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Analytical Methods for the Detection of Toxic Elements in Dry Paint Matrices--A Literature Survey

Maya Paabo

Center for Building Technology
Institute for Applied Technology
National Bureau of Standards
Washington, D. C. 20234

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Final Report

Prepared for
Office of Policy Development and Research
Department of Housing and Urban Development
Washington, D. C. 20410

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U. S. DEPARTMENT OF COMMERCE, Frederick B. Dent, Secretary

NATIONAL BUREAU OF STANDARDS, Richard W. Roberts, Director

Contents

Page

Abstract iv

1. Introduction 1

1.1. Purpose 1

1.2. Scope of the Literature Search 2

2. Analytical Methods 4

2.1. Sample Preparation 4

2.2. Lead Determination 6

2.2.1. Wet Chemical Methods 6

2.2.1.1. Spot Tests and Microchemical Tests . . 7
2.2.1.2. Gravimetry 9

2.2.2. Spectrophotometric Methods 10

2.2.2.1. Colorimetry 10
2.2.2.2. Atomic Absorption 11

2.2.3. Electrochemical Methods 14

2.2.3.1. Electrolytic Deposition 14
2.2.3.2. Polarography 14
2.2.3.3. Anodic Stripping Voltammetry 15

2.2.4. Neutron Activation Analysis 17

2.2.5. X-Ray Emission Analysis 17

2.2.5.1. X-Ray Fluorescence 18
2.2.5.2. Electron Microprobes 21

2.3. Mercury Determination 22

2.3.1. Wet Chemical Methods-Spot Tests 22

2.3.2. Spectrophotometric Methods 23

2.3.2.1. Colorimetry 23
2.3.2.2. Atomic Absorption 24

Contents (cont.)

Page

2.3.3. Neutron Activation Analysis 24

2.3.4. X-Ray Emission Analysis 26

2.4. Arsenic Determination 26

2.4.1. Wet Chemical Methods-Spot Tests 26

2.4.2. Spectrophotometric Methods 27

2.4.2.1. Colorimetry 27
2.4.2.2. Atomic Absorption 27

2.4.3. Neutron Activation Analysis 28

2.4.4. X-Ray Emission Analysis 28

2.5. Cadmium Determination 29

2.5.1. Wet Chemical Methods-Spot Tests 29

2.5.2. Spectrophotometric Methods 29

2.5.2.1. Colorimetry 29
2.5.2.2. Atomic Absorption 29

2.5.3. Electrochemical Methods-Anodic Stripping Voltammetry 30

2.6. Antimony Determination 30

2.6.1. Wet Chemical Methods-Spot Tests 30

2.6.2. Spectrophotometric Methods 31

2.6.2.1. Colorimetry 31
2.6.2.2. Atomic Absorption 31

2.6.3. Neutron Activation Analysis 32

2.7. Selenium Determination-Spectrophotometric Methods . . . 33

2.7.1. Colorimetry 33

2.7.2. Atomic Absorption 33

Contents (cont.)

		Page
3.	Summary and Conclusions	34
4.	References	39

Abstract

This report is a summary description of the chemical procedures currently available for the analysis of selected toxic elements in dried paint. The elements included in this report are lead, mercury, cadmium, antimony, arsenic, and selenium. The literature search upon which this report is based was directed primarily toward references pertaining to the analysis of dried paint. A bibliography of 57 references to wet chemical analysis, colorimetry, atomic absorption spectroscopy, electrochemistry, neutron activation analysis, and x-ray emission analysis is presented.

Key Words: Analytical methods; antimony; arsenic; cadmium; lead; mercury; review; selenium; toxic elements in paints.

Analytical Methods for the Detection of Toxic Elements in Dry Paint Matrices--A Literature Survey

1. Introduction

1.1. Purpose

The overall intent of the Lead-Based Paint Poisoning Program, as undertaken by the National Bureau of Standards, under sponsorship of the Department of Housing and Urban Development, is to determine the nature and extent of the lead paint poisoning problem in the United States and to recommend methods for its detection and elimination. A literature survey, within the scope of this program, was conducted on analytical methods for toxic elements in dry paints. The toxic elements selected for study, in addition to lead (Pb), were mercury (Hg), arsenic (As), cadmium (Cd), antimony (Sb), and selenium (Se). It has been proposed that paints and other surface-coating materials used for toys be considered hazardous substances if they contain more than 0.5% Pb or a combined total of more than 0.05% Hg, As, Cd, Sb or Se on a dried weight basis [1][1]. Many municipalities have already passed laws prohibiting the sale and use of interior paints having a Pb content of more than 1% as metal in total nonvolatile; and, since the passage of Public Law 91-695 (Lead Based Paint Poisoning Prevention Act) in January 1971, the detection and control of the existing hazard from old lead-bearing paint has been emphasized.

This has created a need for reliable analytical procedures for the determination of Pb and the other five elements of interest in dry, aged

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1 Figures in brackets indicate literature references at the end of this paper.

paint. These procedures are needed in order to determine compliance with the abovementioned limits. Little information is presently available on the relative merits of various methods of analysis of these six elements as applied to aged paint. It is the purpose of this report to review the literature and to establish the current state-of-the-art of methods of chemical analysis for the six toxic elements pertaining to aged paint.

1.2. Scope of the Literature Search

The literature on the analysis of toxic elements in dry paint matrices is not numerous since most of the analytical determinations have been applied to the analysis of liquid paints. An extensive literature review on Pb paint detection methods was made by Greifer [2] in December, 1971. Because there has been an increased interest in the subject since that time, the information contained in reference 2 has been brought up to date and, in addition, the following abstracts and journals were examined.

World Surface Coating Abstracts

National Paint and Coatings Association Abstract Review

Toxicity Bibliography

Activation Analysis Bibliography

Atomic Absorption Bibliography

Biological Aspects of Lead: An Annotated Bibliography

Environmental Research

Environmental Pollution

Environmental Letters

Archives of Environmental Health

To help assure a complete coverage of the literature, the manual search was complemented by computer-assisted searches at four data banks:

MEDLINE and MEDLAR at the National Library of Medicine

TOXICON at the Oak Ridge Toxicology Information Response Center

NTIS of the Commerce Department

NASA Scientific and Technical Facility

The first two data banks are oriented toward medical literature, the third data bank is concerned with research performed at all major Departments and Agencies within the Federal Government as well as private groups with Federal contracts, and the fourth data bank contains information of interest to the aeronautical and space sciences. The response from the computer searches was scanty and did not add any useful citations to the manual coverage.

In order to obtain information on most current activities in the field, personal contacts were made with staff members at NBS, universities, industrial laboratories and trade associations.

The information based on the abovementioned sources was used as the basis for this report. This report includes a bibliography of 57 papers concerned with the analysis of toxic elements in dry paint matrices.

2. Analytical Methods

2.1. Sample Preparation

There are few analytical methods applicable to the analysis of dried paints which are nondestructive and do not require any sample pretreatment. Neutron activation analysis and x-ray fluorescence spectroscopy are two major instrumental methods that can be used for the determination of the metal content in paint samples as received. However, in order to determine the metal content of paints by conventional procedures, such as wet chemical, spectrophotometric or electrochemical methods, the metals must be first converted into soluble forms. One of the major problems encountered in dry paint analysis is the quantitative separation of metals from the large masses of organic paint matrices. The separation involves dry ashing either by heating the sample or fusing it with a flux, at a temperature where the metal is not lost by volatilization, and dissolution of the residue in acids; or, wet oxidation of the organic matrix by various strong acids. As a rule, mixtures of nitric, hydrochloric or perchloric acids have been used by workers in the field to digest the paint matrix and to take up the residue left over after dry ashing or fusion.

Few comparative studies have been made on methods used for the separation of Pb from the dry paint matrix. At NBS, during the course of an experimental evaluation of analytical methods for determining Pb in paint [3,4], several sample pretreatment steps were evaluated. For wet ashing nitric and hydrochloric or mixtures of nitric, perchloric and hydrofluoric acids were used. Dry ashing at 500°C was followed with digestion by nitric acid or a mixture of nitric and perchloric acids.

The percent recovery of Pb was determined by Atomic Absorption (AA), polarography or colorimetry. The most promising wet oxidation method was the use of a mixture of nitric and perchloric acids since the insoluble residue left behind, when dissolved in sulfuric acid and analyzed by Anodic Stripping Voltammetry (ASV), yielded a concentration of Pb <0.1 parts per million (ppm). The dry ashing method at 450-550°C followed by exhaustive extraction of the residue with hydrochloric, nitric, and hydrofluoric acids and with ammonium acetate solution was used for the certification of the Pb content in the powdered Pb-based paint Standard Reference Material (SRM 1579) [5]. The efficiency of the method was checked with emission spectrographic analysis of the insoluble residues to make sure that they did not contain significant quantities of Pb.

Westgate, et al [6], found wet ashing with Caro's acid (formed by dropping concentrated hydrogen peroxide into concentrated sulfuric acid) to be more efficient than dry ashing for destroying the organic matter of paint for Pb determinations.

ASTM Committee D01.21.03 is currently active in evaluating test methods for the analysis of trace levels of heavy elements in paints [7]. In preliminary reports, they recommend the use of the dry-ashing method for paints having a Pb content of 0.01-5.0%. The sample is heated to 500-525°C and the residues extracted with nitric acid and then with ammonium acetate.

The other toxic elements, Hg, As, Cd, Sb and Se, are usually separated from the paint matrices by wet oxidation methods because of the volatility of the elements and some of their salts or by fusion methods

followed by acid digestion of the solid formed with the flux. No systematic studies for establishing the best ashing procedure involving these elements in dry paint matrices were found. Workers in the field have either used the same wet ashing procedures as for Pb or have used a dry fusion method.

Hoffmann preferred the use of the Schoeniger oxygen flask method for igniting paint samples and converting the Hg present into mercuric nitrate or by extraction with hot acetic acid to separate phenylmercuric compounds [8]. Digestion in hot sulfuric acid was found to be satisfactory by Berger [9] for the dissolution of Hg from latex paints.

ASTM Committee D01.21.03 [7] is considering recommending the wet oxidation method using sulfuric and nitric acids for paint samples containing the five elements. For best results the wet ashing is conducted under reflux and the reaction is completed by the addition of nitric and perchloric acids. Studies were also made using the fusion method with the sodium carbonate-borax flux for paint samples containing Cd and Sb to allow solubilization of the elemental constituents. The results of these studies will eventually appear as part of the official ASTM method for determining the toxic elements in paint.

2.2. Lead Determination

2.2.1. Wet Chemical Methods

Wet chemical methods such as gravimetric and volumetric analysis or spot tests were used exclusively for both the quantitative and qualitative

determinations of Pb in paints before modern instrumental methods became popular, and even at present they are being used extensively despite the complex chemical procedures often involved.

2.2.1.1. Spot and Microchemical Tests

Spot tests are the simplest qualitative methods for the chemical determination of Pb in paint material. The dried paint may be tested on location without any previous sample preparation by applying the test solution to a scratch in the painted surface or to a loose paint chip. This method has been applied most widely to the routine screening of Pb, since it is specific, simple and inexpensive.

The most common reagent used is an alkaline solution of sodium sulfide, which precipitates Pb as a black sulfide [10,11,12]. Searle, et al [10] was able to detect Pb concentrations as low as 0.1% by dipping the paint chips into an aqueous solution 1% in sodium sulfide and sodium hydroxide and examining the black line visible in the layer containing Pb paint. Sayre [11,12] estimated percent Pb semiquantitatively from 0.8 to 15% by comparing the shades of grays produced in unknowns with the gradations of gray in paints of known Pb content. Of the other metals under consideration only Hg forms a black sulfide, but the quantity present is usually so small that is does not cause significant interference.

Another way to estimate the Pb content of dried paint is to dissolve the paint and to produce, with an appropriate reagent, a colored spot on filter paper. This procedure permits a better visual comparison of colors with spots obtained with standard solutions. Thioacetamide was

used by NBS for the semiquantitative determination of Pb between 0-5.77% [4]. The readings near the 1% level of Pb were variable because of subjectivity in interpreting the resulting shades of color.

Westgate recommends the use of the potassium-copper-lead triple nitrite or the lead iodide test for determining whether Pb is actually present in significant quantities in dried paint flakes [6].

ASTM Committee D01.21.03 has proposed a method for determining trace quantities of Pb in finishes [7]. They recommend dry-ashing the sample, digesting the residue with hot sodium hydroxide solution and treating a drop of this mixture on filter paper with bromine water and benzidine. A blue color indicates the presence of at least 0.06% Pb.

A modification of the conventional spot tests on the filter paper is the Weisz Ring Oven Technique, used by Locke and Riley for the qualitative analysis of paint pigments [13]. The paint chips are dissolved in aqua regia and the residue taken up by acetic or nitric acid. Pb was identified by the appearance of a violet-red line when the filter paper, to which Na-rhodizonate had been added, was fumed over concentrated HCl.

Instead of producing a colored reaction on the paint film or filter paper, one can use the microchemical test; appearance of a colored precipitate in solution as an indication of the presence of Pb. This method requires the dissolution of the paint sample prior to analysis. Pb can be detected by treating the resulting solution with the following reagents: sulfuric acid, potassium iodide, mixture of sodium sulfide and hydrogen sulfide, or potassium dichromate [14]. The British Standard

Institution has developed a procedure for precipitating lead iodide for the detection of Pb in the range of 1.0 - 1.5% [15]. In the United States, Kaplan and Shaull [16] have worked out empirical conditions for practical screening purposes so that the lead iodide precipitate can be used as a positive test to indicate the presence of 1% Pb or more.

2.2.1.2. Gravimetry

The only quantitative method involving wet-chemical procedures for the determination of Pb in dried paints is the gravimetric method. Lead is isolated as lead chromate and the weighed precipitate is used for calculating the Pb content. Searle, et al [10] used the method of Scott [17] for determining Pb in samples containing approximately 2% Pb. The standard deviation of 10 determinations of 0.5g samples was found to be 0.28%. Westgate improved the standard chromate method by digesting dry paint films containing about 1% Pb with Caro's acid [6]. A preliminary titration for screening purposes on a portion of the Pb solution, using ammonium molybdate solution as titrant and tannic acid as an indicator, was used to indicate if the Pb level was below or above 1%. The accurate gravimetric method based on lead chromate was used to determine the exact Pb content.

The Westgate method, however, was found to be unsatisfactory by an ASTM working group [18] which was set up to select a method for determining Pb at the 1% level. The method was found to suffer from poor reproducibility. They preferred the determination of Pb by electrolytic deposition.

2.2.2. Spectrophotometric Methods

2.2.2.1. Colorimetry

In addition to characteristic, insoluble compounds, Pb also forms colored complexes suitable for analytical purposes. Hoffmann studied the feasibility of determining Pb colorimetrically as PbS in alkaline solution by comparing visually the colors formed with those of standard solutions or by determining the absorption at 390 nm [19,20]. It is not a quantitative method but allows an estimation of the Pb content to be made at low concentrations, from 0.003 - 0.3%. A very accurate method for the determination of Pb in paint employs the color of the Pb-dithizone complex in chloroform near 510 nm. The reagent is capable of detecting 0.05 ppm Pb in solution. Since dithizone forms complexes with many metals, the method requires extensive chemical manipulations to obtain high selectivity. Barker, et al [21] used ammoniacal dithizone in the presence of cyanide for the routine determination of Pb in paints which were being used for school materials and toys. By comparing the colors of the sample solutions with colors of standard solutions he was able to readily detect 100 ppm Pb. An alkaline dithizone method was used by Barltrop and Killala [22] for the analysis of paint samples in connection with their study of lead poisoning in children. They followed the procedure of Browett and Moss [23] for the determination of the Pb content in urine. A semi-automated analyzer was utilized to measure the color of the chloroform extract at 505 nm. An extensive study of the application of the dithizone method to the analysis of dry paint was made

by NBS [3,4]. They used the ASTM E 35-63 method [24] for separating the Pb complex in chloroform from interfering metals. This method utilizes an ammonium citrate-cyanide solution as the masking agent. Photometric measurements were made near 520 nm. The dithizone measurements had a tendency to show a small positive error but the precision and accuracy were thought to be adequate for the purpose of determining Pb in paint at the 1% level.

2.2.2.2. Atomic Absorption

Although Atomic Absorption (AA) has found wide application for the determination of Pb in various types of samples, it is only recently that AA has been used for the analysis of Pb in dry paints and related materials. The principal advantages of this technique are its high sensitivity and specificity. Quantitative analysis of any one metal can be made in small amounts of material even in the presence of large amounts of other substances. The detection limit for Pb is 1 ppm or less, depending on experimental conditions. Unfortunately, most procedures require sample pretreatment and almost no work has been done directly with solid samples.

In 1969 Searle [10] worked out a simple, rapid method for determining Pb in paint scrapings by AA. After dry-ashing the sample the residue was taken up with nitric acid. A dilute solution was aspirated into an air-acetylene flame and the spectral line at 283.3 nm was used for analysis. Standard lead nitrate solutions were used to calibrate the instrument. The standard deviation by the AA procedure for 10 measurements, for samples containing about 2% Pb, was 0.05%. A modification of Searle's

method is presently being used by the Chicago Board of Health for the determination of Pb in paint and plastic chips [25]. In England, Hodson and Lord [26] used a method similar to Searle's for the routine screening of toxic metals in paints on toys. The Sherwin-Williams Research Center [27] analyzed 89 commercial paints for Pb by the AA method. The detection limit was 0.0005%.

At the NBS, AA was among the methods evaluated for determining Pb in paint [3,4] and was one of the methods used for certification of the powdered Pb-based paint Standard Reference Material (SRM 1579) [5]. A detailed method was developed for determining micro and/or macro amounts of Pb in paint (0.5 to 100 ug of Pb/ml in final diultion) by measuring the 283.3 nm resonance line of the atomic vapor in a stoichiometric air-acetylene flame [3]. The AA spectrophotometer was calibrated by means of a standard lead nitrate solution prepared by dissolving high purity Pb (NBS SRM-59e) in nitric acid. When the paint samples contained less than 0.005% Pb, an extraction with ammonium pyrrolidine dithiocarbamate in acidic solution was recommended. In a comparison of four instrumental mehtods for determining Pb in paint films [4], AA was found to be a method of satisfactory precision (2-11%) for measuring paints containing up to 5.77% Pb. The major discrepancies were attributed to loss of lead during various sample pretreatment steps. During the course of certification of the powdered Pb-based paint reference material, the oxidation of the paint matrix was accomplished by the dry ash method, and the standard deviation of the AA analysis was 0.13% [5]. When the SRM paint material (containing

11.87% Pb) was analyzed by the AA method at seven different laboratories using 9 different ashing procedures, the results varied from 1.57 to 13.52%, indicating the need for a standardized ashing procedure.

In order to avoid sample pretreatment, an AA method employing a West type carbon rod flameless sample holder was evaluated at the NBS [3] for the analysis of solid paint samples. Samples of paint chips were either analyzed directly or mixed with graphite, but the lead content could only be determined qualitatively. Work is underway to evaluate the best procedure for the application of the flameless carbon rod method to paint analysis. A rapid screening of pencil paint for Pb was attempted by McDuffie [28], who sampled the paint directly by placing the pencil in the edge of the AA burner flame. The AA response was compared to the values obtained for Pb by digesting the paint with acid solution and analyzing the solution by AA. A Pb content below 0.2% could not be detected and the test was strictly qualitative.

An extensive study is being carried out by ASTM Committee D01.21.03 [7], which has recommended the use of the AA method of analysis for determining Pb in dry paints. Paints having a Pb content between 0.01 and 5.0% are to be analyzed by the method described in reference 3. Paints having a Pb content between 0.0001 and 0.1% are to be analyzed by the Delves cup method, which involves sampling the dried paint film directly. The solid sample in a microsampling cup is ignited near the AA flame and vaporized directly in the air-acetylene flame. During preliminary studies, 95% Pb recovery was obtained with paint spiked with known amounts of a Pb drier, and a standard deviation of $\pm$0.002% between duplicates was observed.

2.2.3. Electrochemical Methods

2.2.3.1. Electrolytic Deposition

Before the advent of AA, electrogravimetric analysis was thought to be an excellent technique for the analysis of Pb in paint as compared to spectroscopic, polarographic and colorimetric methods. A procedure for determining Pb at the 1% level was developed by the ASTM working group by comparing gravimetric, colorimetric and various electrolytic methods [18]. The tentative method for determining low concentrations of Pb in paint consisted of electrolytic deposition of Pb as the dioxide on a platinum anode from a solution containing ammonium nitrate and copper sulfate. It was later accepted as the official ASTM method D 2088-68 [29]. The method is not free of interferences and carefully controlled conditions must be maintained to prevent contamination or incomplete deposition. Manganese must be removed as a precipitate to prevent its deposition; and, to avoid incomplete deposition of Pb, any Hg present must be removed by high temperatures during the ashing step. A repeatability of 0.03% Pb can be expected by this method.

At NBS, electrolytic deposition was used as a check method for the powdered Pb-based paint reference material [5]. The average result of 11.92% compared favorably with the certified value of 11.87%.

2.2.3.2. Polarography

Even though no references were found to the previous use of this electrochemical method for the analysis of Pb in a dry paint matrix, polarography was included at NBS in the program of evaluation of

analytical methods for determining Pb in paints [3]. Polarography was found to be a suitable method since the only experimental difficulties encountered were during sample dissolution steps. Experimental details were worked out for the use of a differential cathode ray polarograph [4]. Pb in an acidic solution containing ascorbic acid, was reduced with a linear voltage sweep applied to the last few seconds of a growing mercury drop. The peak current was measured on the cathode ray tube. The method required the simultaneous analysis of a blank solution. Standard solutions of Pb were needed for establishing the calibration curve. A preliminary analysis of 23 samples containing 0 to 5.77% Pb indicated that a precision better than 7% could be obtained. Thus, polarography was chosen as one of the methods of analysis for certification of the Pb-based paint reference material [5]. The average of 16 determinations was 11.93% Pb, with a standard deviation of 0.13% Pb.

The ease of applying polarography to the determination of Pb in solutions was used also by Lukaszewski and Szymanowska [30] for determining whether paints used on ceramics contained Pb. They extracted Pb from the paint with acetic acid and proceeded with the usual polarographic procedure

2.2.3.3. Anodic Stripping Voltammetry

Anodic Stripping Voltammetry (ASV) is one of the most powerful electrochemical approaches to trace analysis and is usually applied to concentration ranges below those found for heavy metals in paint. Once the sample has been brought into solution, the analysis can be carried out very rapidly, and the basic sensitivity of the technique for lead is approximately at the sub-nanogram level.

An electrochemical system and procedure for employing ASV for analysis of Pb in dried paint matrices has been developed by Matson [31]. He recommends the wet ashing procedure by nitric and sulfuric acids. Diluted aliquots of the digest are run on the ASV system, plating at the composite mercury-graphite electrode versus the silver/silver chloride reference electrode at -0.8V for 5 minutes and stripping at 80 MV/sec. The concentration of Pb is determined by the standard addition method using lead nitrate solution. Modifications to the procedure can be made to avoid interferences, for example, from TiO_2. The method can be used for determining Pb in the range of 0.01 to 10% depending on the size of the aliquot used for analysis.

A recent study by Schaplowski [32] concerning the potential hazard of paint on pencils as a source of lead poisoning used the services offered by Matson at the Environmental Sciences, Inc. Laboratory for determining the lead content in paint by the ASV method. Analysis was performed in sodium acetate solutions at -1.1 Volts for 30 minutes with a sweep rate of 55 MV/sec. The Pb content for four brands of pencils varied from 0.03 to 12.5%. A similar technique has been used by the New Orleans Department of Health to analyze paint samples for Pb [33]. An application of ASV was made by Lux, et al [34], for the investigation of the age and place of origin of old paintings. Minute samples of white lead from paintings were taken and Pb was determined at the levels of 5×10^{-7}g and 3×10^{-6}g with standard deviations of $\pm$3.4 and 2.4% respectively.

2.2.4. Neutron Activation Analysis

One of the two instrumental methods for the analysis of Pb in paint that require no previous sample preparation is Neutron Activation Analysis (NAA). The method is potentially more sensitive, at least by an order of magnitude, than either colorimetric or spectrographic methods.

Of the metals concerned, Pb has the lowest sensitivity for thermal neutron reactions. It can be detected at the 1-3 ug level at a thermal-neutron (n·) flux of 10^{13} n· cm^{-2} sec^{-1} for a 1 hour period [35]. Since the stable isotope of Pb, however, does not undergo reactions with thermal neutrons that are useful for analytical purposes, Lutz investigated the use of fast neutrons using ^{252}Cf as the source [36]. The induced nuclear reaction $^{204}Pb(n,n')\ ^{204m}Pb$ was followed by gamma spectrometry with a Ge(Li) detector. Irradiation for 2 hours with the 600 ug ^{252}Cf source and 100 minutes of counting with a 60 cc Ge(Li) detector was required to detect 1% Pb in a 1.5 g paint sample. This technique was also used to confirm the Pb content in the powdered lead-base paint Standard Reference Material (SRM 1579) [5]. The average value of Pb for 4 samples was 11.1% as compared to the certified value of 11.87%.

2.2.5. X-Ray Emission Analysis

The second group of instrumental methods for the analysis of Pb in paint that require no sample preparation involves the characterization of x-ray emission lines. By measuring the radiation emitted between 0.1 and 5 nm, the technique is applicable for the determination of all elements heavier than and including magnesium (atomic number 12).

2.2.5.1. X-Ray Fluorescence

With the development of high resulution solid state x-ray spectrometers, where the excitation source is a primary x-ray, qualitative analysis of metals in paint by x-ray fluorescence can be carried out on a routine basis. McGinnes, et al [37] studied the quantitative aspect of x-ray emission analysis by trying to overcome the complicating matrix effect. He compared the intensities of spectra emitted by dry thin films of paint of known and unknown composition and determined the elemental concentrations of major pigment elements. The percentages obtained for Pb in an alkyd resin agreed to within 6% with the values determined by chemical analysis.

The use of radioisotope excitation sources has led to many practical applications of x-ray emission analysis. For example, Pb in the pigment of old paintings can be detected by interpreting the fluorescent x-ray spectrum resulting from irradiation by a ^{109}Cd source [38]. Development of portable instruments consisting of a radioactive source and a solid state detector have made possible the *in situ* determination of Pb on painted surfaces. Reece, et al [39] used portable x-ray fluorescence analyzers containing a ^{57}Co source and NaI(Th) detector for in field inspection during his study of elevated blood Pb levels in children in the Cincinnati area. Pb contents ranging from 0.2 to 30.8 mg/cm^2 were reported in various interior and exterior paints. In antifouling marine coatings, Pb was easily detected in the presence of large quantities of cuprous oxide [40]. Laurer, et al [41,42] described the development of such an instrument for the detection of Pb in wall paint. It utilized

^{109}Cd - ^{109}Ag as the source of γ-rays to stimulate the emission of the K_β series x-rays of the Pb atoms, which were then detected by a solid state Ge(Li) detector.

The instrumental response is directly related to the weight of Pb per unit area; it was capable of detecting 0.26 mg of Pb/cm^2 of paint (approximately 3% by weight) in a 1 minute determination. The system was calibrated by measuring sprayed paint samples of known composition (2.5, 14 and 64 weight % Pb) or by comparing the instrument readings to the results of chemical analysis of the paint samples. Of the several available instruments, Berry [43] describes an x-ray fluorescence analyzer designed to use a ^{57}Co x-ray source and NaI(Tl) detector. The estimated detection limit is expected to be 0.5 mg Pb/cm^2 of area. The instrument was used to determine Pb in paint on various locations and the results were compared with those of chemical analysis. The data indicated that in no case was the chemically established Pb content underestimated by using the radioisotope measurement. Barltrop, et al [44] describes an instrument manufactured in England and its application to the analysis of paint films. The instrument contains a ^{238}Pu source and a NaI detector with Ga or Ge filters. The instrument was calibrated by standard additions of a Pb compound to liquid samples and by observing the count rates of dried films with a Pb content between 1 and 31%. The accuracy of the readings was $\pm$0.2% in the range of 0%-5% Pb. When, however, the results for commercial paint films were correlated with chemical analyses using the 95% confidence limit the scatter of the data was too great to allow application

of this technique to Pb screening programs. The study of the masking effect of overlying paintlayers indicated that a film of 77 mg/cm^2 (corresponding to about 9 thin layers) will cause a Pb content of 31% to appear to be zero.

At NBS, in the course of evaluating laboratory procedures for accurately determining Pb in dry paint, the x-ray fluorescence method was also investigated [3]. In order to be able to use a single calibration curve, zinc oxide was added to all samples to reduce the differences caused by various paint matrices. A general purpose, single-channel x-ray fluorescence spectrometer was used. The Pb content in unknowns was estimated by comparing the K_β x-ray intensities to those of standard samples containing known amounts of zinc oxide, titanium dioxide and red Pb oxide powders. The total analytical error was not expected to exceed $\pm$10% for Pb at the 1% level. A study of 20 samples showed an average negative error about 9% [4]. The method was used in testing the homogeneity of the powdered lead-based paint standard reference material, SRM 1579 [5]. As an extention of the investigation mentioned above, Rasberry [45] evaluated commercial portalbe x-ray fluorescence analyzers to ascertain their detection limits and precision with which they can be used for determining Pb on painted surfaces. The four design types were classified as : (1) scintillation detector - balanced filter energy discrimination, (2) noncooled detector - pulse height analysis, (3) lithium-drifted germanium detector - pulse height

analysis, and (4) high purity germanium detector - pulse height analysis. The analyzers were compared by determining the weight % of Pb in terms of mg/cm^2 on 27 samples coated with paints of known composition. The amount of Pb added was varied between 0 and 6.6 mg/cm^2. Some of the specimens had several overlayers of paint containing no lead in order to simulate field conditions. Standard deviations for the four types of analyzers for 14 of the specimens to which less than 1.00 mg/cm^2 of Pb was added were 0.46, 0.33, 0.15 and 0.21 mg/cm^2 and the detection limits 0.9, 0.6, 0.3, and 0.4 mg/cm^2 respectively. Tolerance limits for determining 1 mg/cm^2 Pb for the four types were also calculated. It was concluded that walls covered with paint containing Pb in excess of 1 mg/cm^2 could be identified, but the numerical values should be considered only semi-quantitative since errors of 30% to 50% are not uncommon. Similar conclusions were arrived at by Challop and McCabe who commented on four commercial instruments tested by the AEC Health and Safety Laboratory [46]. The statistical limits at the 90% confidence level for measuring painted surfaces of Pb content 1 mg/cm^2 or less varied from ± 0.41 mg/cm^2 to ± 1.0 mg/cm^2.

2.2.5.2. Electron Microprobe

A special case of x-ray emission analysis, when the excitation source is an electron emitter, is electron probe microanalysis. It can be used for a rapid qualitative or semiquantitative determination of the elemental composition of each individual paint layer. Whiteley, et al [46] illustrated the use of this method for determining the number, thickness

and composition of multiple coated substrates; Pb was detected among other metals. Elzinga-Ter Haar [48], analyzing cross-sections of paint samples from various objects of art, found Pb to be present in the range of 20-44 wt %. The quantitation was made by comparing the count rates with those of a reference standard.

2.3. Mercury Determination

2.3.1. Wet Chemical Methods - Spot Tests

Fewer chemical methods have been developed for the determination of Hg in dry paint matrices than for Pb. For purposes of the field detection of HG in weathered paints, Vind and Drisko [49], after digesting the paint in concentrated nitric acid, detected the presence or absence of Hg by using cuprous iodide paper which develops an orange color with Hg. An alternative method, based on the principle that mercuric salts catalyze the corrosion of aluminum, was also used because of its relative simplicity even though it was less sensitive than the cuprous iodide test. Both tests were considered reliable for the positive detection of Hg and negative results obtained with paints specified to contain Hg were explained by the assumption that Hg biocides can be lost rather rapidly from exterior paints during the weathering process.

Hg in dried paint chips has also been identified qualitatively with the Weisz Ring Oven Technique by developing a violet-blue color on the filter paper treated with nitric acid and an alcoholic solution of diphenyl-carbazone [13].

2.3.2. Spectrophotometric Methods

2.3.2.1. Colorimetry

Two similar complexing reagents have been employed for the colorimetric determination of Hg in dried paint. The colored complexes of diphenylcarbazone with inorganic mercuric salts and phenylmercuric compounds have been utilized by Hoffmann in a semiquantitative manner [8]. He isolated either the total mercuric compounds or the phenylmercuric compounds by the Schoeniger oxygen flask method or by successive extractions with acetic acid and benzene respectively. The color formed by the sample solution with diphenylcarbazone was matched with the color of standard solutions. The detection limit for Hg by this method in a 100 mg paint film was approximately 0.04% as phenylmercuric compound. When films containing between 0.04 and 0.3% Hg were analyzed, the results for total Hg tended to be about 4% higher than theoretical amounts, whereas the results for phenylmercuric compounds were considerably lower (25-50%) than theoretical amounts.

A quantitative method of high sensitivity and good accuracy for assaying Hg in dry paint films was developed by Berger [9] using diphenylthiocarbazone (dithizone) as the complexing agent. The paint samples were digested with sulfuric acid and the mercury extracted with a chloroform solution containing dithizone. The mixed color method was used by making spectrophotometric measurements at 475 nm for absorption of light by the Hg complex and at 605 nm for excess dithizone in the solution. The experimental results for eight samples containing Hg at the 1% level were within 0.2% of the theoretical amount with a standard deviation of 0.70%.

2.3.2.2. Atomic Absorption

Although several techniques have been developed for determining Hg by AA and have been applied successfully for the analysis of many different types of materials, the method has not found wide application so far for the analysis of Hg in dry paint matrices.

A flameless AA method, following wet oxidation of dry paint films, was used by the Sherwin-Williams Research Center for the survey of a series of commercial paints [27]. The experimental procedure of Hatch and Ott was followed [49], which employed sodium chloride-hydroxylamine sulfate medium to reduce the mercury to its elemental state and measured the absorption of the 253.7 nm line of atomic Hg vapor. The detection limit for Hg in the paint samples was 0.00005%.

ASTM Committee D01.21.03 is considering adopting AA as a standard method for determining low levels of Hg in dry paint matrices [7]. The use of stannous chloride for the chemical generation of monatomic Hg vapor is preferred instead of the use of the air-acetylene flame. The details of the wet oxidation steps and the following analysis by AA are being assessed by several laboratories before acceptance of the method.

2.3.3. Neutron Activation Analysis

The nondestructive feature of activation analysis, along with the high sensitivity and the very small sample size required, have prompted the use of NAA in the forensic sciences where characterization of paint samples is being used in the course of crime detection. Elements at trace levels can be detected with a flux of thermal neutrons when

a nuclear reaction of sufficient cross section occurs. The nuclear reaction of $^{196}Hg(n,\gamma)^{197,\ 197m}Hg$ has been used as an analytical indicator in paint analysis. Hg can be detected at the 1 - 3 x 10^{-3} ug level at a thermal-neutron flux of 10^{13} n$\cdot$ cm^{-2} sec^{-1} for a 1 hour period [35].

Snow, et al studied the qualitative and quantitative significance of various elements found in black paints [51]. By irradiating 78 different paint films with a thermal-neutron flux of approximately 10^{13} n$\cdot$ cm^{-2} sec^{-1} and by measuring the gamma-ray emission with a NaI(Tl) detector, they were able to detect Hg at the 2.6 ppm level (avg. dev. 7.7%). In a separate study Snow and Washington [52], comparing 300 samples of various colored paints, detected Hg at the same level with the same precision. Schlesinger, et al [53] also reported on the effective application of NAA for the comparison of 155 different paint samples from motor vehicles, interior and exterior walls, woodwork and other sources. The samples were irradiated at a thermal neutron flux of 1.8 - 2.8 x 10^{12} n$\cdot$ cm^{-2} sec^{-1} and NaI(Tl) was used as the detector. Among 19 elements detected, Hg was measured at the 51 ppm level.

Another interesting application of NAA has been the investigation of old paintings with respect to their age and origin. Minute samples of pigment from Flemish-Dutch and Venetian paintings were subjected to NAA by Lux, et al [34]. By irradiating the samples at 2 x 10^{13} n$\cdot$ cm^{-2} sec^{-1} and using Ge(Li) as the detector, Hg (in this case the nuclear reaction of $^{202}Hg(n,\gamma)\ ^{203}Hg$) was detected at 0.5-5 ppm, depending on the sample size.

2.3.4. X-Ray Emission Analysis

The only reported case of analysis of Hg in dry paints by X-Ray fluorescence has been in a study of antifouling coatings. Hg was detected below the 0.05% level in the presence of large quantities of cuprous oxide [40].

2.4. Arsenic Determination

2.4.1. Wet Chemical Methods - Spot Tests

The most popular method for determining As in trace quantities in various materials has been the Gutzeit method or some modification of it. The method is very sensitive and can be used for determining As at the ug level. It requires rendering the sample soluble before arsine can form a colored compound with mercuric chloride. The major interference is caused by the presence of Sb, and separation of As by distillation is required. Barker [21] employed the Gutzeit method for the routine determination of As in paints used for toys and school materials. From the colored stains formed, he was able to detect the presence of As in the samples at a concentration as low as 20 ppm. The Gutzeit stain method was also used [27] in a survey of paints for their heavy metal content. The detection limit was 0.0001%. For the qualitative analysis of paint chips using the Weisz Ring Oven Technique, Locke and Riley included the Gutzeit test for the detection of As when As and Sb would likely not be present together [13].

2.4.2. Spectrophotometric Methods

2.4.2.1. Colorimetry

A characteristic soluble complex of As was employed by Hodson and Lord [26] in their screening procedure for the determination of toxic elements in toys. The As contained in the dry paint film on toys was determined colorimetrically by a dry fusion of the sample with sodium carbonate, dissolving the ash in a mixture of nitric and hydrochloric acids, and measuring the colored comples formed with silver diethyl-dithiocarbamate at 522 nm. The concentration of arsenous oxide was estimated with the help of a standard curve. The method was adequate for the determination of As at the 250 ppm level.

2.4.2.2. Atomic Absorption

Conventional AA has not been applied to the analysis of small amounts of As found in paint matrices. The detection limit for As using an air-acetylene flame is about 1 ug/ml and the resonance lines for As are in the low wavelength region where acetylene flame absorption occurs. ASTM Committee D01.21.03 [7] is considering the use of an argon-hydrogen flame and the 193.7 nm spectral line for the determination of As at low concentrations in paint matrices. The details of the sample pretreatment and the measurement technique will have to be worked out and assessed.

2.4.3. Neutron Activation Analysis

The principal instrumental method used for determining As in paint matrices that does not require any sample pretreatment is Neutron Activation Analysis (NAA). The high sensitivity of the method is especially applicable for the determination of As at trace quantities. The nuclear reaction of interest is $^{75}As(n,\gamma)^{76}As$ and its detection limit at a thermal-neutron flux of 10^{13} n$^{\circ}$ cm^{-2} sec^{-1} for 1 hour is 1-3 x 10^{-4}ug [35]. Schlesinger, et al [53] irradiated 155 paint samples with a thermal neutron flux of 1.8 - 2.8 x 10^{12} n$^{\circ}$ cm^{-2} sec^{-1} and detected As in the concentration range of 6.3 to 42 ppm among a total of 19 elements. Substituting a NaI(Tl) detector with a Ge(Li) detector improved the resolution of As and Sb peaks [54]. Snow and Washington [52], in their survey of 300 paint samples, detected As at the 72 ppm level with a standard deviation of 5.5% when samples were irradiated with a thermal neutron flux of about 10^{13} n$^{\circ}$ cm^{-2} sec^{-1} and the γ-ray emission was measured with the NaI(Tl) detector.

2.4.4. X-Ray Emission Analysis

The second instrumental method used for As analysis in dry paint matrices that does not require sample pretreatment is x-ray fluorescence. Driscoll and Freiman [40] report that the detection of As in antifouling coatings is easily accomplished at the 0.02% level.

2.5. Cadmium Determination

2.5.1. Wet Chemical Methods - Spot Tests

The only reference found for a wet chemical method for determining Cd in dry paint is by Locke and Riley [13], who detected Cd qualitatively in paint chips by the Weisz Ring Oven Technique. When the dissolved sample, on filter paper, is treated with ferrous dipyridyl-iodide reagent the formation of an intense red color stain indicates the presence of Cd.

2.5.2. Spectrophotometric Methods

2.5.2.1. Colorimetry

The high selectivity of dithizone for the characterization of metals has been found useful for the determination of the metal contents of paints. In addition to the detection of Pb, Barker [21] used the dithizone reaction for detecting Cd in paint on toys and school materials. In order to separate Cd from Pb with sufficient selectivity, Cd was extracted from an alkaline solution in the presence of tartrate as the masking agent. The intensity of the dithizone complex with Cd was compared with that of the blank and standard solution. Cd at a concentration of 100 ppm was easily detected by this technique.

2.5.2.2. Atomic Absorption

Even though AA is the most commonly used method for determining Cd in many types of materials because of its extreme sensitivity and freedom of interference effects, it has not found wide application for determining the metal in dry paint matrices. Hodson and Lord [26] used the AA method for screening paints for their Cd content. Cd was

detected by using an air-acetylene flame and by measuring the absorption of the 228.9 nm resonance line. A sensitivity of 0.02 ug/ml was observed. When 89 paint samples were surveyed for their metal contents, essentially by the same method used at the Sherwin-Williams Research Center, Cd was detected between 0.002% and 0.004% in three samples [27]. The detection limit was 0.0006% if a sufficient quantity of sample was available. ASTM Committee D01.21.03 [7] is also considering the recommendation of the method for determining Cd in dry paint films following the wet ashing procedure. The method is being tested on two samples containing 98 and 179 ppm Cd.

2.5.3. Electrochemical Methods - Anodic Stripping Voltammetry

The use of electrochemical methods has found little application for the characterization of Cd in dry paint films. Matson [31], during the ASV analysis of paint for Pb, simultaneously determined the amount of Cd present in the sample extract.

2.6. Antimony Determination

2.6.1. Wet Chemical Methods - Spot Tests

Sb has been identified qualitatively in dry paint chips by the Weisz Ring Oven Technique. Locke and Riley [13] detected Sb after an extensive separation scheme, when potassium iodide and Rhodamine B solutions were added to the filter paper containing the dissolved paint sample. Sb was identified by the blue-violet stain developed on the filter paper. A blank should be run for comparison.

2.6.2. Spectrophotometric Methods

2.6.2.1. Colorimetry

The presence of trace amounts of Sb in dry paints has been estimated colorimetrically by Barker [21] using the color reaction with iodide in the presence of sodium hypophosphite. The quantity of Sb could be estimated at the ppm level when the color developed after a specific time period was compared with solutions containing known amounts of Sb. A more quantitative colorimetric method was used by Hodson [26], who determined the concentration of Sb in paint samples by the brilliant green method. The optical density at 640 nm of the sample solutions was compared with a reagent blank. The sensitivity of the method permitted an estimation of the Sb concentration at the ug/ml level with the aid of a calibration curve.

2.6.2.2. Atomic Absorption

An entirely satisfactory AA method of analysis for determining Sb in dry paints has not yet been developed. AA was used at the Sherwin-Williams Research Center [27] for the analysis of a series of dry paint samples. The air-acetylene flame and the absorption of the 231.1 nm resonance line were utilized. The Sb content detected varied between 0.001 and 1.95%. In samples which were dry ashed and only the acid soluble Sb was determined, the highest concentration of Sb detected was 0.02%, with a detection limit of 0.001%. In samples which were ashed by the fusion method and the total amount of Sb was determined,

the concentration of Sb varied between 1.12% and 1.95% with an undetermined detection limit. ASTM Committee D01.21.03 [7] is considering the use of AA following a wet oxidation procedure as an approved method for determining Sb in paints. Test samples containing 99 ppm to 247 ppm Sb are being analyzed using the air-acetylene flame and the absorption of the 231.1 and 217.6 nm resonance lines. Different ashing methods are being evaluated at the same time. It is expected that at a later date ASTM will publish the optimum method.

2.6.3. Neutron Activation Analysis

The third method employed for the analysis of Sb in paints is NAA. The nuclear reaction of analytical interest is $^{121}Sb(n,\gamma)^{122}Sb$ with a limit of detection of about 4-9 x 10^{-4} ug at a thermal-neutron flux of 10^{13} n$^{\cdot}$ cm^{-2} sec^{-1} for a 1 hour maximum. Snow, et al [51,52] detected Sb in dry paints at 52 ppm with an average deviation of 4.4% by irradiating the films with a thermal neutron flux of approximately 10^{13} n$^{\cdot}$ cm^{-2} sec^{-1} and measuring the γ-ray emission with a NaI(Tl) detector. Schlesinger [53,54], during the analysis of 155 different paints, detected Sb at 3.4 ppm to 126 ppm when the films were irradiated with a neutron flux of 1.8 - 2.8 x 10^{12} n$^{\cdot}$ cm^{-2} sec^{-1} and a NaI(Tl) detector was used. Lux [34,35], during the study of old paintings, also detected Sb in pigment samples. The detection limit for Sb was 10^{-5} µg.

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2.7. Selenium Determination - Spectrophotometry

2.7.1. Colorimetry

A quantitative method for determining small amounts of Se in dry paint films has been the codeine sulfate reaction. When codeine is added to a solution of Se in concentrated sulfuric acid a characteristic bluish color is produced. An adaptation of the technique developed for biological samples [56,57] was used to survey commercial paints for the Se content [27]. Concentrations detected varied between 0.0014% and 0.0322% with a detection limit of 0.0010%.

2.7.2. Atomic Absorption

No references to the AA analyses of Se in dry paint were found. ASTM Committee D01.21.03 [7] is considering an AA method for the determination of Se by using an air-acetylene flame and the absorption of the 196.0 nm resonance line. No experimental data are yet available.

3. Summary and Conclusions

This report was written for the purpose of reviewing various analytical approaches that have been used for the detection and measurement of toxic elements in dry paint matrices. The numerous methods described have been arranged according to each element of interest and are summarized in table I. The majority, about forty, of the published methods refer to the analysis of Pb in dry paint and many of these are only qualitative or semi-quantitative. There are relatively few references to the other five elements.

A major problem in the analysis of all the elements is the separation of the elements from the organic paint matrices with which they are associated. The ashing and digestion steps seem to be sources of considerable error as compared to the subsequent instrumental determinations. It is obvious that the poor precision of several methods can be traced to incomplete oxidation or losses sustained during the oxidation processes. There is a definite need for a proven, reliable oxidation procedure for each element under consideration. In addition to dry ashing at a high temperature or wet ashing with strong mineral acids, the use of atomic oxygen for the low temperature ashing of the organic paint matrix should also be considered.

Of the wet chemical methods described, the spot test offers the greatest number of advantages for a rapid qualitative field determination. A practical semi-quantitative field test has been worked out for Pb determination only, utilizing the black sulfide precipitate formation on a paint chip. A second simple procedure for paint samples for Pb

Table I

Analytical Methods Employed for the Analysis of Dry Paint Matrices

	Pb	Hg	As	Cd	Sb	Se
Spot Test	x	x	x	x	x	
Gravimetry	x					
Colorimetry	x	x	x	x	x	x
Atomic Absorption	x	x	(x)[a]	x	x	(x)
Electrolytic Deposition	x					
Polarography	x					
Anodic Stripping Voltammetry	x			(x)		
Neutron Activation Analysis	x	x	x		x	
X-Ray Fluorescence	x	x	x			
Electron Microprobe	x					

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a - Parenthesis indicate tentative method.

involves the iodide precipitate formation, this time from a solution containing the paint extract. Other elements can also be identified by colored spot formations and the technique has been used for all the elements except Se. However, since the other elements are present in trace quantities as compared to Pb, the procedures involved are either too complex or the reactions are not specific for the determination of several elements simultaneously. The Weisz Ring Oven Technique offers the simplest technique for the extraction of the metals from the paint and separation of the metals before the final identification is made.

Colorimetry is the only method that has been applied to the determination of all the six elements in dry paint, but the method usually requires extensive chemical manipulations that have to be carried out in a laboratory if the results are to be quantitative. The sensitive dithizone reaction seems to be the best choice for the determination of Pb, Hg and Cd; As and Se each require a different complexing agent.

The wet chemical methods are being replaced preferentially by a variety of instrumental methods, AA being the most promising one. With proper care as to sample pretreatment, all the elements concerned can be determined by AA, using the air-acetylene flame for five elements and either a flameless or cold vapor technique for Hg analysis. In order to eliminate the losses encountered during sample pretreatment steps and to avoid the problems associated with flame absorption or emission interferences when the elements are present in low concentration in the sample, there has been increased emphasis on the development of

flameless solid sampling techniques. A modification of the sampling boat, the Delves cup method, has been recommended for Pb analysis at concentrations below 0.1%; direct sampling of paint by the flame has been attempted; and the West type carbon rod flameless sample holder for solid samples is being evaluated. Hopefully these attempts will result in an accurate AA method of analysis for solid paint samples that can be used to replace the conventional procedure of aspirating an aqueous solution into the flame.

Electrochemical methods have been applied to the analysis of Pb only, although polarography and ASV are both suitable for Cd determination.

Another instrumental method of great sensitivity that has been employed for aged paint analysis is NAA. Pb is the least sensitive metal and the method has been used mostly for the detection of Hg, As, and Sb in trace quantities. The method has found only limited application for the analysis of dry house paints since few laboratories have intense neutron sources available.

Currently the most popular nondestructive screening method for in situ measurement is x-ray fluorescence. The method has been applied mainly for Pb determination; and in one reported case also for the detection of Hg and As. X-ray fluorescence could be used for determining the other five elements with the required sensitivity if the elements were first concentrated by proper chemical means. Several commercial instruments developed for the determination of Pb in painted surfaces have been evaluated extensively. At the present state of development,

portable x-ray fluorescence analyzers yield only semi-quantitative data. The presence of Pb is determined in units of mass per surface area which can only be converted into a weight fraction if the exact composition of the paint is known. An accepted convention that 1% Pb in a layer of paint gives a reading of 0.08 mg/cm^2 is often used for interpreting experimental results. The x-ray fluorescence technique must be developed further before an accurate determination of Pb in dry paints is possible.

A closely related method, electron probe microanalysis, has also been applied to the detection of Pb on a few occasions. The ability of this method to simultaneously determine the elemental distribution and the thickness of paint films should make it useful in surface coating analyses.

In terms of future work, emphasis should be placed on the development of sampling techniques and detection methods for toxic elements in dry paint matrices, specially for Cd and Se. Reliable chemical analyses are essential for the fundamental understanding of the hazards posed by the toxic elements present in paints and for the protection of the public against such hazards.

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16. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)

This report is a summary description of the chemical procedures currently available for the analysis of selected toxic elements in dried paint. The elements included in this report are lead, mercury, cadmium, antimony, arsenic, and selenium. The literature search upon which this report is based was directed primarily toward references pertaining to the analysis of dried paint. A bibliography of 57 references to wet chemical analysis, colorimetry, atomic absroption spectroscopy, electrochemistry, neutron activation analysis, and x-ray emission analysis is presented.

17. KEY WORDS (Alphabetical order, separated by semicolons)

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