Application Note

Analysis of Environmental Water Samples using Graphite Furnace AA with ULTRA-PULSE Background Correction

Introduction

The analysis of trace metals in environmental samples often presents analytical problems due to the unknown matrix components of such samples. The concentrations of the components may vary considerably and the number of potential contaminants may be difficult to assess due to the sampling protocol employed. As a result, the analytical chemist is commonly required to determine trace metal concentrations in samples containing high total dissolved solids. Of all the possible applications, `brine samples' present a major challenge. The purpose of this paper is to assess the analytical behavior of chromium, cadmium and selenium in two different brine solutions (0.1% m/V sodium chloride and 1% m/V sodium chloride) when determined by graphite furnace analysis.

Chromium is generally atomized at a relatively high temperature (approximately 1400°C) and for most analytical situations it does not require a modifier. Cadmium is a volatile element and is atomized at a relatively low temperature (approximately 700°C). It may require matrix modification to reach stabilization and allow atomization at a higher temperature. Usually di-ammonium hydrogen phosphate is used as the modifier.

Selenium is a very volatile element and always requires a matrix modifier, such as nitrates of nickel, magnesium, calcium, lanthanum, palladium, platinum or others, to ensure a high atomization temperature and to reduce any chemical and spectral interference[3].

Iron and phosphate are the most common causes of spectral interference encountered in selenium analysis.

Experimental

Instrumentation

A GBC Avanta Σ atomic absorption spectrometer, equipped with the unique ultra-pulse deuterium arc background correction system and System 3000 were used. The System 3000 consists of the GF3000 graphite furnace power supply and PAL3000 programmable automatic sample loader. The GBC data station with Avanta Σ software provides control of the spectrometer, furnace and autosampler, allowing 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 optimize furnace conditions. All graphics traces for standards and samples are stored on the computer hard disk, as are method applications, results files and graphics files, allowing recall for method assessment and refinement. The instrumental conditions for chromium, cadmium and selenium determination are given in Table 1a. GBC total pyrolytic graphite platforms were used for all analyses. Cadmium and selenium Super Lamps (Photron Pty Ltd, Australia) and a chromium standard hollow cathode lamp (GBC Scientific Equipment Pty Ltd, Australia) were used.

Reagents

1000 µg/mL of cadmium, chromium and selenium standard solutions, Aristar grade nitric acid and analytical grade sodium chloride and nickel nitrate were used. All chemicals were obtained from BDH Chemicals (Australia). The de-ionized water was obtained via a reverse osmosis, mixed-bed de-ionizing unit supplying Type 1 ultra pure water (Modulab, Reagent Grade Model Water System, Continental Water Systems Pty Ltd, Australia).

Sample and Standards Preparation

Samples were prepared from the United States Environmental Protection Agency (USEPA) Performance Evaluation Sample WS 378 (a drinking water quality control sample). Sample 1 was prepared by taking 10 mL of concentrate and pipetting it into a one litre volumetric flask containing 5 mL of concentrated HNO3 and made up to volume with de-ionized water. Samples 2 and 3 were prepared by adding 10 mL of concentrate to a one litre volumetric flask containing 5 mL of concentrated HNO3 and made up to volume with distilled water containing 0.1% m/V Na   and 1% m/V Na respectively as the chloride salts. Sample 2 contains a 1000 mg/mL (1000 ppm) sodium matrix and Sample 3 contains a 10,000 mg/mL (10,000 ppm) sodium matrix. A direct calibration was used. A 1000 mg/mL stock standard for each element was diluted to provide a suitable concentration range for each analyte in WS 378. The standard additions method was not necessary. The sample volume used is specified in Table 1, and a GBC graphite platform was placed in a furnace tube to allow the sample to be dried, ashed and atomized.

	Cadmium	Chromium	Selenium
Wavelength	228.8	357.9	196.0
Slit Width	0.5	0.5	1.0
Background Correction	ON	ON	ON
Measurement Mode	Peak Height	Peak Area	Peak Area
Sample Volume (uL	15	15	16
Modifier Volume (uL)	Nil	Nil	5

Table 1: *Parameters for Cadmium, Chromium and Selenium analysis in brine samples, 1, 2 and 3. Inert gas was Argon*

Results

Method development for cadmium and chromium in brine solution was performed without the use of a matrix modifier, even though a matrix modifier allows ashing and atomization at a higher temperature and reduces the background matrix. This allowed for the effectiveness of the ultra-pulse deuterium arc background correction system to be assessed. As shown in Table 2, the appearance temperature of cadmium was altered when 1.0% NaCl was used as the matrix.

Matrix	Appearance Temperature (°C)	
	Cadmium	Sodium Chloride
0.5% HNO$_3$	470	
0.5% HNO$_3$ and 0.1% NaCl	470	670
0.5% HNO$_3$ and 1% NaCl	670	670

Table 2: *Appearance temperature of cadmium and sodium chloride in 0.5% nitric acid and cadmium and sodium chloride in 0.1% sodium chloride with 0.5% nitric acid and 1.0% sodium chloride with 0.5% nitric acid.*

Matrix	Appearance Temperature (°C)	
	Chromium	Sodium Chloride
0.5% HNO$_3$	400	
0.5% HNO$_3$ and 0.1% NaCl	400	670
0.5% HNO$_3$ and 1% NaCl	500	670

Table 3: *Appearance temperature of chromium in 0.5% nitric acid and chromium in 0.1% sodium chloride with 0.5% nitric acid, and in 1.0% sodium chloride with 0.5% nitric acid.*

Analyte	Sample	Measured EPA Conc.	True EPA Conc.	95% Confidence Interval
Cadmium	1	7.1	7.4	5.3–8.8
	2	6.7	7.4	5.3–8.8
	3	7.1	7.4	5.3–8.8
Chromium	1	61	67	56.5–77.3
	2	70	67	56.5–77.3
	3	61	67	56.5–77.3
Selenium	1	9.7	9.3	5.8–11.6
	2	9.5	9.3	5.8–11.6
	3	7.6	9.3	5.8–11.6

Table 4: Results of cadmium, chromium and selenium for analysis in EPA WS378 water sample diluted in 0.5% HNO3 (Sample 1), 0.1% NaCl with 0.5% HNO3 (Sample 2) and 1.0% NaCl with 0.5% HNO3 (Sample 3). Results are compared with EPA certified values for cadmium, chromium and selenium. All concentration values are mg/L.

The increase in appearance temperature resulted in the cadmium signal appearance time being similar to that of the NaCl background trace. In this situation the overlap of the analyte signal and background should present a difficulty for a conventional background correction system (Figure 1). The change in the appearance time of the cadmium signal suggests that the NaCl interacts with cadmium to delay its appearance temperature. In this work, a matrix modifier was purposely not used to allow Cd to atomize simultaneously with the evolution of Na(Cl) off the platform.
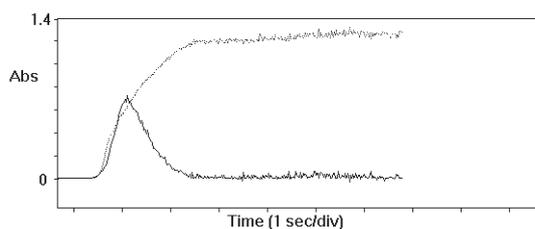
Figure 1: Cadmium trace

The resolution of the analyte peak shows that the ultra-pulse deuterium arc background correction has successively corrected for the high background absorbance (1.2 absorbance units). There is no over-correction effect for the signal trace (Figure 1). The results in Table 4 indicate that the method provides good results when compared with certified values, and all results fall within the published 95%

confidence intervals. The analytical precision for the samples was very good.
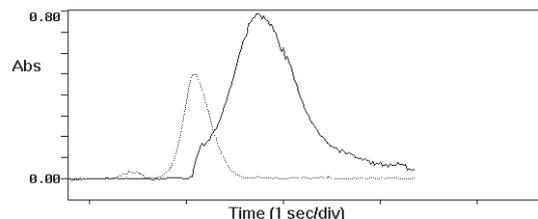
Figure 2. Chromium trace

Chromium is a more refractory element than cadmium and is volatilized at 1400°C while the sodium chloride salt vaporized at a lower temperature of 670°C (Table 3). The analyte and background signals consequently were well separated and presented no difficulty for the ultra-pulse deuterium background correction system (Figure 2). The results in Table 4 for chromium are within the EPA 95% confidence intervals and show good agreement with the respective true value.

Selenium can be very difficult to analyse due to matrix inferences. One percent m/V nickel nitrate was used as the modifier, as this is the USEPA recommended modifier[4]. The results for selenium in each salt matrix were well within the specified 95% confidence for the WS 378 in each matrix (Table 4). Even though the signal and background traces overlapped, the Ultra-pulse background correction system was able to accurately correct the background to produce an acceptable signal trace (Figure 3).
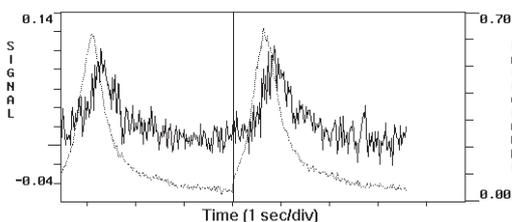
Figure 3. Selenium trace

Furnace Parameters

Cadmium Graphite Furnace parameters

	Final Temp.	Ramp Time	Hold Time	Gas Type
Step 1	90	1.0	10	Inert
Step 2	120	20	5.0	Inert
Step 3	120	0.5	0.5	None
Step 4	1200	0.7	5.0	None
Step 5	2600	1.0	2.0	Inert

Chromium Graphite Furnace parameters

	Final Temp.	Ramp Time	Hold Time	Gas Type
Step 1	90	2.0	3	Inert
Step 2	120	30	5.0	Inert
Step 3	600	10	5.0	Inert
Step 4	600	0.5	0.5	None
Step 5	2700	2.0	1.0	None
Step 6	2800	1.0	2.0	Inert

Selenium Graphite Furnace parameters

	Final temp.	Ramp Time	Hold Time	Gas Type
Step 1	90	1.0	10	Inert
Step 2	110	20	5.0	Inert
Step 3	1350	15	5.0	Inert
Step 4	1350	0.5	0.5	None
Step 5	2300	1.0	2.0	None
Step 6	2600	1.0	2.0	Inert

Discussion

The injection of brine directly into the graphite furnace without matrix modification or dilution can result in severe analytical difficulties due to background interferences. Care must be taken to carefully dry and ash the sample matrix. Alteration of the analyte form during the ashing stages may affect the accuracy and precision of analysis. Furnace conditions must therefore be carefully determined to minimize loss of the volatile metal chloride species that are formed so that at atomization a representative signal trace occurs. The background level of such a sample is particularly high and may adversely affect the accurate determination of these three diverse elements due to over-correction effects. However, none of the analyte graphical traces show any over-correction effect, and are reproduced here as representative traces.

Conclusion

The purpose of this paper was to prepare a sample in a salt matrix, a difficult environment for analysis, and to assess whether the instrument was able to accurately analyse these samples under difficult conditions. The analytical results and signal traces (Figures 1, 2 and 3) illustrate that the objectives have been achieved without difficulty, utilizing ultra-pulse background correction. It is important to understand that in order to prevent over-correction, a high background correction speed (200 Hz) is essential when encountering analytical conditions that cause the analyte signal and background to overlap.

References

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4. Methods for Chemical Analysis of Water and Wastes, USEPA, 600/4-79-020, Revised March, 1983. Method 270.2.