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Determination of cadmium in geological samples by aerosol dilution ICP-MS after inverse aqua regia extraction

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Abstract

The determination of cadmium (Cd) in geological samples by inductively coupled plasma mass spectrometry (ICP-MS) is suffered to significant Mo and/or Zr based oxide interference. We have developed a valid method for Cd determination using Ar aerosol dilution ICP-MS after extraction with inverse aqua regia. Over 90% of the Zr was removed in the extraction procedure, and the residual Zr-hydroxides and Mo-oxides or hydroxides were successfully eliminated by adding an amount of Ar to the sample aerosol prior to the plasma. Compared to the conventional mode without adding Ar, the amount of oxide and hydroxide ions formed in the plasma was reduced by up to 90%. The relative yields of the interfering oxides and hydroxides were as low as 0.005% (MoOH/Mo or MoO/Mo) and 0.007% (ZrOH/Zr). Under the optimized dilution gas flow rate (0.85 L min^{-1}) and carrier gas flow rate (0.24 L min^{-1}), the limit of detection (LOD,3σ) for ^{111}Cd was 1.6 ng g^{-1}. The proposed method was applied to the determination of Cd in 81 soil, sediment, and rock standard reference materials (SRMs). The results for 68 of these geological SRMs were in good agreement with the reference values. The Cd levels in 10 limestone SRMs (GSR-22, GSR-23, GSR-24, GSR-27, GSR-28, GUI-1, GUI-2, GUI-2, DIAN-1, DIAN-2, and DIAN-3) were reported for the first time, and reference Cd values for other 3 geological SRMs (GSD-7, GSD-19, and GSM-1) were updated by this method. The results showed that this method has great potential for Cd determination in geological samples.

Introduction

Cd is an important trace element in the study of environmental geochemistry, and is implicated in environmental quality and human health [1] as it is a highly toxic metal, even at very low concentrations [2, 3]. The abundance of cadmium is just 0.08 μg g^{-1} in the Earth's crust [4]. Therefore, the accurate determination of Cd in geological samples is often a challenge due to its low concentration and the presence of complex sample matrices [5].

Inductively coupled plasma mass spectrometry (ICP-MS) has been shown to be the most applicable technique for the determination trace elements in various geological samples, due to its high sensitivity, multi-element capability, and wide dynamic range.[6-17] However, the measurement of all isotopes of Cd is interfered by various isobaric ions and/or oxide or hydroxide ions of Pd, Sm, In, Zr, Mo, Ru, Nb, and Y. Specifically, the two common isotopes of ^{111}Cd and ^{114}Cd suffer interference from the polyatomic ions $^{95}Mo^{16}O^+$, $^{94}Mo^{16}OH^+$, $^{94}Zr^{16}OH^+$, $^{98}Mo^{16}O^+$, $^{96}Mo^{18}O^+$ and $^{97}Mo^{16}O^+$, and the isobaric ion $^{114}Sn^+$) (See ESI† Table S1).[18] In typical geological samples the contents of these interfering elements are hundreds to thousands of times higher than that of Cd, as the abundances of Zr and Mo are 132 and 0.8 μg g^{-1}, respectively, in the Earth's crust,[4] which causes erroneous results in Cd determination by ICP-MS method.[19] Several techniques can be used to minimize this interference, such as solvent or solid phase extractions,[20, 21] precipitation,[5] volatile species generation,[22] electrothermal volatilization (ETV),[23, 24] membrane desolvation,[25] addition of carbon-containing compounds to modify the argon plasma,[26] isotope dilution,[27, 28] and dynamic reaction cell techniques (DRC). [20, 29] Although these methods can remove the matrix elements and polyatomic ion interference, they are either time consuming or require special instrumental set-ups. Recently, an alternative method employing online dilution of the sample aerosol with Ar before it enters the plasma has been shown to reduce oxide formation without significantly compromising detection limits.[30] When a dilution gas was used, the aerosol entering the plasma contains much less water (and acid) than a conventionally diluted sample, resulting in much hotter plasma and as much as ten times lower oxide formation. [31] This technique was shown to alleviate interference from the oxides of lower atomic number lanthanoids on the detection of the heavy-lanthanoids in the analysis of airborne particulate matter, but only a limited level of interfering species (ca. 20-fold) was addressed in this study.[31]

In this work, a method for the direct determination of trace-level Cd in geological samples based on aerosol dilution ICP-MS (in combination with sample pre-treatment by boiling in inverse aqua regia extraction) was developed, aiming to eliminate the complicated polyatomic interference from Zr and Mo based oxides and hydroxides. The optimization of the technique and its application to the determination of trace Cd in a series of geological standard reference materials (SRMs) are discussed in detail.

Materials and methods

Instrumentation, regents and standards

An Agilent 7700x ICP-MS (Agilent Technologies, USA) with an aerosol dilution system (Fig. 1), a MicroMist nebulizer and a Peltier cooled (2 °C) quartz Scott-type double pass spray chamber was used for this work. The operating parameters for ICP-MS were optimized prior to the determinations with a tuning solution containing 1.0 ng mL^{-1} of Ce, Co, Li, Mg, Tl and Y, and the oxide production rate, calculated as the ratio of CeO^+/Ce^+ was reduced from 3.0% to less than 0.3%. The optimized instrument operating parameters are listed in Table 1. High purity water (18.2 MΩ cm^{-1}) used for the preparation of all blanks, standards and samples was obtained from a Millipore water purification system (Millipore, France). HNO_3 (99.999%), HCl (99.999%), and HF (99.999%) were purchased from Alfa Aesar Ltd. (Tianjin). Single element stock solutions (Cd, Mo, Zr, and Rh, *etc.*) were purchased from the National Center for Analysis and Testing of Steel Materials (NCATSM, China). The accuracy of the method was assessed by using two rock SRMs (andesite AGV-2 and basalt BCR-2) obtained from the United State Geological Survey (USGS, USA), two SRMs (metal-rich sediment SdAR-M2 and gabbro GSM-1) obtained from the International Association of Geoanalysts (IAG, UK), and 77 Chinese geological SRMs (details given in Table S2, see ESI†), from the Institute of Geophysical and Geochemical Exploration (IGGE, China).

Sample preparation by boiling inverse aqua regia extraction

0.2000 g of the homogenized sample powder (200 mesh) was weighed into a 10 mL polyethylene tube, to which 3.0 mL of a freshly prepared inverse aqua regia solution

(HNO_3:HCl=3:1) was added. The capped tube was then placed in a water bath at 95 °C for 2h. After cooling to room temperature, the solution was diluted to 10 mL with high purity water. The solution was centrifuged to remove the undissolved solid particles, and 1.0 mL of supernatant was transferred to a 10 mL polyethylene tube. Water (4.0 mL) was added, and the tube was shaken vigorously. For comparison, a conventional complete digestion method employing closed pressurized digestion with a mixture of HF + HNO_3 was also used (see ESI† Table S3).[32, 33]

Results and discussion

Optimization of aerosol dilution ICP-MS after inverse aqua regia extraction

^{111}Cd was selected as the isotope for ICP-MS analysis because it is the only isotope of Cd without isobaric interference. The major problem encountered in the determination of ^{111}Cd is interference from Zr and Mo polyatomic ions (i.e., $^{95}Mo^{16}O^+$, $^{94}Mo^{16}OH^+$, and $^{94}Zr^{16}OH^+$).[34] In this study, the elimination of the interference from Zr/Mo-oxides using aerosol dilution was investigated for the analysis of the geological samples. As shown in Fig. 2, there is a significant decrease in the ratios of oxide species ($^{95}Mo^{16}O^+/^{95}Mo^+$, $^{94}Mo^{16}OH^+/^{95}Mo^+$, and $^{94}Zr^{16}OH^+/^{94}Zr^+$) formed in the plasma with increasing gas dilution. At the optimized dilution gas rate (0.85 L min^{-1}), the ratios of ($MoOH^+ + MoO^+$)/Mo^+ and $ZrOH^+/Zr^+$ are 0.005% and 0.007%, respectively, which is 10 times smaller than that observed with the conventional standard mode (i.e., dilution gas = 0) (Fig. 2). The signal contribution to m/z 111 from different elements under the standard mode and the aerosol dilution mode was compared. As shown in Table 2, under standard mode, the signal intensities for m/z 111 are 12328 cps, 2987 cps, and 12080 cps for Cd (1 ng mL^{-1}), Mo (200 ng mL^{-1}) and Zr (1000 ng mL^{-1}), respectively. Conversely, under aerosol dilution mode, the signal intensities for m/z 111 are 1754 cps (Cd), 24.8 cps (Mo), and 91.5 cps (Zr). Compared to the conventional ICP-MS method (without aerosol dilution), the signal intensity of Cd dropped by 7 times, but the signal background ratio (SBR) increased from 0.82 to 15.1 by addition of the dilution gas (Table 2). Aerosol dilution ICP-MS was evaluated by the analysis of geological SRMs with high Zr and/or Mo contents (i.e. Zr content / Cd content >3000, and Mo content /Cd content >90). Table 3 lists the results obtained by aerosol dilution ICP-MS and standard mode ICP-MS following the conventional complete digestion procedure. The Cd values obtained by aerosol dilution ICP-MS are much closer to the certified values than those obtained by standard mode ICP-MS, due to the reduction of the Zr or Mo based oxide levels. When the proposed aerosol dilution ICP-MS technique coupled with the conventional complete digestion method is employed, unsatisfactory results are obtained for all selected SRMs with a Zr content /Cd content> 1500. However, the result was satisfactory for the stream sediment SRM (GSD-3a), which possesses a relatively low Zr content /Cd content ratio (566). Most geological samples have a high Zr content (Zr content /Cd content ratios > 1500) and a low Mo content (Mo content /Cd content ratios <100). Therefore, use of the aerosol dilution technique can effectively reduce the Mo based interferences, but it cannot completely eliminate Zr based interferences. Therefore, further study should be conducted to obtain more accurate results.

In our recent paper, a pre-treatment procedure based on extraction with boiling aqua regia was established to alleviate the interference from matrix Zr on As determination in DRC ICP-MS.[29] As was extracted almost completely (>98%) but the Zr recovery was <5%. This is because Zr is a lithophilic element which is strongly bound in silicate minerals and cannot be dissolved out by this procedure.[29] A similar result for Ag and Cd determination in environmental samples with low Zr content /Cd content ratios was reported by Li *et al.*[35] To evaluate the feasibility of this preparation method, three geological SRMs (soil GSS-4, stream sediment GSD-9, and rock GSR-2) were extracted with boiling aqua regia (HCl: HNO_3 = 3:1) or inverse aqua regia (HCl: HNO_3 = 1:3). Table 4 shows that the recoveries of Zr are less than 10% using both extraction methods. However, much larger amounts of Zr (>95%) are dissolved by the conventional complete digestion procedure, which results in the positively biased results for Cd determination in standard mode ICP-MS. As can be seen from Table 4, some little positive bias for Cd was observed using this extraction procedure, which originates from the residual or dissolved Zr (<10%) and Mo (>60%).

Residual Zr and Mo were completely eliminated using the proposed aerosol dilution technique. It can be seen in Table 5 that the values obtained for the geological SRMs containing high levels of matrix Zr and/or Mo using aerosol dilution ICP-MS after inverse aqua regia extraction, without any correction, are in good agreement with the certified values. Although the values of Zr content /Cd content for GSS-3 and Mo content /Cd content for GSD-3 are high at 4100 and 920, respectively, our obtained values for Cd content are 0.054 ± 0.001 and 0.093 ± 0.013 μg g^{-1}, which agree well with the certified values of 0.060 ± 0.009 and 0.100 ± 0.020 μg g^{-1}, respectively. The results clearly show that the proposed method based on aerosol dilution ICP-MS combined with the boiling inverse aqua regia extraction is reliable. The extraction procedure separates most of the Zr matrix (>90%) from the analyte, and the remaining Zr (<10%) and Mo are eliminated by the subsequent aerosol dilution technique.

Analysis of geological SRMs

The signal background ratio (SBR) of Cd increases 200-fold (from 0.82 to 160, as shown in Fig. S1, see ESI†) by our proposed method compared to conventional mode ICP-QMS employing the complete digestion procedure. The limit of detection (LOD, 3σ) is 1.6 ng g^{-1} (taking into account the 250-fold dilution factor). This sensitivity is sufficient for trace-level Cd determination of solid geological samples, in which the Cd levels typically range from 0.02 to 2.0 μg g^{-1}.

Two USGS SRMs (andesite AGV-2 and basalt BCR-2) and two IAG (metal-rich sediment SdAR-M2 and gabbro GSM-1) were assessed using the proposed method, as shown in Table 6. For comparison, the reference values and those reported in the literature are listed. As shown in Table 6, the Cd contents determined for AGV-2 and BCR-2 are in agreement with the USGS reference values. However, the Cd levels in AGV-2 and BCR-2 obtained using the conventional ICP-QMS coupled with the complete digestion procedure (0.121 μg g^{-1} and 0.227μg g^{-1} for AGV-2, 0.082 μg g^{-1}

and 0.75 μg g^{-1} for BCR-2) [36, 37] are significantly higher than the USGS reference values (0.061 μg g^{-1} and 0.140 μg g^{-1}, respectively) and our reported values (0.058 ± 0.004 μg g^{-1} and 0.148 ± 0.007 μg g^{-1}, respectively). For the two IAG SRMs SdAR-M2 and GSM-1, which were used as an international proficiency test for analytical geochemistry laboratories in 2014 (*GeoPT*36),[38] our analysis yielded values of 5.10 ± 0.20 μg g^{-1} and 0.072 ± 0.004 μg g^{-1}, respectively. The value for SdAR-M2 is consistent to the IAG reference value (5.10 ± 0.19 μg g^{-1}), but the Cd level determined value for GSM-1 (0.072 ± 0.004 μg g^{-1}) is lower than the recommended value (0.128 ± 0.012 μg g^{-1}). Ten separate aliquots of this SRM were analysed over a period of three months, and consistent results (0.070-0.076 μg g^{-1}) were obtained (Fig. S2, see ESI†). GSM-1 (gabbro) is a basic intrusive rock, which differs from BCR-2 (basalt), which is a basic extrusive rock. The efficiency of Cd extraction from the different basic rocks may be influenced by its crystallization process, and further study is required to explain this phenomenon.

The proposed method was also employed to determine Cd levels in 77 Chinese geological SRMs, comprising 28 soils, 30 sediments, and 19 rocks. The measured Cd levels in 65 geological samples are in good agreement with their certified values (Fig. 3). Although Cd in present at ultra-trace levels (< 0.20 μg g^{-1}) in 40 of the geological SRMs, the measured values are consistent with the certified values (see inset of Fig 3). Detailed results for these SRMs are given in Table S2 (see ESI†). Table 7 shows the values determined for two stream sediments (GSD-7 and GSD-19), which are inconsistent with the IGGE certified values. In addition, ten limestone SRMs

(GSR-22, GSR-23, GSR-24, GSR-27, GSR-28, GUI-1, GUI-2, DIAN-1, DIAN-2, and DIAN-3) have no current reference values or literature values, and the recommended values of these SRMs are provided by this work (Table 7). The results of repeated analysis, in which the SRMs were extracted and re-analysed ten times over a period of three months, are consistent (Fig. 4), which indicates that our recommended values are reliable. This method also could be used for the determination of other trace elements, such as Ag (Table S4, see ESI†).

Conclusions

A method for the determination of trace-level Cd in geological samples using aerosol dilution ICP-MS after extraction with boiling inverse aqua regia was developed. The significant interfering Zr or Mo based oxides and hydroxides was effectively reduced by the proposed method, compared to conventional ICP-QMS coupled with the complete digestion method, the SBR of Cd improved by two orders of magnitude. The proposed method was employed to analyse 81 geological SRMs, and the results of 68 samples were in good agreement with the certified or literature values. The Cd levels of 13 other SRMs have been provided for the first time by this method. The developed method shows great potential for the direct determination of trace levels of Cd in geological samples.

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Figure captions

Fig. 1. Schematic diagram of our aerosol dilution system.

Fig. 2. Effects of dilution gas flow rate on oxide formation ratios (($^{94}Mo^{16}OH^+$ + $^{95}Mo^{16}O^+$)/$^{95}Mo^+$ and $^{94}Zr^{16}OH^+$/$^{94}Zr^+$) and the signal background ratio (SBR).

Fig. 3. Cd values determined for 65 geological SRMs by the proposed method vs. their certified values. The inset shows the 40 geological SRMs containing ultra-trace levels of Cd (< 0.20 μg g^{-1}).

Fig. 4. Stability of Cd values obtained through the proposed method in 12 geological SRMs: two stream sediments: GSD-7 (a) and GSD-19 (b), and ten limestones SRMs: GSR-22 (c), GSR-23 (d), GSR-24 (e), GSR-27 (f), GSR-28 (g), GUI-1 (h), GUI-2 (i), DIAN-1 (j), DIAN-2 (k), and DIAN-3 (l). For each SRM, ten separate aliquots of the samples were analysed over a period of three months.

Table 1. Instrument operating parameters

ICP-MS instrument	Agilent 7700x ICP-MS
RF Power, W	1450
Plasma gas flow, L min^{-1}	15
Nebulizer gas flow, L min^{-1}	0.24 for aerosol dilution mode; 1.09 for standard mode.
Dilution gas flow, L min^{-1}	0.85 for aerosol dilution mode; 0 for standard mode.
Sampling depth ,mm	7.0
Sample uptake rate, mL min^{-1}	0.3
Dwell time, ms	30
Sweeps	100
Readings	1
Replicates	3
$^{140}CeO/^{140}Ce$ ratio (%)	< 0.3 for aerosol dilution mode; < 3.0 for standard mode.
Isotope monitored	^{111}Cd

Table 2. Signal contribution to m/z 111 by different elements (n=3)

Signal intensity	Elements								Signal background ratio (SBR)
	Blank, pure water		Cd, 1 ng mL-1		Mo, 200 ng mL-1		Zr, 1000 ng mL-1		
	Intensity, cps	RSD, %	Intensity, cps	RSD, %	Intensity, cps	RSD, %	Intensity, cps	RSD, %	
Conventional ICP-MS	6.67	9.1	12328	0.9	2987	1.3	12080	1.2	0.82
Aerosol dilution ICP-MS	1.11	8.5	1754	1.2	24.8	6.5	91.5	5.6	15.1

Table 3. Results of Cd levels in six geological SRMs obtained through aerosol dilution ICP-MS after conventional complete digestion.

Geological SRMs	Zr/Cd	Mo/Cd	Cd, µg g^{-1} (n = 3)		
			Aerosol dilution ICP-MS	Certified Value	Standard mode ICP-MS
GSS-3, yellow-brown earth soil	4100	5	0.113 ± 0.001	0.060 ± 0.009	0.303 ± 0.006
GSS-6, red soil	1692	138	0.180 ± 0.010	0.130 ± 0.030	0.402 ± 0.012
GSS-22, soil	3923	10	0.113 ± 0.003	0.065 ± 0.012	0.330 ± 0.020
GSD-3, stream sediment	2200	920	0.128 ± 0.007	0.100 ± 0.020	0.425 ± 0.002
GSD-3a, stream sediment	566	96	0.520 ± 0.010	0.500 ± 0.060	0.770 ± 0.040
GSR-4, quartz sandstone	3567	13	0.094 ± 0.012	0.060 ± 0.016	0.340 ± 0.020

Table 4. Results for Zr, Mo, and Cd levels in geological SRMs obtained through conventional ICP-MS without aerosol dilution using different sample preparation methods.

Geological SRMs	Elements	Cd, µg g^{-1} (n = 3)			
		Complete digestion	Extraction with aqua regia	Extraction with inverse aqua regia	Certified values
GSS-4, soil	Zr	531 ± 5	16.6 ± 0.4	23.0 ± 0.8	500 ± 42
	Mo	2.30 ± 0.4	2.60 ± 0.02	1.80 ± 0.10	2.60 ± 0.30
	Cd	1.05 ± 0.05	0.420 ± 0.010	0.393 ± 0.005	0.350 ± 0.06
GSD-9, sediment	Zr	387 ± 8	8.32 ± 0.04	10.1 ± 0.1	370 ± 20
	Mo	0.750 ± 0.010	0.537 ± 0.005	0.610 ± 0.010	0.640 ± 0.110
	Cd	0.680 ± 0.020	0.330 ± 0.01	0.320 ± 0.010	0.260 ±0.040
GSR-2, rock	Zr	93.0 ± 2.0	9.70 ± 0.70	7.30 ± 0.40	99.0 ± 11.0
	Mo	0.600 ± 0.020	0.350 ± 0.020	0.351 ± 0.004	0.540 ± 0.090
	Cd	0.142 ± 0.005	0.088 ± 0.005	0.080 ± 0.003	0.061 ± 0.014

Table 5. Results for Cd levels in six geological SRMs obtained through different ICP-MS methods after extraction with boiling inverse aqua regia.

Geological SRMs	Zr/Cd	Mo/Cd	Cd, μg g^{-1} (n = 3)		
			Aerosol dilution ICP-MS	Certified value	Standard mode ICP-MS
GSS-3, yellow-brown earth soil	4100	5	0.054 ± 0.001	0.060 ± 0.009	0.069 ± 0.013
GSS-6, red soil	1692	138	0.134 ± 0.007	0.130 ± 0.030	0.179 ± 0.004
GSS-22, soil	3923	10	0.058 ± 0.003	0.065 ± 0.012	0.074 ± 0.002
GSD-3, stream sediment	2200	920	0.093 ± 0.013	0.100 ± 0.020	0.242 ± 0.006
GSD-3a, stream sediment	566	96	0.493 ± 0.005	0.500 ± 0.060	0.587 ± 0.005
GSR-4, quartz sandstone	3567	13	0.055 ± 0.005	0.060 ± 0.016	0.065 ± 0.005

Table 6. Cd levels in four geological SRMs (μg g^{-1})

Geological SRMs	This study (N=10) [a]	Ref. [b]	Literature values
USGS AGV-2, andesite	0.058 ± 0.004	(0.061)	0.121 [c], 0.082 [d],
USGS BCR-2, basalt	0.148 ± 0.007	(0.14)	0.227 [c], 0.75 [d]
IAG SdAR-M2, sediment	5.10 ± 0.20	5.10 ± 0.19	/
IAG GSM-1, gabbro	0.072 ± 0.005	0.128 ± 0.012	/

[a] Mean ± SD, the SD is the standard deviation for ten separate aliquots of the samples analyzed over a period of three months

[b] Reference value by USGS and IAG

[c] Literature value with convention inductively coupled plasma quadrupole mass spectrometry method by Marx and Kamber [37]

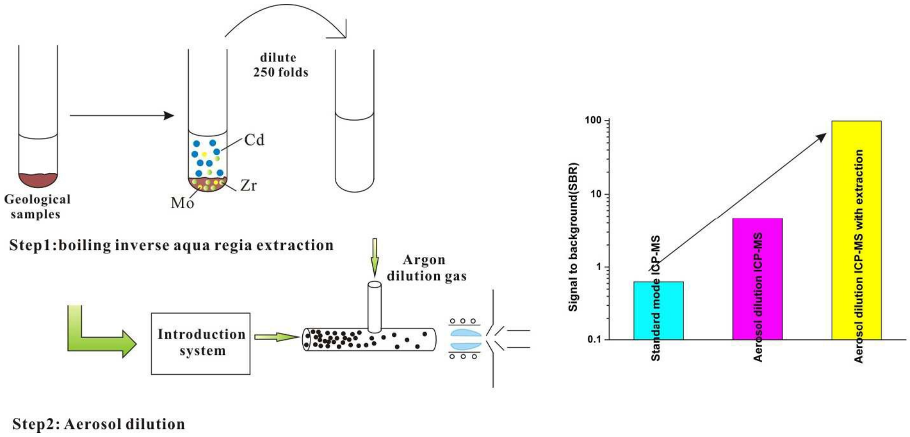
[d] Literature value with convention inductively coupled plasma quadrupole mass spectrometry method by Hu and Gao [38]

Table 7. Recommended Cd values for 12 geological SRMs determined in this work (μg g^{-1})

Geological SRMs	This work (N=10)	Reference values
GSD-7, stream sediment	1.20 ± 0.06	1.05 ± 0.06 [a]
GSD-19, stream sediment	0.088 ± 0.007	0.120 ± 0.01 [a]
GSR-22, limestone	0.121 ± 0.011	/ [b]
GSR-23, limestone	0.770 ± 0.040	/ [b]
GSR-24, limestone	0.063 ± 0.006	/ [b]
GSR-27, limestone	0.550 ± 0.050	/ [b]
GSR-28, limestone	0.510 ± 0.030	/ [b]
GUI-1, Limestone	0.042 ± 0.005	/ [b]
GUI-2, Limestone	0.160 ± 0.017	/ [b]
DIAN-1, Limestone	0.520 ± 0.030	/ [b]
DIAN-2, Limestone	0.366 ± 0.027	/ [b]
DIAN-3, Limestone	0.209 ± 0.015	/ [b]

[a] Recommend value

[b] No reported value



Developed a valid method based on aerosol dilution ICP-MS after inverse aqua regia extraction for direct determination of trace levels of Cd in geological samples.
224x96mm (300 x 300 DPI)

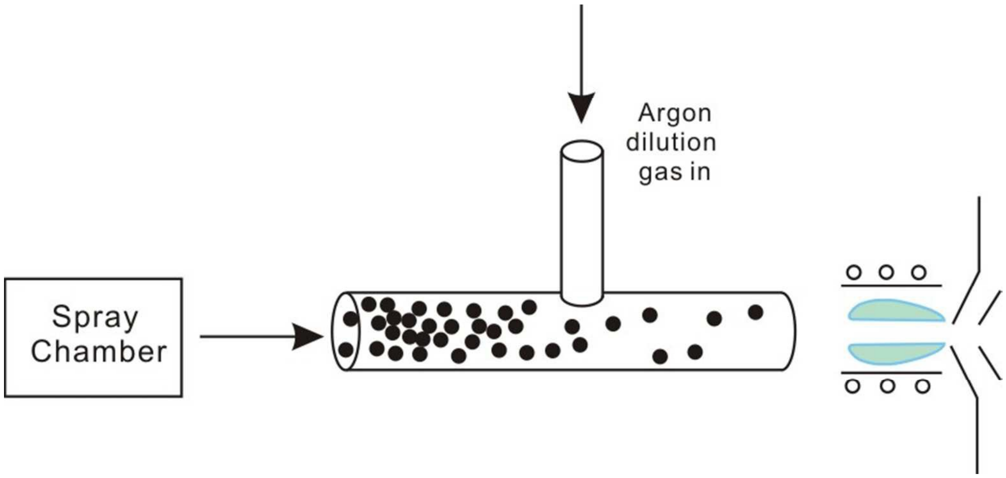


Fig. 1. Schematic diagram of our aerosol dilution system.
75x35mm (300 x 300 DPI)

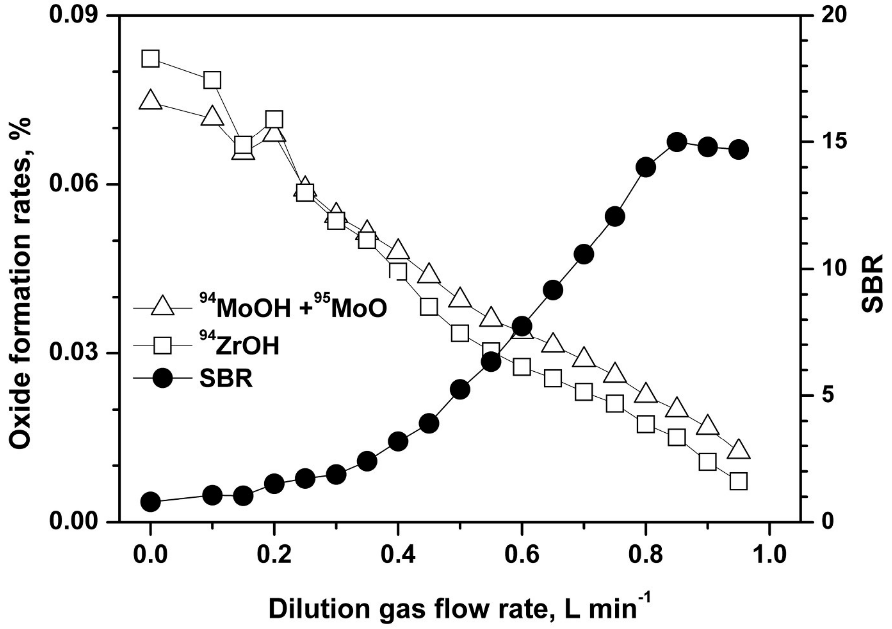


Fig. 2. Effects of dilution gas flow rate on oxide formation ratios ((94Mo16OH+ + 95Mo16O+)/95Mo+ and 94Zr16OH+/94Zr+) and the signal background ratio (SBR).
209x148mm (300 x 300 DPI)

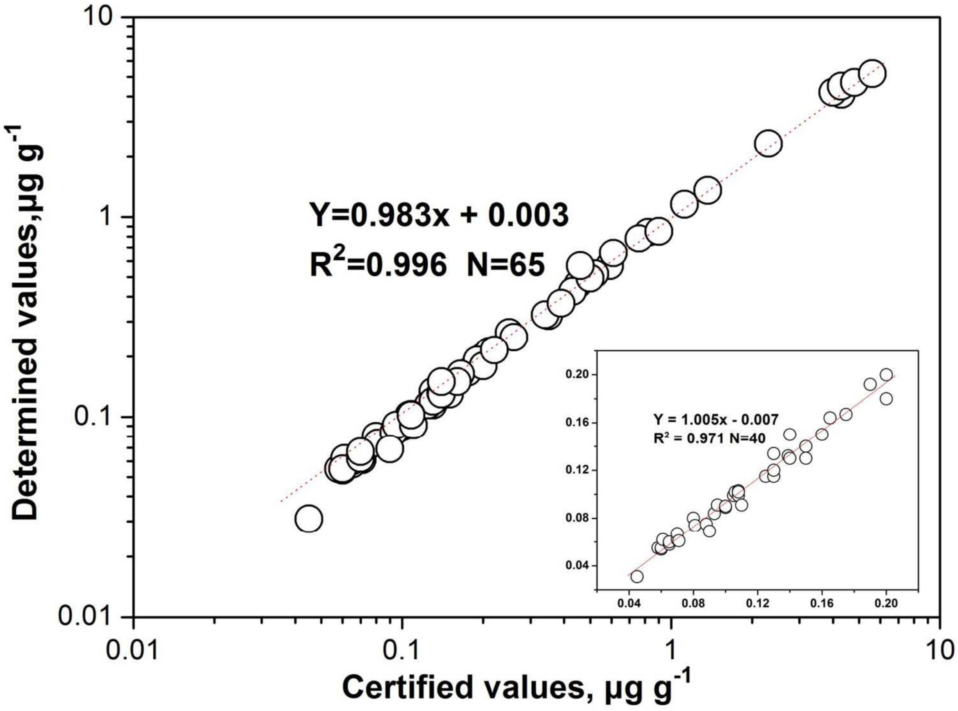


Fig. 3. Cd values determined for 65 geological SRMs by the proposed method vs. their certified values. The inset shows the 40 geological SRMs containing ultra-trace levels of Cd (< 0.20 µg g^{-1}).
156x118mm (300 x 300 DPI)

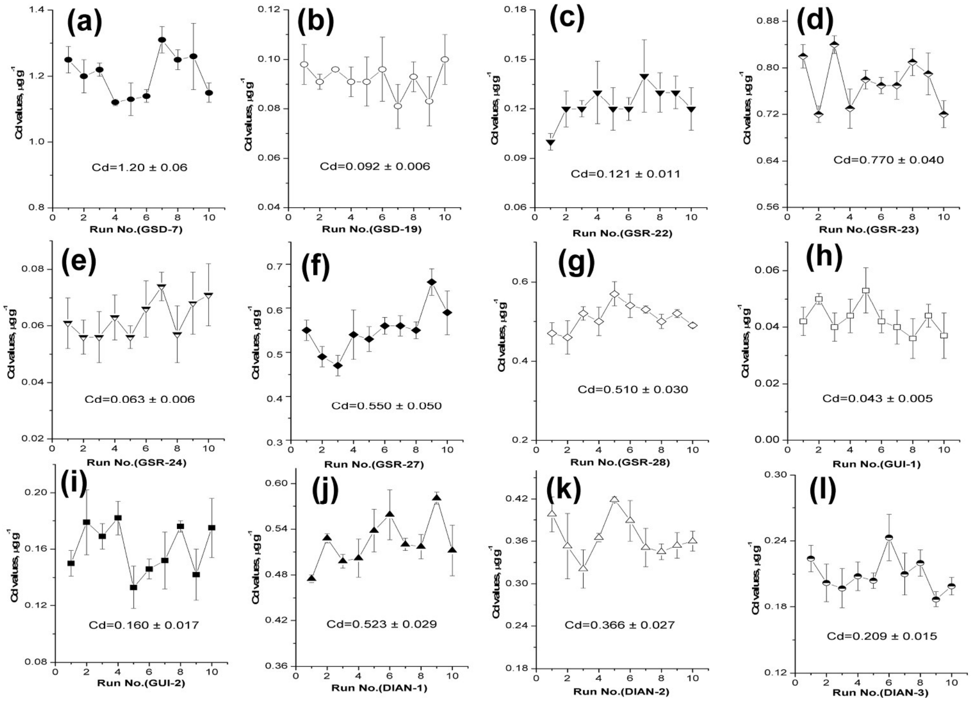


Fig. 4. Stability of Cd values obtained through the proposed method in 12 geological SRMs: two stream sediments: GSD-7 (a) and GSD-19 (b), and ten limestones SRMs: GSR-22 (c), GSR-23 (d), GSR-24 (e), GSR-27 (f), GSR-28 (g), GUI-1 (h), GUI-2 (i), DIAN-1 (j), DIAN-2 (k), and DIAN-3 (l). For each SRM, ten separate aliquots of the samples were analysed over a period of three months.
210x148mm (300 x 300 DPI)