



ORIGINAL ARTICLE

Determination of heavy metals in soil by inductively coupled plasma mass spectrometry (ICP-MS) with internal standard method

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Abstract: Soil, the carrier of agricultural production and important part of the ecological environment, is heavily contaminated with hazardous heavy metals. Therefore, it is obliged to research analytical techniques that could efficiently determine the total content of heavy metals in soil. The determination of heavy metals in soil was disturbed by matrix elements or spectral interferences. In this study, this problem was solved by internal standard method. GBW07402, GBW07448, GBW07423, GBW07428, GBW074079 soil samples were chosen to be the Certified Reference Materials, soils were prepared by microwave digestion with mixed acid following analyzed for determination of the content (Cr, Cu, Pb, Ba, Ni, Mn) by Inductively coupled plasma mass spectrometry in 50 µg/L internal standard concentration, the method was validated by comparing with certified values, method contrast (standard addition method versus internal standard method scan the same prepared solution) and recovery check. The results of internal standard method are in excellent agreement with the indicative values and the data obtained from standard addition method, respectively. Recoveries were adequate being in the acceptable range of 90-99% and RSD of <6.7% for all the elements at three levels of 5, 20 and 50 mg/kg with quantified by standard addition method and internal standard method. Finally, the graphs of quality control (n=100) were obtained to guide internal quality control in laboratory.

Key words: Soil; Heavy metal; inductively coupled plasma mass spectrometry; internal standard method

Introduction

With the rapid development of the global economy, the heavy metal pollution in soil is becoming a crucial environmental problem. Industrial, traffic and municipal wastes were the primary source of heavy metal for soil¹⁻³. These heavy metals were accumulated in waters and plant tissues, which will migrate into the food chain finally. Studies have shown that heavy metals pose a hazardous risk to the health of humans when in excess.

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amount⁴⁻¹⁰. Therefore, the emphasis has been given by many researchers to explore various techniques for analysis of heavy metals.

Up to present, different Analytical techniques for estimation of heavy metals in soil including atomic spectroscopy analysis and chemical method of analysis have been widely researched. chemical method of analysis ,based on the substance chemical reaction and and characterized of high accuracy, applied to to the samples which relative content more than 1%. For the trace component ,the analytical techniques has great advantage ,such as Inductively Coupled Plasma Optical Emission

Spectroscopy (ICP-OES), Inductively Coupled Atomic emission Spectroscopy (ICP-AES), Inductively Coupled Mass Spectroscopy (ICP-MS), Atomic fluorescence spectrometry (AFS), Absorption Spectrometry (AAS)¹¹⁻¹⁵. All of the quantification techniques were have proved to be efficient with good detection limits .Despite the inductively coupled plasma mass spectrometry has been successfully applied to complicated matrices soil sample .The accuracy of the analysis results were inevitable disturbed by the spectral interference and non-spectral interference. Internal standardization as a correction for matrix effects and multiplicative effects in general is becoming the first choice in ICP-MS. Several workers has proved that internal standard undergo an equal relative matrix-induced signal intensity shift and achieve accuracy of the results¹⁶⁻¹⁷.

This paper concentrate on developing a internal standard method for detecting the total amount of Mn、 Cr、 Pb、 Cu、 Ni、 Ba in soil simultaneously by the means of ICP-MS . The method was validated according to the Certified Reference Materials、 different method (internal standard method and standard addition method) and the percentage of recovery at three different spike levels.

1. Materials and methods

1.1 Reagents and materials

Standard stock solutions of Ni, Mn, Cr, Cu, Pb, Ge, In, Rh, Bi at the 1000ug/mL concentration were obtained from Guo biao (Beijing) Testing & Certification Co, Ltd. (GBTC , China). The commercially available nitric acid 、 hydrochloric acid 、 hydrofluoric acid and hydrogen peroxide were purchased from Baker-Instra analyzed(USA). Ultrapure water was prepared by a Milli-Q system from Millipore(USA). The Performance Solutions Kit were from Perkin Elmer (USA).

Mixed working solution (containing Ni, Mn, Cr, Cu, Pb , Ba) and internal standard solution (including Ge, In, Rh, Bi) in 2% nitric acid aqueous solution were prepared. Calibration standards were prepared by diluting mixed standard solution to reach the quantitative concentrations ,which added internal standard solution to the concentration level of 50 ug/L.

2.2 Samples

Five candidate reference soil samples were acquired from Geophysiochemistry Prospecting Institute of Academy of Geological Science of China which containing GBW07402 (chestnut soil), GBW074079(laterite soil), GBW07423(lake sediment), GBW07428(basin soil), GBW07448(brown desert soil). Soil samples were collected from the main representative soil zones and different geological backgrounds or mineralized areas in China. The certified values for every heavy metal in each soil were analyzed and the expire time is 2020.

2.3 Sample preparation

Approximately 0.2g Soil samples (or spiked soil) were weighed into a PTFE beaker. 6 ml of nitric acid , 2 ml of hydrochloric acid and 2 ml of hydrofluoric in a combination have been used for the simultaneous extraction of a large

number of metals in soils. The solution was digested by the Microwave digestion instrument (CEM, MARS 6, USA) in the following procedure: heated to 120°C in 8 minutes and holding 3 min ; raising the temperature to 150°C maintaining 5min ; increase the temperature to 190 °C keeping 35 min . After cooling ,2 ml of H₂O₂ was added to the digested mixture then taken to heating block in 140°C until the residue solution left about 1 mL. Finally, the solution was transported into 50 mL volumetric flasks, brought to volume with water and mixed fully . The determination of metals was performed by ICP-MS with internal standard method and standard addition method.

2.4 Instrumentation

The Inductively coupled plasma mass spectrometric (Perkin Elmer ,NexION 300,American) was carried out to analyzed the contents of target elements in the standard mode. Operating conditions (parameters) are summarized in Table 1.

Table 1 ICP-MS operating conditions and acquisition parameters

operating conditions							
Nubulizer Gas Flow		0.88ml/min					
Auxiliary Gas Flow		1.20ml/min					
Plasma Gas Flow		18.00					
Deflector Voltage		-11.00v					
ICP RF Power		1250w					
Analyzer Vacuum		5.0×10 ⁻⁷					
acquisition parameters							
		Pb,Bi ^a	Cu,Ge ^a	Cr,Ge ^a	Mn,Ge ^a	Ba,In ^a	Ni,Ge ^a
Measured m/z		206,208	63,65	53	55	137,138	60
Calibration	range	5-50	5-50	20-200	100-1000	5-500	10-100
		/ug/L					
Intenal	std	50	50	50	50	50	50
concentration							

^a used as an internal standard element

2.5. Measurement procedures

For the measurements of the elements , the digested solution were diluted to 1/10 with 2% nitric acid aqueous. Internal standard method :The sample were analyzed after adding 50ug/L mixed internal standard . Standard addition method: adding a serials of standard solution(the final solution is equal to the internal standard method calibration range for each element) into the same sample ,then scan the standard solution .Draw standard curve which not pass zero point, from the calibration equation we can calculate the each heavy metal level¹⁸⁻¹⁹. Sample and blank were analyzed in triplicate.

3.Results and Discussion

3.1 Evaluation of the method by Certified value and standard addition method

To verify the efficiency of the method ,five quality control soil samples were digested and quantified by internal standard method and standard addition method. The results were tabulated in the table 2.

Table 2 Results for the total content analysis of 5 candidates reference materials compared to certified concentrations

Element	Sample	The level of heavy metal (mg/kg)		
		Ist value	Ast value	certified value
¹³⁷ Ba	GBW07402	924±37	932±24	930±50

	GBW07407	178±9	175±6	180±27
	GBW07423	514±19	518±13	520±43
	GBW07428	603±9	611±7	608±13
	GBW07448	33.2±6.8	32.7±5.3	34±14
¹³⁸ Ba	GBW07402	928±31	932±24	930±50
	GBW07407	179±14	175±6	180±27
	GBW07423	531±26	518±13	520±43
	GBW07428	607±8	611±7	608±13
	GBW07448	33.2±4.9	32.7±5.3	34±14
⁵³ Cr	GBW07402	44.6±3.2	45.8±2.7	47±4
	GBW07407	403±14	409±8	410±23
	GBW07423	72.8±4.3	74.2±2.9	75±5
	GBW07428	68.5±2.6	69.0±1.8	70±3
	GBW07448	47.1±1.6	49.3±1.3	49±2
⁶³ Cu	GBW07402	15.6±0.68	16.2±0.57	16.3±0.9
	GBW07407	93.9±4.5	95.9±3.1	97±6
	GBW07423	23.7±1.1	24.7±1.6	25±3
	GBW07428	26.4±0.67	26.5±0.9	27.4±1.1
	GBW07448	16.2±0.29	16.0±0.48	16.0±0.5
⁶⁵ Cu	GBW07402	16.0±0.78	16.2±0.57	16.3±0.9
	GBW07407	94.7±4.2	95.9±3.1	97±6
	GBW07423	24.0±2.1	24.7±1.6	25±3
	GBW07428	28.3±0.89	26.5±0.9	27.4±1.1
	GBW07448	15.7±0.31	16.0±0.48	16.0±0.5
²⁰⁶ Pb	GBW07402	18.9±2.4	21.4±2.7	20±3
	GBW07407	14.5±1.9	13.8±1.5	14±3
	GBW07423	24.0±1.6	23.8±2.0	25±3
	GBW07428	30.5±0.56	31.0±0.90	31±1
	GBW07448	18.0±0.78	19.1±0.51	18.7±0.9
²⁰⁸ Pb	GBW07402	20.7±1.9	21.4±2.7	20±3
	GBW07407	15.0±1.4	13.8±1.5	14±3
	GBW07423	24.7±2.0	23.8±2.0	25±3
	GBW07428	30.4±0.68	31.0±0.90	31±1
	GBW07448	18.2±0.57	19.1±0.51	18.7±0.9
⁵⁵ Mn	GBW07402	500±13	507±10	510±16
	GBW07407	1729±90	1745±76	1780±113
	GBW07423	514±12	517±16	520±24
	GBW07428	679±14	690±12	688±15
	GBW07448	520±7	510±9	518±13
⁶⁰ Ni	GBW07402	19.0±0.79	18.9±1.1	19.4±1.3
	GBW07407	271±9	269±8	276±15

GBW07423	31.2±2.1	32.1±1.4	33±3
GBW07428	32.4±0.90	31.7±1.6	33±2
GBW07448	19.7±0.68	20.4±0.49	21±1

Asd stand for the date of standard addition method

Isd stand for the date of internal standard method

Certified value are taken from refs²⁰

Uncertainties are expressed as standard deviation(n=6)

As can be seen, determinations were carried out using the isotopes of ¹³⁷Ba, ¹³⁸Ba, ⁶³Cu, ⁶⁵Cu, ⁵³Cr, ²⁰⁶Pb, ²⁰⁸Pb, ⁵⁵Mn, ⁶⁰Ni and the square of correlation coefficient R² was more than >0.9995. The internal standard method results are in the range of the certified values and excellent agreement with the standard addition method date.

3.1 Recovery Checks

To determine the accuracy of the methods used in the determination of the metals in the soil extracts, known-amounts of the elements studied were added to the soil. Recovery test was done at fortification levels of 5, 20, and 50 mg/kg with three replicates. The Mean recovery rate and RSD were listed in the table 3.

Table 3 Mean recovery (%) and RSD (%) of the selected elements in soil at different fortification levels (n=3)

Element	Sample	Fortification					
		5mg/kg		20mg/kg		50mg/kg	
		Asd Mean(%)	Isd Mean(%)	Asd Mean(%)	Isd Mean(%)	Asd Mean(%)	Isd Mean(%)
¹³⁷ Ba	GBW07402	91(3.7)	92(4.2)	97(1.0)	96(0.9)	94(1.0)	95(1.3)
	GBW07407	94(2.5)	97(1.5)	103(5)	91(2.1)	99(2.4)	99(2.7)
	GBW07423	90(1.0)	90(3.0)	97(4.6)	92(5.7)	98(3.1)	97(1.5)
	GBW07428	96(4.3)	99(5.5)	91(2.7)	93(1.5)	99(2.6)	98(2.4)
	GBW07448	95(2.8)	98(0.9)	94(5.4)	99(3.2)	93(0.9)	94(3.8)
¹³⁸ Ba	GBW07402	97(1.9)	99(1.2)	92(6.7)	98(1.7)	97(1.1)	91(2.6)
	GBW07407	93(1.4)	94(1.8)	98(1.7)	99(4.2)	95(1.4)	97(1.1)
	GBW07423	97(2.6)	96(3.6)	96(4.3)	98(4.8)	90(1.9)	94(1.9)
	GBW07428	99(1.5)	95(1.4)	97(1.2)	98(3.4)	99(2.7)	92(3.7)
	GBW07448	94(0.6)	96(1.8)	96(3.5)	91(4.1)	91(1.5)	95(1.5)
⁵³ Cr	GBW07402	98(4.8)	98(2.6)	97(2.3)	94(0.9)	98(3.8)	93(1.7)
	GBW07407	92(2.7)	97(1.7)	90(1.1)	94(2.6)	94(1.1)	92(3.6)
	GBW07423	97(5.8)	98(2.4)	92(2.4)	94(3.8)	95(2.4)	94(2.4)
	GBW07428	93(4.2)	98(1.3)	96(4.6)	93(1.1)	98(1.3)	96(0.9)
	GBW07448	97(3.1)	99(3.2)	93(1.3)	97(2.2)	91(2.8)	91(3.0)
⁶³ Cu	GBW07402	96(1.6)	97(3.6)	99(3.2)	98(1.0)	98(3.6)	92(1.7)
	GBW07407	90(5.3)	98(1.7)	91(4.6)	96(0.9)	94(1.9)	96(2.8)
	GBW07423	94(1.5)	95(1.1)	91(0.9)	96(1.7)	97(1.4)	99(1.3)
	GBW07428	93(3.6)	96(3.5)	97(1.7)	98(4.4)	94(3.6)	92(1.7)
	GBW07448	93(4.2)	97(1.2)	95(2.4)	95(1.5)	97(2.7)	94(2.4)
⁶⁵ Cu	GBW07402	96(5.3)	95(0.8)	90(4.2)	96(3.8)	98(1.9)	94(3.1)

²⁰⁶ Pb	GBW07407	90(3.3)	98(1.2)	97(1.3)	98(4.1)	96(4.4)	93(3.6)
	GBW07423	92(1.2)	99(3.6)	97(2.7)	95(2.7)	93(1.0)	97(1.7)
	GBW07428	99(1.7)	96(1.9)	93(3.5)	97(0.9)	91(2.3)	97(2.9)
	GBW07448	90(2.5)	94(2.5)	97(1.6)	98(1.3)	96(1.6)	96(1.5)
	GBW07402	99(3.2)	96(0.9)	97(2.7)	94(4.0)	99(0.8)	96(3.6)
²⁰⁸ Pb	GBW07407	99(1.9)	99(5.3)	94(4.9)	97(2.5)	99(3.5)	96(2.4)
	GBW07423	93(4.7)	97(3.4)	98(5.6)	92(3.8)	90(2.9)	99(1.0)
	GBW07428	93(1.1)	91(2.6)	97(3.8)	97(1.3)	91(1.6)	96(1.3)
	GBW07448	95(3.5)	92(2.6)	92(4.5)	96(5.3)	95(3.4)	95(0.9)
	GBW07402	99(1.8)	91(3.7)	97(1.0)	97(0.9)	95(3.1)	90(2.6)
⁵⁵ Mn	GBW07407	94(2.6)	92(4.2)	90(2.7)	92(0.7)	98(1.2)	97(1.3)
	GBW07423	94(1.9)	91(2.7)	91(3.0)	99(4.5)	93(3.4)	93(2.7)
	GBW07428	96(0.9)	96(1.6)	98(1.7)	91(1.4)	99(1.1)	90(1.2)
	GBW07448	95(5.3)	95(1.0)	90(3.9)	99(1.1)	99(2.5)	98(2.6)
	GBW07402	90(1.2)	92(2.3)	96(2.7)	94(1.9)	91(2.3)	95(1.3)
⁶⁰ Ni	GBW07407	93(1.5)	95(2.7)	95(5.4)	95(4.6)	91(1.5)	96(3.5)
	GBW07423	91(4.3)	95(3.2)	97(1.3)	95(4.8)	93(3.7)	93(2.9)
	GBW07428	99(2.9)	99(1.9)	91(2.9)	98(4.7)	90(1.2)	97(1.0)
	GBW07448	95(3.6)	96(3.4)	99(1.2)	97(2.4)	91(2.5)	93(3.3)
	GBW07402	91(4.7)	99(3.2)	97(4.4)	92(3.8)	99(0.9)	94(2.8)
	GBW07407	95(1.6)	96(1.9)	98(5.8)	95(1.0)	97(2.6)	95(1.2)
	GBW07423	92(2.8)	98(2.5)	95(1.4)	97(1.9)	98(1.9)	92(2.7)
	GBW07428	90(1.3)	93(4.7)	97(1.6)	99(2.1)	93(3.4)	92(1.5)
	GBW07448	91(2.1)	91(0.8)	93(2.7)	96(5.3)	97(1.3)	98(2.4)

Asd stand for the recovery date of standard addition method

Isd stand for the recovery date of internal standard method

Relative Standard deviation (RSD) were tabulated in the brackets

A satisfied results were found for all the elements .The recovery percentage were more than 90% for each elements in fortification levels of 5, 20 and 50 mg/kg. The date of RSD $\leq 6.7\%$ for all the chemicals.

3.3 The date of quality control graphy

Graphy of quality control based on the fact that the experimental data distribution is close to Gaussian distribution is one of effective measures to guarantee the analytical quality²¹⁻²².The chart is completed by horizontal lines derived from the normal distribution $N(\mu, \sigma^2)$ that is taken to describe the random variations in the plotted values. $\mu, \mu\pm\sigma, \mu\pm2\sigma, \mu\pm3\sigma$ were selected to construct the chart, which were called centre line(CL)、asistant line(AL) ,warning limit (WL)and control limit(CL). The chart is obtained values of concentration measured are plotted on a vertical axis

against the run number on the horizontal axis. The results in the range of $\mu\pm2\sigma$ is satisfied; Attention should be paid if the measure values were located in the region from $\mu\pm2\sigma$ to $\mu\pm3\sigma$, however the values are acceptable; the experimental date were unbelievable if the date exceed the section of $\mu\pm3\sigma$,it regard as “out of control”. To Certified Reference soil from a system in statistical control over 100 runs for internal quality control in lab is shown in table 4.

Table 4 The date of quality control(n=100)

Element	Sample	The date of quality control(mg/kg)
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		$\mu \pm \sigma$	$\mu \pm 2\sigma$	$\mu \pm 3\sigma$
¹³⁷ Ba	GBW07402	926±34	926±64	926±102
	GBW07407	175±6	175±12	175±18
	GBW07423	513±20	513±40	513±60
	GBW07428	599±10	599±20	599±30
	GBW07448	32.8±5.9	32.8±11.8	32.8±17.7
¹³⁸ Ba	GBW07402	925±39	925±78	925±117
	GBW07407	175±17	175±34	175±51
	GBW07423	528±29	528±58	528±87
	GBW07428	598±11	598±22	598±33
	GBW07448	33.6±5.1	33.6±10.2	33.6±15.3
⁵³ Cr	GBW07402	444±3.7	444±7.4	444±11.1
	GBW07407	400±15	400±30	400±45
	GBW07423	71.8±4.9	71.8±9.8	71.8±14.7
	GBW07428	67.7±3.1	67.7±6.2	67.7±9.3
	GBW07448	46.8±2.0	46.8±4.0	46.8±6.0
⁶³ Cu	GBW07402	15.1±0.81	15.1±1.62	15.1±2.43
	GBW07407	92.9±4.5	92.9±9	92.9±13.5
	GBW07423	22.6±1.6	22.6±3.2	22.6±4.8
	GBW07428	26.0±0.78	26.0±1.56	26.0±2.34
	GBW07448	15.9±0.32	15.9±0.64	15.9±0.96
⁶⁵ Cu	GBW07402	16.2±0.87	16.2±1.74	16.2±2.61
	GBW07407	94.1±4.7	94.1±9.4	94.1±14.1
	GBW07423	23.9±2.7	23.9±5.4	23.9±8.1
	GBW07428	27.8±0.90	27.8±1.8	27.8±2.7
	GBW07448	15.9±0.53	15.9±1.06	15.9±1.59
²⁰⁶ Pb	GBW07402	18.5±2.3	18.5±4.6	18.5±6.9
	GBW07407	14.7±2.0	14.7±4.0	14.7±6.0
	GBW07423	23.7±1.4	23.7±2.8	23.7±4.2
	GBW07428	31±0.76	31±1.52	31±2.28
	GBW07448	17.9±0.86	17.9±1.72	17.9±2.58
²⁰⁸ Pb	GBW07402	20.9±2.2	20.9±4.4	20.9±6.6
	GBW07407	15.4±1.7	15.4±3.4	15.4±5.1
	GBW07423	24.5±1.6	24.5±3.2	24.5±4.8
	GBW07428	30.5±0.74	30.5±1.48	30.5±2.22
	GBW07448	17.9±0.64	17.9±1.28	17.9±1.93
⁵⁵ Mn	GBW07402	503±15	503±30	503±45
	GBW07407	1768±87	1768±174	1768±261
	GBW07423	517±14	517±28	517±42
	GBW07428	684±12	684±24	684±36
	GBW07448	513±9	513±18	513±27

⁶⁰ Ni	GBW07402	18.7±0.56	18.7±1.12	18.7±1.68
	GBW07407	267±11	267±22	267±33
	GBW07423	30.2±2.5	30.2±5	30.2±7.5
	GBW07428	31.9±0.86	31.9±1.72	31.9±2.58
	GBW07448	18.7±0.98	18.7±1.96	18.7±2.94

μ is population mean

σ is population standard deviation

n is run number

Conclusion

The work verify an efficient ICP-MS-based internal standard method to quantify the presence of Cr,Cu, Pb,Ba,Ni,Mn in soils . In this study , Certified Reference analysis、 different method contrast and recovery experiment has been carried out .Overall results indicate that the presented method has satisfactory reproducibility, recovery, and accuracy for Cr,Cu, Pb,Ba,Ni,Mn analysis in five categories soils.Thus, the proposed method can be used successfully to monitor above six heavy metal in soil.

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