

A Simple Method for the Simultaneous Determination of Trace Cadmium and Silver in Soil Samples by Dynamic Reaction Cell Inductively Coupled Plasma Mass Spectrometry

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INTRODUCTION

Soils are important indicators of environmental changes. Cadmium (Cd) and silver (Ag) are well-known pollutants that are introduced into the environment through both geochemical and anthropogenic activities (1-2), can have toxic effects and affect human life (3-4). Therefore, the accurate monitoring of trace Cd and Ag in soils is essential.

Several detection techniques including inductively coupled plasma mass spectrometry (ICP-MS) (5-6), inductively coupled plasma optical emission spectrometry (ICP-OES) (7-8), and atomic absorption spectrometry (AAS) (9-10) have been introduced for the determination of Cd and Ag in environmental samples. Compared to AAS or ICP-OES, ICP-MS has excellent detection limits, multi-element capabilities, the ability to measure isotope ratios (11-12), and has emerged as a useful technique for trace Cd and Ag analysis of soils. Unfortunately, the concentrations of Zr, Mo, Nb, and Y are many orders of magnitude larger than the Cd and Ag in soils, they may form oxide and/or hydroxide ion interferences, such as $^{95}\text{Mo}^{16}\text{O}^+$, $^{94}\text{Mo}^{16}\text{OH}^+$, $^{94}\text{Zr}^{16}\text{OH}^+$ on $^{111}\text{Cd}^+$, $^{98}\text{Mo}^{16}\text{O}^+$, $^{97}\text{Mo}^{16}\text{OH}^+$ on $^{114}\text{Cd}^+$, $^{91}\text{Zr}^{16}\text{O}^+$, $^{90}\text{Zr}^{16}\text{OH}^+$, $^{89}\text{Y}^{18}\text{O}^+$ on $^{107}\text{Ag}^+$ and $^{93}\text{Nb}^{16}\text{O}^+$, $^{92}\text{Zr}^{16}\text{OH}^+$, $^{92}\text{Mo}^{16}\text{OH}^+$ on $^{109}\text{Ag}^+$. Even interference correction equations are unable to solve interference problems for Cd and Ag (13-14), which

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ABSTRACT

A simple method based on the dynamic reaction cell (DRC) technology to eliminate the spectral interference in the simultaneous determination of trace cadmium and silver in soil samples by ICP-MS was established. Under the optimized O_2 flow rate (2.7 mL min^{-1}) and the DRC rejection parameter RPq (0.8 for Ag, 0.7 for Cd), the interference caused by Zr, Nb, and Mo (such as $^{95}\text{Mo}^{16}\text{O}^+$, $^{94}\text{Mo}^{16}\text{OH}^+$, $^{94}\text{Zr}^{16}\text{OH}^+$ on $^{111}\text{Cd}^+$ and $^{93}\text{Nb}^{16}\text{O}^+$, $^{92}\text{Zr}^{16}\text{OH}^+$ on $^{109}\text{Ag}^+$) could be effectively eliminated, and the background signal was reduced up to 100-fold at m/z 109 and 111. The limit of quantitation (LOQ, 10σ) for $^{109}\text{Ag}^+$ and $^{111}\text{Cd}^+$ was 0.1 and 0.2 ng g^{-1} , respectively. The proposed method was applied to the direct determination of Ag and Cd in soil standard reference materials, and the results were in good agreement with the certified values.

could lead to significantly erroneous results.

To solve this problem, matrix separation procedures have been proposed. Duan et al. (15) established a new technology combining two separation methods to remove the spectral interferences and matrix effects in soil and geological samples. Liu et al. (16) established load diphenylthiourea foam-selective enrichment for the separation of Au and Ag from other interfering elements in geological samples. Christophe et al. (17) minimized matrix effects and spectral inter-

ferences using a sequential procedure in the determination of Cd. However, these methods are time-consuming, expensive, and/or require additional equipment.

An alternative method based on the dynamic reaction cellTM (DRCTM) techniques has proven to be effective for the alleviation of these metal oxides or hydroxide interferences (18-20). The aim of this work is to utilize O_2 as the reaction gas to eliminate the oxide and hydroxide interferences for the simultaneous and accurate determination of Cd and Ag in soils by DRC-ICP-MS. The optimization of this technique, the analytical performance, and its application to the simultaneous determination of Cd and Ag in standard reference materials are discussed.

EXPERIMENTAL

Instrumentation

A PerkinElmer® ELAN® DRC-e (Dynamic Reaction Cell) ICP-MS instrument was used (PerkinElmer Corporation, Shelton, CT, USA), equipped with a cyclonic spray chamber (PC3, Elemental Scientific, USA) sample introduction system, and using a 1.0-mm i.d. quartz injector. The operating parameters of the DRC-ICP-MS used for this work are summarized in Table I. The ICP-MS and DRC conditions were selected and the maximum ion signals of the elements studied while reducing the background to a minimum. A CEM MARS X-press (CEM, Matthews, NC, USA) microwave apparatus, equipped with Teflon® vessels, was used to digest the samples.

Reagents and Standard Solutions

High-purity water (18.2 M Ω ·cm⁻¹) was used throughout the work and obtained with a Millipore® Milli-Q® Direct 8 water purification system (Millipore Corporation, France). Nitric acid (HNO₃, 65–70%, w/w, 99.9999%) and hydrofluoric acid (HF, 40%, 99.99%) were purchased from the Beijing Chemical Reagent Research Institute. The single-element stock solutions (Ag, Cd, Zr, Nb, Mo, and Rh) were purchased from the National Center for Analysis and Testing of Steel Materials, P.R. China. The DRC O₂ gas was purchased from Praxair, Investment Co., Ltd., P.R.China (99.999% purity). The soil standard reference

materials (GBW07402, GBW07403, GBW07404, GBW07406, GBW07407, GBW07408) were obtained from the Institute of Geophysical and Geochemical Exploration, Langfang, P.R. China.

Microwave-assisted Digestion Samples

Approximately 50 mg of the accurately weighed sample powder was placed into the Teflon® vessel, then 3.0 mL HNO₃ and 1.0 mL HF were added, and the vessel was sealed. The digestion program given in Table II was used. After the vessel had cooled, it was opened and heated at 120 °C to dryness on a hot plate. Then 1.0 mL HNO₃ was added, evaporated to dryness to

help remove Si and HF. The final solution was made up to 50 mL by addition of 2% HNO₃ and 0.5 mL of 1 mg L⁻¹ Rh internal standard solution. A reagent blank solution was prepared in the same way.

RESULTS AND DISCUSSION

Spectral Interferences

It is well-known that high concentrations of Zr, Mo, and Nb could cause interference by formation of oxides or hydroxides, affecting accuracy in the determination of trace levels of Cd and Ag. The interferences include ⁹⁵Mo¹⁶O⁺, ⁹⁴Mo¹⁶OH⁺, ⁹⁴Zr¹⁶OH⁺ on ¹¹¹Cd⁺ and ⁹³Nb¹⁶O⁺, ⁹²Zr¹⁶OH⁺ on ¹⁰⁹Ag⁺. In this work, the interferences were checked under the standard ICP-MS mode, with the results shown in Table III. It can be seen that the signal intensity of m/z 109 and 111 was 4863 and 1379 cps for 1 ng mL⁻¹ Ag and Cd; however, 500 ng mL⁻¹ Nb and 2000 ng mL⁻¹ Zr was the equivalent of 9.43 and 0.42 ng mL⁻¹ Ag and the intensities were 45838 and 2034 at m/z 109, respectively. And 500 ng mL⁻¹ Mo and 2000 ng mL⁻¹ Zr was the equivalent of 1.03 and 1.48 ng mL⁻¹ Cd with intensities of 1419 and 2042 at m/z 111, respectively. Therefore, the presence of these elements results in significant positive bias for the simultaneous determination of Ag and Cd and the interferences should be removed.

Removal of Spectral Interferences by O₂ DRC

In this work, the DRC technology was used to eliminate oxide/hydroxide interference for Ag and Cd determination with O₂ as the reaction gas. The flow rates of the reaction gas and the DRC rejection parameter q (RPq) were two important parameters. The effect of these parameters on the signal of 1 ng mL⁻¹ Ag, Cd, and the matrix blank at m/z 109 and 111 are shown in Figure 1. In this figure, the back-

TABLE I Instrumental Operating Parameters

ICP-MS	PerkinElmer ELAN DRC-e
Sample introduction	PFA-400 Micro Flow nebulizer
Spray chamber	Cyclonic spray chamber (PC3Peltier Chiller), room temperature
Injector tube	1.0 mm i.d. quartz
RF power	1350 W
Plasma gas flow	16 L min ⁻¹
Auxiliary gas flow	1.0 L min ⁻¹
Nebulizer gas flow	0.81L min ⁻¹
O ₂ reaction gas flow	2.7mL.min ⁻¹
Rejection parameter, q	0.8 for ¹⁰⁹ Ag, 0.7 for ¹¹¹ Cd, 0.25 for ¹⁰³ Rh ⁺
Rejection parameter, a	0
Auto lens	On
Dwell time	50 ms
Sweeps	32
Readings	1
Replicate	3
Cones	Ni
Monitored ions	¹⁰⁹ Ag ⁺ , ¹¹¹ Cd ⁺ , and ¹⁰³ Rh ⁺

TABLE II Microwave Digestion Program for Soil Samples

Parameters	First Stage	Second Stage	Third Stage
Temperature (°C)	120	160	200
Power (W)	800	800	1600
Ramp (min)	10	10	10
Hold Time (min)	5	5	20

ground equivalent concentration (BEC) was used as the criterion for determining the optimum conditions while monitoring $^{109}\text{Ag}^+$ and $^{111}\text{Cd}^+$. The solution of 500 ng mL $^{-1}$

Nb, 500 ng mL $^{-1}$ Mo, and 2000 ng mL $^{-1}$ Zr was treated as matrix blank to simulate the interfering elements.

TABLE III
Interferences on m/z 109 and 111 With Different Elements (n=5)

	m/z 109		m/z 111	
	Signal Intensity (cps)	Equivalent (ng mL $^{-1}$)	Signal Intensity (cps)	Equivalent (ng mL $^{-1}$)
1% HNO $_3$	25±2	0.005	21±1	0.02
1 ng mL $^{-1}$ Ag	4863±42	1	—	—
1 ng mL $^{-1}$ Cd	—	—	1379±19	1
500 ng mL $^{-1}$ Nb	45,838±380	9.43	118±5	0.09
500 ng mL $^{-1}$ Mo	35±4	0.007	1419±31	1.03
2000 ng mL $^{-1}$ Zr	2034±25	0.42	2042±27	1.48

As shown in Figures 1a and 1c, with an increase in O $_2$ flow rate, the signal intensity of the Ag + matrix, Cd + matrix, and matrix blank significantly increased, and then decreased. The reason may be that the formation of more monoxides or hydroxides interferes with the determination at m/z 109 and 111 at the low O $_2$ flow rate. However, the interference was rapidly reduced due to the formation of more dioxide or trioxide at the high O $_2$ flow rate (1, 21-22). When the O $_2$ flow rate was greater than 2.6 mL min $^{-1}$, the signal intensity began to level off, and the value of BEC was at a minimum. Therefore, the

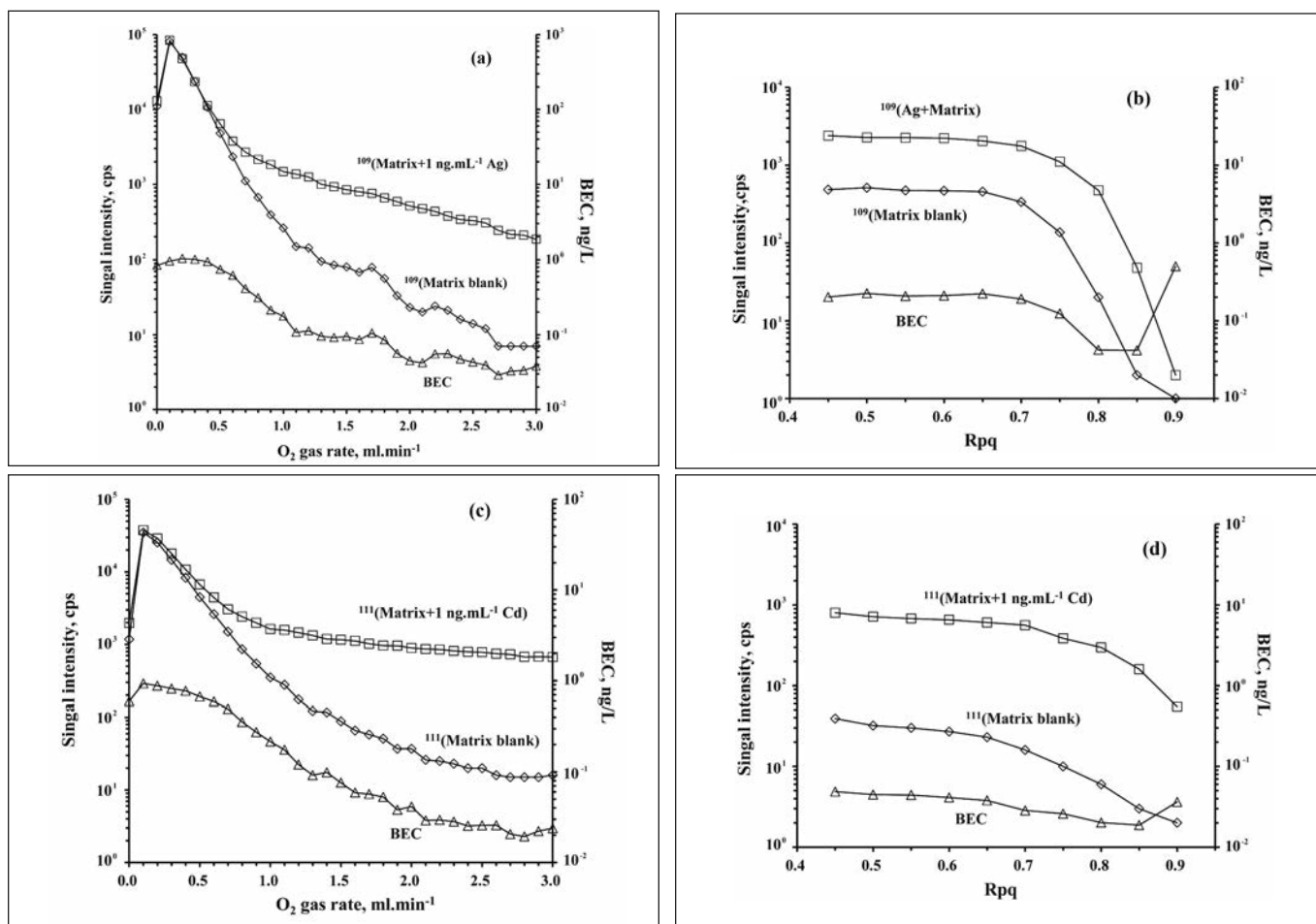


Fig. 1 (a, b, c, d). Effects of O $_2$ gas flow rate (a, c) and rejection parameter q (RPq) value (b, d) on signal intensity of ^{109}Ag +matrix, ^{111}Cd + matrix, matrix blank, and background equivalent concentration (BEC). The concentrations of Ag and Cd were 1 ng mL $^{-1}$. A solution of 500 ng mL $^{-1}$ Nb, 500 ng mL $^{-1}$ Mo and 2000 ng mL $^{-1}$ Zr was used as the matrix blank.

optimized O₂ flow rate of 2.7 mL min⁻¹ was selected. At this flow rate, the interference ions could be reduced up to 100-fold for ¹⁰⁹Ag and ¹¹¹Cd.

The RPq values are important to filter out unwanted precursors of the interfering species from the ion beam and eliminate interferences created in the cell by the reaction gas. With RPq <0.7 (Figure 1b) and <0.65 (Figure 1d), the signal intensity of Ag, Cd, and the matrix blank tended to be constant. However, with an RPq value >0.7 (Figure 1b) and >0.65 (Figure 1d), the signal intensity of Ag, Cd, and the matrix blank began to decrease. The optimized RPq value was 0.8 for ¹⁰⁹Ag and 0.7 for ¹¹¹Cd, where the best background equivalent concentrations (BEC) of ¹⁰⁹Ag and ¹¹¹Cd were 0.02 and 0.03 ng mL⁻¹, respectively.

Analytical Performance

Under the optimized experimental conditions, the limit of quantitation (LOQ and ten times the standard deviation of the produce blank) was 0.1 ng g⁻¹ for Ag and 0.2 ng g⁻¹ for Cd. The LOQ is expressed as the concentration in the samples, thereby taking into account the dilution factor (1000). This sensitivity is sufficient for the trace Ag and Cd determination in soils. The relative standard deviation (RSD) was calculated based on triplicate sam-

ple digestions and analyses, and was generally less than 5%.

Soil Samples Analysis

Table IV summarizes the results for six soil standard reference materials (GBW07402-04, GBW07406-08) which were processed by microwave-assisted acid digestion and followed by DRC-ICP-MS analysis. The obtained values were in good agreement with the certified values by the established method. However, the values using standard mode (i.e., no cell gas or RPq) were much greater than the certified values. This demonstrated that the polyatomic interference could be effectively eliminated by DRC-ICP-MS without the correction.

CONCLUSION

A simple method has been developed for the direct simultaneous determination of trace Ag and Cd in soil samples by DRC-ICP-MS after microwave-assisted acid digestion. The spectral interferences caused by Zr, Nb, and Mo were successfully eliminated by oxide reaction with O₂ in the DRC. This method could be used in environmental samples analysis.

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TABLE IV
Mean and Standard Deviation (n=3) for Ag and Cd in Soil SRMs (µg g⁻¹) by Standard Mode and DRC-ICP-MS

Reference Materials	Soil	Zr/Ag	Nb/Ag	Zr/Cd	Mo/Cd	Ag, g g ⁻¹ (Mean±SD)			Cd, g g ⁻¹ (Mean±SD)		
						This Work			This work		
						ICP-MS	DRC-ICP-MS	Certified Value	ICP-MS	DRC-ICP-MS	Certified Value
GBW07402	Chestnut soil	4056	500	3085	13.8	0.359±0.013	0.055±0.003	0.054±0.007	0.164±0.011	0.072±0.008	0.071±0.014
GBW07403	Yellow brown soil	2703	102	4100	5.2	0.185±0.008	0.093±0.004	0.091±0.007	0.186±0.009	0.063±0.005	0.060±0.009
GBW07404	Limestone soil	7143	543	1429	7.4	0.567±0.012	0.072±0.006	0.070±0.011	1.05±0.05	0.35±0.04	0.35±0.06
GBW07406	Red yellow soil	1100	135	1692	1.4	0.555±0.011	0.21±0.02	0.20±0.02	0.89±0.02	0.14±0.02	0.13±0.03
GBW07407	Latosol soil	5579	1123	3975	36.3	0.791±0.008	0.057±0.004	0.057±0.011	0.62±0.03	0.09±0.01	0.08±0.02
GBW07408	Loess soil	3817	250	1762	8.9	0.331±0.007	0.059±0.003	0.060±0.009	0.93±0.03	0.13±0.01	0.13±0.02

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