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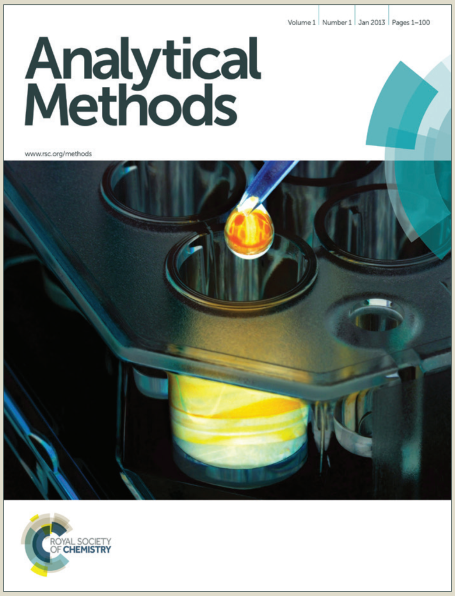

Direct determination of cadmium in geological samples by slurry sampling electrothermal atomic absorption spectrometry

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ABSTRACT

Cadmium (Cd) is an important element for the assessment of environmental pollution. An accurate and high throughput method involving slurry sampling electrothermal atomic absorption spectrometry (ETAAS) was developed to detect trace Cd content in geological samples. After sonication of the sample with 0.5% v/v HNO_3 and 0.5% v/v Triton X-100 solution, the slurry was directly introduced into a graphite atomizer and detected by AAS. This simple method was shown to take 80% less time, and resulted in 90% less reagent waste than the conventional acid digestion method. Under optimized conditions (sample size $\leq$ 75μm, sonication time: 20 min, pyrolysis temperature: 450 °C, and atomization temperature: 1600 °C), the characteristic mass and limit of detection for Cd were 0.8 pg and 0.002 $\mu g\ g^{-1}$, respectively. The proposed method was applied to the determination of Cd in 86 soil, sediment, and rock standard reference materials (SRMs). The results for 78 of these materials were in good agreement with the reference values. The Cd levels in five limestone SRMs (GUI-1, GUI-2, DIAN-1, DIAN-2, and DIAN-3) and one clay SRM (GBW03103) were reported for the first time. The proposed method shows great potential for the direct determination of trace Cd in various geological samples.

Introduction

The assessment of cadmium (Cd) in the environment or geological is important in the study of environmental pollution because of the toxic effect of Cd on human health and the fact that Cd-contaminated crops can grow from polluted soil. [1-3] The abundance of Cd in upper continental crust is only 0.09 μg g^{-1}. Therefore, the concentration of Cd is at trace or ultra-trace levels in natural soils, sediments, and rocks (except for Cd mineral deposits). [4-6] Consequently, highly sensitive and high-throughput analytical methods are needed for Cd determination of solid environmental samples. In addition, accurate determination of Cd is imperative for Cd isotopic analysis, which is vital for the study of cosmology, the tracing of anthropogenic sources, the study of micronutrient cycling, and oceanography. [7]

Two main techniques have been proposed that can be used for the accurate determination of trace Cd in soils, sediments, or rocks in typical geological laboratories. One method is inductively coupled plasma mass spectrometry (ICP-MS), which has high sensitivity, low detection limits, and is capable of simultaneous multi-element analysis. [8-19] However, isobaric and/or polyatomic interferences derived from the presence of high concentrations of matrix elements are significant limitations of this technology. [20] All isotopes of Cd are subject to interferences from various isobaric ions and/or oxide or hydroxide ions of Pd, Sn, In, Zr, Mo, Ru, Nb, and Y. [21] Complicated separation procedures, such as chromatography, precipitation, extraction, and volatile species generation, are usually required to eliminate these interferences [22-25]. Isotope dilution ICP-MS (ID ICP-MS) [26, 27] and dynamic reaction cell ICP-MS (DRC ICP-MS) [28, 29] have been demonstrated as valid methods to accurately detect trace Cd in environmental or geological samples. However, the high cost and complex operating procedures associated with these methods prevent their routine use in a high-throughput geological laboratory. The other method is electrothermal atomic absorption spectrometry (ETAAS), which has emerged as a better technique than ICP-MS for trace Cd determination as it is less subject to interference, more economical, relatively simple, and is capable of direct determination of Cd in complex matrices. [30-33]

Sample preparation is the most time-consuming step for solid environmental sample analysis, and microwave-assisted or high-pressure closed acid digestion has been extensively employed for sample dissolution which avoids analyte losses and contamination. [34] The main drawbacks are the high cost of vessels and ovens, the risk of explosions, low sample throughput, and the long time required for the cooling step. [35] Direct solid sampling ETAAS (DSS-ETAAS) may be used to simplify sample preparation procedures, and to avoid sample contamination. [36-41] However, the DSS-ETAAS method was not widely accepted until recently, owing to the difficulty in handling and introducing small sample masses, the high imprecision of the results due to the heterogeneity of some natural samples, the difficulty in calibration due to the requirement of solid standards with similar matrix composition and structure, the limited linear working range of AAS, and the difficulty in diluting solid samples. [35] Another attractive alternative is the use of slurry sample introduction in ETAAS, which combines the advantages of liquid and solid sampling and avoids many problems associated with direct solid sampling. Here, simple aqueous standards are used instead of solid-sample matrix calibration, the sample concentration can easily be changed by dilution, it can avoid weighted errors and inhomogeneity problems are eliminated, and the analyte concentration falls within the linear range. Furthermore, slurry can be directly sampled using the conventional autosampler used in ETAAS, avoiding the need for specialized expensive equipment such as a microbalance and solid sampling accessories. [42, 43] Slurry sampling ETAAS techniques have been proposed for trace Cd determination in various biological and food materials, such as plant, honey, wheat, and rice. [32, 33, 44, 45] However, limited literature is available regarding Cd determination in environmental soil or sediment samples. [46, 47] Most literature relates to acid digestion procedures but not direct slurry sampling. Therefore, to investigate whether the slurry sampling method is effective for non-soft matrices, such as soil, sediment, and rock, it is necessary to carefully optimize various operating conditions and comprehensively evaluate the accuracy and precision of this method for Cd determination.

The aim of this work was to develop an easy, accurate, reliable, green, and routine method for determination of trace Cd in solid geological samples using slurry sampling ETAAS. The optimization of the technique and its analytical performance, as well as its application to the determination of trace Cd in 86 soil, sediment, and rock standard reference materials (SRMs) are discussed in detail.

Experimental

Instrumentation

All measurements were performed with a PinAAcle^{TM} 900T atomic absorption spectrometer (PerkinElmer, Inc., Shelton, USA), which was equipped with a longitudinal AC Zeeman background correction system, a transversely heated graphite atomizer (THGA), PerkinElmer Cd electrodeless discharge lamps (EDL), and an AS 900 autosampler. A TubeView™ color furnace camera was used to monitor the process of slurry sampling in the graphite tube (Fig. S1, see ESI†).

Materials

De-ionized water used for the preparation of all blank, standard, and sample solutions was obtained from a water purification system (Merck Millipore, Fontenay-sous-Bois, France). The Cd standard solution (1000 μg L^{-1}) was purchased from the National Center for Analysis and Testing of Steel Materials, China. Nitric acid (65–70%, w/w, 99.999%) and Triton X-100 (> 99%) were purchased from Alfa Aesar Ltd. (Tianjin, China). Eighty-six geological SRMs were used to evaluate the accuracy of the proposed method, which covers 26 soil SRMs, 25 sediment SRMs, and 35 rock SRMs. Five of these SRMs were purchased from the United States Geological Survey (USGS) and the remainder from the Institute of Geophysical and Geochemical Exploration of China (IGGE). A detailed description of these SRMs is given in Table S1 (see ESI†).

Slurry sampling procedures

Slurries were prepared by weighing 0.1000 to 0.3500 g of the sample in a 50 mL conical polypropylene tube and diluting to 50 mL with 0.5% v/v HNO_3 containing 0.6% v/v Triton X-100. After homogenizing in an ultrasonic bath (Branson, USA) for 20 min, the uniform slurries were transferred into acid-cleaned propylene autosampler cups. Then, 20 µL of slurry was taken up and delivered to the graphite tube for ETAAS analysis.

For comparison, a conventional digestion method employing closed acid digestion with a mixture of HF + HNO3 was also used (see ESI Table 2S†) [48-50]

Results and discussion

Optimization of slurry sampling ETAAS conditions

To obtain accurate results with the slurry sampling ETAAS techniques, the slurry sampling procedures and graphite furnace heating parameters were optimized in detail. AGV-2, which is an andesite SRM provided by USGS with a certified Cd content of 0.069 μg g^{-1}, was used to optimize all of the parameters. As shown in Fig. 1a, the recovery of Cd from the AGV-2 with HNO_3 was investigated by varying the HNO_3 concentrations from 0.1% and 0.6% (v/v), while other parameters, such as particle size (62 μm), sonication duration (20 min), Triton X-100 concentration (0.5% v/v), and slurry concentration (0.5% m/v), pyrolysis temperature (450 °C), and atomization temperature (1600 °C), were kept constant. As is evident from the figure, the best recovery of Cd is obtained when 0.5% v/v HNO_3 is used.

Sonication and the addition of the stabilizing medium Triton X-100 were used to improve the homogeneity of the sample slurries, and similar optimization procedures as for HNO_3 concentration were performed for Triton X-100 concentration and sonication time, as shown in Fig. 1b and Fig. 1c. Under the optimized Triton X-100 concentration (0.5% v/v) and sonication time (20 min), sample particles formed homogenous and stable slurries (Fig. S2, see ESI†).

It is important to optimize particle size in order to attain quantitative recoveries with the heat extraction procedure. Different particle sizes ranges of a soil sample with a Cd content of 0.230 ± 0.012 μg g^{-1} (determined by the closed acid digestion ETAAS method) were studied. Particle sizes of 83 μm, 75 μm, 62 μm, and 38 μm were investigated, as shown in Fig. 1d, and quantitative recoveries were attained for particles both 38 μm (97%) and 62 μm (98%) in size. 10 min of sample grinding in a ball mill is required to obtain a particle size of 38 μm. However, only 4 min is required to obtain a particle size of 62 μm. Therefore, 62 μm particle sizes (240 mesh) was employed for the rest of this work.

The concentration of slurry suspensions is an important factor, which can affect the measurement precision. Here, a number of suspensions with different percentages of SRM AGV-2 were prepared, and the precision (RSD, %) of the integrated absorbance results was explored. Fig. 1e shows the relationship between precision and slurry concentration in the range 0.1 – 1.0% (m/v). The optimum concentration ranges from 0.2% to 0.7% (m/v). Although quantitative recovery in the slurry sampling procedure is achieved for sample concentrations outside this range (> 0.7% m/v or < 0.2%), a high level of error (RSD > 9.5%) is observed.

As it is a volatile element, Cd is lost from the graphite atomizer at temperatures higher than 300 °C in the absence of a chemical modifier. [51, 52] To increase the thermal stability of Cd and allow higher pyrolysis temperatures for the removal of higher levels of concomitants, $Pd(NO_3)_2$ solution was assayed as a chemical modifier. The effect of the pyrolysis and atomization temperature on the integrated absorbance were studied in experiments on the AGV-2 SRM slurry with or without a $Pd(NO_3)_2$ chemical modifier. As shown in Fig. 1f, the addition of 5 μL 0.05% m/v $Pd(NO_3)_2$ modifier allowed the optimum pyrolysis temperature to increase from 350 °C (without modifier) to 450 °C. The optimum atomization temperature was found to be 1600 °C (Fig. 1f), which is similar to that of without a modifier. In addition to the graphite furnace temperature programs described in Table 1, a pre-pyrolysis step (350 °C) using air was added to avoid carbon residues on the platform of the graphite tube [53].

Analytical features of merit

Calibrations were carried out using aqueous standard solutions with a linear range of 0.1 to 3.0 ng mL^{-1} Cd. The characteristic mass (m_0), defined as the mass of analyte corresponding to 0.0044 absorbance units, is 0.8 pg. The limit of detection (LOD) is 0.002 µg g^{-1}, which was calculated from 20 consecutive measurements of the blank solutions, and a 200-fold sample dilution factor, i.e., a 0.5% m/v slurry concentration. The tube lifetime using the proposed slurry sampling ETAAS method is 785 ± 28 analytical firings, which is only 15% shorter than that with the conventional closed acid digestion ETAAS method. By considering the time taken the preparation of sample slurries (10 samples per each batch spent 0.5 hour) and the determination by ETAAS, the analytical throughput of the method is estimated to be 7 samples per hour. For each sample analysis, only 0.25 mL HNO_3 and 0.30 mL Triton X-100 is required with the proposed method. Conversely, conventional closed acid digestion ETAAS requires 6.0 mL HNO_3 and 2.0 mL HF per sample, representing much higher cost and more waste.

Geological sample analysis

Five USGS SRMs were assessed using the proposed method (Table 2). For comparison, the USGS certified Cd values and those reported elsewhere in the literature are also listed in Table 2. Cd contents determined for SRMs AGV-2, SBC-1, SGR-1b, and BCR-2 are in agreement with the USGS reference values. The reference value of BHVO-2 (USGS) is 0.06 μg g^{-1}, which is lower than our reported value of 0.116 ± 0.011 μg g^{-1}. However, our result is consistent with the value obtained by isotope dilution ICP-MS (0.112 μg g^{-1}), [26] which is regarded as the most reliable method for Cd detection. To further confirm that our reported values are reasonable, ten separate aliquots of BHVO-2 were analyzed over a period of three months, and consistent results (0.093-0.123 μg g^{-1}) were obtained (Fig. 2a). The Cd content of BCR-2 obtained by ICP-MS (0.227 μg g^{-1}, [54] and 0.75 μg g^{-1}, [55] *etc.*) is significantly higher than the USGS reference value (0.14 μg g^{-1}) and the values obtained by ID-ICP-MS (0.136 μg g^{-1} [56]), and our proposed ETAAS method (0.142 ± 0.008 μg g^{-1}). The large errors obtained using the ICP-MS method could be attributed to the presence of large amounts of Zr (Zr/Cd > 1880) and Mo (Mo/Cd > 2510) in BCR-2. Similar results were observed for AGV-2 and SGR-1b, which further confirms that our slurry sampling ETAAS method is more reliable than ICP-MS.

The method we report herein was also used to determine Cd levels in 81 Chinese geological SRMs, comprising 25 soil, 26 sediment, and 30 rocks. The obtained values and their certified values compared in Fig. 3, except for those of one clay (GBW03103), and one ultra-basic rock (GBW07101), and five limestone (GUI-1, GUI-2, DIAN-1, DIAN-2, and DIAN-3) samples, which have no available certified or literature values. As shown in Fig. 3, the Cd levels of 74 of the geological SRMs are in good agreement with the certified values or reference values. The detailed results for these SRMs are given in Table S1 (see ESI†). As shown in Table 3, the Cd content found for the ultra-basic rock GBW07101 is 0.044 ± 0.002 μg g^{-1}, which is nearly twice its reference value 0.024 μg g^{-1}. This SRM was analyzed ten times over a three-month period, and the results ranged from 0.043 to 0.047 μg g^{-1} (Fig. 2b). The proposed method was also used to analyze one clay SRM GBW03103, and five limestone SRMs (GUI-1, GUI-2, DIAN-1, DIAN-2, and DIAN-3), which have no reported Cd value available (Table 3). Our recommended values are 0.108 ± 0.009 μg g^{-1} (GBW03103), 0.056 ± 0.005 μg g^{-1} (GUI-1), 0.176 ± 0.012 μg g^{-1} (GUI-2), 0.134 ± 0.009 μg g^{-1} (DIAN-1), 0.335 ± 0.005 μg g^{-1} (DIAN-2), and 0.244 ± 0.004 μg g^{-1} (DIAN-3), respectively. The results of repeated analysis over a period of three months are very stable (Fig. 4), which further confirms that our reported values are reasonable. In addition, these values are in good agreement with the conventional closed acid digestion ETAAS method (Table 3).

Conclusion

A method using slurry sampling ETAAS to accurately determine trace Cd in various soils, sediments, and rocks was developed and validated. In our method, sample digestion is not needed; thus, the problems related to conventional acid digestion, such as the use of concentrated acids, time consumption, the risk of contamination, and possible analyte loss are avoided. Using of the proposed method, Cd levels were determined for 78 international geological SRMs, and the results were found to be in good agreement with their certified or literature values of the samples. The Cd levels in five limestone SRMs (GUI-1, GUI-2, DIAN-1, DIAN-2, and DIAN-3) and one clay SRM (GBW03103) were reported for the first time in the literature, and the values for one ultra-basic rock SRM (GBW07101) and one basalt SRM (BHVO-2) were updated. In conclusion, our method has great potential for the direct determination of trace levels of Cd in various solid geological samples.

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Figure captions

Fig. 1. Effects of the slurry sampling ETAAS conditions on Cd recoveries from the geological SRM AGV-2. (a) Effect of HNO_3 concentration, (b) effect of Triton X-100 concentraiton, (c) effect of sonication time, (d) effect of sample particle size, (e) effect of slurry concentration, and (f) effect of pyrolysis and atomization temperatures.

Fig. 2. Results of repeated analyses of (a) a basalt SRM BHVO-2, and (b) an ultra-basic rock SRM GBW 07101. The average values of Cd in BHVO-2 and GBW07101 are 0.116 ± 0.011 μg g^{-1} and 0.044 ± 0.002 μg g^{-1}, respectively. Ten separate aliquots of the samples were analyzed during a period of three months.

Fig. 3. Obtained Cd values for 74 Chinese geological SRMs by slurry sampling ETAAS *vs*. their reference values.

Fig. 4. The stability of Cd values obtained by our method in six geological SRMs: (a) clay SRM GBW 03103, (b) limestone SRM GUI-1, (c) limestone SRM GUI-2, (d) limestone SRM DIAN-1, (e) limestone SRM DIAN-2, and (f) limestone SRM DIAN-1. Ten separate aliquots of the samples were analyzed during a period of three months.

Table 1

Graphite furnace temperature programs and spectrometer operating conditions

Step	Temp. (°C)	Ramp. time (s)	Hold time (s)	Inter. flow (mL min^{-1})	Gas type
Drying	110	5	30	250	Ar
	130	15	30	250	Ar
Pyrolysis	350	15	15	50	Air [a]
	450	10	20	250	Ar
Atomization	1600	0	4	0	/
Cleaning	2500	1	3	250	Ar
Wavelengh/nm: 228.8			Measurement mode: Peak area		
Spectral bandwidth/nm: 0.7			Zeeman-effect background correction system		
Cathode lamp intensity/mA: 8			Pyrolytic graphite tubes with platform		
Integration time/s: 3			Injection volume/μL: 20		

[a] Air gas come from the air compressor.

Table 2

Cd detected results of USGS geological SRMs, µg g^{-1}

USGS SRMs	This study (N=15)	USGS Ref. [a]	Literature values
AGV-2, andesite	0.070 ± 0.003	(0.061)	0.121 [b], 0.082 [c],
BHVO-2, basalt	0.120 ± 0.012	(0.06)	0.112 [d]
SBC-1, shale	0.400 ± 0.003	(0.4)	/
SGR-1b, oil shale	0.900 ± 0.040	(0.9)	1.14 [c]
BCR-2, basalt	0.155 ± 0.013	(0.14)	0.227 [b], 0.75 [c], 0.136 [e]

[a] Reference value by USGS

[b] ICP-QMS value by Marx and Kamber [54]

[c] ICP-QMS value by Hu and Gao [55]

[d] ID-ICP-MS value by Makishim et al. [26]

[e] ID-ICP-MS value by Loss et al. [56]

Table 3

Updated Cd values for seven SRMs determined by this method, μg g^{-1}

Geological SRMs	This work (N=10)	Reference values	Closed acid digestion ETAAS method (N=3)
GBW07101, Ultrabasic rock	0.044 ± 0.004	(0.024) [a]	0.048 ± 0.012
GBW03103, Clay	0.108 ± 0.009	/ [b]	0.108 ± 0.029
GUI-1, Limestone	0.056 ± 0.005	/ [b]	0.060 ± 0.012
GUI-1, Limestone	0.176 ± 0.012	/ [b]	0.185 ± 0.015
DIAN-1, Limestone	0.134 ± 0.009	/ [b]	0.142 ± 0.022
DIAN-2, Limestone	0.335 ± 0.005	/ [b]	0.342 ± 0.025
DIAN-3, Limestone	0.244 ± 0.004	/ [b]	0.238 ± 0.018

[a] Reference value by the Institute of Geophysical and Geochemical Exploration of China

[b] No reference or reported value

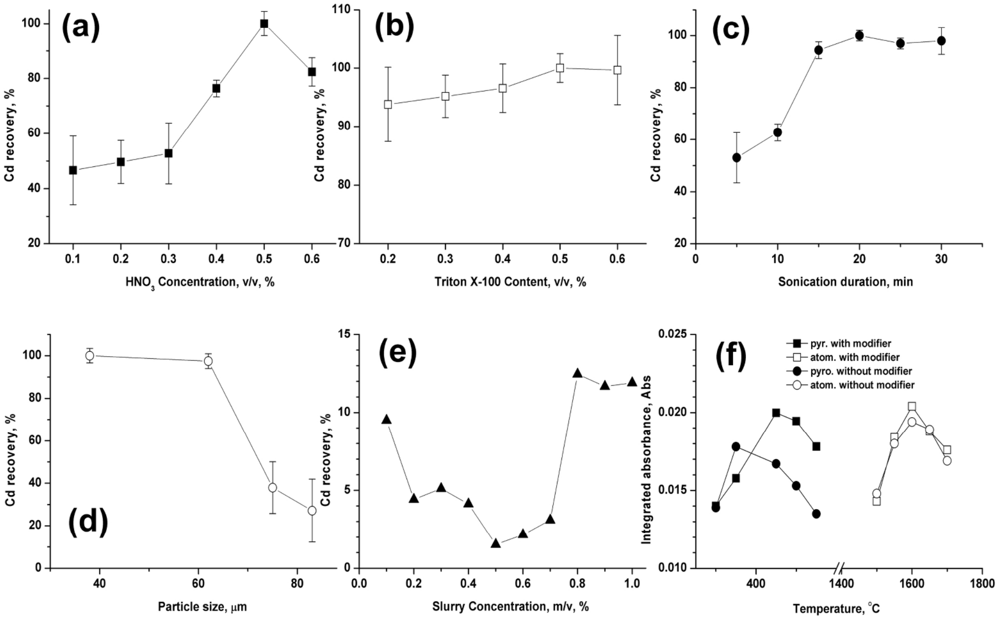

Fig. 1. Effects of the slurry sampling ETAAS conditions on Cd recoveries from the geological SRM AGV-2. (a) Effect of HNO_3 concentration, (b) effect of Triton X-100 concentraiton, (c) effect of sonication time, (d) effect of sample particle size, (e) effect of slurry concentration, and (f) effect of pyrolysis and atomization temperatures.
210x148mm (300 x 300 DPI)

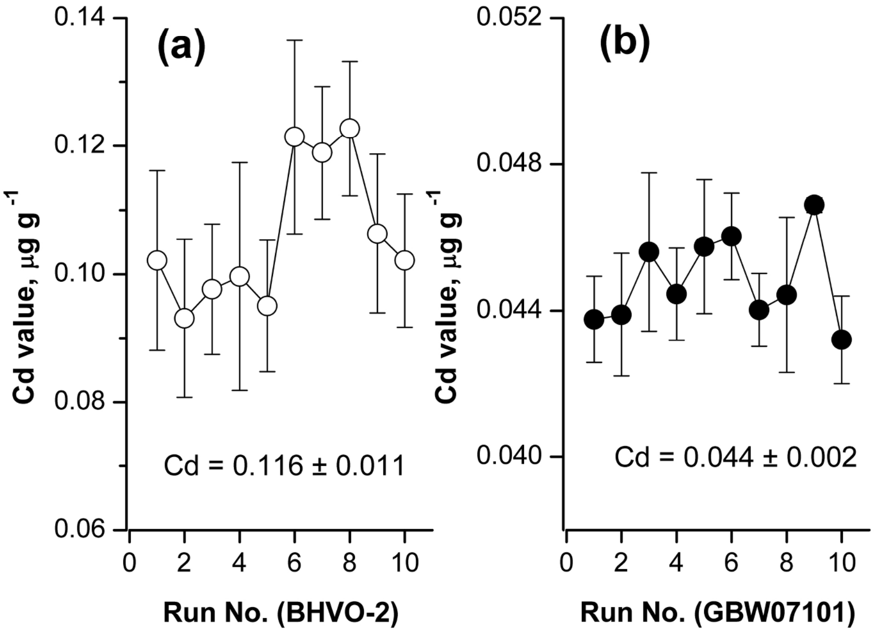

Fig. 2. Results of repeated analyses of (a) a basalt SRM BHVO-2, and (b) an ultra-basic rock SRM GBW 07101. The average values of Cd in BHVO-2 and GBW07101 are 0.116 ± 0.011 μg g^{-1} and 0.044 ± 0.002 μg g^{-1}, respectively. Ten separate aliquots of the samples were analyzed during a period of three months.
210x148mm (300 x 300 DPI)

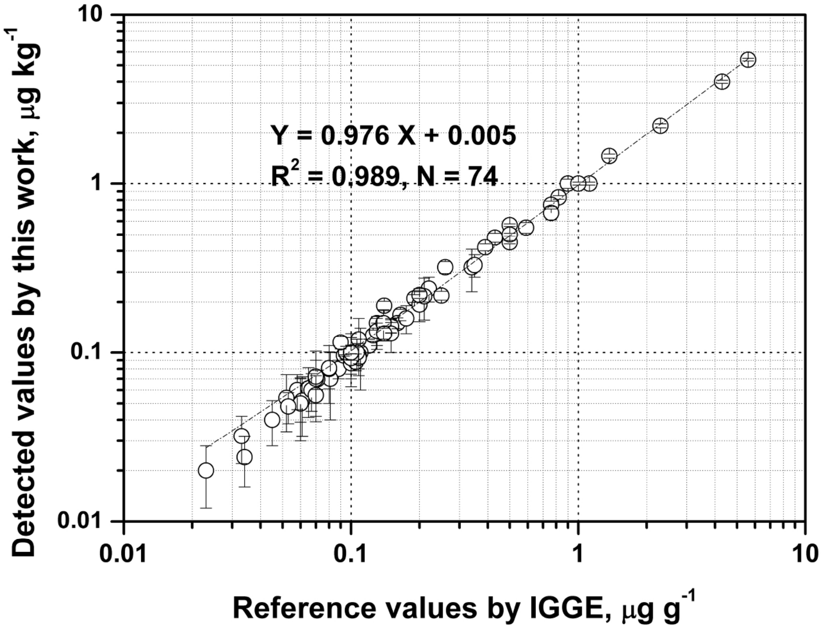

Fig. 3. Obtained Cd values for 74 Chinese geological SRMs by slurry sampling ETAAS vs. their reference values.
210x148mm (300 x 300 DPI)

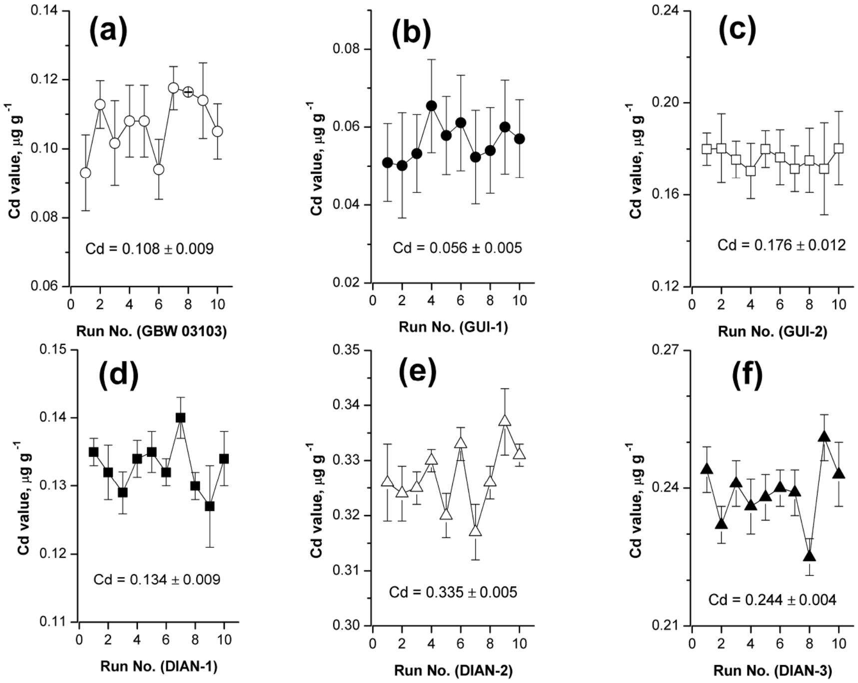

Fig.4 The stability of Cd values obtained by our method in six geological SRMs: (a) clay SRM GBW 03103, (b) limestone SRM GUI-1, (c) limestone SRM GUI-2, (d) limestone SRM DIAN-1, (e) limestone SRM DIAN-2, and (f) limestone SRM DIAN-1. Ten separate aliquots of the samples were analyzed during a period of three months.
209x148mm (300 x 300 DPI)

Graphical Abstract: An accurate and high throughput method involving slurry sampling ETAAS was developed to detect trace Cd content in various geological samples
41x14mm (300 x 300 DPI)