The Determination of the Priority Pollutant Metals Using the CRA-90 Carbon Rod Atomizer

Application Note

Atomic Absorption

Authors

Lucinda M. Voth

Lawrence A. Covick

Douglas E. Shrader

Introduction

Over the past few years, increasing concern has been shown over the potentially detrimental effects of trace metal concentrations in all phases of our environment. Because of this concern, regulation of maximum concentration levels for many elements has been legislatively assigned to various federal and state agencies such as the EPA. The first main area of concern was the safety of public drinking water. Primary Drinking Water Standards were established for the regulation of eight metals (As, Ba, Cd, Cr, Pb, Hg, Se, and Ag). A second area of concern was control of water pollution through regulation of industrial effluents. The Federal Water Pollution Control Act and various amendments are the legislative basis for regulations to control water pollution. These regulations were incorporated into the National Pollutant Discharge Elimination System (NPDES). Operated at the state level NPDES established individual permits for various pollutants for specific industries. Up to 35 metals may be subject to NPDES permits. A third area of concern was the control of pollution from liquid and solid wastes. Most recently, of the 35 metals considered for NPDES permits, thirteen (Ag, As, Be, Cd, Cr, Cu, Hg, Ni, Pb, Sb, Se, Tl, and Zn) have been designated priority pollutants to be monitored and controlled in solid and liquid waste.

Test procedures have been developed to define a hazardous waste. One such test is the Extraction Procedure Toxicity Test. The EP Toxicity test was designed to simulate the leaching process in an improperly designed sanitary landfill. It considers toxic constituents that under these conditions would tend to migrate. For this test, a dry waste sample or liquid waste sample containing greater than 0.5% non-filterable solids must be subjected to an acid extraction involving acidification with acetic acid to pH = 5 followed by a 24 hour shaking and filtration. The resultant extract is combined with any initial filtrate and then analyzed. In the case of metals, if guidelines of 100× the maximum drinking water levels are exceeded, the waste is characterized as hazardous.

Agilent Technologies

While hazardous waste levels can often be analyzed by flame AA methods, the very low concentrations often encountered in the analysis of drinking water and industrial effluents may be extremely difficult or impossible to determine by flame atomic absorption. Because of this, graphite furnace methods, typically 100× more sensitive than flame methods, are part of approved EPA methodology.

In developing a furnace AA method, several factors must be taken into consideration. These include analysis require-ments, sample preparation requirements, analyte instrumen-tal requirements, interferences, and suitable matrix modifiers. Analysis requirements involve questions of accuracy and pre-cision along with the concentration range of interest. The answer lo these questions will determine standard concentra-tions, matrix, number of multiples to be analyzed, and the required sample dilution and preparation. Chemical interfer-ences and background absorption may both be encountered in furnace AA. Each element and sample matrix must be stud-ied to determine whether interferences are present and if so, appropriate corrections must be made. These may include matrix matching, standard additions, the use of background correction, or matrix modification. Modifiers for the elements reported in this paper will be discussed.

In this study, twelve of the priority pollutant metals (Ag, As, Be, Cd, Cr, Cu, Ni, Pb, Sb, Se, Tl, and Zn) were investigated. The only approved method for the thirteenth metal, Hg, is the cold vapor technique. Determinations of each were made in aqueous standards, acetic acid standards such as one might use in the EPA Extraction Procedure, drinking water, Environmental Resource Associates (ERA) Waste Water ref-erence standards, and a very dirty, high-dissolved solids efflu-ent waste water. Optimum parameters, performance, and results for the different sample matrices will be presented along with interference and accuracy data.

Silver

Temperature parameters and necessary matrix modifiers for silver determinations in the various sample matrices are reported in Table 1. The sensitivity* and detection limit** were calculated and are reported in grams. Sensitivity and detection

---

*   Sensitivity or characteristic concentration: The weight in grams of an element which would typically produce an absorbance of 0.0044 (1% absorption) in the peak height mode.

** Detection limit: The weight in grams of an element that produces a reading equal to twice the standard deviation of a series of at least ten determinations near blank level. At the detection limit relative standard deviation is ± 50%.

$$D. L. = \frac{2 \times s.d. \times conc.}{\bar{x}}$$

limits will be reported for all elements determined, and unless otherwise indicated, nitrogen was used as the inert sheath gas for the CRA-90.

Table 1.   Silver

328.1 nm	Sensitivity	0.8×10^{-12}g	
0.5 SBW	detection limit	0.3×10^{-12}g	
Sample	**Matrix**	**CRA parameters**	
Aqueous calibration	Dilute HNO$_3$	5 µL injection	
		Dry 100 °C	35 sec
Acetic acid	Dilute acetic	Ash 500 °C	10 sec
calibration	acid, HNO$_3$	Atomize 1800 °C	1 sec
	Ramp	400 °C/sec	
Drinking water	25% HNO$_3$	5 µL injection	
effluent*		Dry 100 °C	45 sec
		Ash 500 °C	30 sec
		Atomize 2000 °C	1 sec
		Ramp 400 °C/sec	
		300 °C/sec (effluent)	

* Background corrected

The silver calibration curve in distilled water is shown in Figure 1. The calibration is linear up to 0.8 absorbance and precisions were excellent, 0.9–1.9 %RSD for triplicate 5 µL injection volumes. Sensitivity improved with a faster ramp rate but precision was poorer. Both peak height and peak area curves are shown for the acetic acid matrix in Figure 2. Correlation between responses from distilled water and acetic acid was quite good. It was found that adding 1% HNO$_3$ to the acetic acid matrix improved both sensitivity and precision. Precisions are again excellent, 0.8–1.5 %RSD for peak height measurements and 0.3–0.9 %RSD for peak area measurements. (The ERA reference standard did not contain silver so no data is given.)
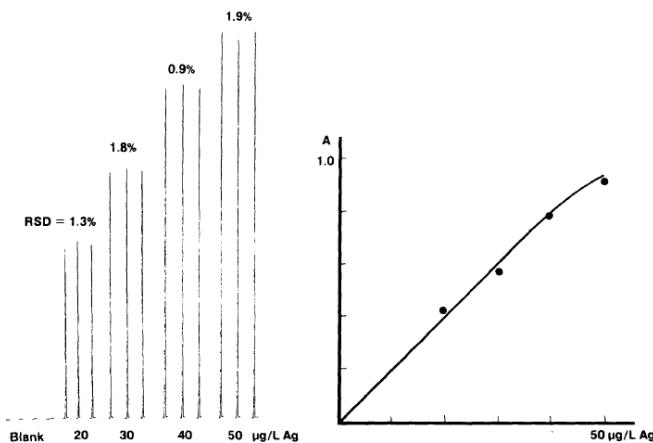

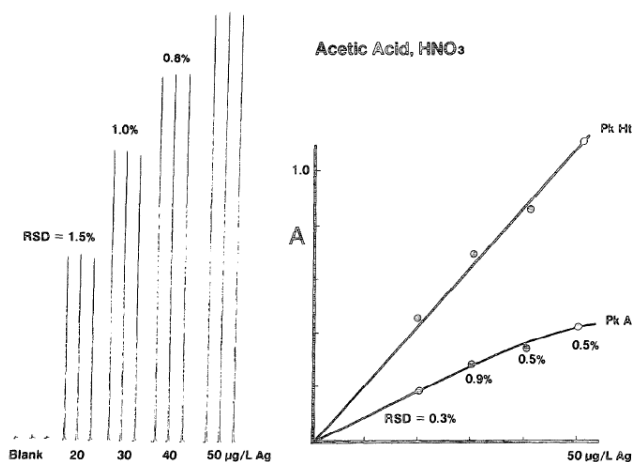*Figure 1.   Silver calibration — 20, 30, 40, 50 µg/L in distilled H$_2$O.*

Figure 2. *Silver calibration — For the EPA recommended separation procedure for liquid and solid waste.*

Silver was not detected in the drinking water sample. When the sample was spiked with silver, double peaks were encountered. A matrix modifier of 25% HNO$_3$ was used to eliminate double peaks and produce good recoveries. For 5, 10, and 20 µg/L Ag spikes the recoveries ranged from 92 to 98% by peak height and from 94 to 104% by peak area.

Silver was not detected in the effluent sample, so again spiked samples were analyzed. The different matrices gave peak height calibration curves which differed dramatically (as shown in Figure 3) probably due to the high chloride concentration in the effluent.
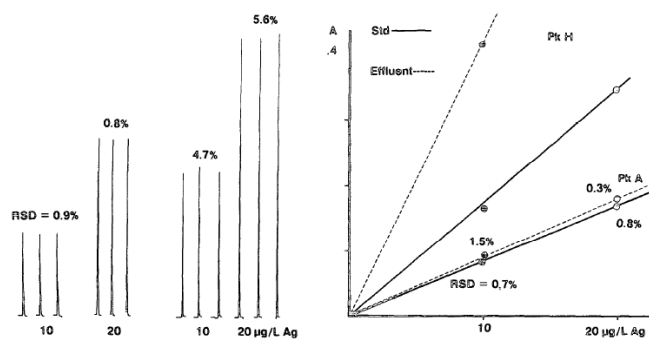
Figure 3. *Effluent matrix effects on silver calibration.*

Peak area measurements not only gave better precision, but produced standard curves of approximately the same slope for both matrices. Thus, measurements should be made by peak area, or alternatively, standard additions would be required for samples of this type. Due to the high dissolved solids content of the effluent, background correction was necessary. It was not needed for the other samples.

Arsenic

Table 2 summarizes the temperature parameters and matrix modifiers that were used to determine arsenic in the various sample matrices. A hollow cathode lamp was used and background correction was applied. Nickel was added to stabilize the As during the ash step. A concentration of 20 µg/mL Ni was found to give the best sensitivity and precision. However, this was not sufficient to retain As in the high salt content effluent sample. Concentrations of 1000, 2000 and 5000 µg/mL were checked, with 5000 µg/mL Ni giving the best results. Temperature programs were adjusted to improve peak shape.

Table 2. *Arsenic*

193.7 nm 1.0 SBW

HCL 5.0 mA	Sensitivity	7.0×10^{-12}g	
Background corrected	detection limit	6.5×10^{-12}g	
Sample	**Matrix**	**CRA parameters**	
Aqueous calibration	Dilute HNO$_3$	5 µL injection	
drinking water	20 µg/mL Ni	Dry	100 °C	35 sec
ERA WasteWatR		Ash	1400 °C	10 sec
Acetic acid	Dilute acetic acid	Atomize	2300 °C	1.5 sec
calibration	20 µg/mL Ni	Ramp	700 °C/sec	
Effluent	Dilute HNO$_3$	5 045L injection	
aqueous	5000 µg/mL	Dry	100 °C	45 sec
calibration		Ash	1500 °C	15 sec
Std. additions		Atomize	2300 °C	1.5 sec
calibration		Ramp	800 °C/sec	

The arsenic calibration curve in distilled water is shown in Figure 4. Absorbance values could be increased by using larger injection volumes. Standards acidified with acetic acid gave somewhat lower responses, thus matrix matched standards should be used for this type of sample.
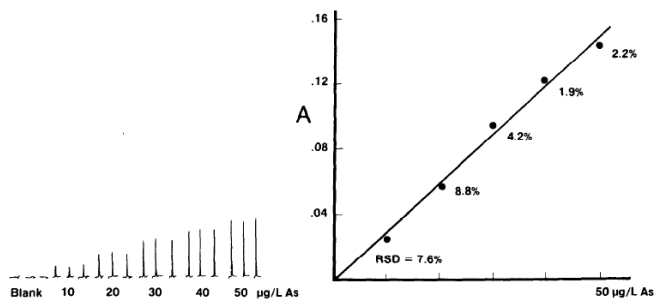

Figure 4. *Arsenic calibration — 10, 20, 30, 40, 50 µg/L As 20 µg/mL Ni.*

As Figure 5 indicates, the ERA reference standard results were excellent for both peak height and peak area modes of measurement.
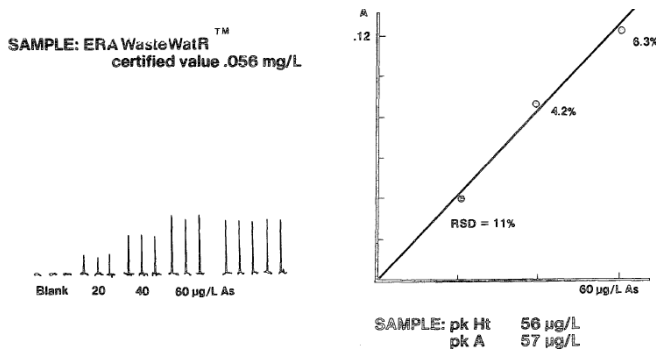

Figure 5. Arsenic calibration — 20, 40, 60 µg/L As.

Arsenic was not detected in the drinking water sample. The recoveries for 5, 10, and 20 µg/L As spikes and precisions (RSD) are shown in Figure 6.

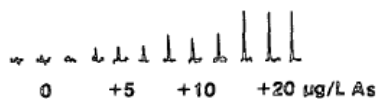| Addition	5 µg/L	10 µg/L	20 µg/L
Recovered	5.2	10.1	21.7
RSD	14.2%	9.2%	3.7%

Figure 6. Arsenic recovery in drinking water — 5, 10, 20 µg/L As.

The effluent sample was diluted 1:1 with 1% Ni solution resulting in a 5000 µg/mL Ni concentration in the sample. Standards were also made up to 5000 µg/mL Ni. Both direct and standard additions calibration gave the same results, 4 µg/L As, or 8 µg/L As in the original sample as indicated in Figure 7. By the more sensitive hydride generation technique, a result of 7 µg/mL As was obtained.
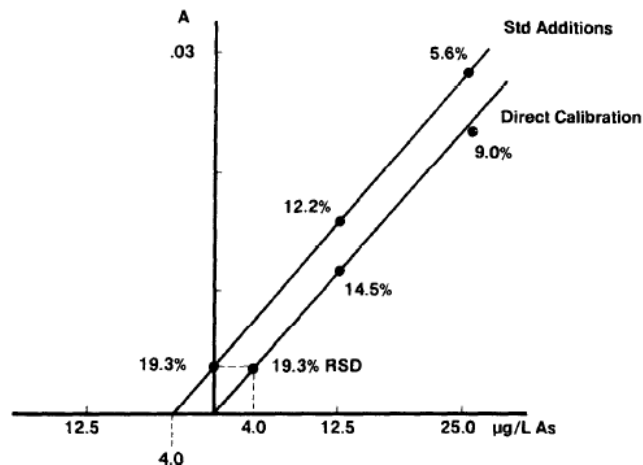

Figure 7. Determination of arsenic in effluent sample.

Beryllium

The temperature parameters and matrix modifiers used for the beryllium determinations are shown in Table 3. The aqueous calibration was prepared with standards of 5, 10, 15 and 20 µg/L Be. The precisions were excellent ranging from 0.2 to 2.0 %RSD. The Be concentration in the ERA reference standard was determined from the aqueous calibration following a 10X dilution. The concentration found of 14 µg/L or 0.140 mg/L in the original sample was an excellent result, (certified value 0.140 mg/L Be).

Table 3. Beryllium

234.9 nm	Sensitivity	0.6×10^{-12}g	
1.0 SBW	detection limit	0.9×10^{-12}g	
Sample	**Matrix**	**CRA Parameters**	
Aqueous calibration	Dilute HNO_3	5 µL injection	
ERA WasteWatR		Dry	100 °C	35 sec
		Ash	1200 °C	10 sec
		Atomize 2300 °C	1.5 sec
		Ramp	700 °C/sec
Acetic acid	Dilute acetic	Dry	100 °C	45 sec
calibration	acid=1% H_2SO_4	Ash	1000 °C	10 sec
		Atomize 2400 °C	1 sec
Drinking water	1% H_2SO_4	Ramp	500 °C/sec
effluent		Ash	1300 °C (effluent)

The dilute acetic acid calibration was significantly less sensitive than the aqueous calibration and precision was poor. The addition of 1% H_2SO_4 did not improve sensitivity but greatly improved precision. Excellent precisions of 0.0–2.9 %RSD were obtained. Matrix matched standards would be required for accurate results.

Beryllium was not detected in either the drinking water sample or the effluent sample, so recoveries were studied. Recoveries for 5 and 10 µg/L spikes in the drinking water sample ranged from 66 to 74% even at low ash temperatures for both dilute acetic and 1% HNO_3 matrices. The addition of 1% H_2SO_4 gave recoveries of 98–99% for 5 and 10 µg/L Be spikes.

The same situation was found in the effluent sample. In a matrix of dilute HNO_3, recoveries averaging 65% were obtained for a 10 µg/L spike. With the addition of 1% H_2SO_4, standard additions was not necessary for the determinations in either the drinking water sample or the effluent sample.

Cadmium

The temperature parameters and matrix modifiers used for cadmium determinations are summarized in Table 4. For the effluent sample, 1% NH_4NO_3 was added to help remove the salt during the ash stage. Ash and atomize conditions were adjusted to produce sharper peaks and to ensure that all residual salt matrix was driven off during the atomize stage.

Table 4.   Cadmium

228.8 nm		
0.5 SBW	Sensitivity	0.16×10^{-12}g
Background corrected	detection limit	0.12×10^{-12}g
Sample	**Matrix**	**CRA Parameters**
Aqueous calibration	Dilute HNO_3	5 µL injection
drinking water		Dry 100 °C 35 sec
ERA WasteWatR		Ash 400 °C 10 sec
Acetic acid	Dilute acetic	Atomize 1200 °C 1 sec
calibration	acid	Ramp 400 °C/sec
Effluent	1% NH_4NO_3	5 µL injection
std additions		Dry 105 °C 45 sec
calibration		Ash 600 °C 15 sec
		Atomize 1800 °C 1 sec
		Ramp 600 °C/sec

Direct aqueous calibration produced excellent results for the ERA reference standard as indicated in Figure 8. The value obtained of 0.168 mg/L closely matches the certified value of 0.170 mg/L Cd. The calibration curve for standards acidified with acetic acid matched the aqueous curve in Figure 8 quite well.
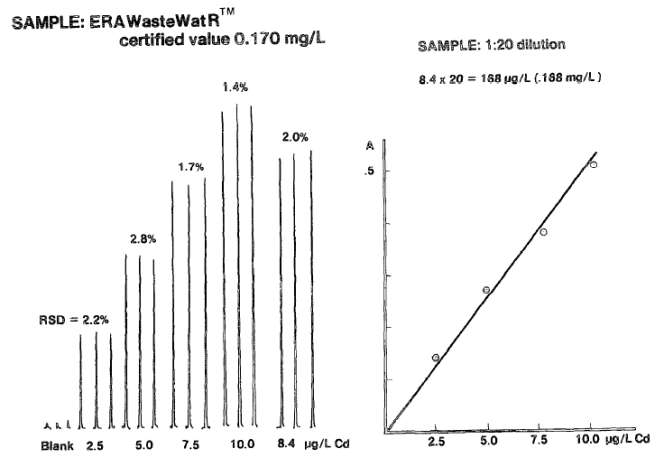

Figure 8.   Cadmium calibration — 2.5, 5.0, 7.5, 10.0 µg/L Cd.

Drinking water results by both direct calibration and standard additions calibration were approximately the same and are shown in Figure 9. Precisions were poorer than previously shown as the concentration of Cd was only 4× the detection limit.
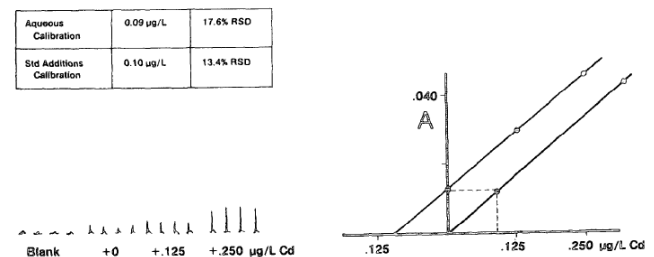

Figure 9.   Cadmium in drinking water.

In the effluent sample, sensitivity was markedly affected by the matrix and the added NH_4NO_3, thus standard additions was the required method of calibration. Results are shown in Figure 10.
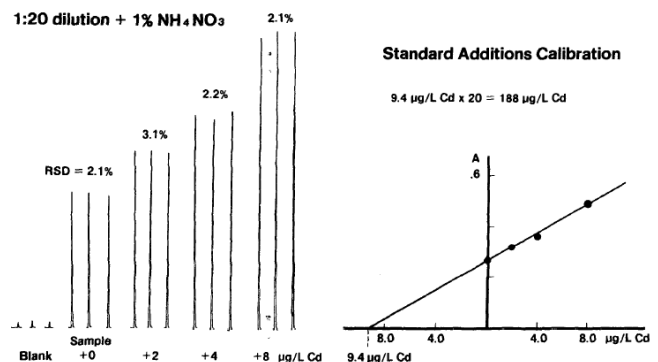

Figure 10.   Determination of cadmium in effluent sample.

5

Chromium

The temperature parameters used to determine chromium in the various samples are shown in Table 5. Because of the fairly high chromium concentration in the ERA reference standard, a smaller injection volume was used to eliminate dilution. Also, the smaller injection volume was used with the effluent to assure that standard additions fell in the linear portion of the calibration curve.

Table 5.   Chromium

357.9 nm	Sensitivity	3.4×10^{-12}g	
0.5 SBW	detection limit	0.67×10^{-12}g	
Sample	**CRA parameters**		
Distilled water calibration	20 µL injection		
standards	Dry	100 °C	55 sec
Tap water	Ash	1300 °C	15 sec
Acetic acid calibration	Atomize	2400 °C	0.5 sec
standards	Ramp	800 °C/sec	
ERA WasteWatR	2 µL injection		
	Dry	80 °C	30 sec
Effluent	2 µL injection		
	Dry	90 °C	30 sec
	Ash	1300 °C	20 sec

Representative peaks and the standard curve for distilled water standards are shown in Figure 11. Standards acidified with acetic acid gave exactly the same response as those in distilled water. Precisions were slightly better.
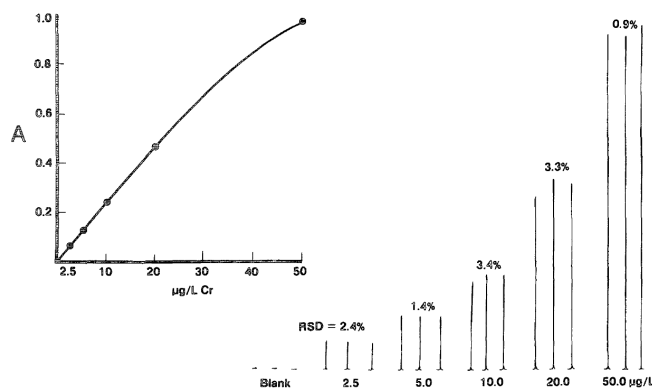

Figure 11.   Chromium calibration – 2.5, 5, 10, 50 µg/L Cr.

As shown in Figure 12, matrix can have a dramatic effect on chromium response. The response of the ERA reference standard was similar to distilled water, producing a standard additions calibration parallel to the aqueous calibration. Due to high chloride concentrations in the effluent, however, peaks evolve much faster resulting in a significantly steeper slope when peak height is measured. If compared to the distilled water calibration, erroneously high results of 42.5 µg/L Cr would be obtained rather than 19 µg/L Cr as determined by standard additions.
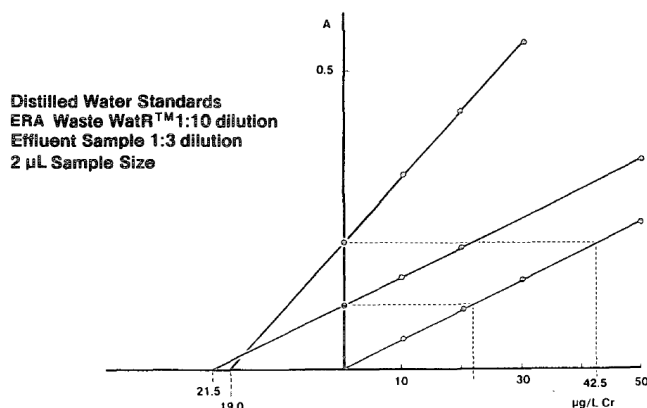

Figure 12.   Effect of matrix on calibration curve.

The tabulated results in Table 6 were calculated from peak height measurements. Direct calibration and standard additions results correlate quite well for the drinking water and ERA standard. Direct calibration of the effluent sample using the peak height mode produced high results. Standard additions gave a lower result of 57 µg/L Cr (19 µg/L × 3). This result was confirmed by peak area measurement and direct calibration. The result of 60 µg/L Cr is very close to the peak height standard additions result of 57 µg/L.

Table 6.   Results of the Determination of Chromium in Water Samples

Sample	Results (direct calibration)	%RSD	Results (standard additions)	%RSD
Tap water	1.6 µg/L	1.2	1.0 µg/L	1.9
*ERA WasteWatR	217 µg/L	3.2	215 µg/L	3.3
Effluent	128 µg/L	1.8	57 µg/L	4.0

* ERA certified value 220 µg/L

Lead

The analysis parameters used for the lead detemination are shown in Table 7.

The aqueous calibration was prepared with standards of 20, 30, 40 and 50 µg/L Pb and precisions for triplicate injections were excellent, ranging from 0.5% to 2.2% RSQ. The ERA WasteWatR standard was diluted 10X and 20X and analyzed using this calibration. The result of 0.540 mg/L Pb (54 µg/L and 27 µg/L in the diluted samples) corresponds well with the certified value of 0.525 mg/L Pb.

Table 7.   Lead

217.0 nm 1.0 SBW **Sample**	Sensitivity detection limit **Matrix**	2.0×10^{-12}g 2.2×10^{-12}g **CRA parameters**		
Aqueous calibration ERA WasteWatr	Dilute HNO$_3$	5 µL injection		
		Dry	100 °C	35 sec
		Ash	500 °C	10 sec
Drinking water		Atomize	1800 °C	1 sec
(peak area)		Ramp	300 °C/sec	
Acetic acid	Dilute acetic	5 µL injection		
calibration	acid	Dry	100 °C	40 sec
		Ash	400 °C	15 sec
Effluent*	1% HNO$_3$	Atomize	1800 °C	1.5 sec
(peak area)		Ramp	400°C/sec	

* Background corrected

The CRA-90 parameters were changed slightly for the acetic acid calibration. Sensitivity measured in peak height was slightly better than that of the aqueous calibration and precisions were excellent, ranging from 0.4% to 2.3 %RSD. If the acetic acid extraction is used, matrix matching is recommended. The acetic acid was found to be contaminated with Pb. A blank was carefully prepared and subtracted from all measurements.

The drinking water sample was analyzed by direct calibration and standard additions calibration. By direct calibration, concentrations of 3 µg/L Pb by peak height and 8.5 µg/L Pb by peak area were obtained. Standard additions produced results of 8.0 µg/L Pb. Either direct measurements by peak area or standard additions would give accurate results.

The high lead concentration in the effluent sample necessitated a 25× dilution of the sample. This greatly reduced the concentration of interfering high dissolved solids. Direct calibration by peak area measurements produced results of 52 µg/L Pb in the diluted sample, confirmed by standard additions as 50 µg/L. With direct calibration by peak height, a low result of 17 µg/L Pb was obtained. In this study peak area measurements gave excellent results using direct calibration.

The interfering matrix was greatly reduced by dilution. If levels are such that dilution is not possible, matrix modifiers such as ammonium nitrate or ammonium oxalate are recommended if lead is to be determined in a high salt matrix [1].

Antimony

Table 8 summarizes the CRA-90 parameters used to determine antimony. The acetic acid calibration showed significantly more curvature than the calibration in dilute nitric, therefore, matrix matching is recommended if the acetic acid extraction procedure is used. All measurements were made in the peak height mode. Standard additions calibration was used for the ERA reference standard and the value obtained of 42 µg/L Sb corresponds well with the reported value of 43 µg/L.

Table 8.   Antimony

217.6 nm 0.2 SBW Background corrected **Sample**	Sensitivity detection limit **Matrix**	7.0×10^{-12}g 2.6×10^{-12}g **CRA parameters**		
Aqueous calibration	Dilute HNO$_3$	5 µL injection		
Acetic acid	Dilute acetic	Dry	90 °C	35 sec
calibration	acid	Ash	1000 °C	10 sec
ERAWasteWatR		Atomize	2100 °C	1 sec
(standard additions)	Dilute HNO$_3$	Ramp	800 °C/sec	
Drinking water	Dilute nitric	5 µL injection		
(standard additions)		Dry	90 °C	45 sec
		Ash	700 °C	10 sec
Effluent		Atomize	2200 °C	1 sec
(standard additions)		Ramp	800 °C/sec	

Antimony was not detected in either the drinking water or the effluent sample, therefore recoveries were studied to determine matrix effects. When peak height absorbances were used, the recoveries in drinking water and the effluent were 115% and 185% respectively. With peak area measurements the situation reversed, with recoveries in both matrices significantly less than 100%. Drinking water yielded an average recovery of 68% and the effluent sample an average recovery of 50%.

It was necessary to decrease the ash temperatures for these samples to 700 °C. Changes in peak appearance time and peak shape were indicative of matrix interference, in this case severest in the high chloride effluent matrix. The addition of a matrix modifier such as ammonium nitrate or ammonium oxalate may remove the chloride interference, or standard additions would be necessary to obtain accurate results.

Selenium

Table 9 summarizes the temperature parameters and matrix modifiers used to determine selenium. A 20 µL injection volume was used to improve sensitivity so that the low ranges required for regulatory requirements could be analyzed (10 µg/L Se). The acetic acid calibration was similar to that in dilute nitric acid and exhibited some curvature even at these low concentrations. The ERA reference standard was analyzed by standard additions with a matrix modifier of 20 µg/mL Ni. The concentration found of 40 µg/L Se corresponds well with the reported value of 43 µg/L.

Table 9.   Selenium

196.0 nm
1.0 SBW; HCl 10 mA

Background corrected	Sensitivity	19×10^{-12}g	
	Detection Limit	9.0×10^{-12}g	
Sample	**Matrix**	**CRA parameters**	
Aqueous calibration	Dilute HNO_3	20 µl injection	
Acetic acid	20 µg/mL Ni	Dry	100 °C	55 sec
calibration		Ash	700 °C	10 sec
ERAWasteWatR		Atomize	2200 °C	1 sec
(standard additions)		Ramp	800 °C/sec	
Drinking water	Dilute HNO_3	20 µl injection	
	200 µg/mL Ag	Dry	100 °C	55 sec
	100 µg/mL Ni	Ash	500 °C	10 sec
Effluent		Atomize	2200 °C	1 sec
		Ramp	800 °C/sec	

Selenium was not detected in either the drinking water or the effluent sample. A recovery study was performed for each sample to determine possible means of overcoming matrix interferences. Additions of 10 µg/L and 20 µg/L Se and the use of a matrix modifier of 500 µg/mL Ni gave average recoveries of 50% in the drinking water sample by both peak height and peak area measurement.

Determination in this matrix could be performed accurately by the method of standard additions. Alternatively the following method developed for the effluent sample could eliminate the need for standard additions.

In the effluent sample less than 10% of spiked selenium was recovered when only nickel nitrate was added, even at concentrations up to 0.5% Ni. A number of other often used matrix modifiers were added individually and in conjunction with 100, 1000, and 10,000 µg/mL Ni. These included 1, 5, and 25% HNO_3 and H_2SO_4, ammonium nitrate, ammonium oxalate, and ammonium citrate. None of these matrix modifiers improved recoveries. Some of them totally destroyed the selenium signal. Good recoveries were obtained from the effluent matrix with the addition of both $AgNO_3$ and $Ni(Ni(NO_3)_2)$. The best recoveries occur if the treated sample is allowed to sit for half an hour prior to analysis.

With silver precipitation of chlorides prior to analysis, the previously reported nickel matrix modifier permits selenium to be determined in high salt matrices. It should be noted that selenium is a natural contaminant of nickel metal. If the nickel nitrate solution is made from nickel metal dissolved in HNO_3 acid, a considerable contamination problem could be encountered. A high quality $Ni(NO_3)_2$ salt is recommended.

Thallium

In the determination of thallium severe interferences were encountered in the presence of NaCl and HCl. Methods of overcoming this interference were investigated by adding 100 µg/L Tl and 0.1% NaCl to various acid matrices including dilute HNO_3, 1% HNO_3, 2% HNO_3, dilute acetic acid, and 0.5% HCl. Recoveries in these matrix acids ranged from 5% to 14%. In 0.5% HCl without the addition of NaCl, 30% of the 100 µg/L Tl spike was recovered. Other matrix modifiers commonly used for NaCl interference such as ammonium nitrate and ammonium oxalate produced similarly poor recoveries. However, the addition of 1% and 2% H_2SO_4 to standards and samples containing 0.1% NaCl gave recoveries of 94% and 97% respectively. The CRA-90 parameters for the 2% H_2SO_4 matrix are given in Table 10.

Table 10.   Thallium

276.8 nm
0.5 SBW
HCl 5.0 mA

	Sensitivity	4.1×10^{-12}g	
	Detection limit	2.6×10^{-12}g	
Sample	**Matrix**	**CRA parameters**	
Aqueous calibration	Dilute HNO_3	5 µl injection	
		Dry	95 °C	35 sec
		Ash	400 °C	10 sec
		Atomize	1800 °C	1 sec
		Ramp	500 °C/sec	
ERAWasteWatR	2% H_2SO_4	5 µl injection	
Drinking water		Dry	100 °C	45 sec
Effluent*		Ash	500 °C	15 sec
Acetic acid		Atomize	2200 °C	0.5 sec
calibration		Ramp	300–400 °C/sec	

* Background corrected.

Other authors have studied the effects of varying concentrations of nitric acid, sulphuric acid, perchloric acid, and sodium chloride. Hydrochloric acid, perchloric acid, and sodium chloride produced severe interferences. Sulphuric acid was investigated as a matrix modifier to remove these interferences. It is assumed that thallium sulphate decomposes to the more stable oxide during the ash stage. While in the presence of hydrochloric acid, perchloric acid, and sodium chloride, thallium forms the volatile chloride and is lost before atomization. In the case of sodium chloride the addition of 0.01% (v/v) sulphuric acid gave good recoveries of thallium in solutions of up

to 100 mg/L NaCl. The addition of 1% (v/v) sulphuric acid allowed good recoveries in up to 1000 mg/L NaCl [2]. The upper limit of tolerable NaCl concentrations in dependent on the ability of the instrument to correct for the high levels of background absorption encountered.

The CRA-90 parameters used are summarized in Table 10. A 5 µL injection volume was used for all calibrations and sample analyses. Calibrations for thallium were prepared in dilute HNO_3 and H_2SO_4 The calibration in 2% H_2SO_4 showed similar sensitivity to that in dilute HNO_3 and precisions were excellent for both ranging from 0.8% to 2.3 %RSD. Argon was used as the inert sheath gas, giving approximately twice the sensitivity of nitrogen. Acetic acid standards such as one might use in the EPA extraction procedure gave poor sensitivity and precision. However, with the addition of 2% H_2SO_4 the acetic acid calibration was similar to that for aqueous calibration.

The CRA-90 parameters were modified for the sulphuric acid calibration. The ash temperature was increased to 500 °C and the atomize temperature was increased to 2200 °C. Though thallium is atomized below 1800 °C apparently residual sulphate salts remaining on the carbon rod decrease sensitivity over repeated firings. Since the atomization peak is very rapid, lower ramp rates gave the best sensitivity and precision. For the drinking water and effluent sample, a ramp of 400 °C/sec was used. For the ERA reference standard, a ramp of 300 °C/sec was used. Accurate background correction was required for the effluent sample because of its high salt content.

In the determination of TI in the ERA reference standard severe interferences were encountered without the 2% H_2SO_4 matrix modifier. Less than 10% of the thallium was recovered. With the addition of 2% H_2SO_4 approximately 90% of the 81 µg/L TI was recovered, 73 µg/L by peak height and 75 µg/L by peak area. The amount of interference was surprising considering the sample was relatively clean. It did not contain sodium chloride, only low levels of other metal salts. Of the priority pollutant metals determined in the ERA sample, only thallium showed interferences from the matrix.

In the drinking water sample without the addition of sulphuric acid, additions of 25 µg/L and 50 µg/L TI could not be detected. From samples spiked with 25 µg/L and 50 µg/L TI, 26 µg/L and 50 µg/L TI were recovered with the addition of 2% H_2SO_4 Also in the effluent sample, without matrix modification, thallium spikes could not be detected. With the addition of 2% H_2SO_4 to the effluent sample, 24 µg/L and 46 µg/L were recovered from 25 µg/L and 50 µg/L thallium spikes. This represents recoveries of 96% and 92% respectively.

Though with the sulphuric acid matrix thallium recoveries in the drinking water and effluent samples ranged from 90% to

104% without the use of standard additions, this may not be true for other samples. Because thallium is susceptible to interferences, the standard additions method of calibration should always be used to check for interferences even with the addition of sulphuric acid. Samples with high levels of dissolved solids may also require dilution as the sulphuric acid does not reduce background absorption.

Copper, Zinc, Nickel

Three of the priority pollutant metals can in most cases be analyzed by traditional flame AA methods. Copper and zinc are included in the Secondary Drinking Water Standards and are regulated at 1.0 and 5.0 mg/L respectively. Industrial effluent levels are regulated by individual NPDES permits at a similar concentration range. Though copper and zinc are regulated at levels attainable by flame AA, nickel could be regulated at levels needing the more sensitive furnace technique. Table 11 summarizes instrument parameters, sensitivities, detection limits and interference data for copper, zinc, and nickel determinations by flame AA.

Table 11.   Determination of Copper, Zinc, Nickel by Flame AA

Instrument	Parameters	Sensitivity detection limit	Drinking water	Effluent
Copper	324.8 nm 0.5 SBW	20 µg/L 2 µg/L D.L.	17 µg/L 18 µg/L (std.addition)	5 µg/L 5 µg/L (std.additlon)
Zinc	213.9 nm 1.0 SBW	4.0 µg/L 0.5 µg/L D.L.	37 µg/L 35 µg/L (std.addition)	44 µg/L 48 µg/L (std.addition)
Effluent background corrected				
Nickel	232.0 nm 0.2 SBW	30 µg/L 5 µg/L D.L.	N.D. Spikes recovered	N.D. Spikes recovered
Effluent background corrected				

N.D = Not detected.

Analysis by standard additions gave results similar to those obtained by direct calibration in the determination of copper and zinc in both samples even at the low levels encountered. Nickel recoveries in both samples were excellent. The only interference encountered was background absorption in the effluent sample for the nickel and zinc determinations. This was easily corrected for by the use of simultaneous background correction.

Table 12 summarizes the CRA-90 parameters used to determine nickel at concentration levels lower than those attainable by flame AA. The aqueous calibration of 20, 30, 40 and 50 µg/L Ni gave excellent precision of 0.9–1.7 %RSD. The nickel calibration in acetic acid was very similar to that in

dilute nitric with precisions only slightly poorer. The nickel concentration was determined in the ERA reference standard and the 0.164 mg/L Ni found corresponds well with the certified value of 0.155 mg/L Ni. Nickel was not detected in the drinking water sample. Spiked additions of 10 µg/L and 20 µg/L gave recoveries of 11 µg/L and 19 µg/L Ni respectively. The effluent was found to contain a low concentration of 3.0 µg/L Ni and standard additions gave similar results. In this study, chemical interferences were found to be minimal for nickel determinations in the samples analyzed.

Table 12.   Nickel

232.0 nm	Sensitivity	10.0×10^{-12}g		
0.2 SBW	detection limit	7.0×10^{-12}g		
Sample	**Matrix**	**CRA parameters**		
Aqueous calibration	Dilute HNO_3	5 µl injection		
Acetic acid calibration	Dilute acetic acid	Dry	100 °C	35 sec
		Ash	850 °C	10 sec
		Atomize	2300 °C	1 sec
		Ramp	600 °C/sec	
ERA WAsteWatR	Dilute HNO_3	Ash	700 °C	10 sec
		Ramp	700 °C/sec	
Effluent*		Ash	700 °C	20 sec
		Ramp	800°C/sec	

* Background corrected

In conclusion, the need to determine very low concentrations of the priority pollutant metals often requires the use of furnace atomic absorption. As has been shown, very accurate results may be obtained in furnace AA provided the analyst keeps in mind potential interferences and makes appropriate changes in sample preparation, calibration, and instrumental parameters if those interferences are present.

References

1   T. N. McKenzie, P. S. Doidge, M. W. Routh, D. E. Shrader, "The Reduction of Chemical Interferences in High Salt Matrices using Chemical Modification in Graphite Furnace AAS", Varian Techtron (1982). (Presented at 1982 Federation of Analytical Chemistry and Spectroscopy Societies Meeting, Philadelphia, USA).

2   C. W. Fuller, "The Effect of Acids on the Determination of Thallium by Atomic Absorption Spectrometry with a Graphite Furnace", Anal. Chim. Acta., 81, 199 (1976).

For More Information

For more information on our products and services, visit our Web site at www.agilent.com/chem

www.agilent.com/chem

Agilent Technologies