

# SIMULTANEOUS DETERMINATION OF NINE METAL ELEMENTS IN RIVER SEDIMENTS AND SURROUNDING SOIL BY ICP-MS WITH QUADRUPOLE COLLISION CELL TECHNOLOGY

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**Abstract.** As people pay more and more attention to environmental pollution, heavy metal pollution of river sediments and surrounding soil is also brought into focus. The traditional methods used to analyze various metal elements as ICP, AFS etc. In this paper, Cu, Zn, Cd, Pb, Hg, Mn, Cr, Ni and As in river sediments and soil were simultaneously determined by ICP-MS with the quadrupole collision cell technology. The analysis efficiency is improved. The collision cell kinetic energy discrimination (KED) model is used to effectively eliminate the mass spectrum interference problem. The matrix effect and signal drift are corrected effectively by using Rh as the internal standard element. The method is verified under the stable instrument conditions. The verification results show that the mass concentration of all elements had a good linear relationship with spectral intensity, and the linear correlation coefficients were all greater than 0.999. The detection limits of 9 elements ranged from 0.01 to 0.3  $\mu\text{g}\cdot\text{g}^{-1}$ . RSD was less than 6.25%, and RE was -7.10% to 7.08%, which proved that the method had good accuracy and precision. It can meet the requirements of determination.

**Keywords:** river sediment and soil, metallic elements, ICP-MS, kinetic energy discrimination model (KED model).

## 1. Introduction

Heavy metals have a serious impact on the environment and human health [1]. At present, with the acceleration of industrialization and urbanization in various regions, heavy metals discharged by human beings into the environment are increasing day by day, which has aroused widespread concern [2]. In China, many highly developed urban agglomerations gather around rivers, and human activities are frequent, which also brings greater challenges to the surrounding environment [3]. River sediment and soil, as carriers of environmental substances, are also affected by heavy metal pollution. Recently, most studies on river heavy metal pollution focus on the analysis and testing of surface water samples, and there are few reports on testing of heavy metal content in sediments and soil [4-5]. Therefore, establishing an accurate determination method of heavy metal content in river sediments and surrounding soil is very important, and it is also an important basis for the investigation of river environmental pollution.

At present, the instruments used in the field of heavy metal detection mainly include four categories: ICP-MS (inductively coupled plasma mass spectrometer), FLAAS (atomic absorption spectrometer), ICP-AES (inductively coupled plasma spectrometer) and AFS (atomic fluorescence spectrometer) [6-9]. Inductively coupled plasma mass spectrometry (ICP-MS) is the most effective and extensive method for the determination of metal elements in soil and sediment samples at present, mainly because ICP-MS is suitable for sample analysis with complex matrix, and has the advantages of high sensitivity, wide linear range, good precision, and simultaneous determination of multiple elements. With the introduction of the collision/reaction cell technology in recent years, the problem of multi-atomic ion interference existing in ICP-MS has been successfully solved, and the use of the kinetic energy discrimination mode (KED) to add helium collision gas has been increasingly applied to solve the mass spectrum interference [10-11].

In this paper, helium is used as the collision gas, the collision cell kinetic energy discrimination mode (KED) is used to eliminate the mass spectrum interference of ICP-MS, and the internal standard element Rh is added to correct the non-mass spectrum interference. A method for simultaneous determination of Cu, Zn, Cd, Pb, Hg, Mn, Cr, Ni and As in river sediments and soils was established.

## 2. Experiment

### 2.1. 1.Equipment

ICP-MS: ICAP-RQ Series (with KED mode) purchased from ThermoFisher US. Using tuning fluid to optimize the instrument, and the optimized working conditions are as follows: the RF power is

1250 W; atomizing gas flow rate 0.82 L·min<sup>-1</sup>; auxiliary gas flow rate 0.7 L·min<sup>-1</sup>; cooling gas flow rate 13 L·min<sup>-1</sup>; collision gas (helium) flow rate 3.2 mL·min<sup>-1</sup>; integration time 0.5 s; semiconductor cooling temperature 2-4 °C; scanning mode peak jump; scan times 100 times.

## 2.2. Materials

National standard materials for analysis of drainage sediment soil composition: GBW07403, GBW07404, GBW07405, all developed by the Institute of Geophysical and Geochemical Exploration, Chinese Academy of Geological Sciences.

Multielement standard solution (includes Cu, Zn, Cd, Pb, Hg, Mn, Cr, Ni, As): 100 µg·mL<sup>-1</sup>, developed by the National non-ferrous metal and electronic material analysis and testing center. The 100 µg·mL<sup>-1</sup> standard solution was diluted step by step to 1.0 µg·mL<sup>-1</sup> multi-element standard secondary diluent. 0.00, 0.025, 0.05, 0.10, 0.25, 0.50, 1.00, 2.00 mL of the 1.0 µg·mL<sup>-1</sup> standard secondary diluent were placed in eight 50 mL volumetric bottles and fixed the volume at 50 mL separately with 3% dilute nitric acid. Shaked to prepare 0.00, 0.50, 1.00, 2.00, 5.00, 10.00, 20.00, 40.00 ng·mL<sup>-1</sup> multi-element standard series.

Nitric acid (superior pure), sulfuric acid (superior pure), hydrofluoric acid (superior pure). Tuning fluid (purchased from ThermoFisher, USA). The experimental water was ultra-pure water (resistivity 18.2 MΩ·cm).

## 2.3. Sample treatment

Three acid digestion system (nitric acid: hydrofluoric acid: sulfuric acid = 1:1:0.1) has been used, accurately weighed a 1.000 g sample and put it in a polytetrafluoroethylene crucible, rinsed with 1 mL deionized water, triacid mixed acid added, put the polytetrafluoroethylene crucible on an electric heating plate with the temperature rise to 120 °C for 0.5 h, heated at 150 °C for 1 h, and finally temperature risen to 280 °C until the triacid evaporates. After cooling, 10 mL of nitric acid solution (nitric acid: water = 1:1) was added for solubilization and extraction, and the volume was fixed at 50 mL with deionized water in a 50 mL volumetric bottle.

## 3. Results and discussion

### 3.1. Optimization of interference problems in ICP-MS

Soil and sediment samples have high concentrations of various salts, the high concentrations of the matrix will affect the determination of metal elements. With the increase of the matrix concentration, the values of the detected signals decreased gradually. The short- and long-term drift of the signal can be monitored and corrected by adding the internal standard substance in the measurement process, and the matrix effect can be compensated. The selection criteria of the internal standard substance are mainly based on two conditions: similar to the mass number of the element to be measured and the content in the sample is very low. Therefore, 103Rh and 185Re were selected as internal standard substances in this experiment. When the internal standard substance is added, the value of each signal to be detected tends to be stable.

The multi-element standard series in 1.2 was used for determination to verify the optimization conditions of the instrument. The standard curve of each element was automatically drawn by the software with the mass concentration as the X-axis and the intensity as the Y-axis, the correlation coefficient was also given. It can be seen from Table 1 that the standard curves of each element to be measured have a good linear relationship, and the linear correlation coefficients are all greater than 0.999.

Table 1

**Standard curve and correlation coefficient**

Element	Equation of linear regression	Correlation coefficient
Cu	$y = 0.9817x + 0.0233$	0.9996
Zn	$y = 0.9903x + 1.152$	0.9994
Cd	$y = 0.9989x - 0.1199$	0.9995
Pb	$y = 1.026x + 0.0353$	0.9997

Table 1 (continued)

Element	Equation of linear regression	Correlation coefficient
Hg	$y = 0.992x + 0.0441$	0.9998
Mn	$y = 0.996x + 0.4011$	0.9993
Cr	$y = 0.9772x + 0.3102$	0.9999
Ni	$y = 0.9943x + 0.3132$	0.9997
As	$y = 0.9214x + 0.1984$	0.9999

### 3.2. LOD and LOQ of the analysis method

LOD (limit of detection) and LOQ (limit of quantitation) were calculated according to the Technical Guidelines for the Revision of Standards for Environmental Monitoring and Analysis Methods of the Ministry of Environmental Protection (HJ168-2010). According to all steps of sample analysis, the blank experiment was repeated 10 times ( $n \geq 7$  specified in the requirements of HJ168-2010). When the sample volume was 0.1 g and the fixed volume was 50 mL, the standard deviations of 10 parallel measurements were obtained by converting each determination result into the concentration of samples, and LOD of each element in the method was obtained according to the LOD calculation formula  $LOD = t(n-1, 0.99) \times s$ . Taking 4 times LOD as LOQ, LOQ of each element in the method was calculated.

Table 2

LOD and LOQ ( $\mu\text{g}\cdot\text{g}^{-1}$ )

Element	LOD	LOQ	Element	LOD	LOQ
Cu	0.10	0.40	Mn	0.09	0.36
Zn	0.30	1.20	Cr	0.11	0.44
Cd	0.01	0.04	Ni	0.12	0.48
Pb	0.16	0.64	As	0.01	0.04
Hg	0.01	0.04	-	-	-

### 3.3. Accuracy and precision of the analysis method

The standard substances GBW07403, GBW07404 and GBW07405 of certified soil and drainage sediment with different concentrations were selected for determination, and each standard substance was measured in parallel 12 times. The results are shown in Table 3. RSD (relative standard deviation) of the determination results of 9 elements was all less than 6.25%, and RE (relative error) was -7.10 to 7.08%. It shows that the method has good precision and accuracy.

Table 3

Accuracy and precision

Sample No.	Element	Standard value, $\mu\text{g}\cdot\text{g}^{-1}$	Measured value, $\mu\text{g}\cdot\text{g}^{-1}$	SD	RSD%	RE%
GBW07403	Cu	11.4	11	0.51	4.47	-3.51
	Zn	31	28.8	0.49	1.58	-7.10
	Cd	0.06	0.062	0.003	5.00	3.33
	Pb	26	27.1	0.51	1.96	4.23
	Hg	0.06	0.058	0.002	3.33	-3.33
	Mn	304	298	13.3	4.38	-1.97
	Cr	32	33.5	1.58	4.94	4.69
	Ni	12	12.85	0.44	3.67	7.08
As	4.4	4.21	0.16	3.64	-4.32	

Table 3 (continued)

Sample No.	Element	Standard value, $\mu\text{g}\cdot\text{g}^{-1}$	Measured value, $\mu\text{g}\cdot\text{g}^{-1}$	SD	RSD%	RE%
GBW07404	Cu	40	41.2	1.32	3.30	3.00
	Zn	210	204	11.1	5.29	-2.86
	Cd	0.350	0.342	0.011	3.14	-2.29
	Pb	58	57.1	2.1	3.62	-1.55
	Hg	0.59	0.58	0.01	1.69	-1.69
	Mn	1420	1398	25.8	1.82	-1.55
	Cr	370	374	12.5	3.38	1.08
	Ni	64	66.1	3.5	5.47	3.28
	As	58	58.5	2.8	4.83	0.86
GBW07405	Cu	144	148.5	3.2	2.22	3.13
	Zn	494	504	15.9	3.22	2.02
	Cd	0.45	0.442	0.024	5.33	-1.78
	Pb	552	548	12.6	2.28	-0.72
	Hg	0.29	0.28	0.01	3.45	-3.45
	Mn	1360	1398	38.4	2.82	2.79
	Cr	118	124	6.8	5.76	5.08
	Ni	40	37.9	2.5	6.25	-5.25
	As	412	435	17.8	4.32	5.58

## Conclusions

Based on the previous research experience, this paper verifies the feasibility of the simultaneous determination of 9 metal elements in river sediments and surrounding soil by ICP-MS with the quadrupole collision cell technology, which can meet the requirements of the Technical Guidelines for the Revision of Environmental Monitoring and Analysis Method Standards of the Ministry of Environmental Protection (HJ168-2010).

Ten sediments and ten soil samples from the Hun River Reach of Shenyang were selected for analysis. The content of Cu, Zn, Cd and Pb were determined by this method to be 26.2-58.5  $\mu\text{g}\cdot\text{g}^{-1}$ , 130-253  $\mu\text{g}\cdot\text{g}^{-1}$ , 0.06-0.13  $\mu\text{g}\cdot\text{g}^{-1}$ , and 13.5-38.1  $\mu\text{g}\cdot\text{g}^{-1}$  respectively. Hg content ranges from 0.07 to 0.13  $\mu\text{g}\cdot\text{g}^{-1}$ , Mn content ranges from 485 to 701  $\mu\text{g}\cdot\text{g}^{-1}$ , Cr content ranges from 67 to 153  $\mu\text{g}\cdot\text{g}^{-1}$ , Ni content ranges from 19.2 to 41.2  $\mu\text{g}\cdot\text{g}^{-1}$ , and As content ranges from 12.5 to 18.4  $\mu\text{g}\cdot\text{g}^{-1}$ .

The application of ICP-MS with the quadrupole collision cell technology to determine river sediment and soil samples can effectively solve the problem of mass spectrum interference in sample testing. Originally 9 elements needed to be tested by several different methods. Now the determination can be completed by only one method, which can greatly improve the efficiency of sample analysis. It can also reduce the pollution of the environment caused by using chemical reagents and the health hazards of the testing personnel.

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