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NATIONAL BUREAU OF STANDARDS REPORT

10 649

REPORT ON LITERATURE REVIEW, SURVEYS, AND CONFERENCES LEAD PAINT POISONING HAZARD DETECTION METHODS

NBS

U.S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

NATIONAL BUREAU OF STANDARDS

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[1] Headquarters and Laboratories at Gaithersburg, Maryland, unless otherwise noted; mailing address Washington, D.C. 20234.

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REPORT ON LITERATURE REVIEW, SURVEYS, AND CONFERENCES LEAD PAINT POISONING HAZARD DETECTION METHODS

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Report To

Lead Paint Poisoning Project
Building Research Division
Institute for Applied Technology
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NATIONAL BUREAU OF STANDARDS

ABSTRACT

A selective listing of analytical methods for the qualitative and quantitative determination of lead in paint and other building materials has been assembled, as a result of a literature review and referral to analytical chemists, instrument manufacturers, and housing inspection personnel in cities having active lead paint analysis programs. Ninety references are listed.

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REPORT ON LITERATURE REVIEW, SURVEYS, AND CONFERENCES LEAD PAINT POISONING HAZARD DETECTION METHODS

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 methodologies for its elimination.

The localization of potentially hazardous environments may be made through an analysis of the circumstances which favor lead poisoning: (a) the presence of susceptible children who may actively seek and eat non-food items, and (b) the presence of lead paint and the condition of the environment that makes it available to those children. The chemical determination of lead in paint and building materials becomes the final step in the overall process of lead paint hazard detection.

There are many procedures for the determination of lead. Some of these methods may be suitable for the analysis of aged paint chips. No information has been available up to now on the relative merits of the various methods for lead analysis as applied to aged, crumbling, peeling, inhomogeneous dried paint chips or painted panels. Municipalities that are faced with a pressing need for information and direction on lead paint analysis[1/] rely on the advertising literature and on the endorsement of the instrument manufacturers, or undertake expensive evaluation programs of their own, without an adequate awareness of work that others have done.

They discover that lead determinations carried out in one city using one method may not agree with lead determinations by other procedures in the same or different cities. It is clear that assistance is required to establish guidelines for the evaluation and application of lead detection methods.

2. OBJECTIVE

The overall objective of the Analytical Chemistry Division's effort on the Lead Paint Poisoning Project is the identification, evaluation, and recommendation of methodologies for determining lead in paint and building materials at the one per cent concentration level. The program is divided into three tasks, each with sub-objectives that relate to specific goals that must be met to attain the overall program objective. These tasks are: Task (1); to review methods for lead analysis and recommend the most promising procedures for direct experimental verification; Task (2); the experimental evaluation of laboratory and field methods for analyzing lead in paint; and Task (3); preparation of standard reference or research materials for calibrating the analytical methods.[2/]

Task (1) itself is divided into three parts. These are: Task (1a): A review of the state-of-the-art of methods for analysis of lead in paint; Task (1b): The identification of performance attributes[3/] for the evaluation and comparison of the various analytical methods; and Task (1c): The preliminary choice of methods[4/] that deserve further experimental study under Task (2) of the program, using the information developed under Tasks (1a) and (1b).

This report is a summary of the results of Task (1a) and is a review of analytical methods for lead that either have been used for the analysis of dried paint films or paint chips, or show promise for that capability.

3. SCOPE OF LITERATURE SEARCH

The literature on lead analysis is very extensive. Therefore, a critical selection of items for review was made on the basis of two considerations: (1) the need for methods that can be used by municipalities for rapid mass screening of dwellings in the field and (2) the need for the methods that are sufficiently precise to be used in support of legal actions by municipalities. Analytical methods that are too slow to process the large anticipated sample loads (e.g., isotope dilution mass spectroscopy), or methods that require an unusually large capital investmant (e.g., photon excitation using a linear accelerator) were not referenced except to indicate the existence of those techniques.

This review contains bibliographic information from library sources, a computer-assisted literature search, conversations with chemists involved with lead paint analyses in cities with active lead poisoning programs, conversations with chemists involved in the evaluation of analytical instruments, and talks with colleagues at the National Bureau of Standards.

This survey includes references to all of the analytical methods found for lead in paint and in some cases for other materials such as atmospheric particulates where the methods could be envisaged as suitable for lead in paint. Some judgment was made however, as to the depth to which individual analytical methodologies were investigated, in accordance with the objective of gathering information selectively and critically.

Only a limited review was made of two areas of test methodology: (1) quality control methods for fresh paints and pigments for which the samples dissolve easily and have minimal interferences from other metals and (2) methods probably unavailable to municipalities such as radioactive methods.

3.1. Literature Abstracted

References were selected primarily from the recent literature on the assumption that the state-of-the-art could best be described by reference to the most advanced techniques. Chemical Abstracts, Analytical Abstracts, and Spectrochimica Acta, however, were reviewed back to 1907, 1954, and 1939 respectively. The other journals were examined only as far back as five to ten years. The journals abstracted were:

Chemical Abstracts
Analytical Abstracts
Analytical Chemistry
Analytica Chimica Acta
The Analyst
Spectrochimica Acta
Talanta
Chemical Titles

In addition, texts, reference books and ASTM Standard Methods were reviewed.

3.2. Computer-Assisted Search

The National Library of Medicine's MEDLARS Search Unit gave references to analytical methods in a search of the literature on lead poisoning. MEDLARS is stored with references to Index Medicus for the current year and two preceding years. It is strongly oriented toward medical literature.

3.3. Public Health Laboratories

Visits and telephone conversations between personnel of the NBS Lead Paint Project and personnel of public health laboratories, hospitals, and housing departments in the District of Columbia, Baltimore, Chicago, New York, Philadelphia, and New Haven were an important part of the information-gathering process. Information was obtained on analytical methods preferred by these and other cities, in their lead paint screening programs.[1/]

3.4. Miscellaneous Sources

Unpublished information was received from the Atomic Energy Commission which evaluated commercial instruments for one particular analytical method (as opposed to a comparison of methods which is the goal of this investigation).[5/] Descriptive literature from instrument manufacturers, while admittedly biased, also provided useful data.

4. CLASSIFICATION OF ANALYTICAL METHODS

Analytical methods are ordinarily classified to be either instrumental or wet chemical methods. Such a clear differentiation may not be possible in the consideration of techniques for the analysis of lead in aged, dried paint samples that contain 20 or 30 layers of different paints. These may require considerable wet chemical manipulation before arriving at a form suitable for instrumental readout. Such materials may be difficult to get into solution and may contain considerable quantities of other interfering metals. Keeping in mind that the instrumental methods themselves may include wet chemical sample pre-treatment, it becomes possible to classify the analytical regimes in the usual manner, that is in terms of the detection and measuring systems: spectrophotometry, electrochemistry, gravimetry, titrimetry, and so on.

5. COLLECTIONS AND GENERAL METHODS

The American Society for Testing and Materials[6/] lists gravimetric and titrimetric methods for determining lead in paints and pigments. ASTM D215-68 covers chemical analysis of white linseed oil paints, ASTM D1301-55 covers white lead pigments, ASTM D49-63 covers dry red lead, ASTM D2742-68 analyzes tribasic lead phosphosilicate pigment, and ASTM D2374-68 covers lead in paint driers. The reservations about the value of methods for fresh paints and pigments apply to these procedures.

Scott's Standard Methods[7/] lists separations, gravimetric methods (precipitations as sulfate, molybdate, chromate), electrolytic determinations, titrimetric methods (ferrocyanide, permanganate, molybdate, chromate, chromate-iodide reactions), colorimetric methods (dithizone, sulfide), and methods for white lead and red lead pigments.

Jacobs[8/] reviews methods for lead as an industrial inorganic poison listing polarography, titrimetry, and other methods. Field tests and detection are covered by tetrahydroxyquinone and potassium copper lead hexanitrite tests. Determinations are by lead sulfide precipitation, lead chromate precipitation, estimation with s-diphenylcarbazide or by iodide-thiosulfate titration.

A standard method for lead in food is given by the Association of Official Analytical Chemists (AOAC)[9/] which calls for ashing, separation of lead either as the dithizone complex or as sulfide, followed by colorimetric determination in comparator tubes or with a spectrophotometer. The problems of interferences and sample preparation are treated extensively. Lees[10/] offers a standard method for lead in food which includes sulfuric acid digestion, citric acid and KCN complexing, extraction with dithizone in chloroform, further treatment with sulfuric-nitric acid, overnight standing in ethanol, filtration, washing, dissolution in ammonium acetate, complexation with KCN, precipitation with freshly prepared sodium sulfide solution. Quantitation is made by comparison with a freshly prepared lead control.

Wilson and Wilson[11/] describe a classical method of lead analysis: gravimetric determination as the sulfate or dichromate; titrimetric determination as ammonium lead acetate against standard molybdate solution using tannic acid as indicator.

These general methods for lead do not consider aged paint films specifically, so their sample preparation schemes are either too simple (fresh paint pigment) or too complicated (foods) for practical application in their present form. Their usefulness lies in their value as a starting point for possible experimental work to derive shortened but still effective sample preparation procedures.

Gettens[12/] described the identification of lead white in the materials of paintings, using microchemical identification, and instrumental methods including emission spectrometry, X-Ray diffraction, neutron activation, X-Ray fluorescence, and X-Radiography. He described the differentiation between old and modern lead white by analysis of the natural radioactivity of lead.

In a review article, Christian[13/] summarized the analysis of lead in clinical samples. After destruction of organic matter by dry ashing or wet digestion, the analyses can be carried out by spectrophotometry, atomic absorption spectroscopy, polarography, neutron activation, and ion-selective electrodes. This and other references to lead analysis in biological materials may not always be applicable to the lead in paint problem because (1) sample preparation must be totally different, and (2) the clinical methods are called upon to determine lead to considerably lower orders of magnitude than are here required. Clinical methods are required to measure 40 μg/ml of blood lead (measuring 100 μg/5 ml blood to ± 10 μg) whereas for lead paint analyses 5 mg may be analyzed in a 500 mg sample to ± 0.5 mg. Only clinical methods that can be used to detect high concentrations of lead in paint will be of value, since it would be unreasonable to dilute milligram lead samples to microgram concentrations. The listing of clinical methods, therefore, will be limited.

6. SPECTROPHOTOMETRIC PROCEDURES

6.1. General

All spectrophotometric procedures for lead in paint or other organic matrices require that the sample first be ashed. Wet ashing is preferred when the highest accuracy is required. Dry ashing is used primarily for convenience and frequently yields low results because of losses of lead by volatilization.

The most frequently used spectrophotometric method for the determination of lead employs a dithizone extraction from a weakly ammoniacal solution in which cyanide is used as a masking agent.[14/] A purportedly simpler method hss been suggested by Dagnall et al[15/] in which lead is isolated as PbI_2 and then determined with 4-(2-pyridylazo)-resorcinol. Both of these methods are relatively complicated and, for our purpose, appear useful only as laboratory referee methods.

In the British Standards Institute method[16/] for 0.2 to 2% lead in dried paint films, the sample is dry ashed, the ash is extracted with acid and the Pb is determined with diethyldithiocarbamate. This reaction is subject to interferences and can undoubtedly be made more selective by using one of the carbamate derivatives in combination with a chelate exchange reaction using Cu^{+2}. The interference of mercury, for example, should be readily eliminated by this additional step. An equally simple method which may have a direct application to the lead-in-paint problem is the one developed by Glasner and Avinur.[17/] This is an ultraviolet procedure in which Pb is determined as $PbCl_4^{=}$.

The two procedures suggested by Hoffman[18,19/] come closer than any to a field method. In the first[18/], acid-soaked or EDTA-soaked filter paper is laid directly on the paint sample and the lead extracted is subsequently eluted and determined turbidimetrically as PbS. This is, at best, only a semi-quantitative method. In a later modification[19/]

the sample containing 0.1-0.3 mg Pb is ashed, the ash is extracted with nitric acid and lead is again determined turbidimetrically as PbS in a cyanide medium.

Finally, spectrophotometric titration procedures in general appear to merit further study. Two especially interesting ones are the EDTA-Xylenol Orange titration[20,21,22] and a Variamine Blue procedure which is carried out in a water-acetone medium.[23]

All sample preparation in the determination of airborne lead is eliminated by Groffman and Wood[24] who collected up to 0.8 mg Pb per cubic meter on a filter, and dissolved it in a $HNO_3 + H_2O_2$ solution in 5 minutes. The lead determination was carried out colorimetrically with dithizone, using lead standards for comparison.

6.2. Atomic Absorption

Atomic absorption spectroscopy is a well established method for the determination of lead in various materials. The method is rapid, and accuracy and precision are easily within the ± 10% range at the one percent lead concentration being observed. There are few interferences in the determination of lead by this procedure, and a minimum amount of sample preparation is required because of the selectivity of the determination.

In common with other chemical methods and subject to the same considerations of lengthy procedures (though less so), the samples are dry ashed, then dissolved in a mixture of $HNO_3 + HF + HClO_4$; or, they can be subjected to a wet oxidation procedure using the same acid mixtures.

Some workers have reported lead losses with the dry ashing techniques unless controls are carefully maintained. In general, wet oxidation is preferred for sample dissolution.

Searle et al[25/] determined lead in paint scrapings by atomic absorption by ashing at 500°C for 1-hour, dissolving the ash in nitric acid and aspirating directly into the instrument flame. Lead was determined at 283.3 nm to a standard deviation of 0.05% at the 2% concentration level. The use of atomic absorption to analyze for lead was described by Chakrabarti, Robinson, and West [26/] who eliminated interferences of anions with EDTA, found no cation interferences, and determined lead at 217.0 nm. In the reverse of normal procedure, they atomized the sample with hydrogen, aspirating into an oxy-hydrogen flame.

Amos et al[27/] have described a new carbon rod atomizer, a flameless sample holder which vaporizes the sample with a pulse of electric current. The carbon rod sample holder is described for the determination of 0.005 μg lead per ml of blood or urine using microliter size drops of solution. If this technique is suitable for the analysis of solid samples it holds promise of simplifying or completely eliminating sample preparation.

Eider[28/] determined multielement organometallic compounds in paint and vinyl additives by atomic absorption spectroscopy without prior chemical separations. Accuracy greater than 1% and precision equal to wet chemistry were claimed. Price[29/] has summarized the application of atomic absorption to the Paint, Oil, and Color Industry, describing the theory, apparatus, procedure, and scope of the method. Nineteen elements were examined in aequous or non-aqueous solution by comparing the spectral absorption with that of a suitable standard solution. The method as described suffers from the same disadvantages already mentioned: pigments must be dissolved in acids.

The use of atomic absorption for lead determinations is well documented for a variety of materials. Lead has been determined in glass and ceramic frit,[30/] airborne particulates,[31/] silicate rocks,[32/] in gasoline,[33/] and in blood and urine.[34/] If sample preparation can be simplified or eliminated, atomic absorption spectroscopy can be a valuable method for the rapid analysis of paint samples.

6.3. Atomic Fluorescence

Atomic fluorescence spectroscopy is closely related to atomic absorption except that the flame in A.F.S. is viewed at right angles to the incident light beam to examine the stimulated fluorescence radiation, while in A.A.S. it is viewed in-line to examine the absorption of the transmitted beam. No references were found to atomic fluorescence determinations of lead in paint. All lead studies appeared to have been carried out on "knowns."

Winefordner[35/] described lead determinations to 0.6 μg/ml using a continuum light source, and to 0.02 μg/ml using a line radiation source at a wavelength of 2833-4056 A. In a review article Winefordner and Elser[36/] compared atomic absorption and atomic fluorescence results for lead: absolute detection limits for lead (in nanograms), sample in aspirated flame, 2 ng for A.A., 2 ng for A.F. Sample in graphite cell, 0.02 ng for A.A., 0.01 ng for A.F., at wavelengths of 2833 and 4058 A.

Browner, Dagnall, and West[37/] determined that 30 cations and anions in 100-fold excess did not interfere with lead determinations by atomic fluorescence and that only Al interfered. A "detection limit" of 0.01 µg/ml of Pb was obtained by measurement of the direct-line fluorescence at 4058 A.

6.4. Fluorometric Techniques

No references to the fluorometric analyses of lead in paint were found, even though fluorometry is a very sensitive and selective technique for the determination of inorganic and organic species. Pringsheim and Vogel[38/] reported in 1940 that lead fluoresces in solution and may be determined analytically by this property. Fluorescence is due not to lead ions but rather to the complex of lead with chloride ions, probably $PbCl_4^=$. Lead levels of 200-2,000 ppm could be determined in this manner. Bhatnagar and Forster[39/] measured the luminescence of metal oxinates and found comparable sensitivity (200 ppm) for the determination of lead as lead oxinate. Goto[40/] also reported qualitative lead analyses in which 0.25 µg of lead reacted with potassium iodide and pyridine or with morin to produce a strongly fluorescing precipitate. Recently, Kirkbright[41/] et al studied the fluorescence of many elements including lead in many media at -196°C, and found that about one ppm lead could be analyzed in HCl. However, Bi, CrVI, CuII, FeIII, MoVI, TlI, V(V), ascorbic acid and metabisulfite interfered at concentrations fifty-fold in excess.

It is quite possible that one of Goto's methods or dyes can be used to determine the presence of lead in the field by only sample dissolution and chemical addition. Under ultraviolet light one would have a fluorescent spot test; but the addition of a fluorometer could result in a quantitative measurement.

7. SPECTROGRAPHIC PROCEDURES

7.1. X-Ray Methods

X-Ray emission (also called X-Ray fluorescence) and absorption have had extensive application in the industrial laboratory for more than 20 years. A general overview of the principles of the method and an indication of the range of application was given by Liebhafsky.[42/] Other useful background information can be found in Carr-Brion's review of X-Ray fluorescence analysis[43/] and current trends in X-Ray fluorescenee are described by Birks.[44/] A good review of X-Ray emission analyzers using radioisotopes has been published by Rhodes.[45/]

McGinness, Scott, and Mortensen[46/] have reported laboratory methods for X-Ray emission analyses of paint films, including the determination of lead. They obtained agreement within about 6% for Pb in alkyd resins. Heinrich[47/] has presented a rapid, semiquantitative X-Ray fluorescence method which can be carried out for Pb in paint chip samples. Accuracy of ± 10% can be obtained.

Solid state, non-diffractive type X-Ray analyzers are especially appropriate for screening wall paints, in situ, for lead. Their good energy resolution characteristics help increase sensitivity and minimize line interferences. Laurer, Kneip, Albert, and Kent[48/] reported their work along these lines on detection of lead in wall paint. Frankel and Aitken[49/] reviewed recent solid state detector technology and non-diffractive X-Ray emission spectroscopy. They mentioned the determination of lead in a masterpiece painting.

Graveson, Sommers, and Wilson[50/] and Graveson[51-54/] have evaluated commercial X-Ray fluorescence instruments suitable for the field measurement of lead in paint. The information was obtained through personal contact with the Atomic Energy Commission and may be unavailable to the public at this time.

Gallagher[55/] has described portable X-Ray fluorescence spectrometers for rapid ore analysis using Pu-238 or Co-57 isotopes to activate lead and give detections, within one minute, down to about 0.5% (weight) limit. Momoki[56/] presented a dilution method for lead in liquid paints for children's toys. An X-Ray fluorescence determination of 0.4-7.0% by weight takes about ten minutes.

Several brochures from manufacturers of solid state nondiffractive X-Ray instruments suitable for field use including one model which operates at any angle[57-59/] described the in-situ measurement of lead in paint.

No references to X-Ray absorption or X-Ray diffraction methods were encountered for lead in paint.

7.2. Optical Emission Methods

Emission spectrochemical methods for the quantitative determination of lead at the one per cent level are used on a routine basis by commercial laboratories. Lead is determined in a variety of materials by this method but specific literature references for the determination of lead in paint have not been found.

Methods for the determination of lead in various other materials are described in the literature.[60/] The procedures are well known and the lead analyses would be rapid and inexpensive but only semiquantitative.

Optical emission would be a good first method to use on an unknown paint sample.

8. ELECTROCHEMICAL PROCEDURES

Eight papers dealing with the electrochemical analysis of lead in paint have been found. Although polarography has been used predominantly in the past, the lack of references to potentiometric methods should not preclude consideration of the use of an ion-selective electrode for lead if it performs well.

All of the electrochemical methods of analysis require prior dissolution of the paint sample which limits the in-field applicability of these techniques. If a simple and rapid dissolution procedure is found, the polarographic method may be made portable, simple and inexpensive.

8.1. Polarography

Abraham and Huffman[61/] have described a polarographic method for 0.04-59% lead in paint pigments using instrumentation assembled at a cost of $45 (exclusive of the galvanometer) using hydrochloric acid digestion of the pigment. Kondratova and Petrashen[62/] determined lead in enamel paint by igniting the sample in a muffle furnace at 500° C followed by igniting the ash for 15-20 min. The ash was dissolved in nitric acid and the lead determined by an electrolytic method. McCallum[63/] studied the leaching rate of antifouling marine paints with a single sweep cathode ray polarograph. Panels coated with the paints were analyzed for lead and other elements after being immersed in sea water for 24 hours. Khalifa and Abdallah[64/] described a "simple, rapid, and reliable" new potentiometric procedure involving the back titration of excess EDTA with Hg(II) using silver amalgam as the indicator electrode. Lead was measured in pigments and extenders in the presence of calcium, magnesium, or barium pigments. An anonymous German reference[65/] described polarographic methods for analyzing paint pigments for lead as Pb(II) in acetic acid - ammonium acetate buffer solution. Baltes and Wiertz[66/] analyzed lead chromate pigments for Pb(II) and CrO_4^{-2} by dissolving the pigments in aqueous KOH and diluting aliquots with a buffer solution containing ammonium chloride, ammonium citrate, and NaOH in equimolar proportions. The polarograms were determined with a dropping mercury electrode. Berger and Cadoff[67/] described the polarographic analysis of lead in white paint pigments in acetic acid - ammonium acetate buffer. Comparison with gravimetric methods showed a 0.5% average relative difference.

8.2. Potentiometry

The availability of liquid ion-exchange lead-selective electrodes,[68/] and the recent development of solid-state lead-selective electrodes may provide a simple, low-cost technique for the determination of lead in paint. This sensor is analogous in operation to the glass pH electrode and can determine lead over a concentration range from 10^{-1} to 10^{-5} M. (10^{-1} M is 2% lead by weight). Although monovalent metal ions interfere to varying degrees, procedures for their elimination probably can be developed. The most likely analytical procedure would involve sample dissolution, addition of ionic strength buffer and masking agents, dilution, and electrode measurement.

Although the use of ion-selective electrodes has not been reported for lead in paint, the successful application of this new tool would provide a very convenient method for such determinations.

8.3. Electrolytic Deposition

The American Society for Testing and Materials lists an electrolytic method for dried paint film in its standard method D:2088-68.[69] The paint film is softened with a suitable solvent (acetone), dried to constant weight, and ashed; the ash is digested in nitric acid and the clear filtrate is diluted, buffered, and electrolyzed onto weighed platinum gauze electrodes. The precision is claimed to be 0.03% about the one per cent (weight) lead level.

The National Paint, Varnish, and Lacquer Association recommends that lead in paint may be determined at the one per cent level by dry ashing the paint in a muffle furnace, and determining lead in the soluble portion by an electroanalytical method involving weighing of platinum gauze electrodes.[70]

9. WET CHEMISTRY

Although wet chemical manipulations such as digestions, separations, complexations, etc. appear to be required for most sample preparations prior to instrumental analysis, this section is concerned with wet chemical methods such as gravimetry, titrations and spot tests, rather than as preludes to instrumental methods.

9.1. General

As is the case with instrumental methods, the lead must first be converted to a suitable form for analysis, and this generally consists of solubilization of the matrix in a proper solvent (neutral, acid, or alkaline) with or without preliminary ashing. Fusion of the sample with appropiate fluxes (carbonates, hydroxides, pyrosulfates, peroxides) followed by solution can also be used. These are laborious and time-consuming procedures, but no substitute forms of sample treatment are as reliable.

After solubilization, lead can be determined gravimetrically as an inorganic or an organic precipitate or by titration. Kraft[71/] summarized gravimetric and titrimetric determinations of lead as is shown in Tables I and II. Scott's Standard Methods[7/] lists the following methods for lead: Detection; separations; gravimetric methods (sulfate, molybdate, chromate); electrolytic determinations; titrimetric methods (ferrocyanide, permanganate, molybdate, chromate, chromate-iodide); and colorimetric (dithizone, sulfide).

9.2. Gravimetry

Gravimetric procedures are used for standard ASTM methods of analysis for lead in paints and pigments. The ASTM lists gravimetric determinations for the chemical analysis of white linseed oil paints (ASTM D215-68), for white lead pigments (ASTM D1301-55), for dry red lead (ASTM D49-63), and for tribasic lead phosphosilicate (ASTM D2742-68).[6/]

Le Giorgia[72/] analyzed dried paint films for lead by ashing, dissolving the pigment in hot HCl, and determining lead as sulfate, iodide, sulfide,

Table 1

Determination of Lead by Gravimetry

As Inorganic = $PbSO_4$; $PbCrO_4$; PbS; $Pb_3(PO_4)_2$, $PbHPO_4$, $PbCO_3$; Pb(OH)CNS; $PbSO_3$; $Pb(CN)_2$; $PbWO_4$; $PbHA_sO_4$; $[Pb_3H_4(IO_6)_2]$; $PbCl_2$.

As Organic = Oxalate; 8-oxiquinolates, Salicylates, Anthranilate; Picrolonic acid; Thionalide; α-Isatinoxime; Mercaptobenzimidazole; Mercaptobenzthiazole; Bismuthiol II; Dithiocarbamic acid derivative; Resorcine; Acridine.

Table II

Determination of Lead by Titrimetry

Titration With = Molybdate; Chromate or Dichromate, Ferrocyanide; Phosphate; Arsenate; Iodate; Periodate; Sulfate; Carbonate; Sulfite; Fluoride; Selenide; Vanadate; Tungstate; Thiosulfate; Ascorbic acid; Lead anthranilate; p-Aminosalicylate; Diethyldithiocarbamate; Diethyldithiophosphate; Mercaptobenzthiazole; Mercaptophenylthiodiazolone; Oxalate; 8-Oxiquinolate; Palmitate; Citrate, Tartrate; Tripolyphosphate.

or dichromate. Westgate et al[73/] reported the determination of one per cent lead in paints by a standard chromate method involving wet-ashing with Caro's acid and extraction of the lead sulfate so formed with ammonium acetate. The British Standard for lead in paints and similar materials calls for nitric acid digestion with precipitation of the lead as lead iodide.[16/] This is similar to Kaplan's procedure for rapidly screening lead in paint scrapings.[74/]

9.3. Titrimetry

Potassium iodide titration is given as an alternate standard method for dry red lead in ASTM D49-63. The referee method of the British Standards Institute for lead in low-lead paints is dry ashing at 500°C followed by separation of Pb by solvent extraction and titration by an indirect method using diethyldithiocarbamate.[16/] The Xylenol Orange - EDTA titration mentioned in the Photometric Analysis section was used by Chaudhuri et al[22/] to titrate a hexamethylene-tetramine lead complex to a lemon yellow end point after solution of the lead pigment in nitric acid. Malevannyi and Shumina[76/] determined lead in pigments by dissolving the paint in HCl, buffering with ammonium acetate and ammonium chloride at pH 9.5-10 and titrating with EDTA to a yellow sulpharsazen end point. The error was reported to be less than 0.5%.

9.4. Spot Tests

Spot tests may be a simple, inexpensive and specific technique for rapidly screening paint samples semi-quantitatively for lead. Sayre[77/] tested painted surfaces and paint chips for lead by applying a drop of

5-8% sodium sulfide solution to sharp, diagonal cuts through all the paint layers and comparing the color changes to a standard color chart to read the approximate per cent lead. Searle et al[25/] described the screening of paint chips prior to atomic absorption analysis by dipping them halfway into an aqueous solution of 1% sodium sulfide in 1% sodium hydroxide, and looking for a black line in the lead-containing layer. Hoffman[78/] detected lead in paint on a wall by extracting with a filter paper saturated with HCl or EDTA solution (20 minutes) and determining the lead in the paper as lead sulfide. Wilson et al[79/] collected lead from metal samples on sodium nitrate wetted filter paper by electrolytic deposition for 15 seconds at several volts and developing it to a yellow color with potassium iodide and sodium metabisulfite.

9.5. Weisz Ring Oven

The ring oven is a microchemical apparatus for rapidly separating metal ions on filter paper for subsequent determination by chemical spot tests. Locke and Riley[80/] developed a separation scheme and identification tests for the chemical analysis of paints using the Weisz ring oven. Lead was separated from Cu, Hg, Cd, Zn, Co, Al, Fe, Sb, As, Cr, Mn, Ti, and Ca.

Lead determinations by Weisz Ring Oven separations have been described by Jungreis and West[81/] and Fugas and Paukovic[82/] for the analysis of solutions and airborne particulates. The separations and particularly the color developments with diphenylcarbazide and with chromate may be applicable to paint analysis.

10. MISCELLANEOUS METHODS FOR LEAD

Some methods, mentioned almost casually in the literature, are interesting enough to consider for possible application to the present investigation. Ziegler[83/] detected lead by selective paper chromatography. Lead nitrate in a sample solution was eluted with a buffered isopropanol solvent on a paper strip through a band of CdS. Only the Pb^{++} passed through the CdS zone and was developed with ammonium sulfide solution.

Lead assay by neutron activation is difficult, since the only practical (n,γ) product is the 3.3 hour ^{209}Pb which has a very low cross section. Lukens[84/] determined lead by neutron activation analysis of samples in vials, using very short-lived nuclides (less than 1-sec half-life). The "detection limit" for lead was 0.4 µg. The reactor used for lead activation would probably not be within the financial reach of municipalities needing a rapid method for lead. Lutz[85/] bombarded environmental samples with high energy photons (20-45 Mev) from a linear accelerator (LINAC) and induced the reaction $^{204}Pb\ (\gamma,n)\ ^{203}Pb$. The ^{203}Pb has a half-life of 52 hours and decays with emission of a 279 Kev gamma ray. The limit of nondestructive determination was about 0.5 ppm of lead.

Blowpipe analysis, involving flaming a sample with a torch is a qualitative procedure for minerals, and may have application to the rapid detection of lead in paint and building materials. Dana[86/] and Smith[87/] gave blowpipe reactions for lead in minerals. Lead was indicated by a yellow deposit on plaster tablets (with or without iodide or bromide fluxes), by metallic globules on charcoal (with sodium carbonate flux), by a yellow to white sublimate on charcoal, and as a yellow borax bead. It is hard to imagine how one could make this test quantitative.

Reinbold and Pearson[88/] describe a most unusual determination of lead by spectropolarimetry. The reagent, D (-) -trans-1,2-diamino-cyclohexane-NNN'N'-tetra-acetic acid determines lead in solution through a stepwise titration at pH = 4.7 by optical rotation at 365 nm.

Infrared spectroscopy, ordinarily considered as a tool for analysis of the organic portion of paints and coatings, can be used to obtain spectra of pigments in the absence of interfering organics. Spectra[89/] are available for basic carbonate white lead, basic sulfate white lead, basic silicate white lead, bssic lead silico-chromate, and lead naphthenate.

Belcher[90/] et al reported the determination of nanogram amounts of lead by gas chromatography, thermal analysis and mass spectrometry of fluorinated lead beta-diketonates. The volatile chelates have high thermal stability but strong column interaction makes quantitative gas chromatography difficult.

11. SUMMARY AND CONCLUSIONS

This review presents ninety references to the analysis of lead in a variety of materials. Twenty of these refer to lead in paints or paint pigments, mostly fresh samples. No more than 8 or 9 references refer to dried paint films or dried paint scrapings.

According to the referenced information, paint scrapings and in situ painted walls were analyzed by atomic absorption spectroscopy, X-Ray fluorescence spectroscopy, and chemical spot tests. This conclusion is in good agreement with information derived from visits to cities with active lead poisoning control programs.[4] New York City uses X-Ray fluorescence; Baltimore uses a potassium iodide test; the District of Columbia uses atomic absorption and X-Ray fluorescence; and Philadelphia uses atomic absorption for analyzing paint chips and screening dwellings. New Orleans uses anodic stripping voltammetry on paint samples as well as blood samples.[75]

The lack of a broad background of analytical methods for lead in paint and building materials is indicative of the small amount of attention that this problem has received, even in recent years. The present concern over the lead poisoning of children undoubtedly will stimulate activity in chemical analysis of lead, and we can expect to see many more references to this subject in the near future.

For the purpose of defining the state-of-the-art of lead paint analysis, this review demonstrates that (1) there has been little work done on the analysis of old, dried paint; and (2) almost all of the analytical methods require that the sample be dissolved and prepared for analysis, often by a lengthy and time-consuming procedure.

The background of literature included in this survey should be a valuable starting point for the forthcoming experimental work on lead paint analysis.

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