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Determination of Six Heavy Metal Elements Such as Co in Solid Waste by ICP-MS

Determination of Six Heavy Metal Elements Such as Co in Solid Waste by ICP-MS

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Abstract. Soil In this paper, tetraacid system -microwave digestion was established as a soil pretreatment method. The analytical methods for simultaneous determination of six heavy metals in Co, V, Sb, Mn, Mo and Tl by inductively coupled plasma mass spectrometry (ICP-MS) were discussed. The results show that the correlation curves of standard curves for soil and sediment Cr, Ni, Cu, Zn, Cd and Pb were determined by ICP-MS method to be 1.0000, 0.9999, 0.9999, 0.9999, 0.9999, and 0.9999, respectively. The detection limits were 0.1 mg/kg, 0.1mg/kg, 0.1mg/kg, 0.1mg/kg, 0.1mg/kg, and 0.1mg/kg, respectively. The relative standard deviations of precision are 1.2%~3.7%, 1.4%~2.9%, 3.7%~6.6%, 1.1%~1.3%, 6.1%~7.6% and 2.7%~7.1%. The accuracy of the standard substance measured values are within the uncertainty range. The laboratory has verified the method of determining heavy metals in soil waste by ICP-MS. The linear relationship, detection limit, precision and accuracy are in line with the standard HJ 766-2015 requirements.

1. Introduction

For the traditional ICP-AES method, it has the characteristics of low detection limit and fast detection speed. However, after a large number of applications, it has been found that in the process of measuring a high concentration of the substrate, it is easily interfered by elements such as Ca, Al, Fe, etc., resulting in low detection accuracy. Therefore, based on ICP-AES, it is necessary to maintain the advantages of traditional detection while reducing the interference of other elements. In this regard, people began to combine vacuum RF spark and mass spectrometry on the basis of ICP. It is considered that mass spectrometry has the characteristics of simple map and moderate resolution. Since then, it has gradually evolved through development and has gradually spread to various industries such as medical, biological, and metallurgical industries. Currently, in the application of ICP-MS, Chen Guojuan (2017) in his published paper applied it to the detection of rare elements in ore to determine Ni, Cu, Zn, and Cd in ore. The content of Sb, Pb, Bi and other elements, and its detection limit is

0.004~0.51µg/g, which greatly improves the accuracy of detection; Wanfei (2010) applies the ICP-MS method to In soil testing, the method is used to determine the content of trace elements in a certain area, which provides a basis and reference for agricultural planting; Wang Yuqing et al focus on soil trace elements in graphite-microwave digestion-ICP mass spectrometry. The accuracy in the determination was verified to further verify the effectiveness of graphite-microwave digestion in the pretreatment of samples; Wang Yunfeng (2016) combined the ICP-MS method to trace trace elements in water system. The measurement further obtained the trace element content in different water systems. Through the above application, ICP-MS has a wide range of uses, and the detection accuracy and precision are high.

2. Experimental part

2.1. Instruments and reagents
Aglient 7700e Inductively Coupled Plasma Mass Spectrometer ICPMS (Agilent, USA); CEM MARS6 Microwave Digestion Apparatus (CEM, USA); Milli-Q Ultrapure Water Treatment System (Millipore, USA); Analytical balance (METTLER TOLEDO, USA); Nitric acid, hydrochloric acid (excellent grade); Environmental Analysis Multi-Element Mixed Standard Solution (Agilent, USA); Soil component analysis standard substance (Institute of Geophysical and Geochemical Exploration, Chinese Academy of Geological Sciences, China); Argon: High purity grade.

2.2. Sample processing
Accurately weigh 0.1~0.2 g (accurate to 0.1 mg) air-dried and ground to a particle size less than 0.149 mm (100 mesh). (Solid or non-dryable solid sample, weigh directly to sample 0.2g, accurate to 0.0001 g), placed in the digestion tank, add 1 mL concentrated hydrochloric acid and 4 mL concentrated nitric acid, 1 mL hydrofluoric acid and 1 mL hydrogen peroxide, put the digestion tank into the microwave digestion device setting program, so that the sample rises within 10 min At 175 °C and held at 175 °C for 20 min (solid waste leachate rose to 165 °C in 10 min and held at 165 °C for 20 min). After digestion, cool to room temperature, carefully open the lid of the digestion tank, then place the digestion tank in the acidifier, and sip the acid at 150 °C until the contents are nearly dry. After cooling to room temperature, dissolve the contents with deionized water. Then, the solution was transferred to a 50 mL volumetric flask, made up to 50 mL with deionized water, and the supernatant was measured by inductively coupled plasma mass spectrometry (ICP-MS).

2.3. Standard curve configuration
Prepare a multi-element mixed standard solution with a concentration of 0, 0.1, 0.5, 1, 5, 10, 20, 50, 100, 200, 500 µg/L with 2% nitric acid; 500µg/L with 2% nitric acid Multi-element (including Rh, In, Re, Lu, Li) internal standard solution.

2.4. Quantitative analysis of samples
Edit the full quantitative analysis method, including selecting the elements to be measured, the number of repeated measurements, and the integration time of each element signal, the reporting method, the measurement method, and the calibration curve table. After the instrument is stabilized, the internal standard tube is placed in the internal standard solution prepared by the nitric acid solution, and the prepared chromium standard use solution series is respectively determined, and the standard series curve is obtained, the sample is measured, and the data is processed.

3. Analysis and discussion

3.1. Linear range

The measured signal intensity is plotted on the ordinate and the concentration is plotted on the abscissa. A standard curve is drawn for the metal element concentration standard solution, and the correlation coefficient is as follows.

Table 1. Metal element standard curve and correlation coefficient

Element	Standard curve concentration point (μg/L)	Calibration curve equation	Correlation coefficient	method Claim
Co	0, 0.2, 1, 5, 10, 20, 50, 100, 200, 500	$y=0.0106*x+5.8081*10^{(-5)}$	1.0000	≥0.999
V	0, 0.2, 1, 5, 10, 20, 50, 100, 200, 500	$y=0.0039*x$	0.9999	
Sb	0, 0.2, 1, 5, 10, 20, 50, 100, 200, 500	$y=0.0032*x+3.9759*10^{(-5)}$	0.9999	
Mn	0, 0.2, 1, 5, 10, 20, 50, 100, 200, 500	$y=0.0020*x+9.9804*10^{(-4)}$	0.9999	
Mo	0, 0.2, 1, 5, 10, 20, 50, 100, 200, 500	$y=0.0036*x+1.9517*10^{(-5)}$	0.9999	
Tl	0, 0.2, 1, 5, 10, 20, 50, 100, 200, 500	$y=0.0270*x+3.9247*10^{(-4)}$	0.9999	

Linearity: A standard curve was prepared by ICP-MS method for the determination of Co, V, Sb, Mn, Mo and Tl in soils waste. The correlation coefficients were 1.0000, 0.9999, 0.9999, 0.9999, 0.9999, and 0.9999, respectively. The correlation coefficients all meet the requirements of the standard HJ 766-2015 correlation coefficient greater than 0.999.

3.2. Determination of method detection limit and determination lower limit

According to 《Technical Guidelines for the Standardization and Revision of Environmental Monitoring and Analysis Methods》 (HJ 168-2010), the detection limit test is performed with all the steps of the sample analysis, and the n (n≥7) blank test is repeated, and the standard deviation of 7 parallel determinations is calculated, and the detection limit of the method is calculated according to the formula 1.

$$MDL=t_{(n-1,0.99)}\times S \quad \text{(Formula 1)}$$

Formula: MDL - method detection limit. n- number of parallel measurements of the sample .

t - degree of freedom is n-1, confidence distribution is 99% of the t distribution (one side).

S - Standard deviation of n parallel determinations. Among them, when the degree of freedom is 6, the value of t with a confidence of 99% is 3.143.

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Table 2. Method detection limit and lower limit test data table   unit: mg/kg

Element	The measurement results							$\bar{x}$	S	t	MDL	The limit of quantitation	standard MDL
	1	2	3	4	5	6	7						
Co	0.003	0.002	0.003	0.002	0.002	0.002	0.002	0.002	0.001		0.1	0.4	1.1
V	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.005		0.1	0.4	0.6
Sb	0.02	0.03	0.03	0.03	0.02	0.02	0.03	0.03	0.002	3.143	0.1	0.4	1.6
Mn	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.009		0.1	0.4	1.8
Mo	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.011		0.1	0.4	0.8
Tl	0.06	0.04	0.04	0.04	0.03	0.03	0.02	0.04	0.013		0.1	0.4	0.6

Annotate: $\bar{x}$: average value; S:standard deviation.

Detection limit: The detection limits of Co, V, Sb, Mn, Mo and Tl in soil and sediment by ICP-MS method were 0.1mg/kg, 0.1mg/kg, 0.1mg/kg, 0.1mg/kg, 0.1mg/kg and 0.1 mg/kg, respectively. The detection limit meets the requirements for Co, V, Sb, Mn, Mo and Tl in the standard HJ 766-2015.

3.3. Method precision

The laboratory analyzed and determined the same type of soil and sediment samples of the same type, and measured according to all the steps of sample analysis. Each sample was measured in parallel six times. The data summary table is shown in Table 3 the data can be found in the attached original record sheet. Calculate the average value, standard deviation, relative standard deviation and other parameters of different samples.

Table 3. Precision test data   unit: mg/kg

element	content	The measurement results						$\bar{x}$	s	RSD (%)	Standard RSD (%)
		1	2	3	4	5	6				
Co	1	8.5	8.4	8.5	8.6	8.6	8.7	8.6	0.2	1.2	6.3
	2	9.5	9.6	9.5	9.3	9.6	9.6	9.5	0.2	1.5	
	3	8.7	8.7	8.5	9.3	9.1	8.5	8.8	0.4	3.7	
V	1	58.1	57.4	59.7	58.9	58.3	59.3	58.6	0.9	1.5	6.2
	2	62.0	61.7	62.1	60.3	61.7	62.8	61.8	0.9	1.4	
	3	51.6	49.9	47.5	50.7	50.6	51.0	50.2	1.5	2.9	
Sb	1	1.0	1.1	1.1	1.0	1.0	1.1	1.1	0.1	3.7	41
	2	1.1	1.0	1.0	1.0	1.1	1.1	1.0	0.1	3.7	
	3	0.9	0.9	1.0	1.0	1.1	0.9	1.0	0.1	6.6	
Mn	1	449	438	446	446	439	442	443	4.6	0.9	2.2
	2	464	459	461	450	461	466	460	5.5	4.0	
	3	447	446	440	453	448	438	445	5.5	2.0	
Mo	1	0.6	0.6	0.6	0.7	0.7	0.7	0.7	0.1	0.3	25
	2	0.7	0.7	0.6	0.6	0.7	0.7	0.7	0.1	0.3	
	3	0.6	0.5	0.5	0.5	0.5	0.5	0.5	0.1	0.3	
Tl	1	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.1	5.5	31
	2	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.1	2.7	
	3	0.3	0.3	0.2	0.3	0.3	0.3	0.3	0.1	7.1	

Precision: The soil waste determined by ICP-MS. The actual samples of the three levels were determined by ICP-MS. The relative standard deviations of Co, V, Sb, Mn, Mo and Tl were 1.2%~3.7%, 1.4%~2.9%, 3.7%~6.6%, 1.1%~1.3%, 6.1%~7.6% and 2.7%~7.1%, respectively. Precision meets the standard HJ 766-2015 requirements for the detection of Co, V, Sb, Mn, Mo and Tl.

3.4. Method accuracy

The laboratory uses the certified reference material samples for analysis and determination to determine the accuracy detection. The two standard levels of certified soil samples GSS-25 and GSS-12 are analyzed and determined according to the whole steps of sample analysis. For the measurement, each sample was measured in parallel six times, and the data summary table is shown in the table. Calculate the average value, standard deviation, relative error and other parameters of different samples of certified reference materials.

Table 4. Test data of certified reference materials

| element | content | The measurement results | | | | | | $\bar{x}$ | μ^a | RE_i (%) |
		1	2	3	4	5	6			
Co	1	12.3	12.2	12.1	12.3	12.1	12.4	12.2	12.0±5	1.7
	2	12.8	12.6	12.6	12.8	12.6	12.8	12.7	12.6±0.3	0.8
V	1	79.3	78.9	77.4	78.5	77.9	80.4	78.7	77.0±4	2.3
	2	85.9	84.4	85.3	87.0	84.9	87.3	85.8	86.0±4	0.3
Sb	1	1.1	1.1	1.0	1.1	1.0	1.1	1.1	1.05±0.07	4.7
	2	1.1	1.1	1.1	1.2	1.2	1.2	1.1	1.13±0.05	2.7
Mn	1	764	757	759	733	787	776	762	774±19	1.6
	2	624	638	628	643	639	629	634	632±21	0.3
Mo	1	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.72±0.07	2.8
	2	1.0	1.0	1.0	0.9	0.9	1.0	1.0	0.96±0.06	0
Tl	1	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.392±0.007	0.6
	2	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.39±0.02	0

Annotate: $\bar{x}$: average value; *S*:standard deviation; RE_i: Relative error; μ^a: Certified standard substance content range

Accuracy: The soil waste were determined by ICP-MS method. The samples with two standard levels were tested. The Co, V, Sb, Mn, Mo and Tl were all within the uncertainty range of the standard materials. Degree meets the standard HJ 766-2015 requires accurate detection of metal Co, V, Sb, Mn, Mo and Tl.

4. Conclusion

The correlation curves of standard curves for soil waste Co, V, Sb, Mn, Mo and Tl were determined by ICP-MS method to be 1.0000 ,0.9999, 0.9999, 0.9999, 0.9999, and 0.9999, respectively. The detection limits were 0.1 mg/kg, 0.1mg/kg, 0.1mg/kg, 0.1mg/kg, 0.1mg/kg, and 0.1mg/kg, respectively. The relative standard deviations of precision are: 1.2%~3.7%, 1.4%~2.9%, 3.7%~6.6%, 1.1%~1.3%, 6.1%~7.6% and 2.7%~7.1%. The accuracy of the standard substance measured values are within the uncertainty range. The laboratory has verified the method of determining heavy metals in soil by ICP-MS. The linear relationship, detection limit, precision and accuracy are in line with the standard HJ766-2015 requirements.

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