Inductively Coupled Plasma Mass Spectrometer ICPMS-2030

Application News

Determination of Mineral and Trace Elemental Contents in Drinking Water by Inductively Coupled Plasma Mass Spectrometry

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User Benefits

◆ A sensitive and reliable method to determine elemental contents in drinking water, using ICPMS-2030 with collision cell technology.

◆ Content levels of regulated analytes far below the maximum contaminant levels, defined by the US EPA (2018) regulations, could be achieved.

■ Overview

In this application work, trace metal and mineral contents in drinking water samples were simultaneously determined by inductively coupled plasma mass spectrometry (ICP-MS). The analysis results of water samples from different common sources were compared against the US EPA regulations. The elemental concentrations were either well below the regulation limits or not detected. The ICP-MS method developed applying helium collision cell technology was verified and it provides a fast, sensitive, and reliable method for water quality and water safety evaluation.

■ Introduction

Clean, fresh drinking water is essential to life. The purity of drinking water is the basic prerequisite for healthy nutrition. On the other hand, the contamination of water mainly from the industrial pollution and then consumed is harmful to the health of human beings. In the past decades, a lot of effort has been made to reduce pollutants in drinking waters. As significant progress in the water treatment has been achieved, reliable measurement techniques are also desired in water safety determination. Heavy metal is one of the major substances in drinking water quality analysis. Elements like Cu, Se, Ca, Mg and Na are considered as micronutrients. Though being essential for a range of physiological functions to human beings, they may cause acute or chronic toxicities at excessive levels. Other heavy metals like Pb, Cd, Hg, As and Al are of particular concern due to their high toxicity and harmful impact on human health. [1]

The United States Environmental Protection Agency (US EPA) has issued a list of regulatory guidelines of heavy elements in drinking water. These values define the maximum level of an element in drinking water at which no known or anticipated adverse effect on the health of the person would occur. [2]

Inductively coupled plasma mass spectrometry (ICP-MS) has been widely used for the analysis of drinking water due to its multielement determination capability, wide dynamic linear range, and superior sensitivity. In this study, a rapid ICP-MS method was developed to determine the content of twenty-four trace and mineral elements in drinking water samples. This application article describes the ICP-MS analysis of twenty-four trace and mineral elements in drinking water, including spike recovery, detection limits, precision and long-term stability referencing to US-EPA 200.8. [3]

Fig. 1 ICPMS-2030

■ Experimental

Analytical conditions

All measurements were performed on Shimadzu ICPMS-2030 coupled with AS-10 autosampler. The instrument configuration and operation parameters are summarized in Table 1. The helium collision cell technology was employed to provide an effective way to remove polyatomic spectral interferences.

Table 1 Conditions and parameters of Shimadzu ICPMS-2030 instrumentation

Parameter	Settings
RF Power	1.20 kW
Sampling Depth	5.0 mm
Plasma Gas	Ar 8.0 L/min
Auxiliary Gas	Ar 1.10 L/min
Carrier Gas	Ar 0.70 L/min
Torch	Mini-Torch
Nebulizer	Nebulizer, 07UES
Chamber	Cyclone Chamber
Chamber Temp.	5ºC
No. of Scans	10 times
Cell Gas (He)	6.0 mL/min
Cell Voltage	-21.0 V
Energy Filter	7.0 V

Sample Preparation

Three water samples were obtained locally. They are tap water, filtered water and bottled water. All water samples were prepared and diluted two times in 1% ultrapure HNO_3 before introduction into ICP-MS.

For mercury, additional 0.5% hydrochloric acid was added in sample preparation to stabilize mercury in water samples. Additional wash steps using 1% HCl was also included to eliminate carryover effect of Hg.

Table 2 Calibration standards and internal standards (Unit: µg/L)

Analytes	Std.1	Std.2	Std.3	Std.4	Std.5	Std.6
Al, Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Mo, Ni, Se, Th, U, V, Zn, Fe	1	5	20	50	100	200
Hg	0.05	0.5	2.5	5	-	-
Na, Mg, K, Ca	100	1000	5000	10000	-	-
Internal Standards	1, 50, 1000					

Calibration Solutions

Multi-element stock solutions from Merck and Sigma-Aldrich were used for calibration standards preparation by serial dilution in 1% HNO_3. Ultra pure water with resistivity >18 mΩ·cm (Milli-Q) and ultrapure nitric acid were used. The calibration levels for each element are listed in Table 2. Bi, Ho, In, Rh and Sc were added as internal standards to correct the possible matrix interferences and instrument drift. The internal standards were added using the T shape internal standard online addition kit.

■ Results and Discussion

Quantitative Analysis of Drinking Water Samples

The determined concentrations in water samples from different sources are listed in Table 3. All measured metal contents were found to be below the maximum contaminant level (MCL) regulated by US-EPA (2018).

Generally, tap water contains the most elemental contents, while bottled water is the cleanest water source as expected. It was also interesting to find that similar heavy metal contents were detected in the filtered water sample compared to the tap water which was from the same water pipe. Some elements were even increased, e.g. Al concentration was found to increase from 17.2 to 29.8 µg/L after filtration. This indicates that the simple water filtration would not help to improve water quality in terms of heavy metal contamination. Toxic elements such as As, Cd, Hg, Pb, Tl measured were either not detected or in rather low levels.

Arsenic, especially in its inorganic form, is one of the most toxic trace elements present in the environment. The As concentrations in the water samples measured were below the limit of 10 µg/L set by the US EPA. The results showed that the tap water contained slightly higher As content of 0.274 µg/L than filtered water of 0.222 µg/L. As was not detected in bottled water.

Table 3 Quantitative analysis results in water samples with MDLs and EPA guideline values (Unit in µg/L)

Element	Concentrations			MDL	MCL EPA (2018)
	Tap water	Filtered water	Bottled water		
Al	17.2	29.8	<MDL	1.8	200
As	0.274	0.222	N.D.	0.02	10
Ba	32.6	36.4	N.D.	0.019	2000
Be	N.D.	N.D.	N.D.	0.006	4
Ca	16360	17540	N.D.	88	--
Cd	0.010	0.012	N.D.	0.006	5
Co	0.009	0.028	N.D.	0.009	--
Cr	0.098	0.142	0.074	0.04	100
Cu	276	26	N.D.	0.1	1300
Fe	7.42	3.44	N.D.	0.2	300
Hg	0.056	0.044	0.038	0.03	2
K	5080	5200	N.D.	15	--
Mg	1482	1428	34.4	1.2	--
Mn	5.6	4.9	N.D.	0.04	50
Mo	0.59	0.133	N.D.	0.03	--
Na	3680	3300	248	21	--
Ni	0.179	0.456	N.D.	0.04	--
Pb	0.458	0.085	N.D.	0.006	15
Sb	0.058	0.020	0.091	0.005	6
Se	N.D.	N.D.	N.D.	7	50
Tl	0.044	0.052	N.D.	0.002	2
U	N.D.	N.D.	N.D.	0.002	30
V	0.378	0.46	N.D.	0.015	-
Zn	25.6	48.6	0.638	0.3	5000

N.D.: not detected

MDL: method detection limits are calculated by LOQ x Dilution Factor (DF)

Table 4 Elements with analyzing mass, internal standards, cell gas mode, correlation coefficients (r), LODs and LOQs (Unit in µg/L)

Element	Mass	Internal standard	Cell Gas	r	LOD	LOQ
Al	27	Sc	On	0.99986	0.3	0.9
As	75	Rh	On	0.99995	0.004	0.012
Ba	137	In	Off	0.99975	0.003	0.009
Be	9	Sc	Off	0.99941	0.0009	0.003
Ca	43	Sc	On	0.99999	13	44
Cd	111	Rh	Off	0.99982	0.0008	0.003
Co	59	Rh	On	0.99949	0.0013	0.004
Cr	52	Sc	On	0.99970	0.005	0.018
Cu	65	Rh	On	0.99987	0.015	0.05
Fe	54	Rh	On	0.99993	0.03	0.11
Hg	202	Bi	Off	0.99993	0.005	0.016
K	39	Sc	On	0.99994	2	8
Mg	24	Sc	Off	0.99999	0.18	0.6
Mn	55	Rh	On	0.99981	0.006	0.02
Mo	98	Rh	On	0.99934	0.004	0.015
Na	23	Sc	Off	1.00000	3	11
Ni	60	Rh	On	0.99988	0.006	0.018
Pb	208	Ho	Off	0.99987	0.0009	0.003
Sb	121	Rh	Off	0.99933	0.0008	0.003
Se	80	Rh	On	0.99960	1.1	4
Tl	205	Ho	Off	0.99994	0.0004	0.0012
U	238	Ho	Off	0.99974	0.0004	0.0012
V	51	Sc	On	0.99987	0.002	0.007
Zn	66	Rh	On	0.99976	0.04	0.14

Cadmium as a carcinogen is toxic to human kidneys, skeletal and respiratory systems. According to the EPA guidelines, Cd concentration in drinking water must be lower than 5 µg/L. About 0.01 µg/L of Cd was detected in tap and filtered water, which were both well below the guideline values.

Copper, Iron and Zinc are secondary drinking water contaminants that could cause cosmetic effects (such as skin or tooth discoloration) or aesthetic effects (such as taste, odor, or color), if intake from drinking water.

Leaching of these minerals from metal components used in water treatment plants and plumbing materials do occur when pH and hardness of water are not adjusted. The concentrations determined in the three water samples were all below the control limits.

Essential elements serve beneficial roles in human physiology. Ca and Mg aid in the mineralization and development of the skeleton while Na is important for proper muscle and nerve function. They were found in large amounts (>5000 µg/L) in tap and filtered water samples but not detected in bottled water.

Table 5 Spike recovery results of targeted elements in tap water and %RSD

Element	Tap Water			
	Spiked Conc. (µg/L)	Recovery	%RSD	Recovery
Al	10	10.1	1.9	101%
As	1	1.07	0.7	107%
Ba	10	10.7	1.9	107%
Be	1	0.95	1.1	95%
Ca	5000	5920	0.8	118%
Cd	1	1.05	2.2	105%
Co	1	1.04	1.0	104%
Cr	1	1.0	0.8	101%
Cu	10	9	0.8	90%
Fe	1	1.15	2.2	115%
Hg	0.5	0.52	1.4	105%
K	2000	1880	0.9	94%
Mg	500	469	5.4	94%
Mn	1	1.14	1.0	114%
Mo	1	1.05	1.3	105%
Na	2000	2250	5.1	113%
Ni	1	1.07	2.2	107%
Pb	1	1.03	0.8	103%
Sb	1	1.06	0.4	106%
Se	10	11.7	3.9	117%
Tl	1	1.07	1.3	107%
U	1	1.18	1.0	118%
V	1	0.99	0.6	99%
Zn	10	10.4	1.3	104%

Calibration Linearity and Detection Limits

Calibrations obtained for targeted analytes showed good linearities with r > 0.9994 as listed in Table 4. LODs and LOQs were calculated by 3 and 10 times the standard deviation of 10 continuous measurement of calibration blank. Sub ppb or ppt levels of LODs and LOQs were achieved for all analytes especially for the hazardous elements such as As, Cd, Hg and Pb, indicating the capability of the ICP-MS method to determine heavy metal for drinking water safety.

Recovery and Precision

Method recovery and precision were assessed by spiking each analyte into tap water sample at various concentrations based on their concentration levels in tap water. Satisfactory recovery rates of 90-118% were achieved as shown in Table 5 for spike recovery test in tap water sample, indicating the method accuracy and absence of interference. Good analysis precisions were obtained with %RSD less than 3% for majority of the analyte elements with a few exceptions of up to 5%.

Stability

Method stability was assessed by analyzing a 5 µg/L quality control solution continuously. The measurement was taken at every 30-minute interval and recoveries were calculated and normalized. Figure 2 shows the stability of the 19 targeted elements over 5 hours. All the normalized recovery values were within the range of 80%-120% during the analyzing period. The limits specified in EPA 200.8 is 70%-130%.

The internal standards intensity was plotted in Figure 3 to monitor the instrument drift normalized to t=0. Throughout the 5 hours, the intensity drift was less than 15%, demonstrating the excellent system stability.
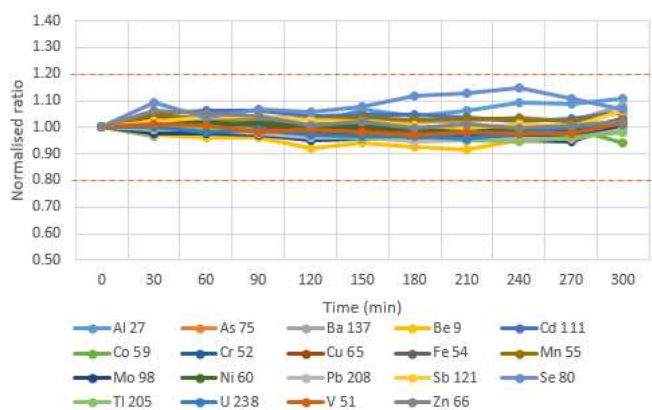

Fig. 2 Normalized recovery tests over 5 hours
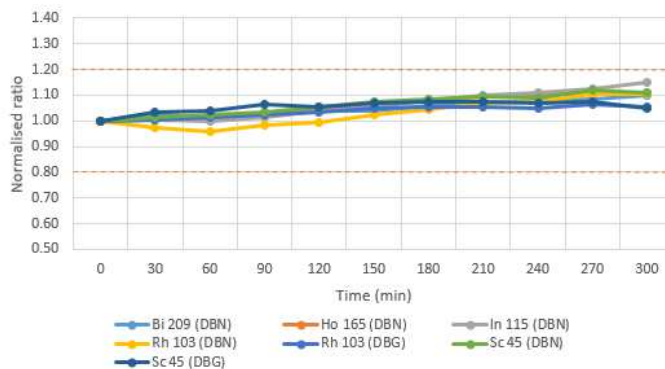(one analysis every 30 min)

Fig. 3 Normalized intensity of Internal standards over 5 hours

■ Conclusion

A high throughput ICPMS method was developed and applied to analyze heavy metals and mineral contents in drinking water under the same instrument condition. The content levels of regulated analytes were compared to the guideline values defined by the US EPA (2018) and were found to be far below the maximum control levels (MCLs). The ICP-MS method developed were evaluated and exhibits good performance with good calibration linearity, good repeatability and low method quantitation limits at ppb to sub-ppb levels. Satisfactory recovery rates and normalized recoveries were obtained within the acceptance range of 80% to 120% in tap water samples. The ICP-MS method established provides a sensitive, accurate, stable and fast way for determination of elemental contents in drinking water.

■ References

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2. US Environmental Protection Agency (EPA). National Primary Drinking Water Regulations, (2018)

3. U.S. EPA. "Method 200.8: Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma-Mass Spectrometry," Revision 5.4, (1994)

■ Acknowledgement