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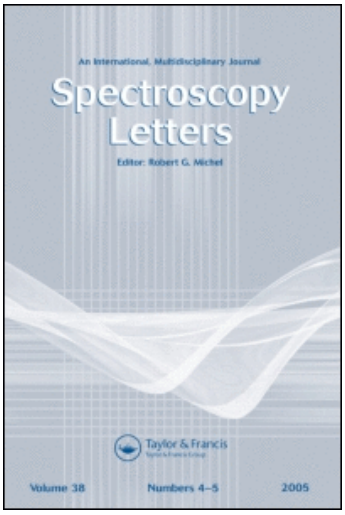


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# DETERMINATION OF PB IN BLOOD AND PRECIPITATION USING A TUNGSTEN WIRE PROBE AND GRAPHITE FURNACE

Key words: wire probe, furnace, atomic absorption spectrometry, Pb, blood, snow

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## ABSTRACT

A W wire coil probe made from 0.33 mm thick wire formed by winding the W wire around a 0.9 mm wire is used to introduce samples into a preheated furnace. Using this device interference from up to 0.4% $MgCl_2$ is effectively eliminated. Detailed procedures are given for the analysis of Pb in blood and melted snow. Results obtained for Pb in blood range from 93 to 106% of the accepted values. Recoveries of Pb spikes from melted snow samples are from 90 to 100%. Each coil may be used for up to 200 firings.



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## INTRODUCTION

Isothermal atomization is one of the main goals of graphite furnace AAS research. Prior to about 1978 graphite furnace AAS equipment was deficient in several respects. As a result procedures developed for its use were subjective, complicated and relatively difficult to reproduce. Procedures established with one manufactures equipment did not necessarly apply using different instrumentation. Recent graphite furnace AAS equipment is much better. In this regard Slavin et al. (1) state "With the advent of the platform furnace technique and the associated control of the other experimental conditions, the graphite furnace technique has finally become a convenient analytical technique."

Features which are essential aspects of this technology are

(1) a fast response photometer with signal integration capabilities
(2) rapid furnace heating (>1500°C)
(3) use of a platform in the tube (to delay atomization until the gas temperature has reached the designated atomization temperature)
(4) temperature control.

For best results Zeeman effect based background correction is also important.

L'vov (2) and others have pointed out the importance of

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atomization occurring under isothermal conditions. Several approaches have been developed to allow an approximation of this condition in modern commercial graphite furnaces. The most important of these is delaying atomization until the gas temperature surrounding the sample has reached the final atomization temperature. In this regard use of a platform and matrix modification are most important.

An important method of obtaining atomization under isothermal conditions is to introduce the sample into the atomizer only after the final atomization temperature has been attained. In this regard Woodriff and Ramelow (3) introduced the sample contained in a small graphite cup into a furnace operated at constant temperature.
L'vov and Pelieva (4) proposed that samples could be introduced into a preheated graphite furnace after drying on a metalic wire. Manning et al. (5), and Slavin et al. (6) investigated this approach for several elements using a W wire with a coil formed on the end to receive the µl sized sample. Giri et al. (7), Slavin et al. (8) and Littlejohn et al. (9) employed a graphite filament in a similar manner for introducing samples into the preheated graphite furnace. The reason for employing a graphite filament rather than a W wire is that the former can tolerate higher atomization temperatures and accommodate larger samples.

Despite this number of investigations little practical application of the important use of probe introduction of samples into preheated furnaces has been recorded. In the following the W wire probe is evaluated for the

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determination of Pb. A detailed procedure is presented for the determination of Pb in blood and snow samples.

## EXPERIMENTAL

### Equipment

A Perkin-Elmer Model 603 atomic absorption spectrometer equipped with $D_2$ arc background correction and a Model 65 recorder was employed. The graphite furnace was a Perkin-Elmer Model 500 with an AS-1 auto sampler. Non-pyrolitically coated graphite tubes were used. The 283.3 nm Pb line was employed.

A 0.33 mm W wire probe was mounted in a hand made holder that fit inside the Auto Sampler arm. The holder was machined from steel capillary tubing. The wire was passed through the tube and a coil made by wrapping the wire around an 0.9 mm wire. A reserve of unused wire was kept above the holder. In ths way when the coil was destroyed a new coil could easily be constructed by simply pulling through a new length of wire to wrap around the 0.9 mm wire. To allow insertion of the coil into the graphite tube without touching the sides it was necessary to enlarge the sample port to 3 mm in diameter. Each new coil must be cleaned by several heatings at the atomize temperature to be used. A blank must then be run to verify that cleaning is complete.

### Reagents

Stock 1000 µg/ml Pb solution was prepared by dissolving 1.0g of high purity Pb metal in a minimum amount of nitric

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acid. Sixty milliliters of $HNO_3$ was added, the solution transferred to a 1000 ml flask and diluted to volume.

A working solution of 2 µg/ml was prepared fresh daily as needed by dilution of the stock solution. This solution was prepared to contain 5% $HNO_3$. A matrix modifier solution was prepared in distilled water to contain 0.02% $NH_4H_2PO_4$ and 0.05%Triton X-100. All reagents were of Reagent Grade purity or better.

Blood samples were supplied by the Ontario Ministry of Labour. These samples were part of an ongoing Pb interlaboratory comparison study.

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## Procedure

Blood samples: blood samples (about 1 ml in volume) are removed from the refrigerator 15-20 minutes prior to the analysis to allow them to reach room temperature before use.

Prepare solutions for analysis by mixing in an autosampler cup 20 µl of whole blood with 100 µl of the matrix modifier solution. (Cups should be cleaned by soaking in 50% HCL for at least 1 hour followed by 5 rinses with distilled water. Clean pipette tips by rinsing with two volumes of 20% $HNO_3$ followed by rinses with two volumes of distilled water.

Place 5 µl samples on the wire coil. Bring the coil close to the furnace to dry the sample. Then insert the coil into the furnace and use the furnace program outlined in Table (1).

Table (1)

Furnace Program for Blood Analysis

| Step | 1 | 2 | 3 | 4 | 5 | 6 | Manual |
|---|---|---|---|---|---|---|---|
| Temp,°C | 340 | 650 | 20 | 2000 | 2000 | 20 | 2000 |
| Ramp, S | 1 | 60 | 1 | 1 | 0 | 1 | 0 |
| Hold, S | 40 | 20 | 7 | 3 | 5 | 5 | 4 |
| Internal gas flow ml/m | 300 | 300 | 300 | 300[a] | 10[a] | 300 | 300 |

[a] read recorder

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Remove the coil from the furnace during step 3. Plunge the coil into the hot furnace 1 second into step five. Clean the coil after the termination of the program with a clean piece of wire. Place the probe back in the furnace and fire at 2000°C to remove any contamination.

Prepare standards by diluting µl aliquots of the 2 µg/ml Pb working solution in 5% $HNO_3$ and the required amount of matrix modifier solution. Use direct comparison of sample and standard peak heights.

Snow Samples: Place a 5 to 20 µl aliquot of acidified melted snow onto the wire coil. (The volume chosen depends on the Pb concentration). Follow the above procedure for blood using the furnace program given in Table (2).

Prepare standards by diluting µl amounts of a 2 µg/ml Pb working solution in 5% $HNO_3$. Use direct comparison of sample and standard peak heights.

Table (2)

Furnace Program for Snow Analysis

| Step | +1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|
| Temp.,°C | 340 | 500 | 20 | 2000 | 2000 | 20 | 2000 | 20 |
| Ramp, S | 1 | 15 | 1 | 1 | 0 | 1 | 1 | 1 |
| Hold, S | 40 | 15 | 7 | 3 | 5 | 5 | 3 | 5 |
| Internal gas flow ml/m | 300 | 300 | 300 | 300 | 10 | 300 | 300 | 300 |

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Considerations in the Formation and Use of W Coil

Manning et al. (5) used a 0.28 mm thick W wire coil supported by a holder in the auto sampler arm. This was also found to be a good approach for the present investigations. The wire thickness chosen for the present work was 0.33 mm. Much thinner or thicker wires were found to be unsatisfactory. In particular thin wires became brittle after only a few firings and also lacked rigidity. Thicker wires had too great a thermal mass.

Coils were formed by wrapping 3 or 4 turns of W wire around a 0.9 mm thick wire. Using this size coil it was possible to use up to a 20 µl aliquot of solution (maximum drop size used by Manning et al. (5) was 10 µl. Giri et al. (7) were able to employ up to a 50 µl drop using a graphite probe). The sample port was enlarged to 3 mm to accommodate the coil. Using this set-up it was possible to obtain up to 200 firings with a single coil.

The coil must be positioned so that it (and when blood samples are run - the abundant carbonaceous residue) do not block the optical beam. This was easily accomplished with the recommended set-up.

Samples of 5 or 10 µl can be dried and charred entirely within the furnace. When 20 µl samples are employed the solution should be evaporated by holding the sample above the heated tube.

## RESULTS AND DISCUSSION

### Sensitivity

The Pb signal was of a similar magnitude for atomization from the wire and a L'vov type platform. This was in turn twice the signal obtained by atomization from the wall. Using a 3mm sample port reduced the sensitivity by up to one-half.

### Interference from $MgCl_2$

Lead standards were mixed with varying amounts of $MgCl_2$, a classical problem substance in Pb determinations. The results obtained are shown in Table (3).

Table (3)

Recovery of Pb in Presence of $MgCl_2$

| %$MgCl_2$ | 0 | 0.3 | 0.4 | 0.5 | 0.6 | 0.8 | 1.0 |
|---|---|---|---|---|---|---|---|
| | | | | Percent Recovery | | | |
| Wall | 100 | 64 | 41 | 23 | 15 | 13 | 8 |
| Platform | 100 | 63 | 56 | 51 | 58 | 58 | 46 |
| Wire | 100 | 102 | 100 | 90 | 87 | 87 | 80 |

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As can be seen no interference was noted until a concentration of 0.5% $MgCl_2$ was employed. Manning et al. (5) record a 95% recovery of Pb at 0.2% $MgCl_2$.

## Considerations in Determining Pb in Blood

Triton X-100 surfactant solution was important in aiding reproducable pipettings onto the wire coil. This is in contrast to the experience of Eaton and Holocombe (10) who document adverse spreading effects on a platform using this reagent. It was also found important for precision to replace the pipet tip frequently.

Frothing of the blood sample was taken as an indication of unsatisfactory drying conditions. For example it was found that whereas drying at 350°C caused frothing drying at 340°C was satisfactory. A 40 second drying time left traces of moisture. To remove the remaining liquid a slow ramp (60s) to 650°C was employed.

## Determination of Pb in Blood

Six blood samples used in an interlaboratory comparison study were used for evaluating the proposed procedure. The results are summarized in Table (4). These values are the means of two to four replications.

These results show recoveries vary from 93 to 106% compared to the accepted values. This means generally good agreement has been obtained. Relative standard deviations of the individual measurements averaged 5% with a range of 2 to 28%. The very large values corresponded to samples showing visible particulate (due to clotting).

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Table (4)

Determination of Pb in Blood (µg/l)

| Sample No. | Result | Acceptable Value | % of Accepted Value |
|---|---|---|---|
| 1 | 156 | 157 | 99 |
| 2 | 286 | 290 | 99 |
| 3 | 395 | 373 | 106 |
| 4 | 344 | 370 | 93 |
| 5 | 489 | 490 | 100 |
| 6 | 593 | 610 | 97 |

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Table (5)

Determination of Pb in Snow (µg/l)

| Sample | Result | % Recovery of 5 µl spike of 40 µg/l |
|---|---|---|
| St. Michael's College | 45 | 100 |
| Queen's Park | 65 | 100 |
| Street slush* (College St.) | 3250 | 95 |
| College St. | 47 | 90 |
| Willowdale | 13 | 100 |
| Oakville | 3 | 100 |
| Kingston | 11 | 100 |

*50 times dilution

Determination of Pb in Snow

Melted, acidified snow samples taken in and around the Toronto city area were analyzed by the proposed procedure. The results are summarized in Table (5). Generally good recoveries of the spikes were obtained.

## CONCLUSIONS

(1) The results obtained on snow and blood samples demonstrate that the wire coil probe method is suitable for the analysis of such samples for Pb.

(2) The wire probe approach with Pb outlined above shows superior interfence suppression (as measured using $MgCl_2$) compared to atomization from the platform or wall.

(3) Up to 200 firings per W coil can be obtained.

(4) Use of a 0.33 mm diameter W wire and coil formed around a 0.9 mm wire with an enlarged (3.0 mm) sample port makes it relatively easy to place up to 20 µl samples reproducibly into the furnace.

(5) The W wire probe can be used with up to 20 µl samples. This compares unfavourably with the up to 50 µl sample sizes permitted using the graphite probe (7). However, the W wire probe can be set up with only minor modifications to the standard furnace equipment.

(6) In contrast to the conclusion of Manning et al. (5), it is our view that the wire probe-in-furnace AAS technique has great potential as a practical trace element analysis technique.

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