversible polarographic waves, but the lead determinations of 3.3% and 4.0% for the coarse and fine solid paints were low.

<u>Results of HNO₃ Digestion:</u> The recorded polarographic waves were ill defined, and interpretation of the results was laborious. The lead content of the coarse and fine solid paint samples were 3.0% and 4.5% respectively, also a bit low.

Results of $HC10_4$ -HNO₃ Digestion: The polarograms were difficult to interpret because of the irreversibility of the polarographic waves. For this reason a chloride supporting electrolyte is recommended. The lead concentration in the coarse sample, 10504D was 4-5%, and the fine sample, 10507D was 6-7% lead. The undissolved residue contained about 10⁻⁷ Molar (less than 0.1 ppm) as determined by anodic stripping voltammetry of a sulfuric acid solution of the residue.

Results of HNO₃ Digestion with HCl Uptake: The polarographic waves were well defined and readily interpretable. The lead content for samples 10504D and 10507D was 3.5% and 4.5% respectively. Only a trace of lead was found in the insoluble residue by anodic stripping voltammetry.

TABLE I. Polarographic Analyses of Paints

Paint Designation	Expected Pb (%)	HClO ₄ -HNO3 Digestion	HC1 Digestion	HNO3 Digestion	HNO ₃ -HCl Digestion	Dry Ash HNO ₃ -HC1 Digestion
Coarse, aged scrapings (10504)	1	4-5%	3.3	3.0	3.5	4.6
Fine, aged scrapings (10507)	1	6-7%ª/	4.0	4.5	4.5	I
Liquid Paint (4C)	20.2					$15.5\frac{b}{2}$
Liquid Paint (4C)	20.2					17.5 <u>c</u> /
Liquid Paint (M)	6•0					66°0
Dry Pigment (S30)	1.6					1.25
Dry Pigment (S31)	0					0.08

<u>a</u>/Insoluble residue dissolved in H₂SO₄, lead determined to be 10⁻⁷M (<0.1 ppm) by anodic stripping voltammetry.

 \underline{b}/By polarography (based on total wet weight).

 \underline{c}/By anodic stripping voltammetry (based on total wet weight).

Results of Dry Ash with HNO₃ Digestion and HCl Uptake: The lead in the coarse 10504D aged paint sample after 10 minutes dry ashing at 500°C, boiling to dryness in conc. HNO₃, and dissolution in 0.1M HCl was determined to be 4.60%. The acid insoluble residue contained only a trace quantity of lead (by ASV). The liquid paint No. 4C (20% Pb nominal) contained 15.5% and 17.5% as determined by polarography and A.S.V. respectively; liquid paint No. M (0.9% Pb nominal) contained 0.99% lead; and white pigments S30 (2% Pb nominal) and S31 (no lead) contained 1.25% and 0.08% lead respectively.

3.2.3. Potentiometry (Ion-Selective Electrode)

A. User Attributes

Although more sensitive to possible interferences, lead ion-selective electrode measurements should prove to be highly sensitive (to 10^{-7} M or 0.02 ppm) yet requiring a minimum of skill for operation, i.e., operation is analogous to making pH measurement with a glass electrode. These sensors can make direct measurements precise to 1 or 2% in a laboratory environment (or 0.1% using a more laborious titration procedure) and 2 to 5% in the field.

As in the case of polarography, dissolution of the paint samples is the most time-consuming operation in the analysis procedure. In this case, the final take up of the sample is done with HNO_3 to avoid chlorocomplexes of the lead. The actual analysis time (not including sample preparation) using the standard addition technique is about 5 minutes.

The greatest advantages of using direct lead electrode measurements is the simplicity of the technique, the portability of the equipment, and the low cost (about \$800). In fact, since most laboratories have pH meters available to them, the only initial expense is the cost of the electrode (\$250), which should have a lifetime of one year.

B. Equipment for the Potentiometric Measurement of Lead in Paint

- (a) Solid-state lead ion-selective electrode
- (b) Double junction reference electrode; a 1M NaNO3 solution

is used as the electrolyte in the outer chamber of the reference electrode.

- (c) Specific ion meter
- C. <u>Characterization of Pb⁺⁺-Selective Electrode over</u> Optimum Concentration Range

the state of the state of the state of the state of the

- (a) The Nernstian response of the lead ion-selective electrode was tested over the concentration range from 10⁻¹ to 10⁻⁷ M Pb⁺² by making potentiometric measurements (absolute emf's) on standard solutions of Pb(NO₃)₂ adjusted to constant total ionic strength of 0.10 molar through the addition of NaNO₃ solution. These measurements result in a calibration curve for the electrode, in terms of absolute cell potential, E, vs. molar concentration of Pb⁺², which can be used for the determination of unknown concentrations of lead in test solutions derived from real samples of paint. More importantly, a knowledge of the slope of the calibration curve so obtained is paramount in the assessment of the error in the lead concentration measurement due to the electrode's deviation from ideal Nernstian behavior.
- (b) Preliminary measurements have been made to investigate pH effects (particularly in solutions of high hydrogen ion concentration) on the performance of the electrode. Since the dissolution of real paint samples for the potentiometric determination of lead necessitates the use of strong mineral acids to convert insoluble lead to its soluble divalent
 - form, levels of hydrogen ion concentration may be encountered during the course of a measurement on any given test solution that may seriously interfere with the determination of dissolved lead.
 - (c) Soluble forms of copper and mercury will interfere with the determination of lead; ionic forms of these two metals must therefore be absent from the solution being tested for Pb⁺². No systematic investigations have been made to

date regarding the nature of this interference or even the levels of either Cu^{++} or Hg^{++} that may be tolerated in solutions of Pb⁺².

D. The Measurement of Total Lead Ion Concentration

There are essentially two ways to determine unknown concentrations of lead, using the specific ion meter in conjunction with the lead ion-selective electrode.

- (a) Direct potentiometric measurements, using the absolute potential scale of the meter. In this mode of operation, emf readings obtained on an unknown solution of Pb⁺² are directly related to a calibration curve. Conditions of analysis relative to the unknown must be identical to the conditions of the measurement carried out on the appropriate standard solutions to produce a valid result.
- (b) Two measurement scales available with the specific ion meter permit standard addition techniques to be applied to the determination of lead in paint. Using either the logarithmic concentration scale or the known increment scale, the lead concentration of an unknown sample solution is obtained as a direct readout when a known volume increment (typically 1.0ml) of a standard lead solution is added to a known volume (typically 100ml) of an unknown lead solution. This mode of concentration measurement is the preferred one; it minimizes matrix errors in the measurement and is particularly attractive due to its simplicity.

3.2.4. Results of Potentiometric Analysis

A. <u>Determination of Lead in Mixed Paint Pigments of Known</u> Composition

To date a limited number of analyses has been performed on dry mixed pigment samples of known lead concentration. The analysis on Pigment #30 corresponding to 1.6 % lead (nominally) showed no apparent difficulty when lead was determined in samples of this particular matrix. The results indicated lead to be present to the extent of 2.8 per cent (average value of two determinations) based on the dry sample weight. <u>However</u>, Pigment #31 containing no lead (nominally) gave the same results, about 3% lead.

The readings appear to be the result of interferences and are invalid.

B. Determination of Lead in Dry Paint Samples

No results of analysis are avaliable at this time. The response of the solid state lead electrode was non-Nernstian, and the data obtained in solutions derived from dried, aged Philadelphia paint samples 10504 and 10507 were unsatisfactory. Interference effects are suspected, particularly electrode membrane poisoning by ions of copper and mercury and direct electrode interference by Fe (III).

3.2.5. Summary and Conclusions, Electrochemical Analysis

The investigation of sample dissolution procedures was a most significant part of the electrochemical study. Liquid paints, dried chips, or scrapings were ignited for only 10 minutes at 500°C, then digested in conc. HNO₃, to yield solutions suitable for a variety of analytical procedures. This is an improvement over classical digestion methods which call for heating in a muffle furnace for several hours or overnight to boil away interfering organic materials.

As a laboratory procedure, classical polarography can yield results both accurate (using standard addition calibration) and precise to about 1-5% of the true value. Except for periodic cleaning of the dropping mercury electrode, instrumental problems should be minimal. Safety considerations are significant from both the sample pretreatment steps, i.e., the use of acids and high temperatures, and in the handling of mercury. Operation requires a skilled technician in a laboratory environment.

Original equipment costs are approximately \$2K with additional operational costs for chemicals (acids, mercury) and sample tubes. Single sample analysis would require about 1 to 1-1/2 hours for sample preparation, measurement, and calculations. Concurrent operations on large numbers of samples would reduce the analysis time to about 5-10 minutes per sample.

Unexpectedly, the potentiometric results show clearly that much work remains to be done to make this method suitable for analyzing paint samples. The suspected poisoning of the solid state lead electrode by copper, mercury, and other heavy metal ions in the dried paint sample shows a need for investigations into complexation of these interfering metals in solution, before potentiometry can work reliably with the electrode system used. For this reason, potentiometry should <u>not</u> be considered satisfactory for lead determinations in paint, at its present state of development. No further investigation of this procedure is planned.

The polarographic results are satisfactory, and this method can be developed into a reliable procedure for either laboratory or field analysis, even to the inclusion of a direct reading system requiring a minimum of operational skill.

3.3. X-Ray Fluorescence Methods

3.2.1. Laboratory Procedure for Accurately Determining Lead in Paint

Experimental investigations of both laboratory methods and on-the-wall techniques have been carried out to examine at first hand their suitability for determining lead in dried paint films. This section describes the laboratory procedure, and the following section, 3.3.2 describes procedures using portable X-ray analyzers. A. Preparation of Samples:

Approximately 1 g of specimen is required; this allows for some loss in crushing and the possibility of running duplicate samples.

Paint compositions vary widely - the two extreme compositions, relative to X-ray fluorescence determination of lead, are ZnO-based paints and TiO₂-based paints. The lead $L\beta_1$ X-ray line measured in

this method (see Section B) is more highly absorbed in a ZnO matrix than in TiO₂, resulting in a reduced intensity for lead from the ZnO matrix. In order to reduce the differences in paint compositions to a common matrix, we add ZnO to all samples before measurement. This makes possible the use of a single calibration curve for all types of paint, without knowing their matrix a priori.

Cellulose is also added to the sample to aid efficient pulverization and mixing. Equal weights of cellulose (extender) and ZnO (absorber) are mixed and 3 g of the mix is used in each preparation together with 0.3 g of powdered paint sample. The extender and the absorber can be made up in advance as a ready-to-use mixture in 3 g preweighed units.

The preparation procedure for each sample is:

- 1. Crush paint chip sample
- 2. Weigh out 0.3 g of crushed sample
- Load 3.0 g of absorber-extender mix into polycarbonate mixing jar together with 5 polycarbonate mixing balls
- 4. Add 0.3 g crushed sample to mixing jar
- 5. Shake mixture in mixer-mill for 5 minutes
- 6. Transfer mixture to sample cup
- 7. Label sample cup
- B. Instrumentation and Procedure:

The instrument used in developing this method is a generalpurpose, single-channel X-ray fluorescence spectrometer. The parameters for the analysis are given in Table II. Utilization of a different spectrometer might cause need for revising portions of the electronic set-up.

Each sample cup is, in turn, loaded into the X-ray fluorescence spectrometer and a fixed-time (100 sec.) count is obtained for the PbL β_1 X-ray line. The lead concentration is obtained from the measured X-ray intensity and an empirical calibration curve. The calibration curve can be established by using standards which are prepared according to the procedure given in Section A, but where, instead of

TABLE II. X.R.F. Instrument Parameters

Parameter	Selection or Adjustment
Tube target	tungsten
Tube voltage	49 kV
Tube current	49 mA
Detector type	scintillation
Detector voltage	1000 V
Primary collimator	0.005" x 4"
Exit collimator	0.040 x 1 1/2"
Crystal	LiF 200, $2d = 4.027 A$
Wavelength, angle	0.9822 A PbL β_1 , 2 Θ = 28.24
Spectrometer path	air
PHA window	1.5 V - 10.0 V
Amplifier gain	adjusted to produce 3 V pulse

a paint chip, carefully weighed quantities of ZnO, TiO₂, and red lead powders are substituted.

C. Results and Testing of the Laboratory Method

In Figure 1, calibration curves are shown for a variety of paint compositions and absorber additions. These were obtained during testing to determine what addition of absorber to make. As can be seen, an addition of ZnO absorber (90% by wt.) to a TiO₂ paint chip sample produced a calibration curve which is within about 2% of that obtained on ZnO paints. With reasonable care, additional errors arising from random sources and sample preparation should not cause the total analytical error to exceed ±10% for lead at the 1% level. Compacting the powder into pellets showed no advantage, other than ease in storage, over analysis of loose powder.

The laboratory procedure has been tested and shown to be free of spectral line interferences, and it is insensitive to differences in the chemical form of the lead.

3.3.2. <u>Portable X-Ray Analyzers for Qualitative, In Situ</u> Screening of Paint Films for Lead

More than a half-dozen manufacturers are now marketing portable X-ray analyzers with potential application for field detection of lead. The present costs for these instruments center around five thousand dollars. They are relatively trouble-free, safe, and portable; their use is simple enough so that an operator can be trained in a few minutes - no sampling or sample preparation is required.

The main question concerning these devices is how reliably and accurately they can detect lead in paint on walls and other building materials. An answer to this question was sought by trying several of the instruments to gain first-hand information on their practical limitations. So far, limited tests have been made with three portable X-ray analyzers which were borrowed for short periods, varying from one to four days. Two of the units were based on detecting an L line of lead, while the third detected a K line.



A. Results of In-Situ Experiments

In the first L-line instrument tested, the detection limit for lead was determined to be about 1%, which is so high that further study of the unit did not seem warranted.

The detection limit for lead, using the second L-line instrument, was less than 0.5%. Figure 2 shows data obtained with this analyzer. From these data, one sees that underestimation of lead becomes acute even with only two overlayers of TiO₂-based paint. The situation would be much worse if the overlayers were ZnO-based paints.

Systems based on L-line measurement are <u>not</u> <u>satisfactory</u> in the presence of overlayers of non-leaded paint.

Turning to the K-line instrument, data for this device are given in Figure 3; note here the lessened effect of overlayers of non-leaded paint. Calibration is still a problem with this analyzer, as it was for the previous one, with both analyzers reading low. It is possible that if the manufacturer of these analyzers had better standard reference materials for calibration, these biases could be reduced.

We have no reason to believe that in situ tests with portable X-ray analyzers could be made more reliably than about $\pm 50\%$ of the amount present. In situ measurement is further limited in that if the paint thickness and density are not known, the results can only be given in terms of mg/cm², which is the actual unit of measurement for portable X-ray analyzers. The difficulties in the in situ procedures arise from several reasons, among which are the variability of paint thickness, texture, and sequence of leaded and non-leaded coats, differences in the substrate, and shape of the painted surface. These difficulties and limitations are discussed in the following section. B. Comments on Wall Inspection by X-Ray Fluorescence

The following comments on portable X-ray instrumentation for the detection of lead in painted walls and other objects are derived from the Internal Report of R.T. Graveson, K. Sommers, and F.C. Wilson to the Atomic Energy Commission.^{4/} Since this report was obtained in confidence, its contents should not be mentioned or used in publications.



'True Lead Concentration (mg/cm²)

Figure 2. Portable X-ray analyzer test, L-line instrument. Note the bias of all the in-situ measurements in the direction of underestimating the amount of lead present. The bias is worse when the lead paint is overcoated with non-lead paint.



Figure 3. Portable X-ray analyzer test, K-line instrument. The in-situ measurements underestimate the lead concentration but the bias is not as great as with the L-line instrument (Fig. 2). Two overcoat layers of non-lead paint do not cause an increase in the bias. The A.E.C. authors investigated four devices, three of which were based on excitation with Co 57, and detection with scintillation counters (using differential filters), while the fourth was based on a germanium detector, and excitation with Cd 109. The latter device is also the object of an article by Lauer et. al. $\frac{5}{}$

From these sources it becomes evident that portable devices such as described can detect lead concentrations of 1% or less in walls; however, it does not appear that these measurements can yield more than a gross estimation of the amount of lead present.

The principle of a portable X-ray fluorescence instrument involves flooding the wall cross-section in front of the device with hard X-rays and collecting the Pb K-radiation reemitted from any lead in the wall. Since the instrument does not know how thick the paint layer is, and since thicknesses of paint layers will vary, it obviously is impossible to estimate the lead content on any basis other than in terms of mg/cm². This is inherent in the technique. It is true that due to the scatter of measurements, and given a spread of thickness around an average, a set of measurements such as in the paper may correlate about as well with percentage of lead as with mg/cm². However, the measurement is of a cross-section, and an abnormal paint thickness would give a gross error. As far as the child is concerned, the mg/cm² units may be just as meaningful as per cent (see Figure 4).

However, the published results $\frac{4,5}{}$ also indicate the possibility of gross systematic errors. For instance, in reference 5/ the test panels prepared as standards give an average signal twice as high as the field samples (see Figure 5).

It appears also from the available measurements that hand painted panels are of varying paint thickness, and hence not reliable as standards. Of course, if in the field the wall paints differ by factors up to two, a measurement in a real situation would not have to be accurate to say, 10%. On the contrary, sprayed paint layers are said to be much more uniform; if paint panels are to be preferred to other standardization devices, spraying would thus be better than painting.





22

XRF Signal Intensity (Counts/min)

It is obvious that the use of lead K-radiation is far more advantageous than the use of L-radiation, since L-radiation is too soft to emerge from deeper layers. Excitation sources used include Co 57 (122 kV) and Cd 109 (88 kV). Detectors are usually scintillation type; one instrument uses a Ge detector. This gives a lower detection limit and a signal that is less susceptible to interferences, since the spectral resolution is higher than can be achieved with scintillation detectors, but the device is cumbersome and must be cooled with liquid N₂.

An important aspect is the effect of background on the detection of low levels of lead. Here, it appears that the design can considerably influence the detection limit. The problem is due to the variation of background with the wall material. The higher the atomic number of the wall material, the higher the background. Here again, the Ge detector would effect an improvement through its high sensitivity and resolution.

In summary, portable X-ray fluorescence instruments seem to have sufficient sensitivity (0.2 to 2 mg/cm² Pb), but not high accuracy. It is best tothink of them as screening devices. In this function they could certainly be very useful.

3.3.3 User Attributes of X-Ray Fluorescence Instruments

Table III lists the characteristics of laboratory and field X-ray fluorescence instruments. In the field method, consider a nondiffractive, radio-isotope excited X-ray emission instrument using a solid state detector. In the laboratory method consider a tube-excited X-ray emission instrument using a crystal spectrometer, with the sample prepared by grinding and the matrix adjusted as described above.

3.3.4. Summary and Conclusions, X-Ray Fluorescence

An economical and rapid laboratory method of determining lead in ground paint samples has been demonstrated. <u>Dissolving the paint</u> <u>sample is not required</u>; instead, the sample is pulverized and mixed with an extender and common matrix in a motorized mixer mill. Lead can be determined in a one gram sample of dry paint chips to an accuracy of ±10 per cent at the one per cent level, by a technician who can handle 80 samples per day.

Although the initial cost for laboratory X-ray fluorescent equipment is large, (between \$25K and \$100K) there seem to be several althernatives to purchasing equipment for local lead detection programs.

TABLE III. User Attributes of XRF Instruments

	Field Method	Laboratory Method
Portability	Good	Not portable
Skills Required	No lab experience	Lab experience reqd.
Sample Preparation	None required	Grinding, matrix adjustment,10/hr.
Automation	Not required	Good
Safety	Some radiation hazard	Some radiation hazard
Initial Cost	\$5 - 10K	\$25 - 100K
Operating Cost	Personnel, about 50¢/sample	Personnel, about \$1/sample
Destructive	No	Yes
Detection Limit	Less than 0.1%	Less than 0.01%
Accuracy	<u>+</u> 50%	<u>+</u> 5% to <u>+</u> 10%

These include the use of commercial X-ray laboratories, and using equipment in state agency and university laboratories. It may be possible to modify the laboratory method mentioned above so that less expensive portable X-ray analyzers can be used.

Considering all the difficulties in calibration, paint overlayers of unknown nature, texture, shape, and quantity factors, and differences in substrates from sample to sample, it appears that portable L line analyzers are of little value for field use; and that portable K line analyzers may often yield readings which are in error by ±50% of the amount of lead present. Thus, even the portable X-ray analyzers for detecting K radiation, which are enjoying great popularity in some lead screening programs, are only qualitative screening devices when measuring leaded paint on the wall.

For these reasons, portable X-ray fluorescence instruments should be considered as only qualitative indicators of the presence of lead in situ. However, an interesting possibility exists for improving the accuracy of on-site lead detection with portable X-ray analyzers by adapting the laboratory sample preparation method for on location use. This has not yet been tried, but it is reasonable to expect that results similar to those obtained in the laboratory may also be possible in the field.

3.4. Atomic Absorption Spectrometry

3.4.1. Solution Aspiration into Flame

In the past two years atomic absorption spectrometry has been established as the leading method for the determination of lead in paint and related building materials. The method is rapid, accurate, and precise with relatively few interferences. It is described in some detail in the Appendix.

Various types of commercial atomic absorption instrumentation are available. One company has an instrument which can operate on ac or a 12-V battery and weighs less than 60 pounds. This instrument is portable and sells at a cost of less than \$3,000. The cost of up-keep and repairs for this equipment is very low. Some workers have reported that no repairs were required over a two-year period of operation.

A. Dry Ashing of Sample $\frac{a}{}$

The sample (a chip or liquid paint) was dry ashed at 500°C for 1 hour. The ash was treated with nitric acid and heated to boiling. Then the solution was transferred to a volumetric flask and diluted to calibrated volume. The clear solution was nebulized into an airacetylene flame and the absorbance of lead measured at a wavelength of 2833 A by the atomic absorption spectrometer.

The elapsed time required for an analysis including dry ashing, dissolution and measurement was less than three hours. The analysis can be performed by a technician at the rate of 50 samples per day. B. Wet Digestion of Sample $\frac{a}{a}$

Transfer 0.5g of paint scrapings to 100-ml Teflon beaker. Add 10ml of HNO_3 and digest for 30 minutes. Add 5 ml of HF, 5 ml of HNO_3 and 10ml of $HCIO_4$ and evaporate to strong fumes of perchlorate, cool, and dilute to 25ml with water. Filter using Whatman No. 42 filter paper and transfer effluent to volumetric flask. Dilute flask to calibrated volume with water. Determine lead by atomic absorption spectrometry and check results by the standard addition method.

To check the residue for losses of lead, dissolve the residue in HNO_3 and H_2SO_4 and determine the lead by atomic absorption spectrometry.

C. <u>Results of Solution-Aspirated A.A.S. Analyses of Paint Scrapings</u> and Liquid Paints

Duplicate samples of aged paint scrapings from Philadelphia, No. 10505 (Coarse fraction) and 10508 (Fine fraction) were analyzed by atomic absorption spectrometry using the wet ashing procedure. Table IV presents the results of analyses. The wide variation in duplicate samples is thought to be caused by inhomogeneity of the sample. The residue from wet ashing was found to contain less than

 $[\]frac{a}{The}$ dry-ashing and wet ashing were carried out before the results of the sample dissolution experiments were available.

TABLE IV. A.A.S. Analysis of Dried Paint Chips

Sa	ample <u>a,b/</u>	Y.	<u>Pb, %</u>
10505	(Coarse)		2.62
10505	(Coarse)		1.11
10508	(Fine)		4.84
10508	(Fine)		3.21

TABLE V.	. Con	npariso	on of	A.A.S	S. and	Dithizo	one M	lethods
for	Aged	Paint	Chips	and	Fresh	Liquid	Pain	ts

		Pe	er Cent Lead
<u>Sample</u>	Lead <u>Expected</u>	AAS	Spectrophotometry
10505 (Coarse) <u>a,c</u> /	-	2.78	2.7
10508 (Fine) <u>a,c</u> /	-	7.25	7.2
Liquid paint, 4D	0	0.3 <u>d</u> /	Trace <u>d</u> /
Liquid paint, 4C	20 %	18.9 <u>d</u> /	19.9 <u>d</u> /

 $\frac{a}{b}$ Same as samples 10504 (Coarse) and 10507 (Fine). $\frac{b}{P}$ Paint chips wet-ashed. $\frac{c}{P}$ Paint chips dry-ashed. $\frac{d}{B}$ Based on wet-weight.

0.1 per cent of the lead in the paint.

Separate samples of the dried Philadelphia paint scrapingo, coarse and fine fractions, were dry ashed and the lead content determined both by atomic absorption spectrometry and by spectrophotometry (colorimetric Dithizone method). In addition, two liquid paint samples containing no lead and 20 per cent lead (from Building Research Division) were analyzed by both methods.

Table V presents the results of this method comparison.

There is good agreement between the Dithizone spectrophotometric method and atomic absorption spectrometry.

D. Summary and Conclusions for Solution-Aspirated A.A.S.

Atomic absorption spectrometry is capable of determining lead over the concentration range of 0.01 to 100 percent with a precision of better than 2 percent. Due to the high sensitivity of the method, only a few milligrams of sample are required for an analysis and a very minimum amount of sample preparation is needed. However, whenever sample heterogeneity is suspected, large samples may be used with aliquots taken for analysis.

There are relatively few chemical interferences in the determination of lead when an air-acetylene flame is used. A large excess (>5 mg/ml) of many cations will change the burning characteristics of the flame and produce a slight suppression. With an air-acetylene flame, no interference has been found with nitrate, perchlorate, sulfate or phosphate.

The use of hydrofluoric and perchloric acids for wet ashing is routine in steel industry laboratories and may be considered safe in the hands of well trained workers under close supervision. The dry/wet ashing procedure described in Section 3.2.1. probably can be used here.

3.4.2. <u>Wire Coil Sample Holder (Microliter Solutions</u>) A. General

The procedure described in this report was designed to permit the analysis of small volumes of sample of less than 1 to 10 microliters $(\mu 1)$, containing a total amount of several hundredths to several micrograms of lead. The matrix considered here was solutions of Pb

containing paints. Since the volume of analytical solution required is small, the procedure described should be of particular interest for the examination of specimens from sources where the volume of sample is critical.

In this procedure the sample solution is applied with a micropipet (10 μ 1) on a platinum-rhodium (13 percent) wire coil. The solution is first dried on the coil and then is introduced into a premixed acetylene-air flame where it is kept until the entire sample is volatilized (20/sec).

The radiation absorbed by the flame during this time interval is measured by a spectrometer provided with a photomultiplier, followed by a synchronous amplifier, and a recorder. A lead hollow cathode lamp and a lock-in chopper are placed on the optical axis of the spectrometer. The radiations are integrated during the entire process of evaporation and excitation of the sample from the platinum coil and the corresponding photo current is recorded.

The instrument is calibrated with solutions of known content of lead, dissolved in a matrix similar to that of the analytical samples, and applied to the platinum coil as described in the foregoing. B. Instrumentation

The instrumentation developed to excite the sample is illustrated in Figure 6, and consists of the platinum coil adapted at the extremity of an arm which can swing for about 90°, carrying the coil in and out of the flame. The flame used is a premixed acetylene-air flame produced with an induction burner. Before entering the flame, the platinum coil can be positioned over an electrical heater where the solution is dried.

The critical part of the instrumentation is the sample supporting coil. It is made from a 3-inch long and 0.030-inch thick wire coiled in a spiral with 4 turns (outer diameter of spiral 3/8 inch) which is silver brazed to a vertical brass rod at 1/8-inch distance from an end (diameter 1/8 inch, length 3/4 inch). The loop is made from a platinum-rhodium (13 percent) alloy which proved to withstand well





the temperature of the acetylene-air flame, and to remain free of contamination with sodium or potassium from the analytical samples even after many repeated usages. Attempts to use pure platinum demonstrated that the wire could readily melt in the flame, while iridium indicated a peculiar memory effect.

The shape and approximate size of the swinging arm which carries the platinum coil at an extremity is not critical and is illustrated in Figure 6 and Figure 7. It is made of aluminum with a stainless steel (316) head in which an appropriate slot is cut to accept the platinum coil with its brass rod.

The arm can swing for about 90° and is operated manually in its three positions: away from the flame to accept the sample, then over the electric heater to evaporate the solution, and finally, into the flame.

The premixed acetylene-air flame is produced here for convenience, simplicity, and economy, with a commercial induction burner. The resulting flame is of sufficient stability and its production requires only one gas under pressure, namely, the acetylene, since the stoichiometric amount of oxygen necessary for the combustion is drawn from the surrounding air by a venturi effect produced by the acetylene flow. Any other burners producing stoichiometric premixed acetylene-air flames of good stability and reproducibility can be substituted for this burner.

The electrical drier illustrated in Figure 6 is made from several turns of resistance wire (chromel A) 0.040-inch diameter and 0.414-ohm/foot. Sufficient heat is produced when the wire is supplied with 2.3v and 10 amp from an appropriate transformer. When the platinum coil carrying 10 μ l of sample solution is placed at 1/8 inch above the heater, the solution will evaporate in 60 seconds.

C. Operation and Results

The instrumentation described in the foregoing is assembled as shown in Figure 6 on the optical bench in front of the spectrometer slit and the image of the flame is projected in the usual manner, on the slit or on the dispersing element (prism or grating). It is essential that the entire volume of flame be included within the



Figure 7. Schematic Diagram of Swinging Arm and Platinum-Rhodium Coil Carrying the Sample. solid acceptance angle of the spectrometer used. The light chopper and hollow cathode are not seen on this figure.

The flame is ignited, and a volume of 10 μ l of sample solution is applied on the coil with the micropipet. The pipeting and transfer of the sample solution onto the coil is critical and requires the experience and attention common to micromeasuring techniques. The coil is moved over the electric heater by rotating the supporting arm, and held over the heater for 60 seconds.

The coil with the dried sample is then introduced into the flame by a rapid, but controlled, manual movement while the recorder is operating. It is essential that the recording is operating before the platinum coil is introduced into the flame. A recording time of 20 seconds was found to be necessary where 10 μ l of solution are applied to the platinum coil.

The following factors must be controlled to obtain good results:

The stoichiometric, premixed acetylene-air flame must be stable and reproducible.

The flame must be within the solid angle of the spectrometer.

The measurement of the sample volumes and their transfer to the platinum coil should be done in a quantitative manner.

The drying of the sample must be complete before it is introduced into the flame.

The platinum coil must be introduced always in the same position into the middle of the flame, some 1/8 to 1/4 inch above the blue cones.

The electronic and recording system must always be in operation before the introduction of the sample into the flame.

The integration time of 20 sec. is sufficient to completely evaporate the sample from the platinum coil and should be kept constant.

The instrument is calibrated by placing on the coil 10 μ l of standard solutions containing known amounts of lead, the resulting calibration curve being illustrated in Figure 8.

Under our instrumental conditions using the direct reading spectrometer described in NBS Technical Note 544 (1970), it was



solutions on wire coil sample holder.

found that 0.05 μ g of lead produced an absorption of 0.025.

Numerous determinations have been carried out using solutions containing lead in concentrations corresponding to those found in conventional paints. The results have shown that standard deviation not exceeding ±10 percent can be produced with the method and instrumentation described in this Report.

A detailed discussion of various microprocedures including a method similar to the one described here will be found in a previous work $\frac{6}{}$

D. User Attributes of A.A.S. with Wire Coil Sample Holder Cost of Equipment

The cost of the equipment described in Figure 6 is estimated at approximately \$250. This equipment can be adapted to the conventional atomic absorption spectrometers provided with a pen recorder.

Speed of Analysis (100 Samples per Day)

Sample weight and solubilization: 90 min. elapsed time Transfer to loop and measurement: 3 min. Calculation of results per sample: 2 min. Total 95 min.

Sample Pre-Treatment

Acid digestion; or Schöniger flask ashing.

Sample Required

Chip, painted panel, wet or dried paint. The procedure is destructive.

Portability

The entire instrument can be designed and built as a portable instrument. The approximate weight should not exceed 25 Kg. The power required to operate the instrument is 115v and 15 amp. a.c. 60 cps. The alignment is not critical.

Skill Required to Operate

Skilled technician.

Safety

The conventional wet-ashing procedure requires the handling of perchloric and nitric acids. Toxic fumes can be produced, and there is some danger of explosion.

E. Summary and Conclusions. A.A.S. with Wire Coil

The wire coil sample holder for atomic absorption spectrometric determination of lead in paint (after acid dissolution) is rapid, permitting a 5-minute turnaround time between samples. The procedure comprises a very inexpensive (\$250) accessory to atomic absorption instruments, and may be quite competitive with other methods of determining lead in paint.

3.4.3. Atomic Absorption Spectroscopy Using Carbon Rod Flameless Sample Holder

The carbon rod atomizer was evaluated for the determination of lead in (1) aqueous medium, and (2) directly on solid paint samples without dissolution. Seven replicate determinations were made of 0.002 μ g of Pb in solution using a Mini-Mossmann carbon rod. $\frac{7}{}$ The solid paint samples were analyzed on a West type of carbon rod, $\frac{8}{}$ after mixing with graphite for matrix correction.

A. Results of Carbon Rod Lead Determinations

The seven replicate determinations of 0.002 μ g of Pb in solution gave an absorption of 46.5 ± 1.0 per cent. From this and subsequent data the carbon rod atomizer was judged to be capable of determining Pb in aqueous solution with a relatively high degree of precision.

The solid samples containing 0.1 to 10 per cent Pb were mixed with graphite for direct combustion on the carbon rod. By using one mg of sample a calibration curve wasprepared. The calibration curve turned out to be non-linear which would indicate that the most optimum operation conditions had not been attained.

Samples of Philadelphia paint chips (10508) were analyzed directly, and mixed with graphite. Lead was determined only qualitatively. Additional work will be required before quantitative

results can be obtained with solid paint samples on the carbon rod flameless sample holder. Additional study is under way to evaluate the advantages and best procedure for this application.

3.5. Spectrophotometry: (Dithizone Method)

The dithizone method for lead is regarded as being precise and accurate enough to serve as a standard ASTM method, $\frac{9}{}$ yet is slow and time consuming, requiring the services of a skilled chemist. It was used on the dried, aged paint samples and the liquid paint samples to provide reference values for comparison with the results of the other procedures.

3.5.1. Experimental

The sample is weighed into an open 3" porcelain dish, placed in a cold muffle furnace, heated slowly to 500° C (over a period of 3-4 hours), and held at this temperature for one hour. The sample is cooled and weighed. Then, the lead is leached out of the ash with 2 ml H₂0 + 5 ml HNO₃ by refluxing for several hours in the covered porcelain dish (watch glass). A shorter time may be sufficient for this application. The solution is diluted with 40 ml H₂0 and warmed, then filtered into a volumetric flask and made up to volume.

The lead in an aliquot of the above solution is determined by the standard ASTM method. $\frac{9}{-}$

3.5.2. Results Dithizone Determinations of Lead in Paints

The results of eleven determinations of lead in paint samples are summarized in Table VI. The results are consistent with other information obtained on these samples.

3.5.3. <u>Performance Attributes of Spectrophotometric (Dithizone)</u> <u>Method</u>

A. General Considerations

1. Accurate, but time consuming method.

2. Expensive in labor alone; 8 samples per eight hour day.

3. Method trouble free when used by experienced chemist.

4. Proper precautions in handling chemicals must be observed.

			•
SAMPLE	DRY ASHING PROCEDURE (Time) (Temp C)	LEAD EXPECTED <mark>C</mark> / (%)	LEAD DETERMINED (%)
Coarse chips ⁴	1 hr. 500	-	2.7
Coarse chips <mark>a</mark> /	1 hr. 500	-	2.6
Coarse chips $\frac{a}{}$	12 hr. 500	-	2.6
Fine chips ^{b/}	1 hr. 500	-	7.1
Fine chips ^{b/}	1 hr. 500	-	7.0
Fine chips ^{b/}	12 hr. 500	-	7.3
Liquid paint 1A	12 hr. 600	1	0.89 <u>d</u> /
Liquid paint 1A	12 hr. 600	1	0.95 <u>d</u> /
Liquid paint 4C	12 hr. 600	20	21.4 ^d /
Liquid paint 4C	12 hr. 600	20	19.8 <u>d</u> /
Liquid paint 4C	12 hr. 600	20	18.9 <u>d</u> /
Liquid paint 4C	12 hr. 600	20	19.3 <u>d</u> /
Liquid paint 4D	12 hr. 600	None	Trace <u>d</u> /

TABLE VI. Spectrophotometric Determination of Lead in Paints (Dithizone)

a/Actual sample from Philadelphia housing: aged, dried paint off door sill, coarse sieved -40+100, No. 10505.

b/Actual sample as above, fine sieved -100, No. 10508.

c/Nominal values from Building Research Division.

d/Based on wet-weight of samples.

B. Scientific Performance

- Reliability: Method produces accurate, repeatable determinations. Care must be exercised in selecting lead free reagents, and in handling chloroform and cyanide solutions.
- Sensitivity: Suitable for determination of lead from 0.1% to 10% in paint. Interferences are bismuth, thallium, indium, and tin which are not ordinarily present in paint.
- C. User Attributes
- Costs: Analytical chemistry laboratory furnace capable of 500°C, spectrophotometer.
- 2. Speed of Analysis: 8 samples per eight hour day.
- 3. Sample Pre-Treatment: Dry ashing, wet chemical handling.
- 4. Sample Required: Chip or liquid paint; destructive.
- Portability: Regular analytical chemistry laboratory facilities needed.
- 6. Skills Required: Experienced analytical chemist.
- 7. Safety: Laboratory hoods required for fumes.
- Aesthetics: Odors present and poisonous chemicals used; however, this is a laboratory method.

3.5.4. Summary and Conclusions, Spectrophotometry

The method provides accurate determinations of lead in paint, as expected, but is not suitable for rapid, routine use because of the extensive wet chemical manipulations required to isolate lead from other metals present in the paint, and from the organic matrix.

Because of the relatively low cost of the instrumentation involved, it is possible that the dithizone method can be used as a backup for more sophisticated instrumental methods of analysis, to serve as a check on their continued calibration and proper performance. 3.6 Spot Tests for Qualitative Lead Detection

Spot tests may be the most simple, inexpensive, and generally useful methodology available for rapidly screening paint samples qualitatively and possibly semi-quantitatively for lead. Two spot

tests are receiving widespread attention in lead paint screening activities: (1) sodium sulfide solutions which give a black precipitate of lead sulfide on dried paint chips or painted surfaces $\frac{8,9}{}$ and (2) potassium chromate precipitation of yellow lead chromate on crushed paint chips. $\frac{10}{}$

In addition, blowpipe analysis has been suggested as a means of detecting lead in paint in a fashion analogous to the procedure used for ore analysis. $\frac{11,12}{}$ In this method, samples are burned in either an oxidizing or a reducing flame, with or without added fluxes, and colored combustion products are noted as being characteristic of the metals sought.

3.6.1. Procedures

Initial experiments were carried out on sodium sulfide and chromate spot tests, and on blowpipe reactions. The sodium sulfide solutions used were an 8% solution recommended by Sayre $\frac{8}{}$ and a 1% solution in NaOH suggested by Searle et al. $\frac{9}{}$ These solutions were carried into housing areas in Washington, D.C. and used to detect lead in paint chips scraped from walls. They were used also to detect the presence of one per cent lead carbonate in dry titanium oxide pigments formulated for the purpose.

Confirmatory experiments were made with a commercially available chromate spot test kit on paint chips known to contain a fairly high but unknown level of lead.

Blowpipe tests were carried out on lead-bearing paint chips on a charcoal block substrate. The torch used was a micro butane-oxygen torch instead of the classical blowpipe. Yellow combustion products on the charcoal would denote the presence of lead in the paint.

3.6.2. Results of Spot Tests

The sulfide solutions gave consistently positive reactions (black stains) on painted woodwork and scrapings from doors and window sills in housing known to contain lead. They did not detect one per cent lead in the dry titanium oxide pigments as a sharp color change, but gave a faint grey color instead of a strong black, due to the

excellent hiding power of titanium oxide pigment. This result indicates that paint chips with fresh fracture surfaces or scratches in paint films can give strong positive detections for lead through the exposure of highly leaded paint layers at the point of contact; but that the detections can be masked by the bulk of the non-leaded paint pigments if the scrapings are removed from the walls and ground up prior to testing.

Initial results with the chromate spot test kit gave good results except on some old, yellowed paint samples which did not yield a sharp, distinguishable yellow precipitate of lead chromate. Since the test kit method called for crushing the entire paint chip it is possible that non-lead paint layers masked the test through the sheer bulk of non-reacting materials. This test will be explored in more detail.

Blowpipe tests on paint chips caused them to burst into open flame if the torch came too close; it is probable that much lead was volatilized into the air at this point, which would constitute a health hazard for field testing. When the flame was held at some distance from the paint chip yellow deposits were observed on the charcoal block, as expected. This test method will be investigated further, also.

3.6.3. Summary and Conclusions of Spot Tests

The initial experiments were concerned with sulfide and chromate tests because of the ready availability of the reagents and the popularity of these tests for rapid screening. The tests worked well on edges and fracture surfaces of paint chips, less well on ground-up bulk samples of paint chips containing many non-leaded paint layers.

The initial results on blowpipe reactions indicated that open burning of the paint chips was to be avoided for optimum lead detection, and also for safety considerations.

The chemical spot tests and blowpipe reactions are in their early stages, and will be investigated further.

4. SUMMARY AND CONCLUSIONS

Ten analytical procedures are being examined examined experimentally to evaluate their suitability for determining lead in paint and building materials at the one per cent level. The methods are: (1) Polarography; (2) Potentiometry using a lead electrode; (3) Atomic Absorption Spectrometry using conventional solution aspiration of the sample; (4) Atomic Absorption using a spiral coil sample atomizer; (5) Atomic Absorption using a carbon rod atomizer; (6) X-Ray Fluorescence laboratory instrument; (7) X-Ray Fluorescence portable instruments; (8) Spectrophotometry using the Dithizone procedure; (9) Emission Spectroscopy laboratory instrument; and (10) Chemical Spot Tests. The results are summarized in Table VII.

Although comparative analyses were carried out on the same samples of paint scrapings (Philadelphia home, coarse and fine fractions) and on liquid paints containing no lead, one per cent lead, and twenty per cent lead, the main thrust was toward testing and evaluating the analytical methods rather than round robin sample analysis.

As a prelude to the studies on instruments analyzing samples in aqueous solution (No. 1, 2, 3, 4, 8 above) an investigation was made of methods for dissolving paint samples. Traditionally, two methods have been used: dry ashing in a muffle furnace at 500°C for several hours to overnight; and wet ashing, involving mixtures of acids, sometimes in explosive combination. A relatively rapid dissolution procedure for paint was developed involving 10 minutes dry ashing at 500°C followed by 10 minutes wet ashing in conc. nitric acid. For polarographic analysis the nitric acid solution is evaporated to dryness and the sample extracted into hydrochloric acid. This dissolution procedure and variations of it were used to dissolve paint samples prior to instrumental analysis.

1. <u>Polarography</u> was found to be suitable for determination of lead in paint. The polarographic waves were reproducible and no serious interferences were encountered. Except for periodic cleaning of the dropping mercury electrode, instrumental problems are minimal.

1					
		ANALYT	ICAL METHODOLOGY	SUITABILITY FOR QUANT. LEAD DETERMINATION	COMMENTS
L	1.	Polarog	çraphy	Yes	Method well characterized ^{a/}
	2.	Potenti	.ometry (Lead Electrode)	No	Electrode poisoned. Removal of interferences re- quires wet chemistry.
	°.	X-Ray F	luorescence (Lab)	Yes	Method well characterized
	4.	X-Ray F	luorescence (Portable)	No	Accuracy too low. Semi-quantitative for rough screening.
43	5.	A.A.S.	(Solution Aspiration)	Yes	Method well characterized ^a /
	• 9	A.A.S.	(Spiral Coil Atomizer)	Yes	Method requires additional development ^{a,b/}
	7.	A.A.S.	(Carbon Rod Atomizer)	Not Yet	Method requires additional development ^{C/}
	° °	Spectro	photometry (Dithizone)	Yes	Precise, accurate, long and tedious ^a /
	•6	Emissic	n Spectroscopy (Arc)	Yes	Semi-quantitative
	10.	Spot Te	sts	Not Yet	Requires color standards
4	<u>a</u> /Sa HN in de	umple dis VO ₃ for 1 L concd H sired vo	solution no problem, now 0 min., cool, filter. F ACL, dilute to desired vo	 Heat in muffle or polarographic lume. For A.A.S. 	furnace 10 min. at 500 C, cool, heat in conc. analysis, take HNO3 solution to dryness, pick up and Spectrophotometry, dilute HNO ₃ solution to
	n∂/ <u>q</u>	ıantitati	on requires careful cali	bration of coil's	drop-holding capacity.
	<u>c</u> /St pa	cudies re int via	quired on the effect of heating in furnace takes	residual organics too long at 500 (on A.A.S. signal. Removal of all organics from C, loses Pb at higher temperatures.

TABLE VII. Summary of Status of Analytical Methods for Lead

This is a relatively slow laboratory method and requires an extra step of sample extraction into HCl, but large numbers of samples could be handled at a rate of 15 minutes per sample.

2. <u>Potentiometry</u> using a solid-state specific ion electrode for lead gave considerable difficulty. The electrode response was non-Nernstian, and readings in solutions of actual paint samples had little relation to the known or expected lead levels. Potentiometry is not suitable for lead paint analysis in its present state of development.

3. <u>X-Ray Fluorescence</u> laboratory instrumentation gave good lead determinations in solid paint samples mixed with zinc oxide and cellulose for matrix background correction. Calibration curves correcting for titanium oxide and zinc oxide contributions to the paint signal were obtained, of a quality assuring a total analytical error of about ±10 per cent for lead determination at the one per cent level. The method was found to be free of spectral line interferences and was insensitive to the chemical form of the lead. X-ray fluorescence offers a rapid and reliable laboratory determination of lead in ground-up dried paint samples.

4. <u>X-Ray Fluorescence</u> portable instruments using the L X-ray spectral line were not suitable for detecting lead paints in situ when they were covered by one or more layers of non-leaded paint. Portable instruments using the K X-ray spectral line detected lead on painted panels even through two layers of titanium-based paint. However, the accuracy of the determinations was no better than $\pm 50\%$ of the amount of lead present, and the calibration curve was not linear. At the 1.0 mg/cm² level, a K-line instrument with $\pm 50\%$ accuracy would have to read below 0.4 mg/cm² or above 1.8 mg/cm² to define a clear "safe" or "hazard" condition. Moreover, a reading of 1.6 mg/cm² pb on the wall. This uncertainty in instrument readings makes the method only qualitatively valuable for the detection of <u>large</u> lead concentrations, in situ.

5. <u>Atomic Absorption Spectrometry</u> has been established as one of the leading methods for determining lead in paint during the past two years. The conventional procedure which analyzes aqueous solutions

aspirated directly into the flame is accurate, rapid, and has relatively few interferences. The combination dry-ash/wet-ash procedure works well for preparing solid paint samples in a form that can be analyzed easily to a precision of ±2 per cent. The turnaround time for a start-to-finish analysis is three hours, and a technician can accomodate up to 50 samples per day.

6. <u>Atomic Absorption Spectrometry using a Wire Coil Sample Holder</u> is a novel development of National Bureau of Standards research. The procedure permits a 1-10 microliter sample of acid-dissolved paint to be analyzed for lead in a time of 5 minutes. The procedure has attractive possibilities for rapid determinations of lead in paint, in view of its low cost (\$250 accessory for A.A.S.), but it requires some additional development work to assure quantitative results for solutions of aged paints.

7. Atomic Absorption Spectrometry using Carbon Rod Sample Holder gave rapid and reproducible calibration curves with lead nitrate solutions indicating the atomic absorption instrument with carbon rod atomizer is capable of determining lead in aqueous solution to a high degree of precision. Solid samples mixed with graphite gave a nonlinear calibration curve indicating that the operating conditions had not been optimized. Direct analysis of dried paint chips on the graphite rod sample holder gave strong positive indications of lead, but the quantitative values were not reportable due to the non-linear calibration. Some additional work is required before reliable quantitative results can be obtained with solid paint samples.

8. <u>Spectrophotometry using the colorimetric Dithizone procedure</u> was examined as a possible referee method for lead determinations in paint. The procedure, reported as a standard ASTM method, $\frac{9}{-}$ is slow and time consuming and requires the services of a highly skilled chemist, but it is regarded as a precise and accurate analytical method for lead. Eight samples can be accomodated per day, possibly more if the stringent dry-ashing specifications can be modified to accept the more rapid dry-ash/wet-ash paint dissolution procedure described in

the text. The dithizone procedure employs hazardous (cyanide) reagents and is strictly a laboratory procedure.

9. <u>Emission Spectroscopy</u> is a convenient qualitative and semiquantitative method for determining lead in dried paint samples. While no experimental work was carried out on emission spectroscopy per se, the instrument was used to provide a rough backup on the sample analyses. Qualitatively emission spectroscopy provides a rapid survey of all detectable elements in a sample; and semiquantitatively it can determine the presence of lead as being a major constituent, or being present in moderate amount, in low or trace amount, or as being undetectable.

10. <u>Chemical Spot Tests</u> are currently in vogue for lead paint screening, and with good cause for the method ^{is} simple, inexpensive, and requires no technical training for proper use. Two tests and a blowpipe reaction gave good qualitative detections of lead in paint. Fresh fracture surfaces of paint chips, and scratches in painted surfaces gave more pronounced lead detections than entire paint chips which were ground up to average the lead content throughout the entire paint sample, because the non-lead pigments, TiO₂ principally, masked the color change by dint of their good hiding power as pigments. Spot tests and blowpipe reactions are excellent qualitative screening aids; more work is required on development of color standards before they can be made quantitative.

BIBLIOGRAPHY

- "Report on Literature Review, Surveys, and Conferences, Lead Paint Poisoning Hazard Detection Methods," Analytical Chemistry Division Milestone Report 1(a), October 1, 1971.
- 2. "Performance Attributes for Analytical Methodology for Lead Based Paint," Analytical Chemistry Division Milestone Report 1(b), October 1, 1971.
- "Report on Lead Based Paint Detection Methods Chosen for Evaluation," Analytical Chemistry Division Milestone Report 1(c), October 1, 1971.
- "X-Ray Fluorescence Analyzers for Leaded Paint Measurements,"
 R. T. Graveson, K. Sommers, and F. C. Wilson, Internal Report to
 U.S. Atomic Energy Commission, Health and Safety Laboratory, April, 1971.
- 5. "X-Ray Fluorescence Detection of Lead in Wall Paint," G. R. Laurer,
 T. J. Kneip, R. E. Albert, and F. S. Kent, Science, <u>172</u>, 466 (1971).
- "Flame Spectroscopy," R. Mavrodineanu and H. Boiteux, Wiley, New York, (1965), pp. 121-123.
- 7. M. D. Amos, Amer. Laboratory, (August 1970), pg. 33.
- 8. T. S. West and Y. K. Williams, Anal. Chim. Acta. <u>45</u>, 27 (1969).
- 9. "Lead by Dithizone Method," A.S.T.M. Part 32, (1968) pg. 203.
- 10. "Spot Test for Detection of Lead in Paint," J. W. Sayre and
 D. J. Wilson, Pediatrics <u>46</u>, 783, (1970).
- 11. "Determination of Lead in Paint Scrapings by Atomic Absorption Spectrometry," B. Searle, W. Chan, C. Jensen, and B. Davidow, Atomic Absorption Newsletter 8, 126, (1969).

- 12. "Scott's Standard Methods of Chemical Analysis," Sixth Edition, N. H. Furman, Ed., D. Van Nostrand, N. Y. (1962), Vol. I, Page 556.
- "Manual of Determinative Mineralogy," G. J. Brush, 16th edition revised, Wiley, New York, (1907), pp. 87-154.
- 14. "Dana's Mannual of Mineralogy," C. S. Hurlhut, Wiley, New York, (1941), pp. 95-130.

Appendix A. Determination of Lead in Paint by Atomic Absorption Spectrometry

Scope

This atomic absorption method is applicable to the determination of 0.5 to 100μ g of Pb/ml of aqueous solution. The calibration curve is linear over this concentration range; however, a scale expansion factor of ten is required for the concentration range of 0.5 to 10μ g/ml.

There are relatively few chemical interferences in the determination of lead when an air-acetylene flame is used. A large excess (>5 mg/ml) of many cations will change the burning characteristics of the flame and produce a slight suppression. With an air-acetylene flame, no interference has been found with nitrate, perchlorate, sulfate or phosphate.

Principle

Atomic absorption spectrometry is based on the measurement of the absorption of resonance radiation by free atoms in the gaseous state, i.e., of spectral lines corresponding to the transition of atoms between the ground and excited states.⁽¹⁾ For analytical purposes the resonance lines at 2170 and 2833 A are generally used. While the line at 2170 A gives twice the sensitivity as the line at 2833 A, it is prone to more spectral interferences.

Status

This method has been developed for the determination of micro and/or macro amounts of lead in paint and building material using either a single or double beam atomic absorption spectrometer.

The resonance line of lead at 2833 A was chosen because fewer interferences are encountered at this wavelength. The resonance radiation is

A-1

produced with a lead hollow-cathode neon-filled lamp. A hollow-cathode lamp filled with argon produces less resonance radiation and the argon line at 2175 A can interfere with the lead resonance line at 2170 A.

Atomic vapor of the analyte is produced by nebulizing the sample into a premixed burner system using a stoichiometric air-acetylene flame. The type of burner head will depend upon the optical system and concentration of matrix ions. Generally, the three-slot burner (Boling) will provide the optimum conditions for samples with a high solid content.

When samples contain less than 0.005 percent lead, it is necessary to remove the lead from the matrix. Ammonium pyrrolidine dithiocarbamate (APDC) form a stable complex with lead at a pH of 2-3 and can be extracted into MIBK. However, caution must be exercised in using APDC since many other ions will be extracted under the same conditions. The organic solvent is introduced into the nebulizer-burner and the absorption of lead measured. When organic solutions are used, a lead calibration curve is prepared under the same operating conditions as the unknowns. Reagents

Use distilled and/or deionized water in the preparation of the reagent and throughout the procedure.

1. Standard stock solution of lead, 10.00 mg per ml. Dissolve 1.000g of Pb (NBS-SRM-59e) in 10 ml of HNO_3 and dilute to 100 ml with water. Prepare more dilute standard solutions from this stock solution as required by the appropriate dilution with 0.15 <u>M</u> HNO_3 .

2. All other reagents are ACS grade or better.

A-2

Sampling

Transfer a 0.1 to 1g test portion to a 100-ml Teflon beaker. Add 10 ml of HNO_3 , and 5 ml of HF. Digest on a hot plate for 30 minutes. Cool, add 5 ml of HNO_3 and 10 ml of $HClO_4$ and evaporate to moist dryness. Add 5 ml of HNO_3 and warm. Dilute to 25 ml with water and filter to remove insoluble residue. Wash residue with three 15-ml portions of 0.05M HNO_3 . Transfer solution to 100-ml volumetric flask and dilute to calibrated volume.

Preparation of Calibration Curve

Transfer 2-, 5-, 10-, 15- and 20-ml portions of the standard solution that contains 100μ g of Pb per ml to 100-ml volumetric flasks. Add 1 ml of HNO₃ and dilute to calibrated volume with water.

Insert the lead hollow-cathode lamp into the atomic absorption instrument. Adjust the lamp current to its optimum value. Adjust the wavelength of the monochromator to read 2833 A. After the hollow-cathode lamp has become stabilized, then optimize all parameters for lead measurements using an air-acetylene flame with a Boling burner. Aspirate water for at least 10 minutes to allow the burner head temperature to stabilize before final optimization of flame conditions and wavelength settings.

Nebulize into the flame standard solution that contains 2-, 5-, 10-, 15 and 20-µg of Pb/ml. Nebulize blank solution (0.15<u>M</u> HNO₃) after each standard solution. Record absorbance values for each standard solution and blank solution. Repeat the series of standard solutions until the absorbance readings agree within 0.5 percent. Prepare a calibration curve using a least square fit.

```
A-3
```

Analysis of Samples

Transfer duplicate aliquots of the sample that contain 50 to $100 \mu g$ to 10-ml volumetric flasks, A and B. To flask B, transfer an aliquot of a standard that contains $50 \mu g$ of Pb and dilute both solutions to volume. Nebulize the unknown solutions (A & B) into the flame and measure the absorbance of lead. Repeat the calibration curve before and after the unknown solutions. Then determine the unknown concentration from the calibration curve. Check the recoveries of lead by the standard addition method.⁽²⁾

Results

S

Seven samples of paint ranging from 0.1 to 10 percent lead were analyzed by the proposed method. In every case the spiked solutions were completely recovered and the spread in duplicate determination was less than two percent. The same series of samples was determined by polarography. The results of the two methods are as follows:

ample No.	Pb, S	<u>//</u>
	Polar.	AAS
1	0.11	0.12
2	4.18	4.57
3	0.34	0.40
4	0.48	0.54
5	9.63	9.53
6	0.44	0.43
7	0.13	0.15

References

- "Flame Emission and Atomic Absorption Spectrometry," J. A. Dean and T. C. Rains, eds., Vol. 1, Dekker, New York, (1970).
- "Analytical Flame Spectroscopy," (R. Mavrodineanu, ed.), O. Menis and T. C. Rains, Macmillan, London, (1971), pp. 74-75.



