International Journal of Mass Spectrometry 321–322 (2012) 19–24

Contents lists available at SciVerse ScienceDirect

International Journal of Mass Spectrometry

journal homepage: www.elsevier.com/locate/ijms

High accuracy measurements of trace elements in drinking water by exact matching isotope dilution mass spectrometry (IDMS)

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ARTICLE INFO

Article history:
Received 28 February 2012
Received in revised form 16 May 2012
Accepted 16 May 2012
Available online 5 June 2012

Keywords:
Exact matching isotope dilution mass spectrometry (IDMS), Sector field (SF)
ICP-MS
ICP-MS
Water matrix
Intercomparison

ABSTRACT

The accurate determination of trace elements in drinking water (nickel, cadmium and lead) has been achieved by adopting exact-matching isotope dilution mass spectrometry (IDMS) technique. The measurement uncertainty of the method was rigorously investigated and values with less than 2% combined uncertainty ($k = 2$) were achieved for all 3 analytes. These results were submitted for an international intercomparison and were in excellent agreement with the Key Comparison Reference Value (KCRV).

1. Introduction

Water is essential for life and its quality has great impact on public health and safety. In view of the adverse health effects that may be caused by heavy metals in polluted drinking water, World Health Organization (WHO) has published the Guidelines for Drinking-water Quality as the pillar of primary prevention. Singapore, with no natural aquifers or abundance in land, has long recognized the importance in providing sustainable supply of water for its people and hence, safeguarding the quality of drinking water. Therefore, the organization of an Inter-American Metrology System (SIM) intercomparison exercise by National Research Council Canada, Chemical Metrology Institute for National Measurement Standards (NRC), Canada on "Trace elements in Drinking Water" (SIM-QM-S2) served our intended purpose to determine our capability in quantifying trace elements in drinking water. The study targeted three toxic metals: nickel (Ni), cadmium (Cd) and lead (Pb), with concentrations at or near the WHO Guidelines for Drinking-water Quality [1]. The WHO guideline values for Ni, Cd and Pb are 0.07, 0.003 and 0.01 mg/L, respectively.

Inductively-coupled plasma mass spectrometer (ICP-MS) is deemed the most suitable technique for trace multi-element analysis due to its excellent power of detection [2]. Its ability to measure isotope ratios also enables the use of isotope dilution mass spectrometry (IDMS) method, which is well recognized as a definitive analytical technique to provide highly accurate analytical results and precision [3].

Although ICP-MS is known to suffer from spectral interferences, the advancement in technology allows magnetic sector ICP-MS to operate at higher resolution [4] or quadrupole ICP-MS with collision or reaction gas mode [5], both enable effective removal of majority interferences.

The isotope dilution (ID-ICP-MS) technique is the most commonly employed technique in the analysis of heavy metals in water [6,7]. Vapour-phase sample introduction is often coupled with ID-ICP-MS technique to enhance sensitivity and elimination of spectral interferences through matrix separation [7]. Determination of heavy metals content in water has also been achieved by other techniques, such as atomic absorption spectroscopy (AAS), although pre-concentration of the water sample is often required [8].

Our work in quantifying Ni, Cd and Pb in SIM-QM-S2 intercomparison is presented here.

2. Experimental

All the experimental work including sample preparation and analysis was conducted in a clean room with a rating of ISO Class 7.

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1387-3806/$ – see front matter
http://dx.doi.org/10.1016/j.ijms.2012.05.008

In the analysis of Ni, Cd and Pb in drinking water sample, two isotopic pairs were measured for each analyte. A composition screening of the drinking water sample was carried out using ICP-MS to determine any potential interference.

2.1. Methodology

Isotope dilution mass spectrometry (IDMS) is considered the metrological methodology because it is a primary ratio method that provides traceability to the International System of Units (SI) [9]. It is also a 'fit for purpose' method as it supports the appropriate high accuracy measurements with small uncertainties [10]. The IDMS technique employed in this study is an iterative exact-matching IDMS, which is known to reduce many systematic errors, such as mass bias, detector dead time and characterization of the isotopic spike material [11].

The IDMS equations used in this method are given in Eqs. (1) and (2), where all the observed isotope amount ratios are used with mass bias correction.

$$C_X = C_Z \cdot \frac{A_X}{A_Z} \cdot \frac{M_Y M_{ZC}}{M_X M_{YC}} \cdot \frac{R_Y - R_{SB}}{R_{SB} - R_X} \cdot \frac{R_{CB} - R_Z}{R_Y - R_{BC}} \cdot \frac{\sum R_{iX}}{\sum R_{iZ}} \tag{1}$$

For elements with no variation observed in the isotopic composition in nature, this equation can be simplified to Eq. (2), since $A_X = A_Z$, $R_X = R_Z$ and $\Sigma R_{iX} = \Sigma R_{iZ}$.

$$C_X = C_Z \cdot \frac{M_Y M_{ZC}}{M_X M_{YC}} \cdot \frac{R_Y - R_{SB}}{R_{SB} - R_X} \cdot \frac{R_{CB} - R_Z}{R_Y - R_{BC}} \tag{2}$$

where C_X is the concentration of analyte in sample, C_Z the concentration of analyte in standard solution used to prepare calibration blend, M_X the mass of sample added to sample blend, M_{ZC} the mass of standard solution added to calibration blend, M_Y the mass of spike solution added to sample blend, M_{YC} the mass of spike solution added to calibration blend, A_X the relative mass of analyte in sample, A_Z the relative atomic mass of analyte in standard, R_X the isotopic amount ratio in sample, R_Y the isotopic amount ratio in spike, R_Z the isotopic amount ratio in standard solution used to prepare calibration blend, R_{SB} the isotopic amount ratio in sample blend, R_{CB} the isotopic amount ratio in calibration blend, ΣR_{iX} the sum of all isotope amount ratios of analyte in the sample, ΣR_{iZ} is the sum of all isotope amount ratios of analyte in the standard solution used to prepare calibration blend.

2.2. Instrumentation

All isotope ratio measurements were carried out using both Agilent Technologies 7700x ICP-MS system (ICP-MS) (Agilent Technologies International Japan, Ltd., Tokyo, Japan) equipped with an octopole collision cell and Finnigan Element 2 (Finnigan MAT GmbH, Bremen, Germany) sector field (SF) ICP-MS using a self-aspirating PFA MicroFlow nebulizer. The instruments were optimized daily to achieve optimum sensitivity and stability according to manufacturers recommendations. The typical operating conditions and data acquisition parameters are summarized in Table 1. The ICP-MS system was also used to conduct sample composition screening and preliminary analysis by external calibration method.

2.3. Reagents and materials

Nitric acid (67–70% HNO_3, PlasmaPure, SCP Science), which was distilled twice using DST-1000 Sub-Boiling Distillation System (Savillex Corporation, Minnetonka, MN, USA), and Milli-Q Element (18.2 MΩ cm, Millipore Corporation, Bedford, MA, USA) water (Type 1 water) were used in sample dilution. All working solutions were diluted with 5% HNO_3 (v/v). The standard solutions

Table 1
Operating conditions for the measurement of Ni, Cd and Pb ratios using sector field (SF) ICP-MS and ICP-MS instruments.

Parameter	Sector field (SF) ICP-MS			Parameter	ICP-MS		
Analyte	^{60}Ni, ^{61}Ni, ^{62}Ni	^{111}Cd, ^{112}Cd, ^{114}Cd	^{206}Pb, ^{207}Pb, ^{208}Pb	Analyte	^{60}Ni, ^{61}Ni, ^{62}Ni	^{111}Cd, ^{112}Cd, ^{114}Cd	^{206}Pb, ^{207}Pb, ^{208}Pb
RF power		1250 W		RF power		1500 W	
Scanning mode		E-Scan		Carrier gas flow rate	0.77 L min^{-1}	0.75 L min^{-1}	0.75 L min^{-1}
Settling time		1 ms		Makeup gas flow rate		0.35 L min^{-1}	
Resolution	4000 (medium)	300 (low)	300 (low)	Sampling depth		8 mm	
Sample time	50 ms	10 ms	10 ms	Spray chamber temperature		2 °C	
Samples per peak	25	80	80	Ion lens setting		Optimised daily	
Mass window	60	10	10	Helium gas flow		4.5 mL min^{-1}	
Runs	10	20	20	Data acquisition integration time	3 s	5 s	2 s
Passes	10	20	20	Points per peak		1	
Total time per sample	3.5 min	2.1 min	1.4 min	Repetitions	10	5	5