Application Note

The Determination of Beryllium in Drinking Water Using the System 3000 Graphite Furnace

Introduction

In July 1992, the United States Environmental Protection Agency (USEPA) set a new standard of maximum contaminant level (MCL) for beryllium in drinking water of 4.0 µg/L.[1] A rapid and fully automated method for the determination of beryllium in drinking water has been developed to allow simple, accurate and precise measurements to be made below 1.0 µg/L beryllium.

The method was developed using GBC *Elite* AA operating software, incorporating automatic sample spike recovery and check sample analysis. Based on a direct method developed by the USEPA,[2] interference-free analysis can be performed in the range 0 to 5 µg/L with a method detection limit of 0.02 µg/L.

In this application two USEPA Quality Control samples were analysed to verify the accuracy and precision of the method.

Experimental

Instrumentation

A GBC model 906, 908, 909, 932 or 933 atomic absorption spectrophotometer equipped with the unique Ultra-Pulse background correction system and coupled with a System 3000 graphite furnace accessory may be used for the analysis. The System 3000 consists of a GF3000 power supply and PAL3000 automatic sample loader.

GBC Elite software allows control over the entire system, i.e., spectrophotometer, furnace and auto sample loader. After simple method development, applications may be stored for future use. All data accumulated during runs is stored automatically on the computer hard disk. Real-time colour graphics of simultaneous signal absorbance, background traces and furnace temperature plots allows the operator to optimize furnace conditions. Instrumental conditions are shown in Tables 2, 3 and 4. Pyrolytically coated furnace tubes and a beryllium hollow cathode lamp were used for all analyses.

Cleaning of Apparatus

All containers and glassware were soaked in 10% detergent solution for three days followed by rinsing with deionized water. Apparatus was then soaked in a 10% nitric acid solution for three days before rinsing again in deionized water and air drying. Air displacement pipettes were used along with pre-cleaned (as above) plastic tips for all sample, standard and modifier preparation. Ideally, containers that are to be used for storing solutions of low metal concentration (below 1 µg/mL) should not have been in previous contact with strong metal solutions.

Reagent Preparation

Analytical reagent grade chemicals as well as high purity “Aristar” nitric acid were used throughout (Merck Pty Ltd, BDH Chemicals, or equivalent). Type 1 ultrapure water was obtained from a mixed bed, reverse osmosis deionizing unit (Modulab, Reagent Grade Model Water System, Continental Water

Systems Pty Ltd Aust.) and used for reagent preparation and analysis. A working standard of 2 μg/L beryllium was prepared from a 1 μg/mL stock solution of beryllium sulphate (made from 1000 μg/mL atomic absorption standard solution) with 0.1% v/v nitric acid. This standard was prepared daily. The PAL3000 automatic sample loader automatically prepared standards of 0.5, 1, 1.5 and 2 μg/L.

Graphite Tube Treatment and Matrix Modification

The graphite furnace tube was treated prior to sample and modifier introduction according to the tube treatment temperature program given in Table 1. This was performed to eliminate any matrix interference and to improve sensitivity to comply with the new standard for MCL.

Step	Final Temp (°C)	Ramp Time (s)	Hold Time (s)	Gas Type	Read	Signal Graphics
1	140	1	3	Inert	Off	Off
2	400	5	5	Inert	Off	Off
3	2650	5	3	Inert	Off	Off

Table 1: *Graphite furnace parameters for the treatment of the furnace tube.*

The tube treatment solution was made up by weighing 0.184 g ammonium molybdate in a 100 mL volumetric flask and making up to volume with deionized water. The furnace tube was coated with ammonium molybdate by programming the PAL3000 to inject a 100 μL aliquot prior to step number 2 in the furnace program at a rate of 1 μL/second. This "hot injection" procedure was repeated four times, providing a coating which will last for at least 300 firings (according to the criteria that the tube should be replaced when the absorbance is reduced to 50% of the initial absorbance for a specified standard).

The modifier used was ammonium phosphomolybdate. A fresh solution (shelf life is approximately 7 days) was prepared by dissolving 0.5 g ammonium molybdate in 50 mL of dilute ammonia solution (4% v/v concentrated ammonia) and adding 0.5 mL phosphoric acid. The auxiliary (or secondary) modifier was made up by weighing 1.0 g ascorbic acid into a 10 mL volumetric flask and making up to volume with deionized water. To prevent photo-decomposition (indicated by discolouration) the modifier was stored in pre-cleaned amber polypropylene bottles and prepared weekly. A beaker of ascorbic acid was placed in the auxiliary modifier position on the PAL3000 sample loader for separate injection into the furnace.

It must be noted that the two modifiers cannot be mixed prior to injection into the furnace because a dark blue precipitate will form, degrading the reproducibility of atomization. The GBC Elite software allows programming of the auto-sampler to inject the modifiers separately, ensuring that this does not occur.

Sample Preparation

Two water sample concentrates for trace metal analysis, "Trace Metals - AA" Quality Control Samples, TMA 989 and 1-2 TMAA-2, were used as quality control samples during the analysis. These were supplied by Spex Industries, Inc., (N J) and are certified by the United States Environmental Protection Agency.

Samples were prepared according to the manufacturer's instructions. 10 mL of concentrate was pipetted into a 1 litre volumetric flask containing 900 mL deionized water. 1 mL of concentrated nitric acid was added and the flask made up to volume with deionized water. Further dilution was necessary to bring the beryllium concentration within the calibration range. Samples were prepared daily by diluting 1:10 with 0.1% v/v nitric acid, and stored in pre-cleaned polypropylene containers.

A sample blank was prepared by adding 1 mL of concentrated nitric acid to a 1 litre volumetric flask and made up to volume with deionized water. A "GBC" sample was prepared as above with an equivalent concentration of 9.0 μg/L Be. This was considered an internal quality control sample and analysed as a "Check Sample".

All potable water samples were preserved using nitric acid (pH 1–2). This concentration of nitric acid (1–2 mL per litre of sample) will preserve the sample for up to four weeks. An acid digestion procedure adapted from the USEPA Contract Laboratory Program Statement of Work was used to prepare samples for analysis.[3]

An aliquot of 100 mL of well shaken sample is transferred to a 250 mL beaker. 1 mL of 50% concentrated nitric acid and 2 mL of 30% hydrogen peroxide is added. The beaker is covered with a watchglass and heated in a water bath or on a hotplate at 95°C for 2 hours or until the sample volume is reduced to between 25 and 50 mL. The sample is then cooled and filtered to remove insoluble material. Alternatively, the sample may be centrifuged or allowed to settle after dilution and mixing to remove insoluble material. The volume is then adjusted to 100 mL with deionized water and the sample is ready for analysis.

A 2 μg/L Be spiking solution was prepared using the 1 μg/mL Be stock standard solution. However, only 2 μL injection volume was used, hence the actual spike concentration was 0.33 μg/L Be.

Results and Discussion

The GBC Elite software allows complete automation of the analysis. After the tube treatment program was performed, (Table 1) the analytical program was automatically loaded (Tables 2, 3 and 4). The method incorporated calibration, check sample analysis and spike recovery. Peak height measurements was used to quantify the absorption signals. Method development was performed by optimizing the temperature settings (Table 3) for the beryllium samples. Initial settings were obtained from the GBC Furnace Methods Manual[4] and the USEPA Contract Laboratory Program Statement of Work.[5]

System Type	Furnace
Element	Be
Matrix	0.1% nitric acid
Lamp Current (mA)	10
Wavelength (nm)	234.9
Slit Width (nm)	0.5
Slit Height	Reduced
Instrument Mode	Absorbance BC on
Measurement Mode	Peak Height

Table 2: *Instrument parameters for graphite furnace analysis of beryllium in water.*

Step	Final Temp (°C)	Ramp Time (s)	Hold Time (s)	Gas Type	Read	Signal Graphics
1	80	10	5	Inert	Off	Off
2	130	20	10	Inert	Off	Off
3	500	5	5	Inert	Off	Off
4	1300	5	20	Inert	Off	Off
5	1300	0.5	0.5	None	Off	Off
6	2500	1	1	None	On	On
7	2800	1	4	Inert	Off	Off

Table 3: *Graphite furnace temperature program for sample analysis.*

Sample Type	Blank Volume	Std. Volume	Sample Volume	Modifier Volume	Aux-Mod. Volume
Sample	0	0	12	2	3
Blank	12	0	0	2	3
Std. 1	9	3	0	2	3
Std. 2	6	6	0	2	3
Std. 3	3	9	0	2	3
Std. 4	0	12	0	2	3

Table 4: Auto-mix sampler volumes (μL) for sample analysis.

	TMA 989		1-2 TMAA 2	
	Certified	**Actual***	**Certified**	**Actual***
Between-run (n=10)	10.08	10.15 ±0.52	9.89	9.89 ±0.34
Within-run (n=10)	10.08	10.07 ±0.26	9.89	9.76 ±0.23
95% Confidence Interval	7.72–12.44		8.42–11.36	

* Mean ±1 standard deviation
Characteristic Concentration = 0.011 μg/L (20 μL sample injection)
Detection Limit - 0.02 μg/L

Table 5: Analytical results for samples TMA 989 Sample No. 2 and 1-2 TMAA 2. Results are in μg/L.

Table 5 shows the results obtained for the two samples TMA 989 and 1-2 TMAA-2, while Figures 1 and 2 show the peak profiles for the two samples respectively. The background absorbance was found to be negligible for all samples, as it was almost indistinguishable from the baseline trace.

Comparison between analytical data and certified concentration values shows the accuracy of the technique for both within-run and between-run results (Table 5). For all samples and standards, the relative standard deviation was found to be between 1.08% and 5.45% (average of 3.27%). The method detection limit, calculated from obtained data, was 0.02 μg/L based on 100 μL injection volume (well within the Contract Required Detection Limit – 0.2 μg/L from USEPA) while the characteristic

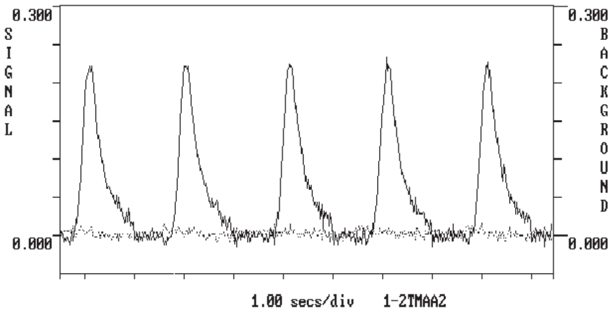

Figure 1: *Typical analyte and background traces for beryllium in Quality Control Sample AA TMA 989 Sample 2.*

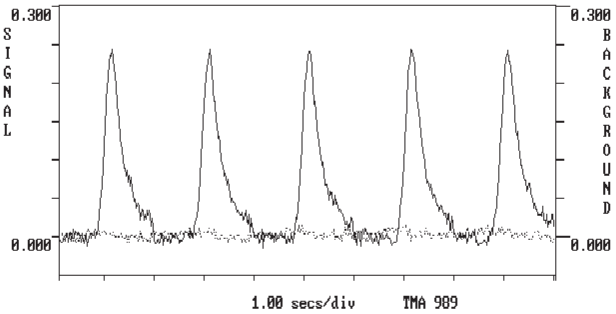

Figure 2: *Typical analyte and background traces for beryllium in Quality Control Sample 1-2 TMAA Sample 2.*

concentration was 0.011 μg/L Be, based on 20 μL sample injection.

Figure 3 shows the effect of various modifiers on the atomization sensitivity. An improvement of 100% over previous methods was achieved using the method described here. Interference studies by D.A. Lytle, et al,2 have proved the use of the tube coating solution and modifiers as suitable for the analysis of beryllium in drinking water. It was shown that minimal interference occurred when using the modifier combination with pyrolytically coated graphite furnace tubes. Table 6 shows the spike recovery values. These were well within the 95% confidence interval, as set out by USEPA, indicating negligible interference effects.

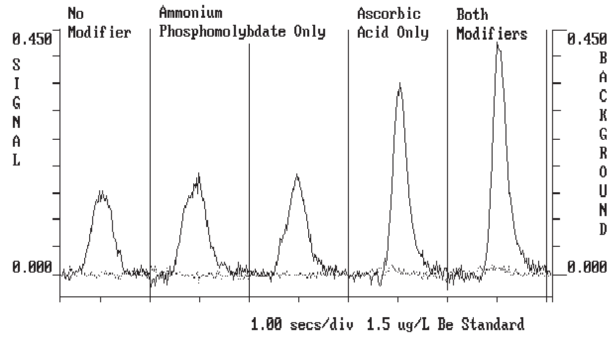

Figure 3: *Signal graphics traces showing the effect of modifiers on sample peaks for beryllium analysis.*

Sample	Beryllium concentration (μg/L)			% Recovery
	Expected	Actual	Post spike	
TMA 989 #2	10.08	10.2	13.4	97.1
1-2 TMAA 2	9.89	9.9	13.3	101.3
GBC sample check	9.0	9.1	12.5	102.8

Table 6: *Spike recovery values determined during analysis.*

Conclusion

With the use of GBC Elite software, the determination of beryllium in drinking water can be performed with a very high degree of accuracy, precision and reliability. Furthermore, the entire method is automated, eliminating the need for operator intervention. Using the two modifiers (modifier and auxiliary modifier), it has been shown that both the Detection Limit and Characteristic Concentration values can be significantly improved. The analytical results obtained show that this method will meet United States Environmental Protection Agency requirements.

References

1. US Environmental Protection Agency. National Primary and Secondary Drinking Water Regulations; Synthetic Organic Chemicals and Inorganic Chemicals, Final Rule 40 CFR Parts 141 and 142. Fed. Reg., 57:138 (July 1992).
2. Lytle, D.A., Schock, M.R., Dues, N.R., Doerger, J.U.Determining Beryllium in Drinking Water by Graphite Furnace Atomic Absorption Spectroscopy, Journal of American Water Works Association, Vol 85, Issue No. 2, page 77-83. 1993.
3. USEPA Contract Laboratory Program Statement of Work for Inorganics Analysis, Document Number ILMO1.O, Exhibit D, Section III Part A. Water Sample Preparation, 1 Acid Digestion Procedure for Furnace Atomic Absorption Analysis.
4. Graphite Furnace Methods Manual.GBC Scientific Equipment Pty Ltd, Australia.
5. USEPA Contract Laboratory Program Statement of Work for Inorganics Analysis. Document Number ILMO1.O Exhibit D Section IV, Sample Analysis, Part B, Atomic Absorption Methods, Furnace Technique Method 210.2 CLP - Modified for Beryllium.