



# AAS

## APPLICATION NOTES

The analysis of lead in drinking water

AAS



## Introduction

The determination of lead in drinking and ground waters is of major importance to assess which sources may contribute to the exposure of the community to this toxic trace element.<sup>1</sup>

In analysing waters for lead content, the analyst's major concern is the precise determination of lead in large numbers of samples. The lead concentration to be determined may range from trace levels to quite high concentrations. Analytical programs may range from day-to-day monitoring of small water supply systems up to large-scale studies of ground-waters. The large number of samples required and the susceptibility of samples to contamination and element loss create special problems for the water analyst.

Atomic Absorption Spectrometry is the preferred method of analysis of lead in water<sup>2</sup> for the following reasons:

- it is fast, accurate, and simple.
- it involves minimal sample preparation.
- it is specific and free from interferences.
- it can be used for both high and low concentrations of lead.

Concentrations of components of water supply systems vary with time, location and depth. In lakes, concentrations vary with depth, location, and temperature. Hence seasonal changes can also be expected. If there is movement of water through the lake the concentrations in the still and moving waters may differ. In rivers, pH changes may occur as the waters progress downstream. This has a significant effect on concentrations of many chemical species. The sediment load varies with speed, and will be different in parts of a river which are moving with differing velocities.

Tributaries and drains will frequently not become thoroughly mixed with the main stream for a large distance downstream from the junction.

Modes of lead in water are defined as:

1. Dissolved: unacidified sample passes through a 0.45 µm membrane filter.
2. Suspended: unacidified sample retained by a 0.45 µm membrane filter.
3. Total: unfiltered sample after vigorous acid digestion. Or the sum of 1 and 2 above.
4. Acid-extractable: treatment of an unfiltered sample with hot dilute mineral acid.

Item numbers 1 and 3 are the most common types of samples for lead analysis in water. Because of the ever-present possibility of contaminating the sample or causing loss of analyte, all stages of sample handling should be executed with due care. The lead concentration in most samples will be present at trace levels and consequently even small amounts of contamination will drastically alter the concentrations of these trace components. Similarly, loss of even a few micrograms of element by adsorption or precipitation will have a very serious effect.

All personnel collecting or handling samples should be well aware of the problems and potential sources of contamination, especially simple sources such as fingers, dust, dirty glassware and pipettes which have been left on a dirty bench. All containers are potential sources of contamination even if they have been thoroughly cleaned. These types of contamination can be checked by analysing a sample of de-ionized water, which has been standing in the container for several days.

It is advisable to prepare samples and standards at a pH of approximately 2. Addition of 2 mL/L of concentrated HNO<sub>3</sub> is sufficient in a neutral unbuffered sample. 5 mL/L may be required for some alkaline or highly buffered samples. Samples should be stored in clean polyethylene containers.

Under these conditions samples with lead concentrations of several mg/L are stable for at least two months. If it is necessary to store very dilute solutions the amount of acid may need to be increased to 1 mL/100 mL of sample. If glass containers are used lead may be absorbed onto or leached from the surface even from acidified solutions. Because of these losses, samples should not be allowed to remain in contact with glassware longer than necessary. Stock standards should be prepared at high concentrations, for example, 100 µg/mL. Working standards, especially those with concentrations less than 1 µg/mL, should be prepared daily.

## **Cleaning of apparatus**

All containers and apparatus coming into contact with very dilute solutions are thoroughly cleaned before use. Preferably these containers will not have been in contact with strong metal solutions. All glassware is soaked for a minimum of 16 hours in 50% nitric acid and then rinsed in reverse osmosis de-ionized water (see Reagent Preparation).

## **Experimental**

### **Instrumentation**

A GBC atomic absorption spectrometer, equipped with the unique Hyper-Pulse deuterium arc background correction system and GBC automated graphite furnace system, may be used for the analysis. The graphite furnace system consists of the graphite furnace power supply (GF) and programmable automatic sample loader (PAL). GBC software provides control of the entire system: spectrometer, furnace and autosampler. It allows the operator to develop furnace methods and to collect and store data. Real-time colour graphics of simultaneous signal absorbance and background traces allow the operator to optimise furnace conditions. All graphics traces for all standards and samples are stored on the computer. All method applications, results files and graphics files are stored on the computer, allowing recall for method assessment and refinement. The instrumental conditions for the determination of lead are given in Table 1, 2 and 3. GBC pyrolytically coated graphite furnace tubes are used for all analyses. A GBC lead super lamp is used to determine lead in the water samples.

### **Reagent preparation**

Analytical-reagent chemicals are used throughout. De-ionized water used for reagent preparation and analysis is from a reverse osmosis, mixed-bed de-ionizing unit that supplies Type 1 ultrapure water.

Working lead standard solutions are prepared from 1000 µg/mL stock solution by dilution in 1% V/V nitric acid. Magnesium nitrate modifier is prepared from a spectroscopic 1000 µg/mL magnesium standard to give a concentration of 40 µg/mL magnesium.

### **Sample preparation**

Two water sample concentrates for trace metals: "Trace Metals - Water Supply" Quality Control Sample WS 378, and "Trace Metals - AA" 989 Sample 1, are used as quality control check samples. Both samples were supplied by Spex Industries, Inc., N.J., and are certified by the United States Environmental Protection Agency. Both samples are prepared according to the following instructions: 10 mL of concentrate is pipetted into a 1 litre volumetric flask containing 900 mL of de-ionized water, 1 mL of concentrated nitric acid is added and the flask made up to 1 litre with de-ionized water. 1 mL of concentrated nitric acid is added to a 1 litre flask and made up to 1 litre with de-ionized water. It is set aside to be used as the blank for lead analysis only. These two samples are analysed for dissolved lead in water.

<b>Wavelength (nm)</b>	283.3
<b>Lamp Current (mA)</b>	8.0
<b>Slit Width (nm)</b>	1.0
<b>Slit Height</b>	Reduced
<b>Measurement Mode</b>	Peak Height

**Table 1: Instrumental parameters for graphite furnace analysis of lead in water**

<b>Program Step</b>	<b>Final Temp</b>	<b>Ramp Time (s)</b>	<b>Hold Time (s)</b>	<b>Gas Type</b>	<b>Read On/Off</b>	<b>Graphics On/Off</b>
1	40	2.0	1.0	Inert	Off	Off
2	90	5.0	5.0	Inert	Off	Off
3	120	10.0	5.0	Inert	Off	Off
4	400	10.0	5.0	Inert	Off	Off
5	400	1.0	1.0	None	Off	Off
6	2000	1.5	2.0	None	On	On
7	2200	1.0	1.0	Inert	Off	Off

**Table 2: Graphite furnace temperature program**

<b>Sample Type</b>	<b>Blank Volume</b>	<b>Standard Volume</b>	<b>Sample Volume</b>	<b>Modifier Volume</b>
Sample	0	0	12	5
Blank 1	12	0	0	5
Std. 1	10	2	0	5
Std 2	8	4	0	5
Std. 3	6	6	0	5

**Table 3: Auto mix sampler volumes (µL)**

All potable water samples are preserved immediately upon collection by acidifying with concentrated HNO<sub>3</sub> to pH 1-2 (add 1 to 2 mL per litre of sample). Samples may be stored for up to four weeks without deterioration.

The measurement of total lead in drinking water requires that total lead is analysed. Hence the procedure requires a vigorous digestion on the unfiltered sample. 50 mL of well mixed preserved sample is placed into a 100 mL Erlenmeyer flask to which 5 mL of concentrated nitric acid and a boiling chip are added. A loose fitting cap is used and the sample digested in an autoclave at 110°C for 30 minutes using the dry cycle. If the sample volume is above 50 mL the previous procedure is performed and the sample boiled down to less than 50 mL. The remaining contents are then transferred to a 50 mL volumetric flask and made up to volume with de-ionized water. The digested sample is then transferred to a polyethylene container. Blank solutions, standard solutions as well as repeat samples are also treated in the same way.

To test Spike Recovery the following samples are prepared. Sample “GBC” is an in-house sample with a concentration of 6.3 µg/L made up in de-ionized water. A second set of water sample concentrates for trace metals is used. “Trace Metals – AA” TMA 989 Sample 1 and Sample 3 are prepared as above except that only 1 mL of concentrate instead of 10 mL is used for each. Also a second type of quality

control concentrate, “Trace Metal – Water Supply” Quality Control Sample WS 378, is prepared as above but also using only 1 mL. This alteration in the standard procedure is to produce a sample, to be tested for spike recovery, at a concentration level near to the Contract Required Detection Limit of 1 µg/L. The concentration of the spike in each case is 12.5 µg/L.

A calibration graph is established from aqueous standards. Peak height measurement mode is used to quantify the atomic signals. The furnace temperature settings (Table 2) are optimised for these particular samples. The temperature conditions were, in general, the recommended settings as specified in the GBC Furnace Methods Manual.<sup>3</sup>

	WS 378 No. 6		TMA 989 No.1	
	Certified	Actual*	Certified	Actual*
<b>Between-run (n=11)</b>	21.9	21.8 ±0.9	50.4	51.9 ±2.9
<b>Within-run (n110)</b>	21.9	22.7 ±0.9	50.4	50.6 ±1.4
<b>95% Confidence Int.</b>	17.5–26.3		40.3–60.5	

\* Mean ±1 standard deviation

Characteristic concentration = 0.19 µg/L (20 µL sample volume).

Detection limit = 0.13 µg/L.

**Table 4: Analytical results for lead in WS 378 concentrate number 6 and TMA 989 sample number 1. All results are in µg/L**

In Table 4 the analytical results for the two EPA certified samples are shown. Typical peak profiles are shown in Figures 1 and 2. The background signals are small and almost indistinguishable from the baseline trace.

The analytical data shows excellent agreement with the certified concentration values for both within-run and between-run analyses. The detection limit achieved (0.13 µg/L) is well within the 1 µg/L Contract Required Detection Limit (CRDL) for ground water in the USEPA Contract Laboratory Statement of Work (CLP SOW) program. The characteristic concentration, 0.19 µg/L, illustrates the excellent sensitivity of the graphite furnace analysis.

Sample	Lead Concentration µg/L			Percent Recovery
	Expected	Actual	Post-spike	
<b>GBC</b>	6.3	6.3	18.4	96.9
<b>TMA 989 No. 3</b>	0	0	11.9	96.2
<b>TMA 989 No. 1</b>	5.1	5.2	18.2	103.6

**Table 5: Spike recovery data for lead in various water samples (refer Sample Preparation)**

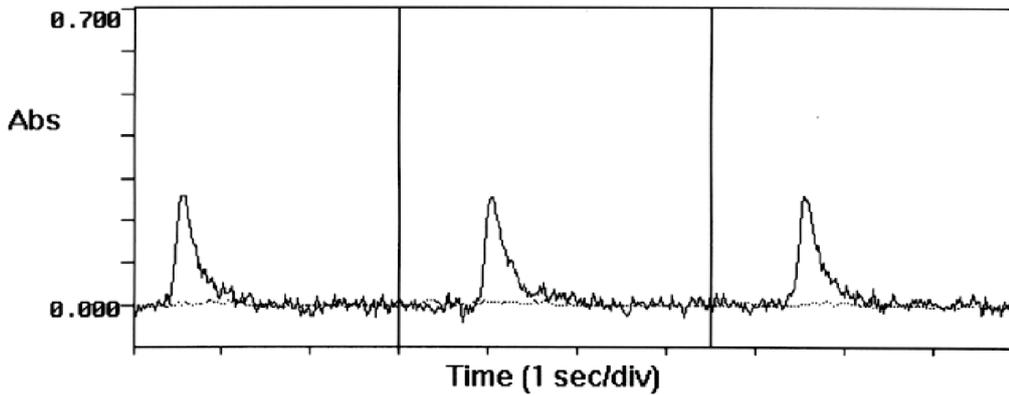


Figure 1: Typical analyte and background traces for trace metals water supply sample WS 378 concentrate 6

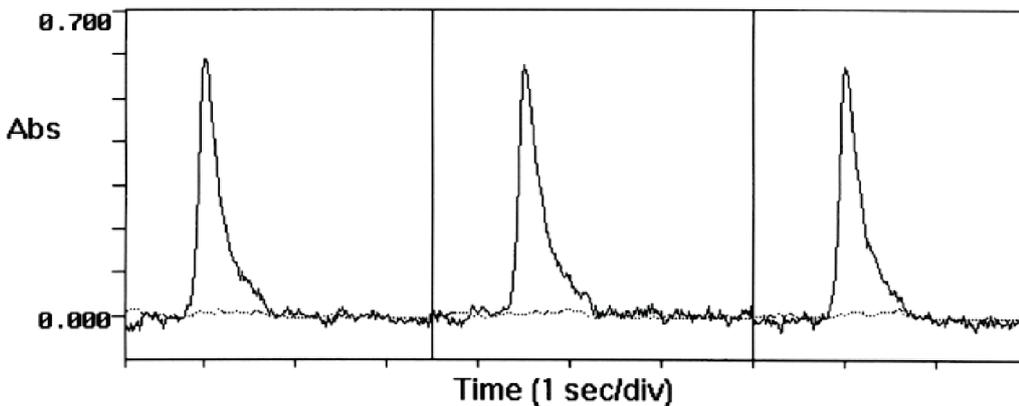


Figure 2: Typical analyte and background traces for trace metals-AA TMA 989 sample 1

In Table 5, Spike Recovery data illustrates the accuracy of the method not only when using an in-house sample but also for two suitable water supply quality control samples.

We have demonstrated that this method is able to analyse lead at concentration levels considerably lower than is required by U.S. government regulations.

## Conclusion

The determination of lead in ground and drinking waters can be performed with reliability and precision by using this simple method to meet United States Environmental Protection Agency requirements.

## References

1. American Public Health Association. Standard Methods for the Examination of Water and Wastewater. 17th Edition, 1989.
2. USEPA Methods for Chemical Analysis of Water and Waste. Method 239.2 for Lead. EPA-600/4-79-020, revised March 1983, NTIS, Springfield, VA., USA.
3. Graphite Furnace Methods Manual, GBC Scientific Equipment Pty Ltd, Braeside, Victoria, Australia.