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Assessment of Homogeneity and Minimum Sample Mass for Cadmium Analysis in Powdered Certified Reference Materials and Real Rice Samples by Solid Sampling Electrothermal Vaporization Atomic Fluorescence Spectrometry

Xuefei Mao,[†,‡] Jixin Liu,[§] Yatao Huang,[†,‡] Li Feng,[§] Lihua Zhang,[†,‡] Xiaoyan Tang,[†,‡] Jian Zhou,[†,‡] Yongzhong Qian,[†,‡] and Min Wang*[,†,‡]

[†]Institute of Quality Standard and Testing Technology for Agri-products, Chinese Academy of Agricultural Sciences, Beijing 100081, China

[‡]Key Laboratory of Agri-food Safety and Quality, Ministry of Agriculture, Beijing 100081, China

[§]Beijing Titan Instruments Company, Limited, Beijing 100015, China

ABSTRACT: To optimize analytical quality controls of solid sampling electrothermal vaporization atomic fluorescence spectrometry (SS-ETV-AFS), the homogeneity (H_E) of rice samples and their minimum sample mass (M) for cadmium analysis were evaluated using three certified reference materials (CRMs) and real rice samples. The effects of different grinding degrees (particle sizes <0.85, <0.25, <0.15, and >1 mm) on H_E and M of real rice samples were also investigated. The calculated M values of three CRMs by the Pauwels equation were 2.19, 19.76, and 3.79 mg. The well-ground real rice samples (particle size <0.25 mm) demonstrated good homogeneity, and the M values were 3.48−4.27 mg. On the basis of these results, the Cd concentrations measured by the proposed method were compared with the results by microwave digestion graphite furnace atomic absorption spectrometry with a 0.5 g sample mass. There was no significant difference between these two methods, which meant that SS-ETV-AFS could be used to accurately detect Cd in rice with several milligrams of samples instead of the certified value (200 mg) or the recommended mass (200−500 mg) of the methods of the Association of Official Analytical Chemists.

KEYWORDS: *cadmium, rice, minimum sample mass, solid sampling, electrothermal vaporization atomic fluorescence spectrometry (ETV-AFS)*

INTRODUCTION

Cadmium is one of the heavy metals most well-known to be toxic to human health from environmental and industrial contaminants.[1] Transferred through the food chain, Cd is known to be persistent in the human body with long excretion half-lives on the order of years.[2] In recent years, Cd contamination in rice has become an increasing concern in some rice producing and consuming-countries such as China.[3,4] As the leading staple food, rice has been identified as one of the major sources of Cd intake in China.[5]

In monitoring efforts for Cd contamination in rice, many laboratories in China started to apply rice certified reference materials (CRMs) for calibration, quality control, and method validation purposes. The CRMs are key materials improving and maintaining a coherent system of measurements. Due to the fact that the standard deviation (SD) of in-bottle homogeneity of CRMs is usually overestimated, the minimum sample mass in the certificate may also be an overestimation.[6,7] As a result, the certified minimum sample mass of rice CRMs for element analysis is usually more than 200 mg. On the other hand, the recommended minimum sample mass for Cd analysis in classical methods, such as flame atomic absorption spectrometry (FAAS),[8] graphite furnace AAS (GF-AAS), inductively coupled plasma mass spectrometry (ICP-MS),[9,10] etc., were usually more than several hundreds of milligrams. However, a larger sample mass consumes not only excessive CRMs and samples but also more toxic and harmful reagents in the digestion process.

At present, some digestion-free analytical methods have been developed and reported, such as instrumental neutron activation analysis (INAA),[11] synchrotron radiation X-ray fluorescence (SRXRF),[12] electrothermal AAS (ET-AAS),[13] electrothermal vaporization atomic fluorescence spectrometry (ETV-AFS),[14,15] etc. Only minute amounts of samples at the milligram or submilligram level are used for a single determination in the above cases. Unfortunately, the maximum sample intakes of these methods are too small to meet the certified minimum values of CRMs, so the required quality control assurances by CRMs cannot be performed.[16]

Sufficient homogeneity of powder CRMs and real samples is considered to be the most crucial prerequisite for choosing the minimum representative sample mass in elemental analysis. Hence, Kurfürst et al.[17] introduced relative homogeneity factors (H_E) to quantify the homogeneity of an element in a certain matrix on the basis of a modification of the Ingamells sampling constant K_S.[18] H_E is frequently selected as a homogeneity indicator in reference material evaluation and production.[19,20]

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Pauwels et al.[21] deduced an equation of minimum sample mass (*M*) for powdered reference materials by measuring elements in subsamples at the milligram or submilligram level. The *M* value mainly depends on the reference material's uncertainty, the relative standard deviation (RSD) of all measurements, and the number and weight of the subsamples. Rossbach and Grobecker[11] applied the Pauwels equation to assess the minimum sample mass of the International Atomic Energy Agency (IAEA) lichen candidate reference material for Cd and Pb measured by solid sampling AAS (SS-AAS). The mean subsample mass ranged from 0.19 to 0.34 mg, while the mean values of *M* were 5.6 and 3.81 mg, respectively. As shown above, the maximum sample intakes were usually lower than 1 mg, so the calculated *M* values by microanalysis methods did not fit themselves. Although worse precision due to sample heterogeneity was able to be compensated by the generally larger set of replicates in microsample analysis,[22] too many replicates of unknown samples were so complicated and impracticable that many direct sampling analytical methods were not suitable for in-field and rapid detection in agrifood due to their incompetent maximum sample intakes.

In spite of that, a large number of studies repeatedly reported the advantages of direct sampling analysis, such as SS-AAS,[23,24] ETV-AFS,[14,15] ETV-ICP-AES,[25] SS-ETV-ICP-MS,[26] SRXRF,[12] INAA,[11] etc. Among these, AFS is a sensitive technique for Cd determination because of its low spectral interference. In 1970, Bratzel et al.[27] first used the tungsten wire loop as an atomizer for AFS. In the ensuing 30 years, the tungsten coil (TC) atomizer for AFS was further developed in many studies.[14,15,28−30] Wu et al.[30] reported a TC ETV-AFS method, which could be used to detect Cd with high sensitivity in liquid and slurry samples. Our previous work successfully established a new method for trace Cd determination in some biological samples by SS-ETV-AFS, which used a graphite felt as the vaporizer and a TC as the Cd trap.[14] Due to the minute amounts (approximate 10 mg) of maximum sample intake for SS-ETV-AFS, it was necessary to develop the homogeneity studies into microscale to demonstrate that the sampling would be representative.

In this work, SS-ETV-AFS was used to detect Cd in rice samples for the purpose of assessing the homogeneity and minimum sample mass. On the basis of the H_E and the Pauwels equations, the H_E and *M* values of three CRMs and several real rice samples for Cd analysis were assessed and confirmed. Here the SS-ETV-AFS method has proven advantageous for Cd determination in rice because it is sensitive, stable and fast. Moreover, it requires a small sample mass, and has an easy operation without digest pretreatment. We believe this method is extremely suitable for in-field and rapid detection in markets and rural areas.

■ MATERIALS AND METHODS

Instrumentation. The solid sampling device of Cd (model DCD-200) and the graphite fiber felt sample boat were made by the Beijing Titan Instruments Co., Ltd. (Beijing, China) and SANYE Carbon Materials Factory (Shandong, China), respectively. A Ni−Cr coil was used as a furnace for sample drying and ashing in an open atmosphere. A sample boat was installed in a 40 mL aluminum cavity, which was sealed and passed through H_2 + Ar to avoid the loss of analyte during the vaporization step. A 2 mm ⌀ × 10 mm 10-circle TC (Xiamen Honglu Tungsten Molybdenum Industry Co. Ltd., Fujian, China) was mounted at the exit of the vaporizer cavity as a trap which was sealed in a small aluminum trap cavity (2 mL). The ashing furnace, vaporizer, and trap were all program-controlled. A 600 mL/min flow rate of 10% H_2 + Ar as the carrier was used to sweep the vaporized Cd into the AFS instrument. The program of the DCD-200 for ashing, vaporization, trapping, release, and cleaning are shown in Table 1.

Table 1. Program of the Solid Sampling Device

no.	program	time (s)	power (W)	signal acquisition
1	ashing	30−100	90	no
2	cooling	5	0	no
3	vaporization/trap	30	70	no
4	vaporization/trap	5	0	no
5	vaporization/trap	15	0	no
6	release	1	30	yes
7	cooling	5	0	yes
8	cleaning	1.5	35	no
9	cooling	5	0	no

The AFS instrument (model AFS 8220, Beijing Titan Instruments Co. Ltd.) was equipped with a Cd-boosted hollow cathode lamp (HCL; 228.8 nm, Beijing Research Institute of Nonferrous Metals, Beijing, China) as the light source. The HCL was operated at 50−80 mA, and the working voltage for the photomultiplier ranged from −360 to −230 V. An approximately 30 cm silicone tube connected the shield quartz atomizer of the AFS with the trap as the interface, and the atomizer was not ignited.

The GF-AAS instrument (model AA800, with a Cd hollow cathode lamp, PerkinElmer, Waltham, MA) was used to determine Cd in rice samples after microwave digestion for the purpose of verifying the results of SS-ETV-AFS in this work. The detailed operating conditions of GF-AAS are listed in Table 2.

Reagents and Samples. A standard stock solution (1000 mg/L) of Cd and three CRMs of the rice component (−80 mesh, GBW10043, GBW10010, and GBW10045) were purchased from the National Standard Center of China (Beijing, China). A working standard solution was obtained by stepwise dilution of the standard stock solution with deionized (DI) water (Milli-Q Integral Water Purification System, Millipore, Billerica, MA). HNO_3 and H_2O_2 (Guarantee reagent, Beijing Chemical Reagents Co., Beijing, China) were used for the digestion of the rice sample, and $(NH_4)_3PO_4$ (Guarantee reagent, Beijing Chemical Reagents Co.) was used as a matrix modifier in GF-AAS detection.

Rice sample no. 1 purchased from a supermarket in Beijing was separated into four parts (about 200 g for each) by grinding and sieving by particle size (<0.85, <0.25, and <0.15 mm, namely, −20, −60, and −100 mesh, and simple grinding at >1 mm, respectively), and the four parts were prepared for assessment of H_E and *M* of powdered rice samples. Four other rice samples purchased from supermarkets in Beijing, named no. 2, no. 3, no. 4, and no. 5, respectively, were ground and sieved to pass 60 mesh for comparison of SS-ETV-AFS with GF-AAS. Detailed information for sample nos. 2−5 is listed in Table 5.

Analytical Procedures for SS-ETV-AFS. A schematic diagram of the analytical procedures for SS-ETV-AFS is shown in Figure 1. First, several milligrams (accurate to 0.01 mg) of sample was put into the sample boat and delivered into the ashing furnace. The sample was dried at approximately 100 °C for tens of seconds to remove water and ashed at approximately 500 °C for another tens of seconds to remove most of the organic matrix (Figure 1, panel 1). At the end of this step, the sample was converted to a gray residue. Then the boat was moved into the vaporizer, which was electrically heated at approximately 1200 °C for tens of seconds to vaporize Cd within the residue (Figure 1, panel 2a). The vaporized cadmium was purged out and trapped on a TC at room temperature to separate the remaining matrix (Figure 1, panel 2b). Finally, Cd was released from the trap and measured by AFS (Figure 1, panels 3a and 3b).

Analytical Procedures for GF-AAS. HNO_3 (6 mL) and H_2O_2 (2 mL) were added to a Teflon vessel (60 mL), to which approximately 0.5 g of rice powder had been added. The closed vessels were put into

Table 2. Instrumental Parameters for GF-AAS

element	wavelength (nm)	slit width (nm)	lamp current (mA)	program	temp (°C)	rise time (s)	keep time (s)	flow rate of Ar gas (mL/min)
Cd	228.8	0.7	4	drying	110	1	30	250
				drying	130	15	30	250
				ashing	500	10	20	250
				atomization	1600	0	5	0
				cleaning	2450	1	3	250

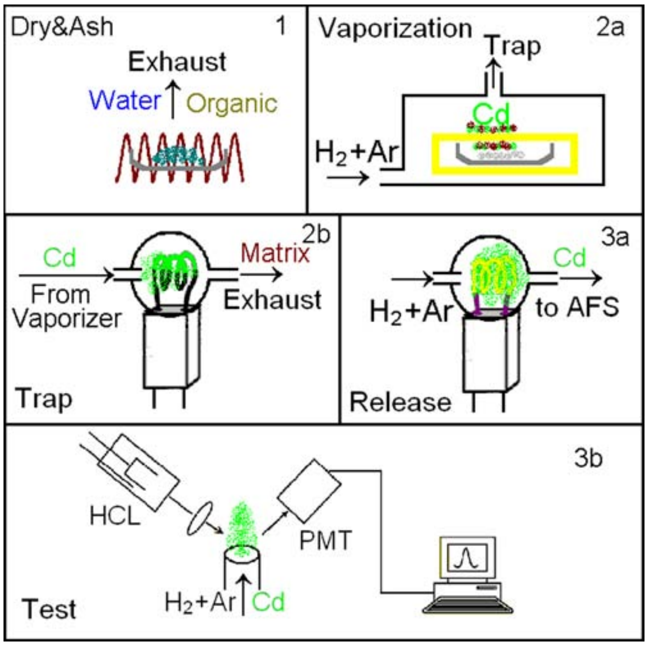

Figure 1. Schematic diagram of the analytical procedures for SS-ETV-AFS.

the microwave digestion system (model MARS, CEM, Matthews, NC), heated to 160 °C in 10 min, and then kept at that temperature for 25 min. After removal of the acid by electrical heating, the digests were transferred and quantitatively diluted to 25 mL after cooling. The solutions were sufficiently homogenized and then subjected to measurement by GF-AAS.

Statistical Analysis. Results from the experiments were statistically evaluated using the statistical software SAS 9.1. The statistical significance of the difference was assessed by Duncan's multiple range test. A probability of 0.05 or lower ($p < 0.05$) was considered as significant.

■ RESULTS AND DISCUSSION

Calibration Curves and Analytical Performance of SS-ETV-AFS. Analytical figures of merit of SS-ETV-AFS for Cd were obtained under the optimal instrumental conditions. To correct for rice matrix effects, the calibration curves were established by adding several milligrams of blank rice matrix with each 10 μL calibration solution. An R^2 (correlation coefficient) of at least 0.995 showed good linearity ranging from 0.2 μg/L to 1.0 mg/L. The LOD was 40 ng/L (0.4 pg), which was equal to 3σ of 10 measurements of 200 ng/L (2.0 pg) working standard solutions. The LOQ was 160 ng/L (1.6 pg), which was equal to 10σ of 6 measurements of blank rice samples added with 200 ng/L (2.0 pg) working standard solutions. The RSDs were less than 5% at 2 μg/L (20 pg) and 20 μg/L (200 pg) working standard solutions from 10 measurements, which indicated good stability of the instrument.

Equation of Homogeneity. The relative homogeneity factor H_E (Kurfürst) is a very important indicator of homogeneity for elemental analysis in a given matrix. A value less than or equal to 10 means a good homogeneity:

$$H_E = (\mathrm{RSD})m^{1/2}$$

RSD = relative standard deviation of all measurements, and m = mean sample mass (mg).

As an example, we have calculated H_E to obtain a 14.3% RSD in repetitive measurements for Cd in GBW10043 samples: RSD of the homogeneity study, 14.3%; mean mass used for the homogeneity study, 1.03 mg.

$$H_E = 14.3 \times 1.03^{1/2} = 14.5$$

Pauwels Equation. The minimum sample mass is the smallest portion drawn correctly from the whole that can be considered as being representative under a certain uncertainty. The equation of minimum sample mass (Pauwels) is assessed from repetitive measurements for an element in a smaller unit of mass of subsamples (always milligram level or less) at a given confidence level:

$$M = (k_2'(\mathrm{RSD})/\mathrm{UNC})^2 m$$

M = minimum sample mass (mg), k_2' is a factor for two-sided tolerance limits of normal distributions as given in a standard statistical textbook,[31] and UNC denotes the uncertainty level at which M should be given.

As an example, we have calculated the M in repetitive measurements for Cd in GBW10043 samples: UNC = 25%; k_2' = 2.549 (P = 0.95, α = 0.05, n = 30); RSD of the homogeneity study, 14.3%; mean mass used for the homogeneity study, 1.03 mg

$$M = [(2.549 \times 14.3\%)/25\%]^2 \times 1.03\text{ mg} = 2.19\text{ mg}$$

Table 3. H_E and M Values of Three CRMs for Cd Analysis

CRM	certified min sample mass (mg)	certified concn (μg/kg)	n	UNC (%)	concn found by SS-ETV-AFS[a] (μg/kg)	RSD (%)	m (mg)	H_E	M[b] (mg)
GBW10043	200	12.0 ± 3.0	30	25.0	9.6 ± 1.4	14.3	1.03	14.5	2.19
GBW10010	200	87.0 ± 5.0	30	5.7	91.6 ± 8.9	9.7	1.05	9.9	19.76
GBW10045	200	190.0 ± 20.0	30	10.5	187.2 ± 14.7	7.9	1.03	8.0	3.79

[a] Average ± standard deviation of 30 replicates. [b] k_2' = 2.549 (P = 0.95, α = 0.05, n = 30).

Homogeneity (in Bottle) and Minimum Sample Mass of Three CRMs. The Cd concentrations in three CRMs, namely, GBW10043, GBW10010, and GBW10045, were repeatedly measured 30 times by SS-ETV-AFS at approximately 1 mg sample mass. The mean Cd concentrations of these CRMs shown in Table 3 are 9.6, 91.6, and 187.2 μg/kg, respectively, and are in good agreement with the certified values.

In Table 3, H_E and M values of three CRMs are given. At a mean subsample mass of 1.03−1.05 mg, the H_E values of GBW10010 and GBW10045 were less than 10, which indicated their good homogeneity. In contrast, the homogeneity of GBW10043 was not so satisfying. The M values of three CRMs were 2.19−19.76 mg, which were obviously much lower than the certified value 200 mg. According to the Pauwels equation, when the sampling number ($n = 30$) and mean weight of the subsamples are relatively identical among the three CRMs, the value of M rests with the RSD of the measurements and UNC of the CRMs. In other words, the smaller the RSD or the higher the UNC, the lower the M value. Hence, although the homogeneity of GBW10043 was the worst, the corresponding M was the smallest one because of the highest UNC. However, the highest M value of GBW10010 was mainly due to its lowest UNC value (5.8%), which was approximately half the M value of GBW10045.

For the uncertainty components of microsample analysis, in addition to the heterogeneity of the samples, the influences of balancing and measuring errors cannot be neglected either. In this work, the RSD of 30 measurements from one piece of nylon cord ($n = 30$, $\overline{m} \approx 1.10$ mg) by microbalance was 3.7%, and the RSDs of 10 measurements of 2−10 μL of water using a micropipet (Eppendorf, Germany) by microbalance ranged from 0.96% to 2.75%. If the above measuring errors were considered, the coefficients of variation merely from the heterogeneity of the samples were possibly smaller than the RSDs in Table 3, so the minimum sample masses of the CRMs were probably lower than the results calculated by the Pauwels equation. The results verified that the recommended minimum sample mass in the certificate was too conservative, which agreed with other studies.[11,12,32,33] According to the results, the quality control of SS-ETV-AFS could be performed with several milligrams of CRMs, which was very important for the further application of SS-ETV-AFS.

Homogeneity and Minimum Sample Mass of Real Rice Samples. According to the above-mentioned sample preparation, rice sample no. 1 with four different grinding degrees (approximately 1 mg for each) was measured 20 times by SS-ETV-AFS, and the results are listed in Table 4. It was shown that the mean Cd concentrations of four treatments ranged from 17.4 to 25.9 μg/kg. Among them, the mean value of the simply ground sample significantly ($p < 0.05$) deviated from those of the others at the 95% confidence level, probably due to its poor homogeneity ($H_E = 99.6$, i.e., $\gg 10$). Although the mean value of the −20 mesh treatment showed no significant difference compared to those of the other two at the 95% confidence level ($p > 0.05$), its homogeneity ($H_E = 29.6$, i.e., >10) was much worse than those of the others ($H_E = 6.8$ and 7.5, respectively).

Table 4. H_E and M Values of Rice Sample No. 1 for Cd Analysis at Different Grinding Degrees

grinding deg (mesh)	n	concn found by SS-ETV-AFS[a] (μg/kg)	RSD (%)	m (mg)	H_E	$M_{10\%}$[b] (mg)
100	20	25.5 ± 1.7	6.7	1.03	6.8	3.48
60	20	24.8 ± 1.9	7.5	1.01	7.5	4.27
20	20	25.9 ± 7.7	29.6	1.00	29.6	66.31
simply ground	20	17.4 ± 17.2	99.1	1.01	99.6	750.91

[a] Average ± standard deviation of 20 replicates at a mean sampling mass of ∼1 mg. [b] $M_{10\%}$ is the minimum sample mass at UNC = 10% and $k_2' = 2.752$ ($P = 0.95$, $\alpha = 0.05$, $n = 20$).

Unlike CRMs, there was no certified uncertainty for real rice samples because of the absence of the certified UNC value. However, for microsample analysis, the relative uncertainty of repeated measurements within ±10% was proved acceptable; hence, 10% was selected as the value of UNC to assess the M values of real rice samples in this work. In Table 4, the $M_{10\%}$ values of −60 mesh and −100 mesh treated samples were 3.48 and 4.27 mg, respectively, which were much smaller than the recommended minimum sample mass of 200−500 mg in AOAC methods.[9] In agreement with the heterogeneity mentioned above, the $M_{10\%}$ values of −20 mesh and simply ground samples were more than 60 and 750 mg, respectively. The results exceeded the designed maximum sample intake of the sample boat for SS-ETV-AFS.

As a result, the minimum sample mass of real rice samples could be decreased to 3−4 mg for Cd analysis by SS-ETV-AFS when the powder particle sizes were smaller than 0.25 mm (−60 mesh), which meant that the calculated M values were fit for the sampling intakes of SS-ETV-AFS. In this regard, the proposed method was remarkably superior to other solid microsampling techniques, such as SS-AAS,[23,24] SS-ETV-ICP-MS,[26] SRXRF,[12] INAA,[11] etc., because the calculated sampling mass of the other methods were usually not fit for the sampling intake of the instruments.

Verification of the Calculated *M* Values. According to the calculated M values in Tables 3 and 4, 3 and 4 mg were chosen as the sampling mass for Cd determination by SS-ETV-AFS in CRMs and real rice samples (nos. 1−5), respectively. Table 5 shows the results measured by SS-ETV-AFS and GF-AAS. Cd concentrations of approximately 3 mg of CRMs found by SS-ETV-AFS were in good agreement with the certified values. Moreover, all analytical results of approximately 4 mg of sample nos. 1−5 from markets measured by SS-ETV-AFS showed no significant difference ($p > 0.05$) from those by GF-AAS at the 95% confidence level. Meanwhile, the mean Cd concentrations of approximately 4 mg of rice sample no. 1 ($n = 4$) were consistent with the results (approximately 1 mg, $n = 20$) in Table 4.

The results demonstrated that the proposed method was a good solid microsample analysis technique to determine trace Cd in rice and avoided troublesome digestion and unnecessary dilution procedures. It was also proved that 3 mg for three CRMs (−80 mesh) and 4 mg for real rice powdered samples of −60 mesh treatment were adequate for sample representation, instead of the certified value (200 mg) and the recommended mass (200−500 mg) of the AOAC methods. Due to the uncertainty of overestimation from in-bottle heterogeneity and the neglect of measurement and weighing errors in the total RSD,[6,34] 3 mg was obviously smaller than the calculated M value of GBW10010 in Table 3, which proved that the real minimum sample mass of a well-ground powdered rice sample could be smaller than that calculated by the Pauwels equation. The results were extremely useful for the further development

Table 5. Verification of Calculated *M* Values in CRMs and Some Real Rice Samples

sample no.	concn found by SS-ETV-AFS (μg/kg)	certified or GF-AAS concn[c] (μg/kg)	variety	place of origin
GBW10043	9.9 ± 0.6[a]	12.0 ± 3.0		Liaoning Province
GBW10010	90.0 ± 1.9[a]	87.0 ± 5.0		
GBW10045	180.7 ± 9.4[a]	190.0 ± 20.0		Hunan Province
1 (−100 mesh)	26.0 ± 1.1[b]	25.0 ± 1.9	japonica rice	Northeast China
1 (−60 mesh)	27.5 ± 1.7[b]	26.6 ± 0.7	japonica rice	
2	86.9 ± 2.7[b]	87.6 ± 2.3	glutinous rice	
3	7.6 ± 0.8[b]	6.5 ± 1.1	japonica rice	Jilin Province
4	6.4 ± 0.7[b]	6.0 ± 1.0	japonica rice	
5	21.8 ± 1.0[b]	19.9 ± 1.8	japonica rice	Heilongjiang Province

[a] Average ± standard deviation of four replicates at a mean sampling mass of ∼3 mg. [b] Average ± standard deviation of four replicates at a mean sampling mass of ∼4 mg. [c] Average ± standard deviation of four replicates at a mean sampling mass of ∼0.5 g.

of SS-ETV-AFS as a novel method for in-field and rapid detection in agrifood.

■ AUTHOR INFORMATION

Corresponding Author

*Phone and fax: +86-10-82106566. E-mail: wangmincaas@126.com.

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Notes

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■ REFERENCES

(1) Lauren, S. J. Chemical food safety issues in the United States: past, present, and future. *J. Agric. Food Chem.* **2009**, *57*, 8161−8170.

(2) International Programme on Chemical Safety. *Environmental Health Criteria 134: Cadmium*; World Health Organization (WHO): Geneva, Switzerland, 1992.

(3) Cheng, F. M.; Zhao, N. C.; Xu, H. M.; Li, Y.; Zhang, W. F.; Zhu, Z. W.; Chen, M. X. Cadmium and lead contamination in japonica rice grains and its variation among the different locations in southeast China. *Sci. Total Environ.* **2006**, *359*, 156−166.

(4) Xu, Y. Pollution and risk evaluation of lead, cadmium and mercury in rice in the markets of Anhui Province. *Jiangxi Food Ind.* **2011**, *3*, 32−33 (in Chinese with English abstract).

(5) Zhang, Z. W.; Watanabe, T.; Shimbo, S.; Higashikawa, K. H.; Ikeda, M. Lead and cadmium content in cereals and pulses in north-eastern China. *Sci. Total Environ.* **1998**, *220*, 137−145.

(6) Xu, J. P.; Hu, X. Y.; Xue, N. Estimation for minimum count of sampling based researching the uniformity of RM. *Metall. Stand. Qual.* **2012**, *50*, 25−27 (in Chinese with English abstract).

(7) *ISO Guide 35:2006: Reference Materials—General and Statistical Principles for Certification*; International Organization for Standardization (ISO): Geneva, Switzerland, 2006.

(8) Ye, Q. Y.; Li, Y.; Jiang, Y.; Yan, X. P. Determination of trace cadmium in rice by flow injection on-line filterless precipitation−dissolution preconcentration coupled with flame atomic absorption spectrometry. *J. Agric. Food Chem.* **2003**, *51*, 2111−2114.

(9) *AOAC Official Method 999.10. Lead, Cadmium, Zinc, Copper, and Iron in Foods Atomic Absorption Sepctrophotometry after Microwave Digestion*; AOAC International: Gaithersburg, MD, 2011.

(10) Perelló, G.; Martí-Cid, R.; Llobet, J. M.; Domingo, J. L. Effects of various cooking processes on the concentrations of arsenic, cadmium, mercury, and lead in foods. *J. Agric. Food Chem.* **2008**, *56*, 11262−11269.

(11) Rossbach, M.; Grobecker, K. H. Homogeneity studies of reference materials by solid sampling-AAS and INAA. *Accredit. Qual. Assur.* **1999**, *4*, 498−503.

(12) Feng, S. L.; Xu, Q.; Lei, Y.; Cheng, L.; Feng, X. Q.; Fan, D. Y.; Sha, Y.; Huang, Y. Y.; He, W. Study of minimum analytic mass of microanalysis reference material with SRXRF. *High Energy Phys. Nucl. Phys.* **2003**, *27*, 105−108 (in Chinese with English abstract).

(13) Bruhn, C. G.; Ambiado, F. E.; Cid, H. J.; Woerner, R.; Tapia, J.; Garcia, R. Analytical evaluation of a tungsten coil atomizer for cadmium, lead, chromium, manganese, nickel and cobalt determination by electrothermal atomic absorption spectrometry. *Anal. Chim. Acta* **1995**, *306*, 183−192.

(14) Feng, L.; Liu, J. X. Solid sampling graphite fibre felt electrothermal atomic fluorescence spectrometry with tungsten coil atomic trap for the determination of cadmium in food samples. *J. Anal. At. Spectrom.* **2010**, *25*, 1072−1078.

(15) Wen, X. D.; Wu, P.; Chen, L.; Hou, X. D. Determination of cadmium in rice and water by tungsten coil electrothermal vaporization-atomic fluorescence spectrometry and tungsten coil electrothermal atomic absorption spectrometry after cloud point extraction. *Anal. Chim. Acta* **2009**, *650*, 33−38.

(16) Zeisler, R. Reference materials for small-sample analysis. *Fresenius' J. Anal. Chem.* **1998**, *360*, 376−379.

(17) Kurfürst, U.; Pauwels, J.; Grobecker, K. H.; Stoeppler, M.; Muntau, H. Micro-heterogeneity of trace elements in reference materials—determination and statistical evaluation. *Fresenius' J. Anal. Chem.* **1993**, *345*, 112−120.

(18) Ingamells, C. O.; Switzer, P. A proposed sampling constant for use in geochemical analysis. *Talanta* **1973**, *20*, 547−586.

(19) Pauwels, J.; Hofmann, C.; Grobeeker, K. H. Homogeneity determination of Cd in plastic CRMs using solid sampling atomic absorption spectrometry. *Fresenius' J. Anal. Chem.* **1993**, *345*, 475−477.

(20) Friese, K. C.; Grobecker, K. H.; Wätjen, U. Development of an electrothermal vaporization ICP-MS method and assessment of its applicability to studies of the homogeneity of reference materials. *Fresenius' J. Anal. Chem.* **2001**, *370*, 499−507.

(21) Pauwels, J.; Vandecasteele, C. Determination of the minimum sample mass of a solid CRM to be used in chemical analysis. *Fresenius' J. Anal. Chem.* **1993**, *345*, 121−123.

(22) Kurfürst, U.; Rehnert, A.; Muntau, H. Uncertainty in analytical results from solid materials with electrothermal atomic absorption spectrometry: a comparison of methods. *Spectrochim. Acta, Part B* **1996**, *51*, 229−244.

(23) Pauwels, J.; Hofmann, C.; Vandecasteele, C. On the usefulness of SS-ZAAS for the microhomogeneity control of CRM's. *Fresenius' J. Anal. Chem.* **1994**, *348*, 418−421.

(24) Lisia, M. G. D. S.; Bernhard, W.; Rennan, G. O.; Araujo, S. D. C. J.; Maria, G. R. V.; Andreas, M.; Irland, B. G. M.; Helmut, B. R. Simultaneous determination of Cd and Fe in beans and soil of different regions of brazil using high-resolution continuum source graphite furnace atomic absorption spectrometry and direct solid sampling. *J. Agric. Food Chem.* **2009**, *57*, 10089−10094.

(25) Chen, S. Z.; Li, F.; Liao, Z. H.; Peng, T. Y.; Jiang, Z. C. Study on the direct analysis of solid powder biological samples using fluorination assisted electrothermal vaporization inductively coupled plasma atomic emission spectrometry with PTFE slurry modifier. *Fresenius' J. Anal. Chem.* **1999**, *364*, 556−559.

(26) Martin-Esteban, A.; Slowikowski, B.; Grobecker, K. H. Correcting sensitivity drift during long-term multi-element signal measurements by solid sampling-ETV-ICP-MS. *Talanta* **2004**, *63*, 667−673.

(27) Bratzel, M. P.; Dagnall, R. M.; Winefordner, J. D. A hot wire loop for atomic fluorescence spectrometry. *Appl. Spectrosc.* **1970**, *24*, 518−521.

(28) Atnashev, Y. B.; Korepanov, V. E.; Muzgin, V. N. A spiral tungsten atomizer in atomic-fluorescence analysis. *J. Appl. Spectrosc.* **1983**, *39*, 1230−1233.

(29) Grazhulene, S. S.; Khvostikov, V. A.; Vykhristenko, N. N.; Sorokin, M. V. Determination of lead in natural and waste waters using a non-dispersive atomic fluorescence spectrometer with a tungsten spiral atomizer. *J. Anal. At. Spectrom.* **1992**, *7*, 105−108.

(30) Wu, P.; Wen, X. D.; He, L.; He, Y. H.; Chen, M. Z.; Hou, X. D. Evaluation of tungsten coil electrothermal vaporization-Ar/H_2 flame atomic fluorescence spectrometry for determination of eight traditional hydride-forming elements and cadmium without chemical vapor generation. *Talanta* **2008**, *74*, 505−511.

(31) Natrella, M. G. Experimental statistics. *NBS Handbook 91*; National Bureau of Standards: Washington, DC, 1966, T.11-T.13.

(32) Huang, D. H.; Xiao, C. J.; Ni, B. F.; Tian, W. Z.; Zhang, Y. X.; Wang, P. S.; Zhang, G. Y.; Liu, C. X. Preliminary study on reference material for microanalysis quality control. *At. Energy Sci. Technol.* **2009**, *43*, 1123−1127 (in Chinese with English abstract).

(33) Nomura, C. S.; Silva, C. S.; Nogueira, A. R. A.; Oliveira, P. V. Bovine liver sample preparation and micro-homogeneity study for Cu and Zn determination by solid sampling electrothermal atomic absorption spectrometry. *Spectrochim. Acta, Part B* **2005**, *60*, 673−680.

(34) Štupar, J.; Dolinšek, F.; Koren, U. Estimation of the homogeneity of reference materials by SS-ETAAS and use of the "tape-sandwich" sample-introduction technique. *Anal. Bioanal. Chem.* **2002**, *374*, 968−976.