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Application News

Inductively Coupled Plasma Mass Spectrometry ICPMS-2050

Determination of Essential and Toxic Elements in Urine by ICPMS-2050

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User Benefits

- Utilizing CRM Urine Control samples streamlines the workflow and minimizes the risk of errors.
- ICPMS-2050 can achieve accurate analysis with lower argon gas consumption and running cost using mini torch.
- Internal standard fluctuation can be readily observed using the Internal Standard Intensity Fluctuation Graph function of LabSolutions™ ICPMS.

■ Introduction

Biomonitoring is the process of measuring specific chemicals or metabolites in biological specimens, such as urine and blood serum. It is an important tool for assessing human exposure to environmental contaminants. One of the methods involves measuring the concentration of trace elements, such as arsenic, cadmium, lead and mercury.

Urine is an ideal sample for biomonitoring because the sample collection is both non-invasive and relatively simple. In addition, many trace elements are excreted predominantly in urine as their original form or metabolites1). Graphite furnace atomic absorption spectrometry (GFAAS) has been used by clinical laboratories to determine trace elements in urine. However, as GFAAS is a mono-elemental technique, the analysis could be time consuming when many samples are measured for multiple element analysis.

In recent years, Inductively Coupled Plasma Mass Spectrometry (ICP-MS) has become the preferred technique for urine analysis due to its ability to detect multiple elements simultaneously, wide dynamic linear range and high sensitivity. Furthermore, with collision/reaction cell technology equipped in ICP-MS, interference such as polyatomic interference can be eliminated. In this study, an ICP-MS method was developed to determine the concentration of nineteen toxic and essential elements in certified reference material (CRM) of urine using Shimadzu ICPMS-2050 (Fig. 1).

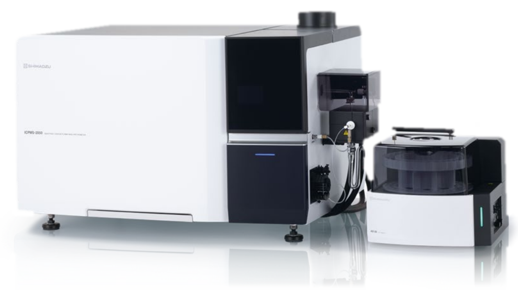

Fig. 1 ICPMS-2050

■ Sample Preparation

Sample

Two RECIPE ClinChek® (München, Germany) Urine Control, lyophil., for Trace Elements were used for this study: Level I and II (Ref: 8847 – 8849, Lot 2502). The control samples are reconstituted with 10 mL of ASTM Type 1 ultrapure water as per the enclosed certificate instructions.

Sample Preparation

The reconstituted samples were prepared using simple dilution with acid diluent. A dilution of 15 times was carried using acid diluent in Table 1 before sample analysis.

Table 1 Components of Acid Diluent prepared in Water*1

Reagent	Description	Purpose
Nitric Acid	65% Suprapur®, Merck, Germany	Stabilizes essential and trace metals
Triton®X-100	Premium grade, Sigma-Aldrich, USA	Homogenizes sample & support lyse of cells
1-Butanol	≥99.5% Sigma-Aldrich, USA	As a carbon source to enhance analytical sensitivity
Gold Standard	1,000mg/L Sigma-Aldrich, USA	Stabilizes mercury (Hg)

*1 All solutions are prepared using ASTM Type 1 ultrapure water (18.2MΩ resistivity, Milli-Q system, Millipore, Germany)

■ Standard Preparation

Calibration Standards

Single-element stock solutions from Merck and Sigma-Aldrich were used to prepare calibration standards through serial dilution using acid diluent in Table 1. The calibration concentration ranges for each element are shown in Table 2.

Internal Standard Solution

Internal standards were used for correcting potential matrix interference and instrument drift. Single-element stock solution of Bismuth (Bi), Germanium (Ge), Indium (In) and Scandium (Sc) were used to prepare internal standard with acid diluent in Table 1. The prepared solution was added to all calibration standards, sample and washing solution with the final concentration of 10 µg/L for each internal standard.

Table 2 Calibration concentration range for target elements

Elements	Calibration Concentration Range (µg/L)
Cd, Cr, Co, Hg, Mn, Ni, Tl	0 – 5
Al, As, Ba, Cu, Fe, Mo, Pb, Se, V	0 – 50
Sb	0 – 10
Zn	0 – 100
Ca	0 – 2,500

■ Instrument and Measurement Condition

Table 3 shows the instrument configuration of ICPMS-2050. A mini-torch, which consume 2/3 less argon gas than a standard torch , was used to reduce running cost.

Table 3 Instrument conditions

Instrument	: ICPMS-2050
Nebulizer	: Micromist DC Nebulizer
Spray Chamber	: Cyclonic Chamber
Plasma Torch	: Mini-torch
Sampling Cone	: Nickel
Skimmer Cone	: Nickel
Autosampler	: AS-20

Table 4 shows the analytical conditions. A few significant changes were made to the default analytical condition, which include increasing the sampling depth to 7 mm from default setting of 5 mm. This change aims to minimize the amount of sample introduced into the system, thereby reducing potential interference. Additionally, argon gas dilution is utilized to account for the effects of the sample matrix. Both measures aim to achieve optimal system robustness while maintaining adequate sensitivity.

Table 4 Analytical Conditions

Sampling Depth	: 7 mm
Plasma Gas Flowrate	: Ar 9.0 L/min
Auxiliary Gas Flowrate	: Ar 1.1 L/min
Carrier Gas Flowrate	: Ar 0.45 L/min
Dilution Gas Flowrate	: Ar 0.40 L/min
Cell Gas	: He 6.0 mL/min H_2 7.0 mL/min
Cell Voltage	: -21.0 V
Energy Filter	: 7.0 V

■ Result and Discussion

Detection Limits

The linear regression (R) values of the calibration curves obtained are shown in Table 5. The R values obtained for all target elements exceeded 0.999, indicating good linearity was achieved under the selected mass number and gas mode. Limit of Detection (LOD) and Limit of Quantitation (LOQ) for the target elements are also shown in Table 5. The LODs and LOQs were calculated based on 3 and 10 times the standard deviation (σ) from 10 replicate measurements of the calibration blank, respectively.

Analysis of CRM

The essential and toxic elements in the CRM urine samples were simultaneously measured using a calibration curve method and the results of the analysis are shown in Table 6. Recoveries of 83 – 118% of the certified values were achieved, indicating the method accuracy and the absence of interference.

Table 5 Linear Regression, LOD and LOQ of each analytical element

Element	Gas Mode	Internal Standard	Linear Regression (R)	LOD (µg/L)	LOQ (µg/L)
^{27}Al	No Gas	^{45}Sc	0.99996	0.02	0.07
^{75}As	He	^{72}Ge	0.99991	0.03	0.09
^{137}Ba	He	^{115}In	0.99984	0.02	0.06
^{44}Ca	H_2	^{45}Sc	0.99997	3	9
^{114}Cd	H_2	^{72}Ge	0.99989	0.01	0.05
^{59}Co	He	^{45}Sc	0.99992	0.003	0.01
^{52}Cr	He	^{72}Ge	0.99998	0.03	0.1
^{65}Cu	He	^{72}Ge	0.99999	0.02	0.05
^{56}Fe	He	^{72}Ge	0.99999	0.06	0.2
^{202}Hg	H_2	^{209}Bi	0.99991	0.009	0.03
^{55}Mn	H_2	^{72}Ge	0.99979	0.008	0.03
^{95}Mo	He	^{72}Ge	0.99999	0.003	0.009
^{60}Ni	He	^{72}Ge	0.99999	0.01	0.04
^{Sum}Pb*1	He	^{209}Bi	0.99990	0.001	0.005
^{121}Sb	He	^{72}Ge	1.00000	0.005	0.02
^{78}Se	H_2	^{72}Ge	0.99988	0.02	0.05
^{205}Tl	He	^{209}Bi	0.99997	0.004	0.01
^{51}V	H_2	^{72}Ge	0.99975	0.02	0.07
^{66}Zn	H_2	^{72}Ge	0.99979	0.2	0.7

LOD = 3 × σ × slope of calibration curve
LOQ = 10 × σ × slope of calibration curve

*1 The summation of signals at 206, 207, and 208 m/z for lead (to compensate for any differences in the abundances of these isotopes between samples and standards)

Table 6 Analytical Results for CRM Urine Sample (RECIPE ClinChek Urine Control, Level I and II)

Element	ClinChek Urine Control, Level I				ClinChek Urine Control, Level II			
	Measured Value (µg/L)	Certified Value (µg/L)	Control Range (µg/L)	Recovery (%)	Measured Value (µg/L)	Certified Value (µg/L)	Control Range (µg/L)	Recovery (%)
^{27}Al	33.0	32.7	26.1 - 39.2	101	73.1	80.8	64.7 – 97.0	90
^{75}As	18.2	16.8	13.4 – 20.1	108	51.8	51.0	40.8 – 61.2	102
^{137}Ba	10.0	10.8	8.66 – 13.0	93	46.9	50.3	40.2 – 60.3	93
^{44}Ca	17,800	17,000	14,100 – 19,800	105	17,700	16,800	13,900 – 19,600	105
^{114}Cd	2.39	2.11	1.68 – 2.53	113	14.8	14.1	11.3 – 16.9	105
^{59}Co	2.09	1.98	1.58 – 2.37	106	9.55	9.46	7.57 – 11.4	101
^{52}Cr	4.01	3.91	3.13 – 4.70	103	10.4	9.85	7.88 – 11.8	106
^{65}Cu	56.5	48.4	38.7 – 58.0	117	106	104	83.2 – 125	102
^{56}Fe	36.9	39.6	31.7 – 47.6	93	205	222	177 – 266	92
^{202}Hg	2.25	-	-	-	6.61	-	-	-
^{55}Mn	4.17	3.85	3.08 – 4.62	108	10.1	9.46	7.57 – 11.3	107
^{95}Mo	19.2	19.4	15.5 – 23.3	99	85.8	93.0	74.4 – 112	92
^{60}Ni	3.19	3.22	2.58 – 3.86	99	15.2	14.6	11.7 – 17.6	104
^{Sum}Pb	27.9	26.3	21.1 – 31.6	106	43.7	52.5	42.0 – 63.0	83
^{121}Sb	6.47	5.50	4.40 – 6.59	118	51.5	47.9	38.3 – 57.4	108
^{78}Se	22.2	23.9	17.9 – 29.8	93	62.7	75.3	56.4 – 94.1	83
^{205}Tl	7.96	7.21	5.77 – 8.66	110	20.9	19.0	15.2 – 22.8	110
^{51}V	20.3	20.6	16.5 – 24.7	99	44.8	50.6	40.5 – 60.7	89
^{66}Zn	170	180	144 – 215	94	477	502	401 - 602	95

Recovery (%) = Measured Value / Certified Value × 100

Spike Recovery Test

To validate the measurement results in Table 6, an unspiked and spiked of CRM urine sample for Level I was quantitatively measured using calibration curves. The spike concentrations and spike recovery results are shown in Table 7. Spike recoveries of 93 – 104% were obtained for all the measured elements. This demonstrates the matrix of the CRM urine sample has minimum effect on the ICPMS-2050 analysis.

Method Stability

When analyzing high-matrix samples over extended periods, the stability of internal standard elements serves as a key indicator for evaluating the robustness of the analytical method. As illustrated by the internal standard intensity fluctuation graph in Fig. 2, the analysis method demonstrated stability throughout the entire 30-sample run, with the intensities of each internal standard fluctuating by no more than 20%. Additionally, a standard check was performed after every 10 samples to ensure the validity of the measured values.

■ Conclusion

This application news highlights that the ICPMS-2050 is well suited for analyzing essential and toxic elements in urine samples. With its high sensitivity and robustness, the ICPMS-2050 facilitates simultaneous analysis across a broad concentration range, from low to high. Additionally, the spike recovery results demonstrate the method's high accuracy.

<References>

1) G.V. Iyengar. (1998) Reevaluation of the trace element content in Reference Man, Radiat Phys Chem, 51(4-6): 545-560

<Related Applications>

1. Determination of 20 Nutritional, Essential and Toxic Elements in Blood Serum by ICP-MS using Alkaline Dilution, [Application News 05-SCA-116-010-EN]

Table 7 Spike Concentrations and Spike Recovery Results

Element	Unspike Measured Value (µg/L)	Spike Concentration (µg/L)	Spike Measured Value (µg/L)	Spike Recovery (%)
^{27}Al	2.61	10	12.9	103
^{75}As	1.22	10	11.1	99
^{137}Ba	0.78	10	11.1	103
^{44}Ca	1180	500	1680	100
^{114}Cd	0.16	1	1.16	100
^{59}Co	0.13	1	1.09	96
^{52}Cr	0.28	1	1.31	103
^{65}Cu	3.67	10	13.7	100
^{56}Fe	2.54	10	12.7	102
^{202}Hg	0.15	1	1.08	93
^{55}Mn	0.27	1	1.29	102
^{95}Mo	1.23	10	10.9	97
^{60}Ni	0.22	1	1.22	100
^{Sum}Pb	1.86	10	12.3	104
^{121}Sb	0.42	2	2.40	99
^{78}Se	1.48	10	11.0	95
^{205}Tl	0.54	1	1.59	105
^{51}V	1.22	10	11.6	104
^{66}Zn	11.8	20	30.3	93

Spike Recovery (%) = (Concentration of spiked sample − Concentration of sample) / Spike-concentration × 100

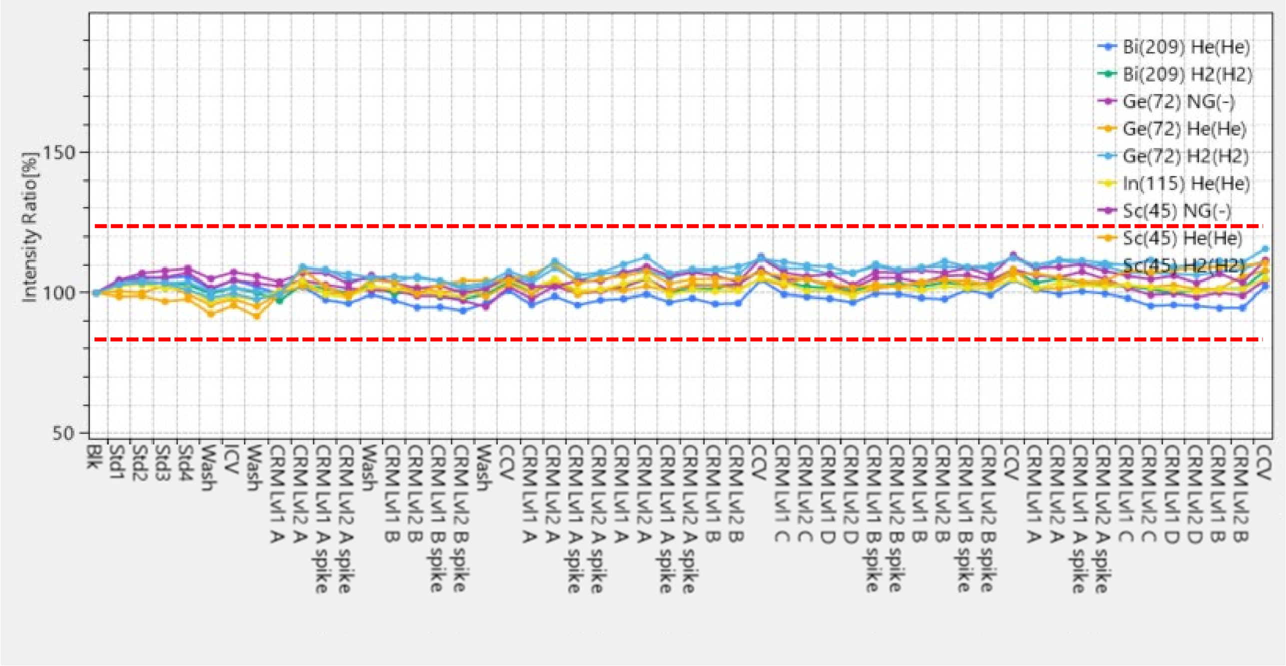

Fig. 2 Internal Standard Intensity Fluctuation Graph

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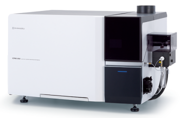

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