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Isotopic Determination of Lead by Secondary Ion Mass Spectrometry

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Interim Report

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This report has been reviewed by the Public Affairs Office (PAS) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

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FOR THE COMMANDER

J. E. Freytag, Colonel, USAF
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A method is described by which samples containing as little as 5 ng of lead can be isotopically analyzed. The procedure was developed for use with lubricating oils containing additives labeled with particular lead isotopes, but it can also be applied to the determination of lead in other materials. It consists of three steps: (1) digestion of the organic sample to release the lead into aqueous solution, (2) anodic deposition of the lead onto platinum electrodes,

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and (3) secondary ion mass spectrometry. Quantitative determination of the amount of lead in a sample can be accomplished by adding to the sample a known amount of a standard lead compound with an isotopic composition different from the sample.

PREFACE

It is a pleasure to acknowledge the assistance of T. J. Murphy and I. L. Barnes of The National Bureau of Standards during the early stages of this program. We also wish to thank Mr. N. Marquez, who carried out the IMMA analyses, and A. T. Finney and R. A. Berg, of the Defense Satellite Communication Systems program office, for their support.

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I. INTRODUCTION

Accurate methods for the determination of trace quantities of lead are necessary for monitoring lead in the environment and in biological and geological samples. Techniques have been developed to remove lead from organic and inorganic materials, usually by variations of an acid digestion.[1,2] Subsequent determination of the lead has been accomplished with a variety of instrumental techniques such as atomic absorption,[3] fluorescence,[4] and thermal ionization mass spectrometry.[5] Not all methods are suitable for isotopic analysis, which is important in work in which particular isotopes of lead are used as tracers. We describe a method for the isotopic analysis of samples containing as little as 5 ng of lead by means of electrodeposition and secondary ion mass spectrometry using an ion microprobe mass analyzer (IMMA).

The samples we investigated were lubricant oils. A lead naphthenate additive had been mixed into the oils to form a 1% by weight lead naphthenate solution in the oil. Lead naphthenate is a common lubricant additive used to provide protection to moving mechanical assemblies under boundary lubrication conditions. The lead naphthenates used were enriched in various natural isotopes of lead so that they could be used to trace migration of the oils through a two-bearing mechanical assembly such as used in some spin-stabilized communications satellites to despin antenna platforms.[6] Our technique was developed with these samples in mind, but it is also applicable to other lead-containing materials.

The procedure consists of three steps. First, the organic lead is treated to release the metal to an aqueous solution. Second, the aqueous lead ions are electroplated onto platinum electrodes. Third, the surfaces of the electrodes are analyzed with the IMMA, which provides data on the relative amount of each mass number component in the sample. Quantitative analysis can be obtained by isotope dilution, adding a known amount of a standard lead compound to the sample. This standard should have an isotopic composition that is distinct from those expected from the samples and from that of natural lead, so that it may be distinguished from these other components of the samples.

II. EXPERIMENTAL

In all trace analysis, extreme care must be taken to avoid contamination of the samples. In lead analysis, this problem is compounded by the widespread presence of lead in the environment. The preparation of the samples for analysis was carried out on a clean bench in a room only infrequently used for projects other than the lead analysis. Cleaning procedures for each step of the process will be detailed during the description of each technique. The nitric acid and perchloric acid used (Ultrex grade) each contained only 1 ppb lead. Electronic grade water that had been produced by filtering through Milli-RO4 and Milli-Q filters was used. It had a minimum resistivity of 10 MΩ cm.

A. DIGESTION

The procedure used for the transfer of lead from the lead-naphthenate-containing oils to aqueous solution is an acidic digestion based on several described earlier.[1,2] Modifications of the reported methods were necessary to make this step compatible with the remainder of the analytical process. The digestion solution is a mixture of 0.3 mmole each nitric and perchloric acids diluted with 15 ml water. Since the amount of lead naphthenate to be reacted is generally less than 10^{-9} mole, this amount of acid is sufficient. The sample is added to the acidic aqueous solution, and the mixture is refluxed for 4 hr. The apparatus used for refluxing (Figure 1) is constructed entirely from Teflon-FEP (fluorinated ethylene propylene), since this material has been shown to absorb lead less readily than glass or other common container materials.[7] The small Teflon bottle with a screw cap is available commercially. A hole punched through the cap permits the attachment of a condenser that is basically a Teflon tube. The condenser is air cooled and is long enough to avoid the possible escape of lead-containing vapors or droplets from the refluxing solution. Teflon can be rigorously cleaned by means of a two-day procedure,[8] which was followed before each use of a condenser or bottle. The Teflon pieces are submerged in a solution of hot 8M nitric acid for 24 hr, and then in hot 6M hydrochloric acid for another 24 hr.

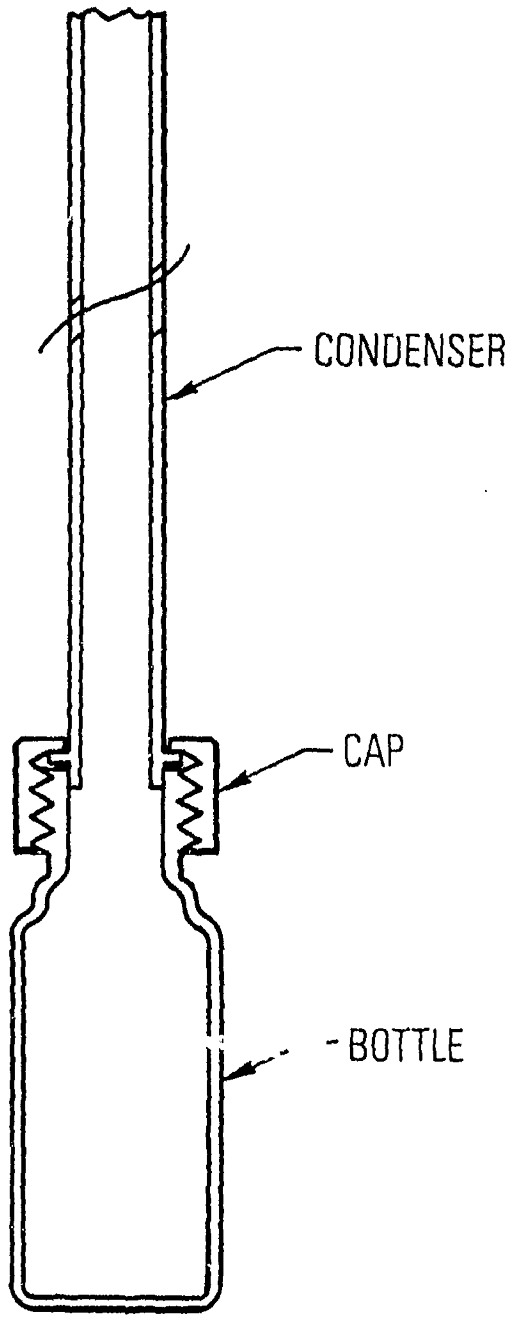

Figure 1. Teflon Digestion Apparatus

B. ELECTROPLATING

The electroplating technique was developed by Barnes, Murphy, Gramlich and Shields.[5] It is an anodic deposition of PbO_2 from an acidic solution of Pb(II) ions. They have shown that the amount of acid in the solution and the volume of the solution affect the yield of the electroplating process; therefore, the acid quantities added to our digestion solution and its volume were chosen to approximate the most effective plating conditions, as well as to be appropriate for the digestion. Plating was carried out in the same Teflon bottle as the digestion, after removing the condenser and adding 10 ml of water. The electrode design is shown in Figure 2. It is 20-mil-diameter platinum wire, enclosed in a low-lead glass sheath that is sealed around the platinum at one end. The wire is cut and polished at this end to be flush with the glass sheath. The electrodes are dipped only a short distance into the solution, and the solution is constantly stirred with a Teflon-coated magnetic stirring bar. Care must be taken to avoid heating of the solution by the stirring motor, as the efficiency of the plating process decreases with increasing temperature.[5] The deposition is carried out at 1.9 V and is reported to be complete after 16 hr.[5] We have determined that a second overnight deposition does not plate a significant amount of additional sample lead from the solution. The electrodes are cleaned between uses by immersion in hot aqua regia and can be used 10 to 15 times before the platinum separates from the glass sheath. After the aqua regia treatment, the electrodes are

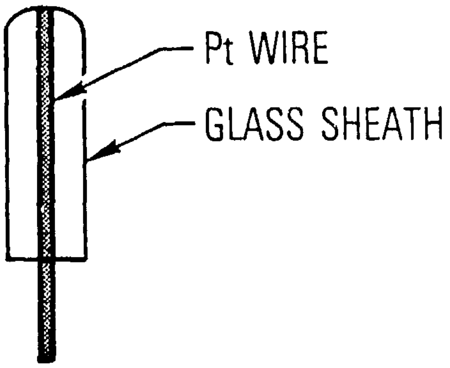

Figure 2. Platinum Electrode

rinsed in water, cleaned in 1M HNO_3, rinsed, cleaned in 1M HCl, and rinsed. Pairs of electrodes are then placed in dilute acidic solutions, and 1.9 V is applied across them for 3 hr. The cathode of this treatment is used as the anode for the PbO_2 electrodeposition.

C. IMMA

The ion microprobe mass analyzer is an Applied Research Laboratories Inc. secondary ion mass spectrometer. It produces a beam of oxygen ions that is magnetically filtered so that only the $^{18}O_2^+$ ions strike the sample. $^{18}O_2$ is used so that the presence of ^{16}O in samples can be observed when desired. The beam is 5 μm in diameter with a 9×10^{-3} mA/cm^2 current density, and can be rastered across the surface of the specimen. Ions sputtered from the surface are collected and analyzed by a mass spectrometer. The ion detector is a modified Daly detector in which the ions produce secondary electrons upon impact with an aluminized target. These electrons are directed into a scintillation tube, and the resulting radiation passes into a photomultiplier. The gain in signal inherent in this process enables the IMMA to detect elements at the parts per billion level; it is also capable of isotopic analysis since it has a resolution of one mass number. The PbO_2-covered electrodes are inserted into stainless steel holders that mask most of the glass area from the ion beam to reduce electrostatic charging of the sample. The primary beam is rastered across an area 20×160 μm^2. The mass spectrometer detector operates in a pulse-counting mode for maximum sensitivity, and the raw data are processed by a minicomputer.[9]

D. QUANTITATIVE ANALYSIS--ISOTOPE DILUTION

A known amount of a particular lead isotope is added to the sample and the entire analytical procedure is carried out as previously described. From the ratios of the intensities of the lead peaks of the sample to those of the isotope standard, the total amount of lead in the sample is calculated. The added lead in these experiments was in the form of lead naphthenate added to the digestion solution before refluxing. In this way, potential losses of lead in the digestion and plating procedures do not affect the isotope ratios.

III. RESULTS AND DISCUSSION

Apiezon C oils containing 1% lead naphthenate enriched in each of the four natural isotopes of lead were used in the development of this technique. The isotope ratios of these substituted lead naphthenates are listed in Table I, along with the isotope ratios of natural lead. The oils were diluted in heptane to make volumetric pipetting of small test quantities into the digestion solution easier and more accurate. Quantities of the oil-heptane solutions that contained 25 ng to 1 μg of lead were analyzed by this method. By the use of a lead sample with a different isotope ratio than that of natural lead, the extent of contamination can be determined by analyzing the isotope ratios measured by the IMMA.

The accuracy of IMMA determinations of isotope ratios was tested by observing the isotope ratios for natural lead. The average isotope ratios for a set of 15 samples containing 50 ng or less natural lead are accurate to ± 3%. If only the four samples containing 15 ng or less natural lead are considered, the measured isotope ratios are accurate to ± 5%.

Typical test results using the substituted lead naphtenates in oil are provided in Table II. The amount of natural lead contamination is presented in two ways. In the second column, it is listed as the percentage of the total amount of lead measured (i.e., sample plus natural lead). In the third column are listed weights of contaminant lead calculated by proposing that the amount of lead listed in the first column is present on the electrode at the end of the procedure. This assumes there were no losses of lead from the isotopically enriched test sample during the procedure. The first three samples were prepared as described in the previous paragraph. The final four samples were prepared by pipetting the oil-heptane solution onto a small polyurethane sponge and permitting the heptane to evaporate. The sample was extracted from the sponge by ultrasonic treatment in a small amount of heptane. The sponge and heptane solution were both included in the digestion mixture. These samples were intended to mimic the samples for which the technique was developed; small sponges had been used to wipe portions of the bearings and other components of the test apparatus to collect oil samples. The amount of contamination is greater for the sponge samples than for the directly pipetted samples, probably as a result of the increase in the number of handling steps.

In order to test the possibility of quantitative determination of the amount of lead in a sample, experiments were carried out in which known amounts of two oils enriched in different lead isotopes were added to the digestion mixture by means of a sponge. With one oil chosen as the "known", the amount of the other oil was calculated using the abundance ratios measured by the IMMA. The results of several of these experiments are provided in Table III. With this method of quantitative analysis, results accurate to within ±6% are obtainable.

Samples collected from the despin mechanical assembly (DMA) were analyzed by means of this technique, and some of the results are presented in Table IV. The samples were collected from various locations in the DMA, and, while some contain only one oil, others contain a mixture of several. In those samples for which the amount of lead was measured, it was always approximately 5 ng. More than 100 of such samples were analyzed to ascertain the transport properties of the lubricant during the life test of the DMA. The results of these analyses will be reported in a subsequent publication.

A new technique for the isotopic determination of lead has been developed. As little as 5 ng of lead can be detected, and isotopic analysis accurate to within a few percent is possible.

Table I. Isotopic Composition of Substituted Lead Naphthenates

Sample	Constituent(%)			
	Pb^{204}	Pb^{206}	Pb^{207}	Pb^{208}
Oil A	42	23	21	14
Oil B	0	100	0	0
Oil C	0	2	92	6
Oil D	0	1	3	96
Natural Pb	1	24	22	52

Table II. Amount of Contamination

Sample	Contamination % of Total Pb	ng
100 ng Pb^{207} (Oil C)	1	1 ± 3
50 ng Pb^{207} (Oil C)	9	5 ± 2
50 ng Pb^{208} (Oil D)	5	3 ± 2
845 ng Pb^{207} (Oil C) (sponge)	5	42 ± 25
100 ng Pb^{207} (Oil B) (sponge)	14	16 ± 3
50 ng Pg^{207} (Oil C) (sponge)	29	20 ± 2
50 ng Pb^{207} (Oil C) (sponge)	26	18 ± 2

Table III. Quantitative Analysis Tests

Pb^{206} from Oil B (ng)[a]	Pb^{207} from Oil C (ng)[a]	Pb^{207} calculated (ng)[b]
224	245	254
224	245	237
224	122.5	123

[a] Known amount added to solution.

[b] Calculated from known amount of Pb^{206} (column 1) and measured Pb^{207}/Pb^{206} ratio.

Table IV. Despin Mechanical Assembly Oil Samples

Sample Number[a]	Sample Composition (%)				Amount Pb (ng)
	Oil A	Oil B	Oil C	Oil C	
R-11-2	0	0	0	100	b
S-8-8	0	12	88	0	b
R-7-6	0	25	75	0	b
R-8-6	0	0	100	0	6
R-8-3	0	0	100	0	5
H-3-3	0	100	0	0	5

[a] These numbers refer to locations in the despin mechanical assembly from which the samples were removed; e.g., R is a bearing reservoir, S is the shaft, and H is the housing of the apparatus.

[b] Not measured.

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