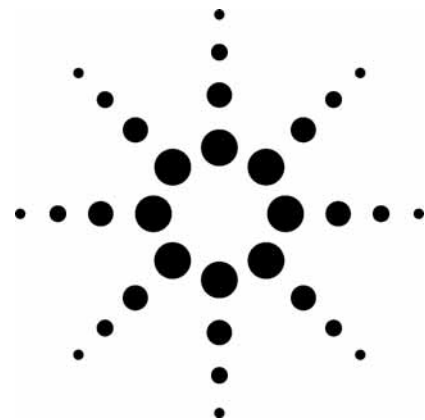


Ultra-Trace Analysis of Beryllium in Water and Industrial Hygiene Samples by ICP-MS

Application

Environmental



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Abstract

Exposure to airborne beryllium can lead to adverse health effects in humans. Consequently, many countries have legislation in place to ensure the health and safety of workers and the wider environment. Because even very low concentrations of Be in air constitute a toxic threat to health, analytical methodology that is capable of extremely high-sensitivity measurement is required. Although trace-level analysis of the element is difficult by some ICP-MS instrumentation, the Agilent 7500ce ICP-MS can achieve Be detection limits in the sub-ppt range directly in water and in acid digests of air filters under routine analytical conditions. Long-term precision and accuracy data recorded over 8 hours of continuous analysis of a highly diluted certified reference material (NIST 1640) is presented. Recoveries were greater than 97% and precision was in the order of 1 to 2%. Comparable performance was obtained when measuring spiked membrane filters, indicating that the method is applicable to the ultra-trace analysis of Be in air samples collected on filters.

Introduction

Workplace exposure to beryllium (Be) can pose significant chronic and acute health risks and is receiving increased scrutiny from regulators and industrial hygiene professionals. Be is a metallic element belonging to Group IIA of the periodic table. It has an atomic weight of 9.012 and is monoisotopic. It occurs naturally in the earth's crust at concentrations ranging from 2 to 10 ppm. The average concentration in U.S. soils is about 0.6 ppm, and during the late 1970s and 1980s Be was measured at between 0.03 and 0.4 ng/m³ in air [1]. In its natural ore state, beryllium is relatively nontoxic. However, all other commercially important Be compounds exhibit significant pulmonary toxicity. Humans are exposed to Be from a number of sources, including food, water, and air. Clinically, the most important exposure pathways are airborne, including smoke from coal combustion, cigarette smoke, and airborne particulates from various Be manufacturing processes. Be use spans numerous industries, including electronics, aerospace, nuclear, and metallurgical. Exposure to airborne Be can lead to pulmonary disease either as Acute Beryllium Disease (ABD) or Chronic Beryllium Disease (CBD), depending on level and duration of exposure. Both can be fatal, and CBD symptoms may only appear after a latency period of up to 25 to 30 years. The U.S. Environmental Protection Agency (EPA) has also classified Be as a "probable human carcinogen" [1]. EPA-developed toxicity values for Be exposure are shown in Table 1. The National Institute for Occupational Safety and Health (NIOSH) exposure limit for Be in air is 0.05 µg/m³. The limit of detection (LOD) by



Table 1. Chemical Toxicity Values for Beryllium Via Oral and Inhalation Exposure Pathways as Determined by the U.S. EPA [1].

Cancer Risk	Non-Cancer Effect	
Inhalation UR*	Oral RfD*	Inhalation RfC*
2.4 per mg/m ³	0.002 mg/kg-day	0.00002 mg/m ³

*UR – (inhalation unit risk): estimate of number of people per million that likely will get cancer from continuous exposure to Be in air at a concentration of 1mg/m³.

*RfD – (oral reference dose): An estimate (with uncertainty spanning perhaps an order of magnitude) of a daily oral exposure of a chemical to the human population (including sensitive subpopulations) that is likely to be without risk of deleterious noncancer effects during a lifetime.

*RfC – (inhalation reference concentration): An estimate (with uncertainty spanning perhaps an order of magnitude) of a continuous inhalation exposure of a chemical to the human population through inhalation (including sensitive subpopulations) that is likely to be without risk of deleterious noncancer effects during a lifetime.

Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) according to NIOSH 7301 [2] is 5 ng/filter, which requires air sampling volumes between 1,250 and 2,000 liters. By contrast, the LOD by ICP-MS using the Agilent 7500ce as described in this paper is 50 ppq in solution (0.00005 ng/mL), which is equivalent to 0.00125 ng/filter or a 4000× improvement in sensitivity.

Analytical Challenges

From an analytical standpoint, Be poses several challenges. Because of the toxicity of very low concentrations in air, extremely high sensitivity is desired. Traditional NIOSH and Occupational Safety and Health Administration (OSHA) methods for Be in airborne samples utilize ICP-OES with approximate detection limits of 0.005 µg/filter (NIOSH 7301), which may require a sampling volume of up to 2,000 liters. By using a much more sensitive technique such as Inductively Coupled Plasma Mass Spectrometry (ICP-MS), adequate sensitivity can be had at much lower sampling volumes and absolute detection limits can be lowered significantly. While ICP-MS can provide numerous advantages over other techniques in terms of sensitivity and throughput, there are some challenges as well. Be exhibits two characteristics that have traditionally made trace-level ICP-MS analysis difficult. Be is low mass and has a high first ionization potential (9.32 eV). Being low mass (atomic weight = 9), Be ions are subject to scattering in the presence of other higher mass ions (space charge effects), for example other metals in the sample. This can limit the sensitivity by an order of magnitude or more on some ICP-MS instruments. High ionization potential has a similar effect. Since the ICP-MS measures ions, elements that are difficult to ionize like Be have much higher detection limits than elements that ionize easily. Therefore, in

order to achieve maximum sensitivity for Be, these two obstacles must be overcome. By specifically designing the plasma and ion optics for maximum ionization and minimum space charge, Agilent Technologies has effectively achieved Be detection limits in the sub ppt range under routine analytical conditions with the 7500 Series instruments. These design characteristics include a unique digitally synthesized 27 MHz RF generator and low flow sample introduction system to ensure maximum plasma temperatures as well as the avoidance of any type of shadow stop in the path of the ion beam that would cause loss of low mass sensitivity.

Instrumentation

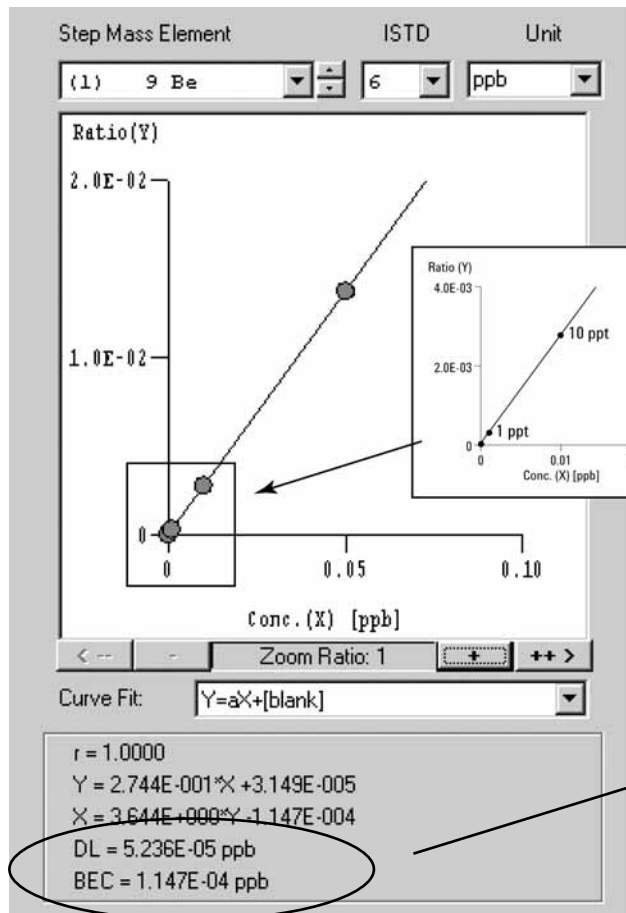
An Agilent 7500ce ICP-MS was used for this work in standard configuration. While the 7500ce is a collision cell instrument, it was used in “no-gas mode”; meaning, the collision cell was unpressurized and no collision/reaction chemistry was employed. The work was done under standard laboratory conditions of cleanliness, no clean room or special apparatus of any type were utilized. Instrument parameters are listed in Table 2.

Table 2. ICP-MS Parameters

Agilent 7500ce Instrument Conditions	
Plasma forward power	1500 W
Carrier gas flow	0.8 L/min
Nebulizer	Glass concentric
Sample flow	400 µL/min
Spray chamber temp	2 ° C
Extraction lens 1	2 V
Extraction lens 2	-110 V
Reaction mode	Off
Isotopes monitored	6, 9, 45
Integration time for ⁹ Be	5 seconds per replicate/3 replicates per analysis
Total run time	3 minutes

Experimental

The initial determination of performance was based on simple calibrations in dilute nitric acid and repeated analyses of diluted certified reference water (NIST 1640) for Be. This is because there are currently no standard reference materials available for Be in air samples. In the initial work, a sequence of 163 separate samples (dilutions of NIST 1640, Figure 2) was performed over 8.5 hours in order to determine the robustness and precision of the method (Figure 3). Calibrations were performed from 1 ppt to 50 ppt as shown in Figure 1.



Conc	Calc Conc	CPS/Count
0.000	0.000	3.222
1.000E-03	1.032E-03	32.74
1.000E-02	1.003E-02	289.4
5.000E-02	4.999E-02	1440

Figure 1. Calibration for Be in dilute nitric acid at 0, 1, 10, and 50 ppt (standard concentrations in the data table at the top right are expressed in ppb). The expanded area shows linearity from 1 to 10 ppt. ⁶Li was used as the internal standard.

Estimated detection limits based on calibration linearity, response factor, and background were calculated to be 5.2×10^{-5} ppb (52 ppq) or 0.000052 ng/mL, compared with published values of 0.2 ng/mL by ICP-OES (NIOSH 7300). Subsequent work included the analysis of spiked 47 mm diameter cellulose ester membrane filters (0.8 μ m pore size) according to the NIOSH 7301 (modified) method. Digestion conditions are outlined in Table 3. The method was slightly modified to use a Hot Block digester and the final diluent was 1% nitric acid. The intent was to determine the suitability and performance of the method to the matrix containing the dissolved filters.

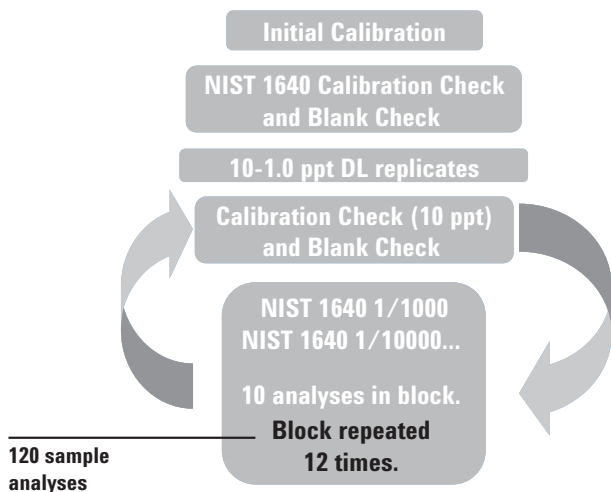


Figure 2. The analytical sequence used to test long-term accuracy and precision through continuous repeat measurements of certified reference material (NIST 1640 water)

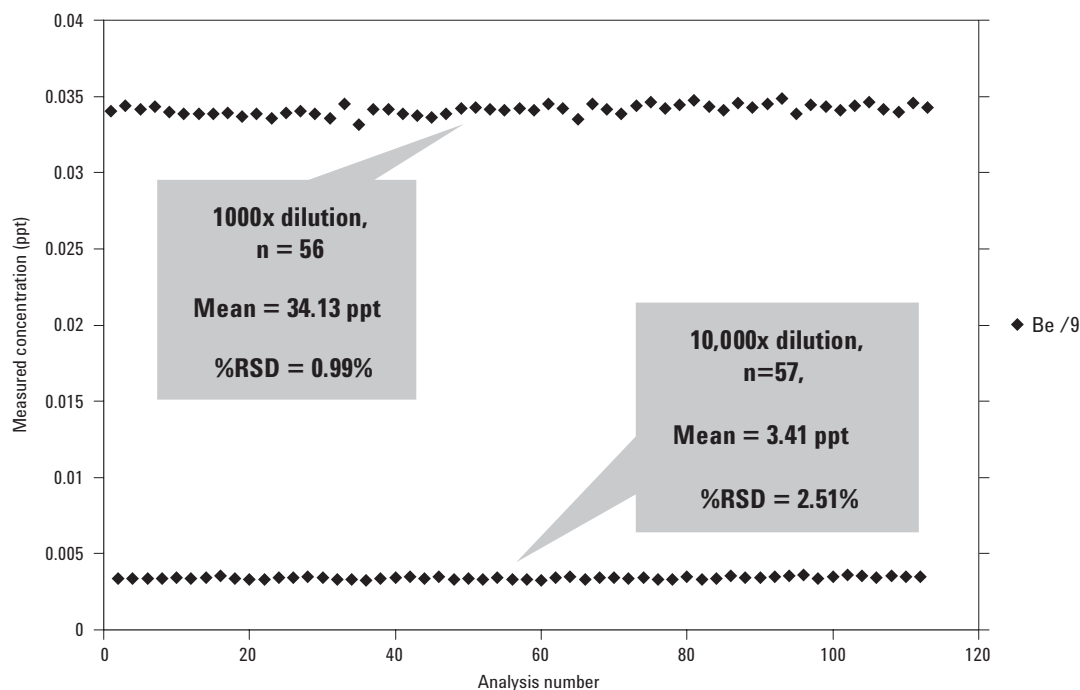


Figure 3. Results of a long-term stability study using repeat analysis of NIST 1640 diluted 1,000 and 10,000×. 1000 and 10,000× samples were analyzed alternately for 8.5 hours. Actual certified concentration in the diluted samples was 34.9 ppt and 3.49 ppt (1000 and 10,000×).

Table 3. Modified NIOSH 7301 Digestion Procedure Utilizing Hot Block Digester for Analysis of Be on Filter Samples by ICP-MS.

Digestion Step	Procedure	Notes
1	Place filter into pre-leached 50 mL poly centrifuge tube. Add 5 mL 1:3 HNO ₃ :HCl. Cover with a plastic watch glass. Let stand 30 min at room temperature.	Start a reagent blank at this step. Some species of Al, Be, Co, Cr, Li, Mo, Sb, W, and Zr may not be completely solubilized by this procedure. Alternative solubilization techniques for these elements can be found elsewhere [2].
2	Heat on hot block (120 °C) until ca. 0.5 mL remains.	Hot block substituted for hot plate.
3	Add 2 mL 1:3 HNO ₃ and repeat step 2. Repeat this step until the solution is clear.	PVC filters will not completely dissolve after repeated additions of ashing acid.
4	Remove watch glass and rinse into the digestion tube with distilled water.	
5	Increase the temperature to ~140 °C and take the sample to near dryness (ca. 0.5 mL)	
6	Bring to final volume of 25 mL with 1% nitric acid.	Final solutions ranged from hazy clear to dark amber. Internal standards added at this point. Solutions allowed to settle overnight prior to analysis of supernatant.

Precision and Accuracy in Waters

Precision and accuracy was evaluated by examining the results of the replicate analyses of the 1,000 and 10,000× dilutions of NIST 1640. The certified value for Be in NIST 1640 is 0.03494 ppm. Therefore, after dilution, values were 0.03494 and 0.003494 ppb. During the course of the analytical sequence (Figure 2), NIST 1640 was analyzed 113 times over 8.5 hours, 56 times at 1/1,000 dilution and 57 times at 1/10,000 dilution. The results are shown in Table 4.

Table 4. Analysis of Be in NIST 1640 – Standard Reference Water. Accuracy and Precision of Replicate Measurements of NIST 1640 at 1,000 and 10,000× Dilution Over 8.5 Hours of Continuous Analysis

DF	n	Average measured concentration (ppt)	%RSD	Average % recovery
1,000	56	34.13	0.988	97.67
10,000	57	3.41	2.51	97.49

Precision and Accuracy on Filter Samples

In order to determine the performance of the method for the analysis of Be contained on membrane filter samples according to NIOSH 7301 (modified), replicate filters (10 filter blanks and 10 5-ppt spiked filters) were analyzed. Spike recoveries were performed since no standard reference materials for Be on filters are available. Results are given in Table 5.

Table 5. Summary Results of Replicate Analyses of Spiked Membrane Filters and Blanks for Be

	n	Mean conc. (ppt)	% RSD	% Recovery
Reagent blank	–	–0.08 (n = 2)	–	–
Blank filters	10	0.481	58.8	–
Spiked filters (5 ppt)	10	5.25	4.73	95.3

Conclusions

The Agilent 7500 Series ICP-MS is capable of measuring Be directly in waters and in acid digests of air filters according to NIOSH 7301 at levels up to 4,000 times lower than the published DLs using ICP-OES. By using proprietary Agilent ion optics designed specifically to minimize the effects of space charge on low mass analytes such as Be and very high plasma temperatures, the obstacles to ultra trace determination of Be by ICP-MS have been overcome, allowing measurements at the ppq level ($<0.0006 \text{ ng/m}^3$ for a 2,000 L sample). In addition, the long term precision and accuracy, as determined by measuring highly diluted certified reference material (NIST 1640) shows recoveries of greater than 97% and precision on the order of 1 to 2% over more than 8 hours of continuous analysis. Similar performance was obtained when measuring spiked membrane filters, indicating that the method is applicable to the ultra-trace analysis of Be in air samples collected on filters. The very high sensitivity and precision can permit the use of shorter sampling times and/or significantly lower limits of detection.

References

1. <http://www.epa.gov/ttn/atw/hlthef/berylliu.html#ref2>
2. NIOSH Manual of Analytical Methods (NMAM), Fourth Edition

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