JAAS

Accepted Manuscript

This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

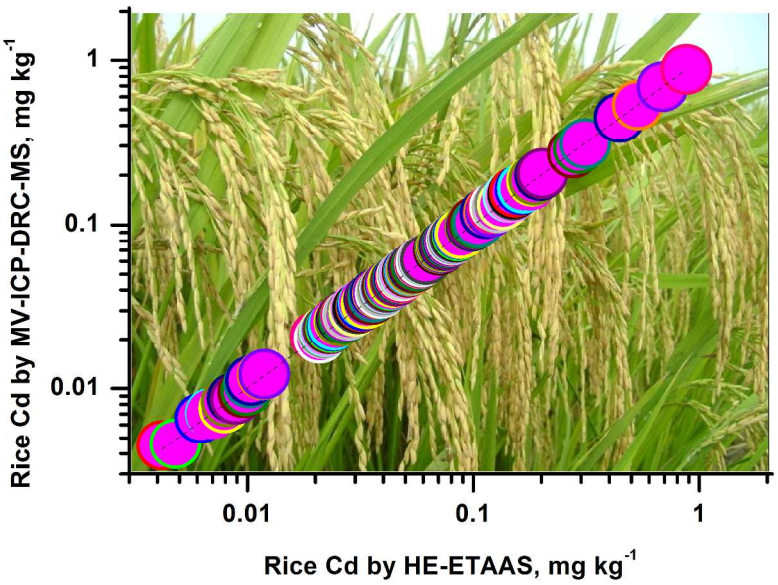
Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/jaas



Graphical abstract: A simple and high throughout method using heat-extraction electrothermal atomic absorption spectrometry (HE-ETAAS) was developed for monitoring rice cadmium (Cd) from Chinese markets.
297x210mm (300 x 300 DPI)

Rice cadmium monitoring using heat-extraction electrothermal atomic absorption spectrometry

Wei Guo [a], Ping Zhang [b], Lanlan Jin [a] and Shenghong Hu *[a]

[a] *State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences, Wuhan, 430074, P. R. China*

[b] *Beijing CKC, PerkinElmer, Inc. 100015, China*

Corresponding Author

*Tel. and Fax: +86-27-67883495. Email: shhu@cug.edu.cn

Abstract

A simple and high throughput method involving heat-extraction electrothermal atomic absorption spectrometry was developed to monitor Cd content in rice, and 184 rice samples purchased from supermarkets in Beijing were surveyed. The main advantages of using a heat-extraction in comparison to slurry sampling are doubling of the graphite tube lifetime and 80% decrease in the background absorbance signal, most likely because the less sample matrix was introduced into the atomizer, avoiding buildup of carbonaceous residues or silicates on the graphite platform. Heat-extraction provides better detection limits and precision than microwave acid digestion. In the heat-extraction method, slurries in 3% v/v HNO_3 were heated on a heating block. After centrifugation, the supernatant was introduced into a graphite tube pretreated with a W-Rh permanent modifier. The optimum conditions for Cd detection were 0.2–5.0% m/v slurry concentration, 3% HNO_3 extract, 10 min heating at 120 °C, rice-particle size < 150 μm (after 3 min of sample grinding), 600 °C pyrolysis temperature, and 1500 °C atomization temperature. The extraction recovery for Cd in rice standard reference materials was 98.4–101.1%. The characteristic masses and detection limit for Cd based on the integrated absorbance for a 2.5% m/v rice sample were 0.7 ± 0.1 pg and 1 ng g^{-1}, respectively. The mean Cd content was 0.076 μg g^{-1} (ranging from 0.004 to 0.876 μg g^{-1}), and only 4.3% of investigated rice samples exceeded the maximum allowable Cd concentration of 0.20 μg g^{-1}. This simple and

rapid method has great potential for monitoring trace Cd in food samples for market survey.

Introduction

Cadmium (Cd) is toxic to humans at low levels because its effects are cumulative. Soil pollution with Cd is a public concern since the daily ingestion of rice with high Cd levels was found to be the main cause of Itai-itai disease in Japan.[1,2] China is the largest rice producer in the world, growing 30.7% of rice produced worldwide.[3] Rice is the most important cereal in Southern China, but its high potential for Cd absorption and accumulation is a cause for public concern. The maximum allowable concentration (MAC) of Cd in rice has been set at 0.2 μg g^{-1} in China.[4] Recently, Cd-contaminated rice was found in Hunan,[5] Jiangsu,[6] and Guangdong [7] in South China. There is a high demand for a rapid and accurate analytical method to monitor Cd levels in rice for market surveys.

Electrothermal atomic absorption spectrometry (ETAAS) and inductively coupled plasma mass spectrometry (ICP-MS) are the two main methods for monitoring trace Cd in rice samples.[8-11] ETAAS has emerged as a useful method owing to less interference, low cost, relative simplicity, and its capability for direct determination of Cd in complex matrices. For solid rice analysis, sample preparation is often the most time-consuming step. Over the past two decades, microwave-assisted acid digestion has been extensively employed for sample dissolution and to avoid analyte losses and contamination.[12] The main drawbacks are the high cost of vessels and ovens, occasional explosions, low sample throughput, and long time required for the cooling step.[13] To simplify sample preparation and avoid

some of the problems associated with dissolution procedures, a slurry sampling ETAAS technique (SS-ETAAS) has been employed for the direct determination of Cd in rice samples.[14,15] As a suspension of insoluble particles, slurries usually exist in acid solutions and/or other media such as Triton X-100, which permit homogenization of the sample and liberation, to some extent, of trace elements into the solution. The advantages of the slurry sampling technique are simplicity, safety, environment friendliness, low cost, reduced time, and low risk of contamination, allowing for low detection limits.[16] To obtain high recoveries with slurry techniques, it is necessary to optimize the particle size, number of particles present in the injected volume, analyte homogeneity, suspension medium, slurry concentration, and sampling depth.[17-19] Because of the buildup of carbonaceous residues or refractory inorganic materials inside the graphite tube, the lifetime of the tube was reduced by 50% compared to that in the digested solution.[20,21] Ultrasound-assisted extraction ETAAS (UAE-ETAAS) is an alternative approach used to analyze rice samples; Cd was totally or partially extracted into the liquid phase when the slurries were sonicated before sampling.[22,23] Compared to the slurry sampling techniques, UAE offers a lower background absorbance, longer tube lifetimes, and lower analytical costs.[13-15] However, some researchers reported that while soft tissues (plankton, algae, and oyster tissues) could be almost completely extracted (>90%), the total extraction was only 60% for cabbage and spruce needles.[24] The required particle size was < 30 μm for this procedure, increasing the sample grinding difficulty.[15] In addition, the sample can be

contaminated by the damaged walls of the centrifuge tubes when higher sonication power and extraction time are required for complex matrices [15].

In this paper, a simple heat-extraction ETAAS (HE-ETAAS) method is proposed for monitoring Cd levels in rice samples. Compared to microwave acid digestion and slurry sampling procedures, it had a higher sample throughput, longer tube lifetime, and lower analytical costs. As a laboratory method, it was used to analyze 184 rice samples collected from Chinese markets

Experimental

Instrumentation

All measurements were carried out with a PinAAcle™ 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 electrodeless discharge lamps (Part No. N3050615), a TubeView™ color furnace camera, and an AS 900 autosampler. The standard THGA tubes (Part No. B0504033) with integrated platforms were used with thermal treatment for W-Rh permanent modifier deposition based on the procedure previously reported by Lima et al.[25] After 300 injection firings, the coated graphic tube platform should be retreated. The operating parameters of the ETAAS in this work are summarized in Table 1.

Reagents and standards

High purity water (18.2 MΩ cm^{-1}) used for the preparation of all blank, standard, and sample solutions was obtained from a Millipore water purification system (Millipore, 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%) was purchased from Alfa Aesar Ltd. (Tianjin). Five rice standard reference materials (NIST1568a, GBW08511, GBW08512, GBW10045, and GBW10046) were used to test the accuracy of the proposed method.

Sampling and sample preparation

A total of 184 rice samples were purchased from several supermarkets in Beijing in 2013. Before reaching the laboratory, the samples were kept in plastic bags and stored in a refrigerator (4 °C). These samples were oven-dried at 60 °C and ground in a ball mill (Retsch, Germany) to obtain the desired particle size (< 150 μm). To evaluate the effect of sample particle size on the proposed extraction procedure, randomly selected rice samples were ground to different particle sizes: $\phi > 250$ μm, $150 < \phi < 250$ μm, $75 < \phi < 150$ μm, $38 < \phi < 75$ μm, $30 < \phi < 38$ μm, and $\phi < 30$ μm.

Heat-extraction procedure

Each of the 184 rice samples (0.2500 g) was accurately weighed into 15 mL conical polypropylene tubes and was subsequently diluted with 3% v/v HNO_3 to a volume of 10 mL. The tubes were then placed on a heating block (120 °C) and heated for 10 min.

Subsequently, the liquid phase was separated by centrifugation (5000 rpm, 5 min), and 1 mL of the supernatant solution was transferred to an autosampler cup.

Slurry sampling and microwave acid digestion procedures

For comparison, the slurry sampling procedure and microwave acid procedure were both employed in this work. The slurry sampling procedure was performed using the following method. Slurries were prepared by weighing 0.2500 g of the sample in a 15 mL conical polypropylene tube and diluting the sample to the mark with 0.05% v/v Triton X-100 containing 0.5% v/v HNO_3. This solution was homogenized in an ultrasonic bath (Branson, USA) for 10 min to break up particle agglomerates. Slurries were transferred to an autosampler cup under sonication. The microwave acid digestion procedure was performed using the following method. The rice sample (0.2500 g) was weighed into a Teflon vessel and 3.0 mL HNO_3 and 2.0 mL H_2O_2 were added. Then, the vessel was sealed. Microwave (CEM, USA) digestion was applied using the following procedures. The temperature was ramped to 120 °C in 10 min at 800 W, held for 5 min, ramped to 160 °C in 10 min at 800 W, and held for 15 min. After cooling, the opened vessel was placed on a heating block (120 °C). The sample was boiled to near dryness and subsequently transferred to a 25 mL volumetric flask and diluted to the scale with a 1% HNO_3 solution.

Results and discussion

Optimization of HE-ETAAS conditions

Preliminary experiments for heat extraction were carried out with rice samples to optimize the extraction conditions of Cd. The recoveries of Cd in rice standard material GBW08511 (Cd content was 0.504 ± 0.018 μg g^{-1}) were used to optimize the extraction conditions such as extracting medium, temperature, and time. HNO_3 concentrations ranging from 1% to 20% (v/v) were also evaluated for the heat extraction procedure, and the extraction curves of Cd in GBW08511 are shown in Fig. 1a. The other conditions were kept constant, such as particle size (< 150 μm), extracting temperature (120 °C), extracting time (10 min), and slurry concentration (2.5% m/v). As shown in Fig. 1a, average Cd extraction was 98% in the 2–10% HNO_3 range. The extraction of Cd slightly decreased at high HNO_3 concentrations (10–20%, v/v). A 3% v/v HNO_3 solution was chosen as the extracting medium for the heat extraction, and this was a compromise between the maximum analyte extraction and graphite tube lifetime. Similar optimized procedures for the extracting temperature and extracting time are shown in Fig. 1b and Fig. 1c. In this study, the temperature and time of the heat extraction procedures were selected to be 120 °C and 10 min to guarantee quantitative Cd extraction from different rice samples, as a high Cd content could diminish the rate of Cd extraction into the aqueous phase. The stability of the extracted solution was also evaluated; the supernatant solution was stored in a refrigerator (4 °C) with occasional agitation. After ten days, an average extraction recovery of 98.7% ± 0.2% (in 3.0% HNO_3) was obtained with the heat extraction.

Because the results showed that Cd was stable in the liquid phase, it is most likely that Cd did not adhere to the rice particles or vessels walls.

Particle size is an important parameter to be optimized to attain quantitative recoveries with the heat extraction procedure. Different particle size ranges of a rice sample (Cd content 0.031 ± 0.002 μg g^{-1} determined by microwave digestion ETAAS method) were studied ($\phi > 250$ μm, $150 < \phi < 250$ μm, $75 < \phi < 150$ μm, $38 < \phi < 75$ μm, $30 < \phi < 38$ μm, $\phi < 30$ μm). As shown in Figure 2, the extraction of Cd was quantitative (> 97%) for samples with a particle size < 150 μm and recoveries of ~95% were attained for particle sizes $150 < \phi < 250$ μm. Only 3 min of sample grinding in the ball mill was required to obtain a particle size of < 150 μm, and this particle size was employed for the rest of this work. However, while sizes < 30 μm are adequate for the slurry sampling or ultrasound-assisted extraction procedure,[15] small particle sizes require a longer time (> 20 min) for sample grinding, and decrease the sample throughput, making them unsuitable for routine analysis with a large number of samples.

The slurry concentration for Cd extraction from the rice standard reference material (NIST1568a) was also explored. The optimum concentration ranges for extraction were 0.2–5.0% m/v for Cd. While quantitative recovery in the heat extraction procedure was achieved for sample concentrations < 0.2% m/v, a high level of error (RSD > 8.2%) was observed. A high slurry concentration (> 5% m/v) may be required for long extraction procedures and more acidic medium, which would

decrease the sample throughput and graphite tube lifetime, making the procedure unsuitable for routine analysis.

Two advantages of heat extraction in relation to slurry sampling are minimization of carbonaceous residue buildup inside the graphite tube and lower background values because significantly less matrix is introduced. In Fig. 3, a comparison of the peak profiles obtained with an injection of 20 µL of 2.5% m/v rice flour SRM NIST 1568a (Cd concentration is 0.022 ± 0.002 µg L^{-1}) extracted, slurry, and digest solutions is presented. As shown in Fig. 3, the absorbance signals were similar for extracted (peak height, 0.0763), slurry (peak height, 0.0758), and digest solutions (peak height, 0.0757). However, the background absorbance (peak height) of the extracted solution (peak height, 0.0124) was only 50% and 21% compared to that of the digest and slurry solutions, respectively.

A matrix modifier is always used to increase analyte thermal stability, providing higher pyrolysis temperatures for removal of high contents of concomitants. Cd is a volatile element that can be lost from the graphite atomizer at temperatures higher than 300 °C in the absence of a modifier. [9] To increase the thermal stability of Cd during pyrolysis, a W-Rh coating of the integrated platform of a transversely heated graphite atomizer could be used as a permanent chemical modifier. The best recoveries in the rice flour SRM (NIST 1568a) extracted solution were obtained with 250 µg W + 200 µg Rh, and this composition was selected for further measurements. Other measurement conditions such as pyrolysis and atomization temperatures were

also optimized for the extraction solution. Fig. 4 shows the absorbance signal as a function of the pyrolysis and atomization temperatures for Cd in extracted, slurry, and digest solutions. The maximum pyrolysis temperature of the analyte in the extracted or digest solutions was higher (>200 °C) than that in the slurry solution (400 °C). Cd may be lost before atomization because of the formation of organic complexes in the condensed phase processes. [15] If Cd is extracted into the aqueous solution, the losses in the condensed phase are reduced, resulting in a higher pyrolysis temperature. As shown in Fig. 4, the optimal pyrolysis and atomization temperatures for the heat extraction procedure were 600 °C and 1500 °C, which were similar to those of the digestion procedure. In addition to the graphite furnace temperature programs described in Table 1, a pre-pyrolysis step (400 °C) was also added, using air to avoid residuals of carbon and chloride.

Analytical performance

Calibrations were carried out using aqueous reference solutions with a linear range extending up to 5.0 ng mL^{-1} Cd. The characteristic mass obtained for the analytes when employing a W-Rh permanent modifier, based on integrated absorbance, was 0.8 ± 0.1 pg Cd. The uncertainties were based on the average of six results obtained on different days with different atomizers. Detection limits (LOD) for 2.5% m/v rice samples were 1.0 ng g^{-1} Cd and were calculated from 11 consecutive measurements of the blank solutions, according to the procedure recommended by IUPAC. Tube lifetimes using different sample preparation procedures with conventional $NH_4H_2PO_4$

+ Mg $(NO_3)_2$ modifiers and a W-Rh permanent modifier are compared in Table 2. The use of a W-Rh permanent modifier prolongs the tube lifetime by 35–65% for all three sample-preparation procedures when compared to the use of conventional $NH_4H_2PO_4$ + Mg $(NO_3)_2$ modifiers. For rice Cd analysis by slurry sampling, the number of analytical firings, when a W-Rh permanent modifier was employed, did not surpass 780. Conversely, when the samples were decomposed or extracted, at least 1260 analytical firings were attained. Remarkable improvements in tube lifetime were attained with heat extraction (Table 2). For a 2.5% m/v rice SRM 1568a extracted solution, the tube lifetime lasted through 1550 firings (versus 790 for slurry sampling, an increase of 96%) for Cd analysis. Although the tube lifetime for microwave digestion with the W-Rh permanent modifier could also be prolonged to last through 1260 analytical firings, sample digestion caused several problems, which could be solved if the analyte was quantitatively extracted into the aqueous phase without drastic decomposition of the sample matrices.

The accuracy of the proposed heat extraction procedure for the determination of Cd was assessed using five rice reference materials (Table 3). For comparison purposes, the microwave digestion method was also employed. The Cd content obtained for the heat extraction method was in agreement with the certified values (Table 3), and the recoveries ranged from 98.4–101.1%. Although Cd recoveries obtained with the microwave digestion method are satisfactory (range from 100–106.3%), the precision is less than that of the heat extraction procedure, likely because of less contamination during pretreatment and low acid interference in the

matrix. Cd in the rice reference material GBW08512 (0.0069 ± 0.0014 μg g^{-1}) could only be detected accurately by the heat extraction method (0.0065 ± 0.0002 μg g^{-1}), and this was attributed to the better detection limits achieved compared to decomposed samples.

Monitoring Cd content in rice samples from Chinese markets

The real samples were analyzed by the proposed HE-ETAAS method, and for comparison, the microwave digestion inductively coupled plasma dynamic reaction cell mass spectrometry (ICP-DRC-MS, for the detailed test procedure, see Guo et al. [26,27]) method was also used. As shown in Fig. 5, there was no difference between the two methods. The mean Cd content was found to be 0.076 mg kg^{-1} (ranging from 0.004 to 0.876 mg kg^{-1}). Only eight samples (4.3%) contained higher levels of Cd than the MAC of 0.20 μg g^{-1}. The results were similar to the report by Fang et al.,[28] who observed a mean level of 0.08 μg g^{-1} (N = 92) in China. However, several studies [29-38] have reported the high mean levels of Cd ranging from 0.10 to 1.91 μg g^{-1} in some areas of Southern China and other countries, which might be due to contamination by industrial pollutants containing heavy metals. Thus, our proposed HE-ETAAS method may be used to monitor even trace levels of Cd in rice in other countries as well.

Conclusions

Superior analytical characteristics such as a simpler and milder operation procedure, low cost, higher sample throughput, lower characteristic masses, detection limits,

longer tube lifetime, and better recoveries of rice samples were obtained with the HE-ETAAS method. This simple and fast method has great potential for the direct and fast monitoring of trace Cd in various food samples for market survey.

Acknowledgements

This work was supported by the National Nature Science Foundation of China (No. 21207120, and 21175120), the National Key Scientific Instrument and Equipment Development Projects of China (No. 2011YQ06010008), and the Fundamental Research Funds for the Central Universities, China University of Geosciences (Wuhan) (No. CUGL140411).

REFERENCES

1. K. Nomiyama, *Sci. Total Environ.*, 1980, **14**, 199-232.

2. M. Murakami, F. Nakagawa, N. AE, M. Ito, and T. Arao, *Environ. Sci. Technol.,* 2009, **43**, 5878-5883.

3. Z. Huang, X. D. Pan, G. P. Wu, J. L. Han, and Q. Chen, *PLOS ONE*, 2013, **8**, e75007.

4. Ministry of Health of the People's Republic of China, Maximum levels of contaminants in foods (GB2762–2012), Beijing, 2012.

5. P. N. Williams, M. Lei, G. X. Sun, G. Q. Huang, Y. Lu, C. Deacon, A. A. Meharg,

and Y. G. Zhu, *Environ. Sci. Technol.*, 2009, **43**, 637-642.

6. H. B. Cao, J. J. Chen, J. Zhang, H. Zhang, L. Qiao, and Y. Men, *J. Environ. Sci.*, 2010, **22**, 1792-1799.

7. P. Zhuang, B. Zou, N. P. Li, and Z. A. Li, *Environ. GeoChem. Health,* 2009, **31**, 707-715.

8. A. A. Meharg, G. Norton, C. Deacon, P. William, E. E. Adomako, A. Price, Y. G. Zhu, G. Li, F. J. Zhao, S. McGrath, A. Villada, A. Sommella, P. M. C. S. De Silva, H. Brammer, T. Dasgupta, and M. R. Islam, *Environ. Sci. Technol.,* 2013, **47**, 5613-5618.

9. P. Wu, C. H. Li, J. B. Chen, C. B. Zheng, and X. D. Hou, *Appl. Spectro. Rev.*, 2012, **47**, 327-370.

10. F. Y. Chen, and S. J. Jiang, *J. Agric. Food Chem.*, 2009, **57**, 6564-6569.

11. D. M. Silvestre, and C. S. Nomura, *J. Agric. Food Chem.*, 2013, **61**, 6299-6303.

12. F. E. Smith, *Talanta*, 1996, **43**, 1207-1268.

13. J. L. Brasil, E. C. Lima, R. C. Veses, and M. M. Tisott, *Atom. Spectrom.*, 2004, **25**, 94-101.

14. P. Vinas, M. Pardo-Martinez, and M. Hernandez-Cordoba, *Anal. Chim. Acta*, 2000, **412**, 121-130.

15. E. C. Lima, F. Barbosa Jr., F. J. Krug, M. M. Silva, and M. G. R. Vale, *J. Anal. At. Spectrom.,* 2000, **15**, 995-1000.

16. J. Sardans, F. Montes, and J. Penuelas, *Spectrochim. Acta Part B,* 2010, **65**, 97-112.

17. N. J. Miller-Ihli, *J. Anal. At. Spectrom.,* 1994, **9**, 1129-1134.

18. F. M. Fortunato, J. A. G. Neto, and G. P. G. Freschi, *Atom. Spectrom.,* 2012, **33**, 138-142.

19. B. Docekal, and V. Krivan, *J. Anal. At. Spectrom.,* 1992, **7**, 521-528.

20. E. C. Lima, Jr. F. Barbosa, F. J. Krug, and U. Guaita, *J. Anal. At. Spectrom.,* 1999, **14**, 1601-1605.

21. E. C. Lima, F. Barbosa Jr., F. J. Krug, and U. Guaita, *J. Anal. At. Spectrom.,* **1999**, 14, 1913-1918.

22. N. J. Miller-Ihli, *J. Anal. At. Spectrom.,* 1988, **3**, 73-81.

23. R. A. Sanchez-Moreno, M. J. Gismera, M. T. Sevilla, and J. R. Procopio, *Phytochem. Anal.,* 2010, **21**, 340-347.

24. C. Maduro, G. Vale, S. Alves, M. Galesio, M. D. R. Gomes da Silva, C. Fernandez, S. Catarino, M. G. Rivas, A. M. Mota, and J. L. Capelo, *Talanta,* 2006, **68**, 1156-1161.

25. E. C. Lima, F. J. Krug, and K. W. Jackson, *Spectrochim. Acta Part B,* 1998, **53**, 1791-1804.

26. W. Guo, S. H. Hu, Y. F. Xiao, H. F. Zhang, and X. J. Xie, *Chemosphere,* 2010, **81**, 1463-1468.

27. W. Guo, S. H. Hu, J. Zhao, S. S. Jin, W. J. Liu, and H. F. Zhang, *Microchem. J.*, 2011, **97**, 154-159.

28. Y. Fang, X. Y. Sun, W. J. Yang, N. Ma, Z. H. Xin, J. Fu, X. C. Liu, M. Liu, A. M. Mariga, X. F. Zhu, and Q. H. Hu, *Food Chem.*, 2014, **147**, 147-151.

29. Y. Du, X. F. Hu, X, H. Wu, Y. Shu, Y. Jiang, and X. J. Yan, *Environ. Monit. Assess.*, 2013, **185**, 9843-9856.

30. F. M. Cheng, N. C. Zhao, H. M. Xu, Y. Li, W. F. Zhang, Z. W. Zhu, and M. X. Chen, *Sci. Total Environ.*, 2006, **359**, 156-166.

31. P. N. Williams, A. Villada, C. Deacon, A. Raab, J. Figuerola, A. J. Green, J. Feldmann, and A. A. Meharg, *Environ. Sci. Technol.*, 2007, **41**, 6854-6859.

32. J. J. Fu, Q. F. Zhou, J. M. Liu, W. Liu, T. Wang, Q. H. Zhang, and G. B. Jiang, *Chemosphere,* 2008, **71**, 1269-1275.

33. P. N. Williams, H. Zhang, W. Davison, S. Z. Zhao, Y. Lu, F. Dong, L. Zhang, and Q. Pan, *Environ. Sci. Technol.*, 2012, **46**, 8009-8016.

34 L. Jorhem, C. Astrand, B. Sundstrom, M. Baxter, P. Stokes, J. Lewis, and K. P. Grawe*, Food Add. Contam.*, 2008, **25**, 284-292.

35 S. Shimbo, Z. Zhang, T. Watanabe, H. Nakatsuka, N. Matsuda-Inoguchi, K. Higashikawa, and M. Ikeda, *Sci. Total Environ.*, 2001, **281**, 165-175.

36 K. A. Wolnik, F. L. Fricke, S. G. Capar, M. W. Meyer, R. D. Satzger, E. Bonnin, and C. M. Gaston, *J. Agric, Food Chem.*, 1985, **33**, 807-811.

37 M. A. Zazouli, M. Shokrzadeh, H. Izanloo, and S. Fathi, *Afr. J. Biotech.*, 2008, **7**, 3686-3689.

38 I. F. Rivai, H. Koyama, and S. Suzuki, *Bull. Environ. Contam. Toxicol.*, 1990, **44**, 910-916.

Figure captions

Figure 1. Effects of extraction conditions on Cd recoveries in rice reference material GBW08511. (a) Effects of HNO_3 concentration, (b) effects of extracting temperature, and (c) effects of extracting time.

Figure 2. Effects of different particle sizes on the recoveries of Cd with the heat extraction procedure. The Cd recovery in rice samples was calculated by normalizing the absorbance value from the HE-ETAAS method to that of the microwave acid digestion ETAAS method.

Figure 3. Cadmium absorbance peak profiles obtained with rice flour SRM NIST 1568a. The solid line represents the Cd signal, and the dotted line represents background absorbance. (a) Heat extraction solution, (b) slurry sampling, and (c) microwave digest solution.

Figure 4. Effects of the pyrolysis and atomization temperatures on the Cd absorbance (rice flour SRM NIST 1568a) with different preparation procedures: heat extraction, slurry sampling, and microwave acid digest.

Figure 5. Difference observed (N = 184) in Cd content ($\mu g\ g^{-1}$) in rice between the proposed HE-ETAAS method and MV-ICP-DRC-MS method.

Table 1 Operating parameters of the graphite furnace and spectrometer

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	400	15	15	50	Air [a]
	600	10	20	250	Ar
Atomization	1500	0	4	0	/
Cleaning	2500	1	3	250	Ar
Wavelength/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 comes from the air compressor.

Table 2 Comparison of the tube lifetimes (N = 3), firings

Sample preparation procedures	Matrix modifier	
	W-Rh	$NH_4H_2PO_4 + Mg(NO_3)_2$
Microwave Digestion	1260 ± 38	920 ± 30
Slurry Sampling	790 ± 44	480 ± 55
Heat extraction	1550 ± 40	1140 ± 35

Table 3 Determination of Cd in rice reference materials by the proposed HE-ETAAS method (N = 5).

Rice SRMs	Certified values	HE-ETAAS		Microwave digestion ETAAS	
		Cd content, μg g^{-1}	Recovery (%)	Cd content, μg g^{-1}	Recovery (%)
NIST1568a	0.022 ± 0.002	0.022 ± 0.001	100.0	0.022 ± 0.003	103.8
GBW08511	0.504 ± 0.018	0.503 ± 0.009	99.8	0.512 ± 0.011	101.7
GBW08512	0.0069 ± 0.0014	0.0065 ± 0.0002	98.6	N.D [a]	N.D [a]
GBW10045	0.19 ± 0.02	0.187 ± 0.004	98.4	0.202 ± 0.012	106.3
GBW10046	0.018 ± 0.002	0.0182 ± 0.001	101.1	0.018 ± 0.005	100

N.D [a] is the non-detectable value.

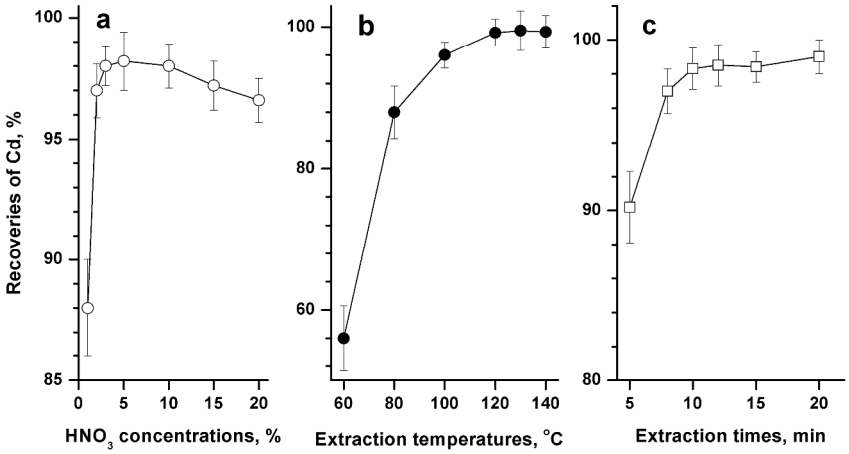


Fig. 1 Effects of extraction conditions on Cd recoveries in rice reference material GBW08511. (a) Effects of HNO_3 concentration, (b) effects of extracting temperature, and (c) effects of extracting time.
297x210mm (300 x 300 DPI)

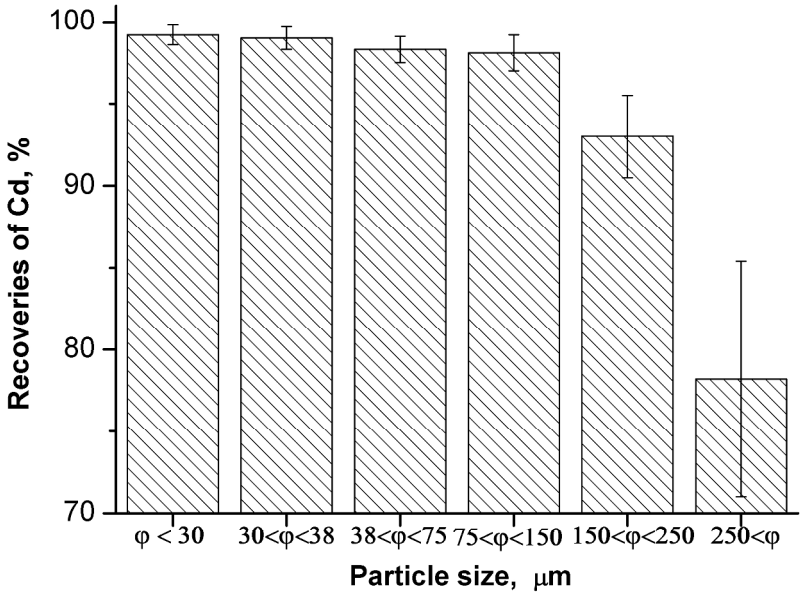


Fig. 2. Effects of different particle sizes on the recoveries of Cd with the heat extraction procedure. The Cd recovery in rice samples was calculated by normalizing the absorbance value from the HE-ETAAS method to that of the microwave acid digestion ETAAS method.
297x210mm (300 x 300 DPI)

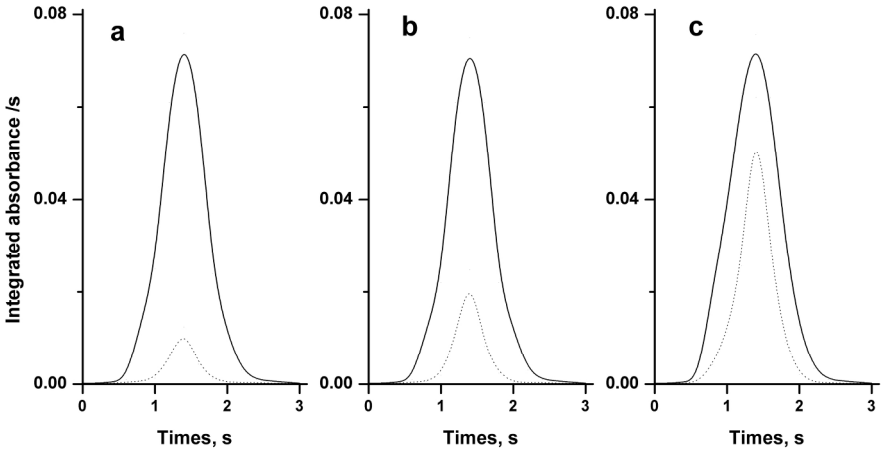


Fig. 3. Cadmium absorbance peak profiles obtained with rice flour SRM NIST 1568a. The solid line represents the Cd signal, and the dotted line represents background absorbance. (a) Heat extraction solution, (b) slurry sampling, and (c) microwave digest solution.
210x148mm (300 x 300 DPI)

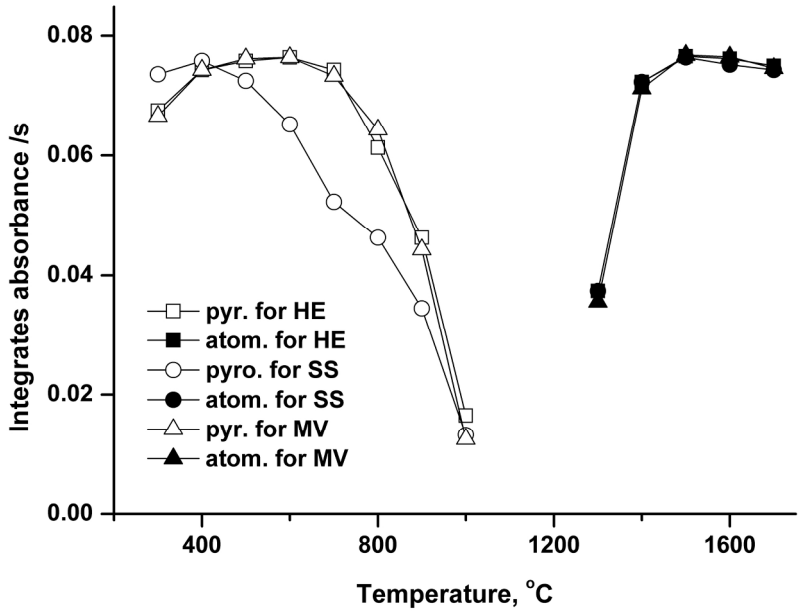


Fig. 4. Effects of the pyrolysis and atomization temperatures on the Cd absorbance (rice flour SRM NIST 1568a) with different preparation procedures: heat extraction, slurry sampling, and microwave acid digest. 210x148mm (300 x 300 DPI)

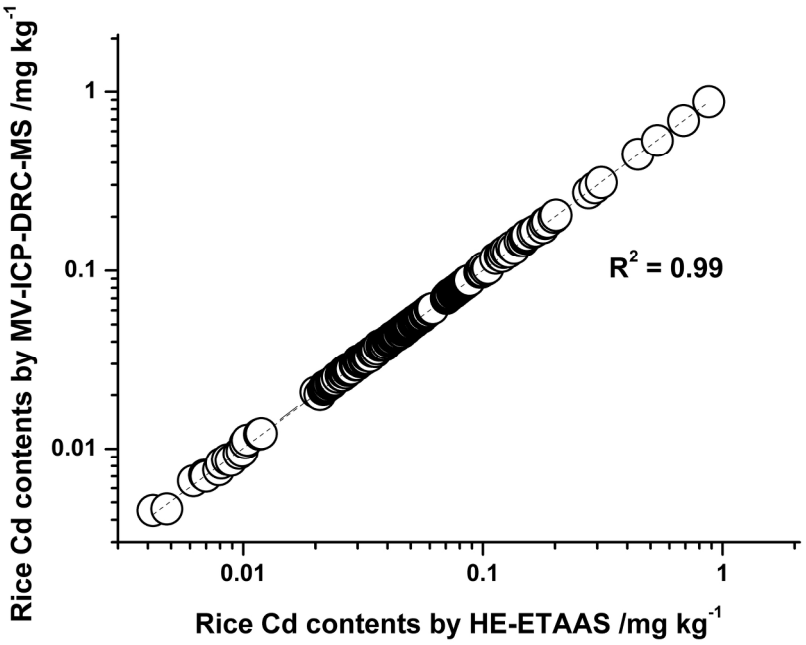


Fig.5. Difference observed (N = 184) in Cd content (mg kg $^{-1}$) in rice between the proposed HE-ETAAS method and MV-ICP-DRC-MS method.
210x148mm (300 x 300 DPI)