The Determination of Toxic Metals in Waters and Wastes by Furnace Atomic Absorption

Application Note

Atomic Absorption

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Introduction

With the increasing awareness of the significance of many trace metals at ultra-trace as well as toxicological levels, there is a continuing need to improve existing methods for determining those elements. Analysts must monitor elements such as arsenic, selenium, lead, and cadmium in a rapidly increasing number of samples.

The maximum allowable concentration levels of these toxic metals in waters and wastes are regulated by the U.S. EPA and individual states. In drinking water, maximum levels range from 0.002 mg/L for mercury to 1 mg/L for barium [1]. NPDES permit levels for discharging effluents vary, depending upon the metal and industry involved. Guidelines for liquid and solid wastes are set at 100 times the drinking water levels [1]. Because of the extremely low concentrations encountered in many samples, furnace atomic absorption methods are part of EPA approved methodology [2].

The Case for Careful Methods Development

Seven metals (As, Ba, Cd, Cr, Pb, Se, and Ag), are regulated in drinking water and may be determined by furnace AA. These same metals are to be determined in liquid and solid waste samples as part of the EP toxicity test used to characterize a hazardous waste [3]. The only approved method for the eighth primary metal in drinking water, mercury, is the cold vapor generation technique.

Graphite furnace atomic absorption techniques, typically 100 times more sensitive than traditional flame AA methods, require that the analyst take extra care in developing his method. Since µg/L (ppb) levels of metals are normally being determined, extreme caution must be used to prevent contamination of solutions. Required precision and accuracy, sample and standard preparation, and Number AA-31 June 1983 possible interferences and matrix modifications must be considered. This study was undertaken to ascertain optimum parameters, necessary matrix modifiers, and performance characteristics of the seven toxic metals listed above.

Instrumentation

The instrumentation used for this study was the Agilent AA-975 Atomic Absorption Spectrophotometer and GTA-95 Graphite Tube Atomizer with programmable sample dispenser. The GTA-95 control unit contains a video display unit. The VDU is used in setting up furnace operating parameters. Temperatures, times, gas flows, and gas type are easily programmed for up to twenty individual steps in the furnace method. The VDU is also used to program sample dispenser parameters. The sample dispenser contains a computer-controlled stepper-motor-driven syringe, which may be programmed to pick up and deliver selected volumes of up to four solutions to the furnace in a single injection.

A typical sample dispenser program is shown in Figure 1. Normal calibration was accomplished by injecting variable volumes of a single stock standard. Variable blank volumes were included to keep total injection volume constant. A matrix modifier was automatically added.

The sample dispenser may also be programmed to automatically spike samples for analysis using the method of standard additions for calibration (Figure 2). The sample dispenser therefore saves the analyst time by automatically preparing solutions and provides better answers by eliminating potential dilution errors and contamination.

During operation, a temperature profile is displayed on the VDU, overlaid with the analytical signal from the AA, providing a quick and convenient means of determining optimum furnace parameters. An example of this display is shown in Figure 3.

SAMPLES AND STANDARDS			BLANK	MODIFIER
TYPE	LOCATION	VOLUME	VOLUME	VOLUME
BLANK	– –	– –	20	5
STD 1	51	6	14	5
STD 2	51	12	8	5
STD 3	51	20	0	5
STD 4				
STD 5				
SAMPLES	– –	20	0	5

LAST SAMPLE NO. = 45
NO. OF REPLICATES = 4
RESLOPE RATE = 0
FIRST SAMPLE NO. = 1
MULTIPLE INJECTIONS = 1
LAST DRY PHASE STEP = 2
INJECTION TEMP. = AMB

Figure 1. Sample parameters, normal calibration.

SOLUTION	STANDARD VOLUME	SAMPLE VOLUME	BLANK VOLUME	MODIFIER VOLUME
BLANK	– –		12	
ADDN. 1	2	3	7	
ADDN. 2	3	3	6	
ADDN. 3	4	3	5	
ADDN. 4				
ADDN. 5				
SAMPLE	– –	3	9	

LAST SAMPLE NO. = 40
NO. OF REPLICATES = 4
SINGLE SAMPLE NO. = 31
MULTIPLE INJECTIONS = 1
LAST DRY PHASE STEP = 2
INJECTION TEMP. = AMB

Figure 2. Sample parameters, standard additions.

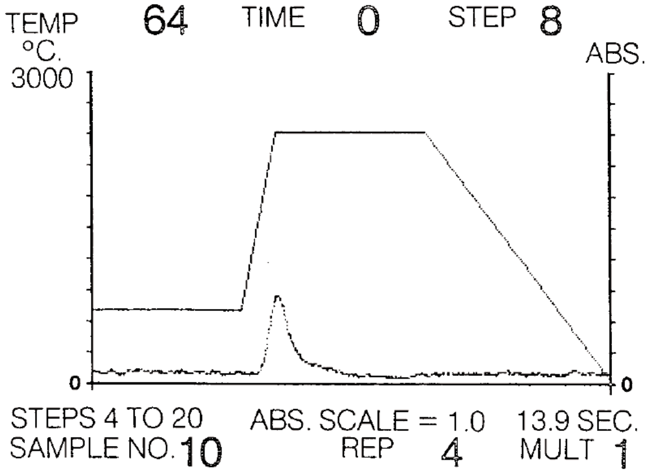

Figure 3. Temperature profile and analytical signal from the AA.

Results

For each of the seven elements studied, optimum furnace operating parameters were determined. These parameters were used for dilute nitric acid solutions and acetic acid solutions such as those encountered in the test for characteristic of EP toxicity applied to liquid and solid wastes [3]. Recoveries of the seven elements were determined in drinking water and in a complex, high dissolved solids effluent. All results were obtained using the automatic capabilities of the sample dispenser for solution preparation. Injection volumes varied from 10 to 40 µL. Unless otherwise noted, results were derived from peak height measurements of the atomic signal.

Arsenic

Table 1 illustrates the optimum temperature program for As. Maximum ramp rate to the atomize temperature of 2500 °C, along with stop-flow of the normal gas, nitrogen, was used. Temperature programs for other elements were similar with changes made in ash and atomize temperatures as appropriate.

Representative peaks and calibration curves for As are shown in Figure 4. Precisions ranged from 2.5 to 4 %RSD. A matrix modifier of 20 mg/L nickel was used. Responses for As were similar in both dilute HNO_3 and acetic solutions. This was true for most elements with the exception of Cr. For utmost accuracy, however, acid type should be the same for both standards and samples.

In drinking water, recoveries ranged from 100 to 104%. Low As recoveries were initially obtained from the effluent. However, by increasing the Ni concentration to 1000 mg/L in the effluent and standards, recoveries greater than 90% were achieved.

Table 1. Furnace Operating Parameters for Arsenic

Step no.	Temperature (°C)	Time (sec)	Gas flow	Gas type	Read command
1	75	5.0	3.0	Normal	
2	120	50	3.0	Normal	
3	1000	1.0	3.0	Normal	
4	1000	4.0	3.0	Normal	
5	1000	1.0	.0	Normal	
6	2500	.8	.0	Normal	*
7	2500	2.0	.0	Normal	*
8	2500	2.0	3.0	Normal	
9	40	11	3.0	Normal	
10					

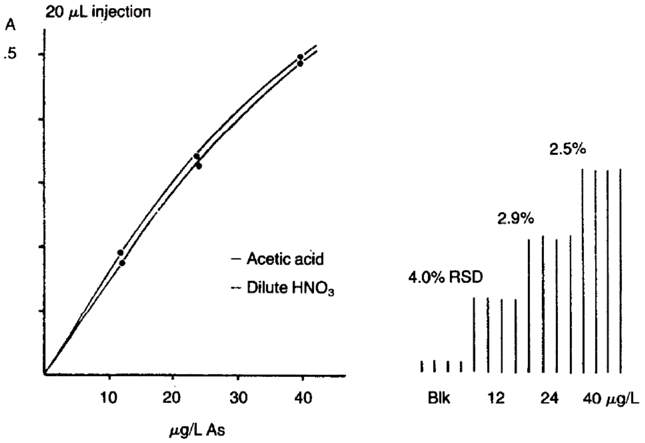

Figure 4. Arsenic calibration.

Barium

In order to reduce the sensitivity for Ba and cover the concentration range up to 1 mg/L (the maximum drinking water level), 0.5 L/min. of argon (as alternate gas) was used during the atomize step, rather than stop-flow conditions. Furnace operating parameters for Ba are shown in Table 2.

The programmability of the GTA-95 permitted less expensive nitrogen to be used during the dry steps, switching to argon prior to the atomize steps for maximum sensitivity and tube life. An ash temperature of 1300 °C and atomize temperature of 2500 °C were used. Precisions ranged from 0.9 to 4.1 %RSD.

Low recoveries for Ba were obtained in both drinking water and effluent. Matrix modification did not alleviate the problem. Accurate results were obtained, however, when the method of standard additions was used for calibration.

Table 2. Furnace Operating Parameters for Barium

Step no.	Temperature (°C)	Time (sec)	Gas flow	Gas type	Read command
1	75	5.0	3.0	Normal	
2	130	45	3.0	Normal	
3	1300	1.0	3.0	Normal	
4	1300	5.0	3.0	ALT.	
5	1300	1.0	.5	ALT.	
6	2500	.6	.5	ALT.	*
7	2500	2.0	.5	ALT.	*
8	2500	1.0	3.0	ALT.	
9	40	12	3.0	ALT.	
10					

Cadmium

Optimum ash and atomize temperatures for Cd were 300 °C and 1800 °C, respectively. The use of a slower ramp rate (500 °C/sec) to the atomize temperature and peak area measurement of the atomic signal resulted in precisions better than 1 %RSD. Representative peaks and calibration curves for Cd are shown in Figure 5.

Ammonium nitrate was found to be the best matrix modifier for Cd, but standard additions was also necessary to achieve 100% recoveries from the effluent.

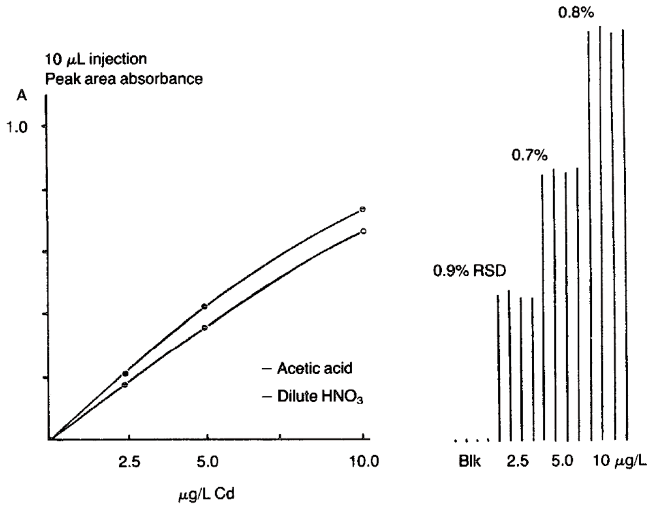

Figure 5. Cadmium calibration.

Chromium

Precisions obtained for Cr ranged from 1.1 to 1.6% RSD. Ash and atomize temperatures were 900 °C and 2500 °C respectively.

Recoveries for Cr from drinking water were excellent (99–100%). Recoveries of 96 to 100% were obtained from the effluent when ammonium nitrate was used as a matrix modifier.

Lead

Pb precisions ranged from 0.9 to 2 %RSD. As with Cd, a slow ramp rate of 500 °C/sec from the ash temperature (400 °C) to the atomize temperature (200 °C) produced the best results.

With both the drinking water and effluent, standard additions was necessary to obtain recoveries of 96 to 101% for Pb. It is possible that matrix modification with either ammonium nitrate or ammonium oxalate would remove the requirement of standard additions calibration for Pb.

Selenium

Ash and atomize temperatures for Se were 700 °C and 2500 °C, respectively. The analysis of four multiple injections of 10 µL produced signals 170% of those obtained with single 40 µL injections. Over the concentration range of interest (0–12 µg/L Se), precisions were better than 5% RSD.

Low recoveries were encountered in both the drinking water and effluent when Ni alone was used for matrix modification. Levels to 5000 mg/L Ni were checked in this study. Other modifiers normally used also produced low recoveries. It was found that adding 200 mg/L silver nitrate to the samples, allowing chlorides to precipitate for 30 minutes, followed by analysis using 200 mg/L Ni as modifier, gave usable recoveries (85–112%).

Silver

Optimum ash and atomize temperatures for Ag were 600 °C and 2000 °C, respectively. Figure 6 shows representative peaks and calibration curves for Ag. The excellent precisions shown (0.2 to 1.7 %RSD) illustrate the extreme accuracy and repeatability of the sample dispenser as 1, 2, and 4 µL aliquots of a stock standard (automatically diluted to 10 µL with blank solution) were used to build the calibration curves.

Improved reproducibility for the drinking water and effluent was obtained when 5% nitric acid was used for matrix modification. Standard additions was necessary to obtain recoveries of 100% from the effluent.

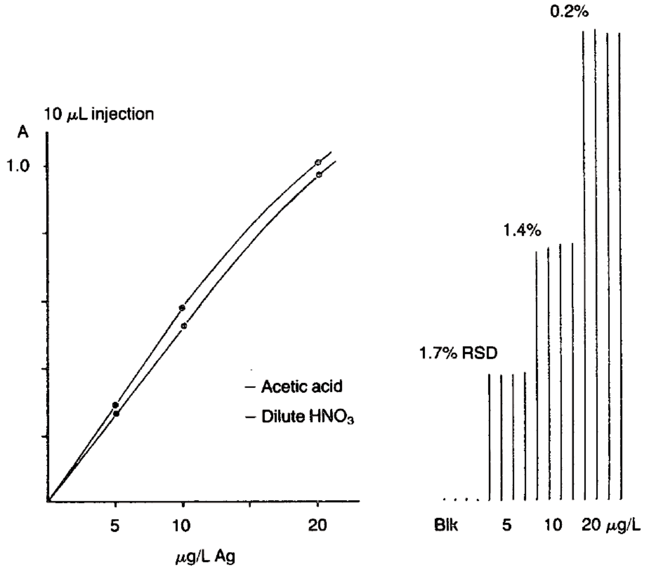

Figure 6. Silver calibration.

Accurate Determinations

Table 3 presents results obtained in a recent ASTM graphite furnace round robin for water. One of the samples supplied was a quality control check sample. The concentrations found for the QC check sample correlate extremely well with reported (true) values. As can be seen from this data (and as shown for the seven toxic metals discussed), accurate results can be obtained with furnace atomic absorption, provided the analyst keeps in mind potential interferences, matches acid matrices if necessary, and uses techniques such as matrix modification and standard additions if interferences are present.

The Agilent GTA-95 Graphite Tube Atomizer with programmable sample dispenser can save the analyst precious time by automatically preparing solutions and can provide more accurate answers by eliminating potential dilution errors and contamination.

Table 3. ASTM Round Robin, Quality Control Check Sample

Element	Reported value (µg/L)	Concentration found
Aluminum	61	65
Arsenic	24	24
Beryllium	24	25
Cadmium	6.5	6.6
Chromium	4.4	4.8
Cobalt	30	30
Copper	8.7	8.5
Iron	16	16
Lead	30	30
Manganese	7.9	8.1
Nickel	8.7	8.5
Selenium	8.7	9.0
Vanadium	78	76

References

1. US EPA, A Handbook of Key Federal Regulations and Criteria for Multimedia Environmental Control, EPA-600/7-79-175(1975).
2. US EPA, Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020 (1979).
3. US EPA, Test Methods for Evaluation of Solid Waste, Physical/Chemical Methods, SW-646 (1980).

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