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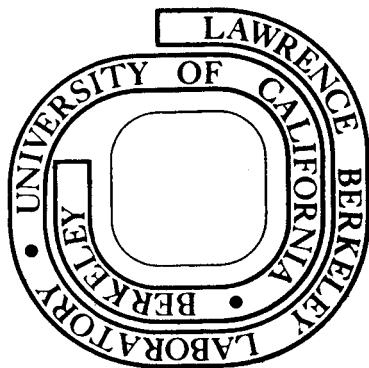
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T. Hadeishi and R. D. McLaughlin

November 1975

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ZAA determination of lead with a dual chamber furnace

T. Hadeishi and R. D. McLaughlin

Abstract

A dual chamber furnace is described that has application to certain analytical problems in atomic absorption spectroscopy. The design of the furnace was chosen to cause introduction of analyte vapors into the absorption region to occur in a more reproducible fashion. More important, the furnace acts like a high temperature chromatograph by separating the analyte from the matrix vapors as the temperature is increased. The operation of this furnace was demonstrated by using the Zeeman atomic absorption (ZAA) technique to determine Pb in 3% salt water solutions and Pb in NBS bovine liver without the usual drying and ashing steps.

Analytical curve data is presented for the ZAA method. The theory of the shape of this curve is discussed and a fit between theory and experiment is displayed. The lower limit of detection was found to be 50 pg of Pb.

ZAA determination of lead with a dual chamber furnace.

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Introduction

Zeeman atomic absorption (ZAA) spectroscopy is a technique that provides background correction capability far superior to methods presently used in conventional atomic absorption spectroscopy. For some time now, ZAA has been used to determine Hg in biological samples by shining light through the smoke and vapors that result when the temperature of the sample is suddenly raised to about 900° C.^{1,2,3,4} In order to maximize the sample size that can be used, a dual chamber furnace has been developed which provides very good relative sensitivities. The signal obtained from this furnace has been shown to be independent of the type of Hg compound.⁵ This paper describes the extension of this technique to elements that are less volatile than Hg.

For the purpose of furnace design, the elements can be grouped into three broad categories: 1) those that are so volatile that they escape with the combustion or pyrolysis products of a biological sample, e.g., Hg, As, Se, 2) those of moderate volatility that, in the main, do not escape with combustion products but some losses do occur, e.g., Pd, Cd and 3) those of such low volatility that losses are not a problem. Two slightly different types of furnaces have been described that perform well for the highly volatile elements.^{5,6} This paper is mainly concerned with a dual chamber furnace for elements of moderate volatility and describes results of Pb determinations in a variety of sample types. Experience thus far indicates that Cd deter-

minations can be carried out in the same manner.

Apparatus

The furnace that is best suited for this type of analysis is a modification of the one developed by H. Massmann⁷ (Fig. 1). Here the upper diagram illustrates the furnace as it is now used in conventional AA spectroscopy. The lower diagram illustrates the modified furnace. Notice we have a dual chamber configuration in which the volume of the outer chamber is approximately 1 ml. This outer chamber was machined so as to provide a tight fit when pressed over the inner chamber. It is also possible to obtain a good fit by sliding Ta foil between the inner and outer chamber. The temperature is then raised until the Ta melts by passing current through the inner chamber. The molten Ta acts like a high temperature glue since, in running samples, it is not necessary to reach temperatures that cause the Ta to liquify again. The second chamber alleviates the following problems inherent in the single chamber furnace: 1) poor reproducibility because of different location of sample, 2) loss of analyte because of escape with vapors during thermal decomposition, 3) light blockage because solid tends to swell into a carbon sphere during ashing. The solid is placed in an outer chamber and dried, ashed and atomized in a single step roughly 30 seconds after the current is applied to the heating element. For Pb and Cd this furnace acts like a single stage gas chromatograph and separates the organic vapors and NaCl from the Pb or Cd vapors. In addition, the outer chamber allows 100 μ l solutions to

be run without a time consuming drying step. This furnace configuration results in a temperature profile such that the midsection is cooler than the ends. This temperature distribution should be advantageous for single chamber use as it will tend to keep large liquid samples in the center of the heating element during the evaporation step, with a corresponding improvement in reproducibility.

Solid samples were transferred into the outer chamber by using a disposable Eppendorf pipette tip as a funnel. The entry port into the outer chamber was 3 mm in diameter, which allowed the narrow end of the tip to be cut off and the remainder would still fit inside the chamber. This arrangement provided a large enough opening to allow free movement of the powdered sample. Samples were weighed on a Kahn electrobalance that had a sensitivity of 0.1 mg. No contribution to the 10% uncertainty of this method could be traced to the weighing or sample transfer procedure. If the analysis of wet samples is required, the procedure of preparing homogenized slurries⁸ can be followed.

The ZAA instrument used for this work is the same as that described previously⁹ with the exception that the Hg light source was replaced by a Pb light source. A separated Pb isotope was not required because the Pb hyperfine structure is so small. The light source consisted of an electrodeless discharge tube containing lead iodide placed between the poles of a permanent magnet with a field strength of about 10 kilogauss. It was necessary to heat the discharge tube to obtain sufficient vapor of lead to excite the spectrum. At the same time, heating of the poles of the magnet would lessen the field strength.

These conflicting requirements were fulfilled by placing the discharge tube in a stainless steel block that was heated by commercially available self-contained, rod shaped, heaters capable of reaching temperatures of 800°C ¹⁰ and water cooling the magnet yoke.

Procedure and Results

The results of determinations of 100 μl solution samples is contained in Table I. Measurements were carried out using 1 ng quantities of Pb in 5 μl of 1% HNO_3 solution. 100 and 200 μl portions of distilled water were added to the furnace after the 5 μl of 0.2 ppm Pb solution was deposited. The DVM reading represents an average of four voltages displayed on the digital voltmeter after volatilizing the solution. The coefficient of variation was obtained by dividing the standard deviation by these values. Notice that there is a greater uncertainty when 100 μl of solution is used but a coefficient of variation of 10% for a 10 ppb sample is still very useful. When 200 μl of water was added, the results were erratic and low. This indicates that with this much solution, the gases generated during the rapid evaporation swept part of the Pb out of the furnace. It should be possible to use larger volumes by going through a slow drying step.

Figure 2 illustrates the dependence of the DVM reading upon the Pb introduced into the furnace. Measurements were made in the range 0.5 ng to 50 ng. The 50 ng point was not plotted because a large amount of scatter resulted when this much Pb was introduced into the furnace. This scatter occurred because so much Pb was in the light path that the

amount of 283.3 nm light was less than 20% of the initial intensity and the AGC circuit could not function with this low a level. In the event that it would be desirable to run samples that produced more than 40 ng of Pb, the density of atoms in the furnace must be reduced. This can be accomplished by increasing the flow rate of Ar through the system and lowering the furnace temperature so that the atoms are volatilized more slowly.

The non-linear dependence of DVM reading upon quantity of Pb is not as bothersome as might first appear. The reason this is true is demonstrated in Figure 3. This curve represents the first half of the curve shown in Figure 1. Many data points were taken in order to define the shape as accurately as possible. An adjustable Eppendorf pipette was used to simplify the task of obtaining so many points; some of the scatter may be caused by inaccuracies in this pipette. In any case, it can be seen that the curve is closely approximated by two straight lines. If the amount of Pb is equal to or greater than 7 ng, the upper straight line relationship is used and if equal to or below 7 ng, the lower line is used. The solid curve in this figure was obtained by graphically fitting the data to the expression:

$$DVM = K[\exp(-k_{\sigma}c) - \exp(-k_{\pi}c)]$$

where DVM is the reading on the digital voltmeter, c is the number of nanograms of Pb volatilized in the furnace, k_{σ} and k_{π} are the absorption coefficient of the σ and π Zeeman components, respectively, and K is a proportionality constant. This expression was used because of the

dependence of signal upon concentration derived earlier.¹ The values of the parameters found from this fit were:

$$K = 3.9$$

$$k_{\sigma} = 0.004$$

$$k_{\pi} = 0.09$$

A more convenient relationship is obtained if logarithmic amplifiers are used to process the signal. This situation is discussed by Koizumi and Yasuda.⁴

The capability of this furnace for the analysis of solid samples was tested by using the National Bureau of Standards standard reference material 1577 - Bovine Liver. A great deal of care had to be exercised to prevent contamination during sample transfer. The major problems were solved by washing the pipette tip in concentrated HNO_3 and by avoiding contact with the outer walls of the furnace assembly during insertion and withdrawal of the pipette tip. Thermal decomposition of the sample was accomplished by heating with 200 amps until most of the smoke had dissipated; after which the current was increased to 300 amps. The whole process of thermal decomposition and atomization required about 30 seconds.

A description of the thermal decomposition process is contained in Figure 4. The lower trace is a monitor of the intensity of the Pb 283.3 mm line and can be equated to the signal that would be obtained from a conventional AA instrument. The upper trace is the ZAA signal. During the decomposition process, the light is totally blocked off by a large amount of smoke, causing a large change in the

total intensity. This effect can be seen in the two sample runs on either side of this slide. The center run represents the signal that is obtained from 5 μ l of the 1 ppm standard solution. The upper trace is slightly displaced in the right hand direction from the lower trace on this chart record. Just how much displacement can be seen by comparing the ZAA and AA signal on the center run. These two peaks would coincide if there were no displacement. The two side runs clearly show that no Pb is coming off with the smoke from the sample. If this occurred, we would start to get an ZAA signal by the time the light transmission had returned to something greater than 20%.

Four consecutive runs were made on the Bovine Liver samples after the sample handling problems were solved. The sample size ranged from 10 mg to 17 mg, which caused the amount of Pb passing through the furnace to range from 3.3 ng to 6.4 ng. The Pb content was determined by comparison with 5 μ l of a standard 1 ppm solution. The Pb content of the NBS standards was found to be 340 ± 40 ppb. This agrees exactly with the value obtained by NBS (0.34 ppm).

A more severe test of the ability of this system to determine Pb without prechemical treatment would be provided by the the analysis of NaCl solutions since these two materials have somewhat similar boiling points (Pb = 1613° C, NaCl = 1413° C). A 3% solution of NaCl in distilled water was prepared using reagent grade NaCl that was certified to contain less than 1 ppm heavy metals. When 100 μ l of this solution was vaporized in the furnace, a signal was obtained that corresponded to a 0.2 ppm Pb content in the solid.

100 μ l portions of 3% NaCl solutions to which 1 ng of Pb had been added were next vaporized and the result was corrected for the reagent blank. The average of four determinations was found to be 1.1 ng with a coefficient of variation of 9%, by comparing with the standard solution. These results were obtained without use of a drying cycle and demonstrate the tendency of the furnace to act like a one stage gas chromatograph. Experience with blood and urine samples indicates that these materials can also be analysed without a drying or ashing step because of the ability of the furnace to separate substances of different volatility.

The lower limit of detection (LLD) (amount of analyte required to produce a signal equal to the noise) varied somewhat depending upon the noise level of the light source. The best value achieved for the 283.3 nm Pb line was 50 pg. Since the LLD represents a measure of the signal to noise ratio of an analytical technique, it would seem to be the most useful parameter for comparisons of ZAA with other methods. In comparing atomic absorption instruments with each other, the sensitivity (amount of analyte needed to cause a change of 1% in the initial light intensity) is often used. The analogous parameter for an ZAA instrument would be the amount of analyte necessary to cause a 1% change in the intensity of the π component of the Zeeman split lines.

Acknowledgments

The graphical fitting of the analytical curve to the difference between two exponentials was carried out by Patricia McLaughlin. We would like to express our appreciation for the insights gained because of her participation. Thanks are also due to Wilton Burlund and Douglas MacDonald for construction of the light source and furnace. Contributions were also made by Donald Johnson of the Ethyl Corporation who provided urine samples of known Pb content that were used to evaluate an earlier version of this furnace.

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Table I

Volume Effects on Furnace Performance

	5 μ L SOLUTION CONTAINING 1 NG PB	100 μ L SOLUTION CONTAINING 1 NG PB
DVM READING	277	283
COEFFICIENT OF VARIATION	$\pm 6\%$	$\pm 10\%$

Figure Captions

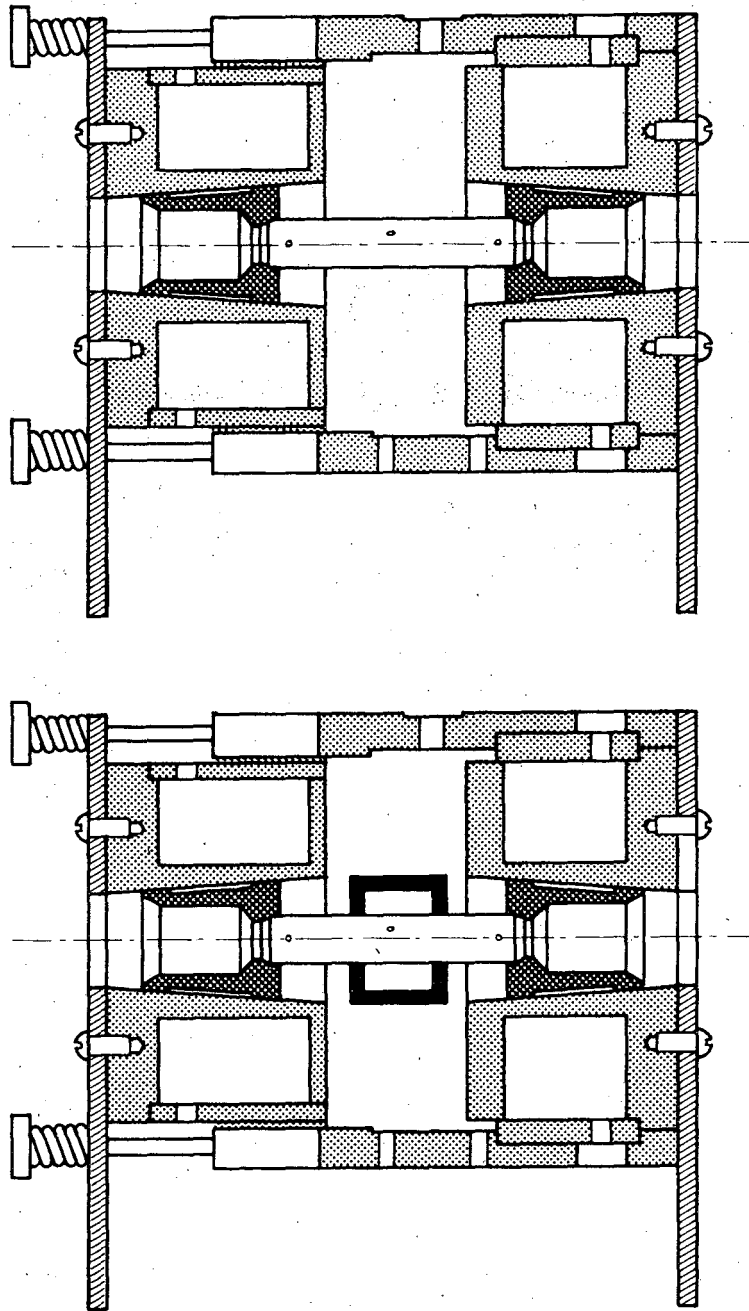
Fig. 1. Upper diagram: Cross section of Massmann furnace. Lower diagram: Massmann furnace modified to provide dual chamber operation.

Fig. 2. Analytical curve for Pb. DVM represents the digital voltmeter reading corresponding to the integrated signal.

Fig. 3. More accurate plot of first half of Fig. 2. The points are experimental. The curve results from a graphical fit to the difference between two exponentials.

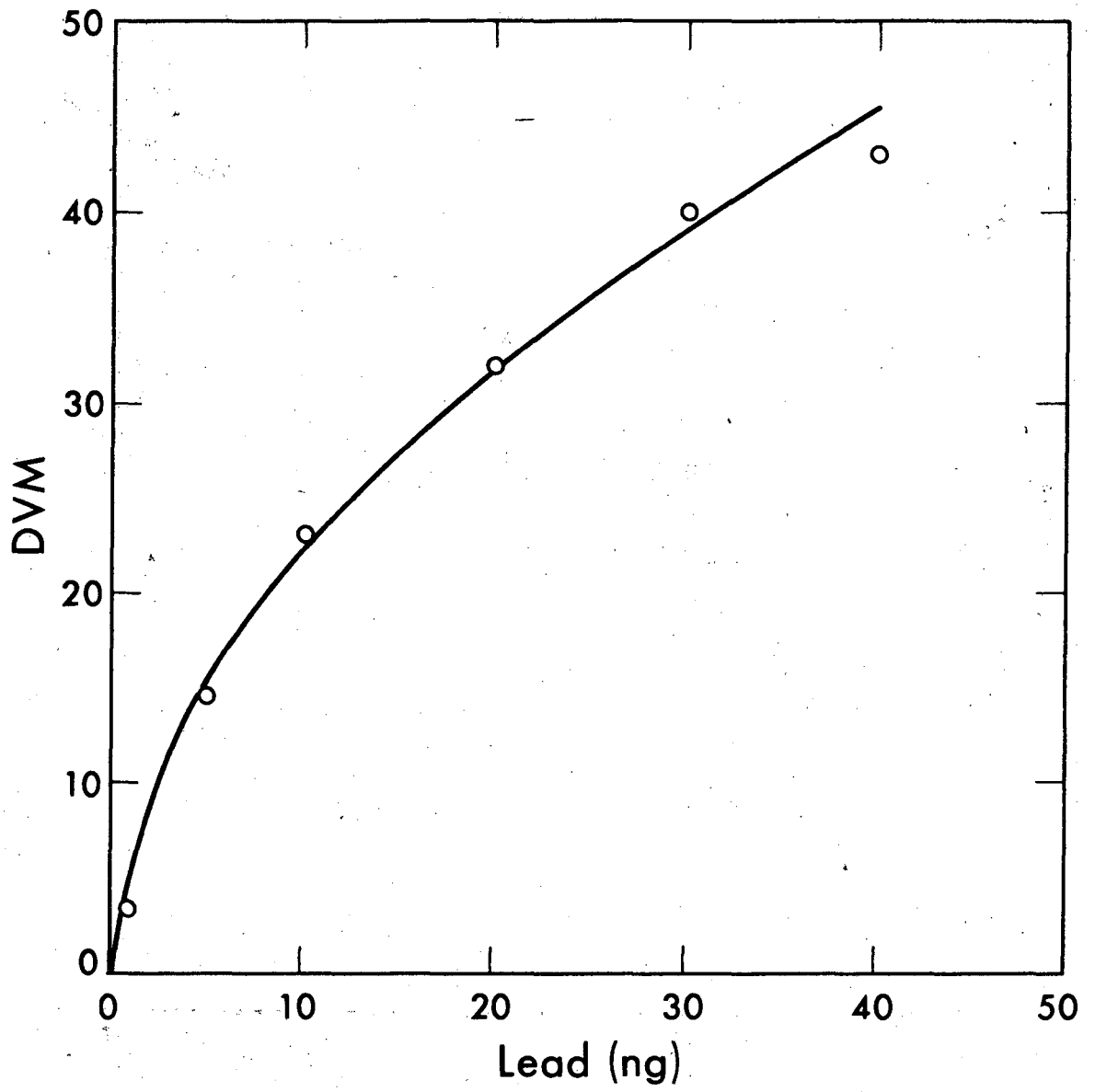
Fig. 4. Type of signal obtained from combustion of liver sample without drying or ashing step. Time increases from left to right. Upper trace represents ZAA signal. Outer peaks result from liver samples; inner peaks from 5 μ l of 1 ppm standard Pb solution.

Oven assembly



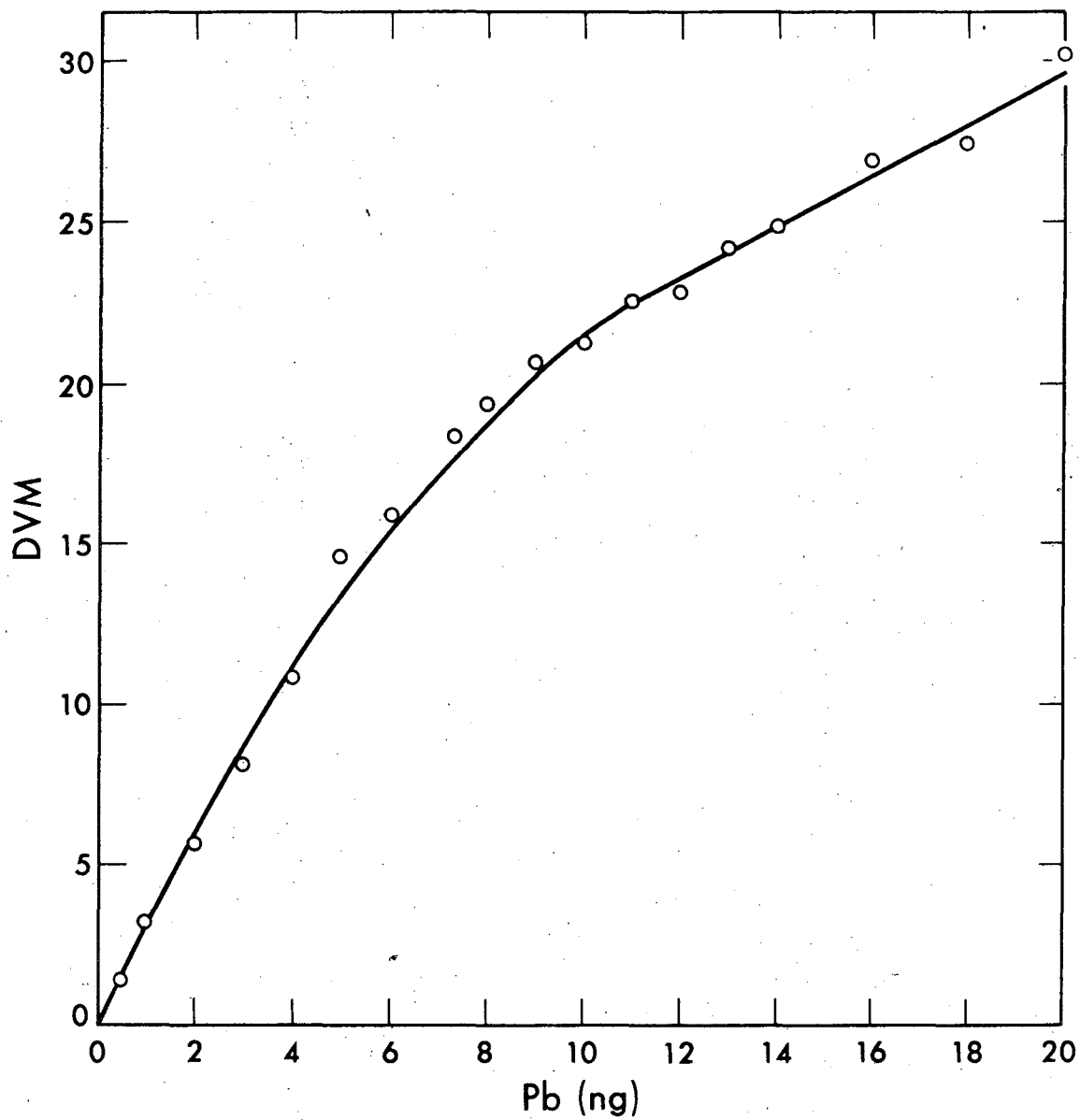
XBL 759-4117

Fig. 1



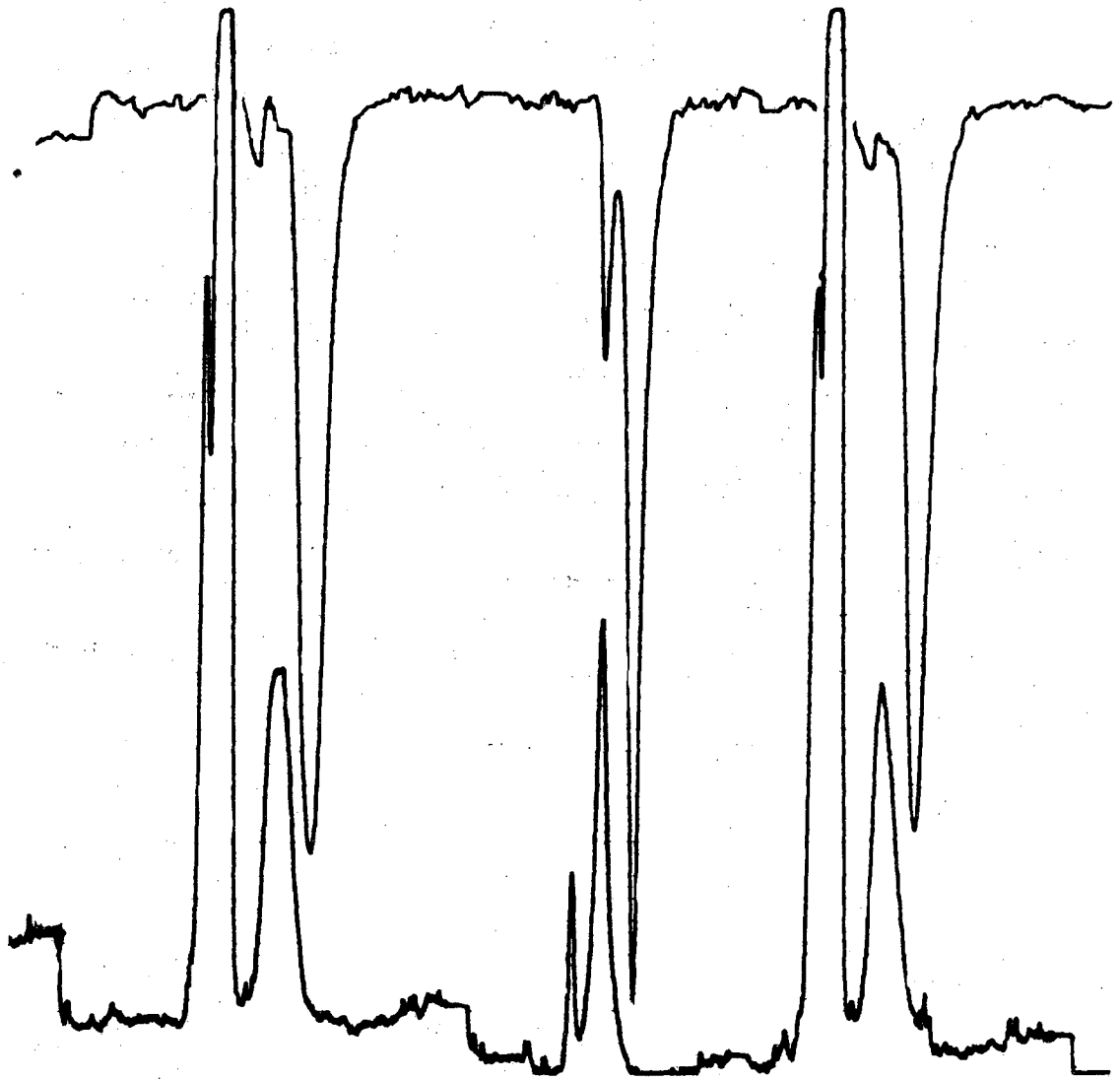
XBL 759-4119

Fig. 2



XBL 7510-8603

Fig. 3



XBL 759-4116

Fig. 4

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