

Slurry Sampling Flow Injection Chemical Vapor Generation Inductively Coupled Plasma Mass Spectrometry for the Determination of As, Cd, and Hg in Cereals

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A slurry sampling inductively coupled plasma mass spectrometry (ICP-MS) method has been developed for the determination of As, Cd, and Hg in cereals using flow injection chemical vapor generation (VG) as the sample introduction system. A slurry containing 6% m/v flour, 0.7% m/v thiourea, 0.4 $\mu\text{g mL}^{-1}$ Co(II), and 2.5% v/v HCl was injected into a VG-ICP-MS system for the determination of As, Cd, and Hg without dissolution and mineralization. Because the sensitivities of the elements studied in the slurry and that of aqueous solution were quite different, a standard addition method and an isotope dilution method were used for the determination of As, Cd, and Hg in selected cereal samples. The influences of vapor generation conditions and slurry preparation on the ion signals were reported. The effectiveness of the vapor generation sample introduction technique in alleviating various spectral interferences in ICP-MS analysis has been demonstrated. This method has been applied for the determination of As, Cd, and Hg in NIST SRM 1567a Wheat Flour reference material, NIST SRM 1568a Rice Flour reference material, and cereal samples obtained from local market. The As, Cd, and Hg analysis results of the reference materials agreed with the certified values. The method detection limits estimated from standard addition curves were about 0.10, 0.16, and 0.07 ng g^{-1} for As, Cd, and Hg, respectively, in the original cereal samples.

KEYWORDS: Inductively coupled plasma mass spectrometry; slurry sampling; chemical vapor generation; cereals; As; Cd; Hg

INTRODUCTION

Inductively coupled plasma mass spectrometry (ICP-MS) is a technique for elemental and isotopic analysis that combines the remarkable characteristics of the ICP for atomization and ionization of injected samples with sensitivity and selectivity of mass spectrometry. The most common sample introduction method for ICP-MS is the pneumatic nebulization of solution. Although it is simple and offers good stability, sample introduction is inefficient, only 1–3% of the sample being introduced into the plasma. Hence, efforts have been made to couple alternative sample introduction systems to ICP-MS to extend its application range. The type of analytical tasks that can be solved by ICP-MS can be extended using a number of other sample introduction techniques that are compatible with ICP-MS. Vapor generation (VG) is one of the sample introduction techniques that are currently employed in ICP-MS (1–8). Several studies have shown that the sensitivity and detection limits of vapor-forming elements are greatly improved when they are introduced into the plasma as vapors. Additionally, it was also shown that appropriate vapor generation conditions can be used to remove or separate the analyte from problematic matrix species, which would otherwise cause spectral and nonspectral interferences (8, 9). Vapor introduction in flow injection mode is a simple and rapid technique that has been coupled to ICP-MS previously (5, 10, 11). In the

present investigation, a simple, laboratory-built vapor generation system is used as the sample introduction device for flow injection ICP-MS.

Rice and wheat are two important foods for human beings in most parts of the world. However, environmental pollution can cause increased levels of toxic elements in these cereals, which result in detrimental effects on human health. Moreover, some of the metals are the subject of food legislation. Thus, the determination of trace elements in cereals, in order to measure the levels of toxic elements, is important. ICP-MS has been applied for the determination of trace elements in various food samples (12–16). Most of the analyses need tedious sample dissolution and pretreatment steps (16). In this work, a slurry sampling technique combined with chemical vapor generation ICP-MS has been proposed as an alternative for avoiding the need for dissolution or mineralization steps (3, 17, 18). Ribeiro et al. employed online hydride generation ICP-MS to determine As, Sb, Se, Sn, and Hg in environmental reference materials as acid slurries (3). Cava-Montesinos et al. applied slurry sampling hydride generation atomic fluorescence spectrometry to the determination of As, Sb, Se, Te, and Bi in milk (18). To the best of our knowledge, there are no slurry sampling VG-ICP-MS applications for trace As, Cd, and Hg determinations in cereals. Compared to traditional sample preparation methods such as acid digestion and dry ashing, slurry sampling offers several benefits including reduced sample preparation time, reduced possibility of sample contamination, and decreased possibility of analyte loss before analysis.

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Table 1. ICP-MS Equipment and Operating Conditions

ICP-MS instrument	Perkin-Elmer Sciex ELAN 6100 DRC II
plasma conditions	
rf power/W	1100
plasma gas flow/L min ⁻¹	15.0
intermediate gas flow/L min ⁻¹	1.10
carrier gas flow/L min ⁻¹	0.99
mass spectrometer settings	
resolution	0.7 amu at 10% peak maximum
isotopes monitored	⁷⁵ As, ¹¹¹ Cd, ¹¹³ Cd, ²⁰¹ Hg, ²⁰² Hg
dwell time/ms	50
sweeps per reading	7
readings per replicate	350
peak signal	integrated
autolens	on
vapor generation system	
sample volume/ μ L	200
slurry	6% m/v flour, 2.5% v/v HCl, 0.7% m/v thiourea, 0.4 μ g mL ⁻¹ Co(II)
carrier solution	2.5% v/v HCl, 0.7% m/v thiourea, 0.4 μ g mL ⁻¹ Co(II)
reductant solution	2.25% m/v NaBH ₄ in 0.2% m/v NaOH
reductant and carrier flow rate/mL min ⁻¹	1.4

The aim of the present work is to develop an accurate and rapid slurry sampling flow injection (FI) ICP-MS method with a vapor generation sample introduction device for the determination of As, Cd, and Hg in cereals. The flour samples were diluted in 2.5% v/v HCl to form the slurry solutions and then determined by flow injection VG-ICP-MS. Optimization studies for the vapor generation of As, Cd, and Hg are reported. This method has been applied for the determination of As, Cd, and Hg in selected cereal samples.

MATERIALS AND METHODS

Apparatus and Conditions. An ELAN 6100 DRC II ICP-MS instrument (PE-SCIEX, Concord, ON, Canada) was used for this study. Vapors generated from samples, after passing through the vapor generation system, were introduced into the ICP torch through Teflon tubing. The operating conditions for the vapor generation and the ICP were optimized by the flow injection method. In this study, a wheat flour slurry solution spiked with 1 ng mL⁻¹ each of As(III), Cd(II), and Hg(II) was selected as the model to optimize the operating conditions. The vapor generation system and the ICP conditions were selected to maximize the signal-to-noise ratio for the elements studied, whereas the appropriate slurries were injected into the ICP by flow injection vapor generation system. The vapor generation and ICP-MS operating conditions used in this work are summarized in **Table 1**. A MARS microwave digester (CEM, Matthews, NC) was used to digest the cereal samples.

In this study, a continuous-flow vapor generation system was coupled with ICP-MS for the determination of As, Cd, and Hg using FI analysis. It was assembled from a six-port injection valve (Rheodyne type 50) with a 200 μ L sample loop. A schematic diagram of the flow injection vapor generator system is shown in Figure S1 of the Supporting Information. A better VG efficiency was obtained by placing about 100 glass beads (5 mm diameter) in the gas-liquid separator to increase the surface area for vapor evolution (19). Vapor generated from the VG system was delivered to the ICP-MS system for As, Cd, and Hg determination via Tygon tubing.

Reagents. All reagents were of analytical reagent grade, and deionized water was used throughout. Suprapur HNO₃ (70% m/m) and HCl (35% m/m), NaBH₄, NaOH, As(V), Co(II), and Hg(II) element standard and thiourea were obtained from Merck (Darmstadt, Germany). NaAsO₂ was from Alfa Chemical (Ward Hill, MA). Dimethylarsinic acid was obtained from Sigma (St. Louis, MO). Methylmercury (CH₃HgCl) was purchased

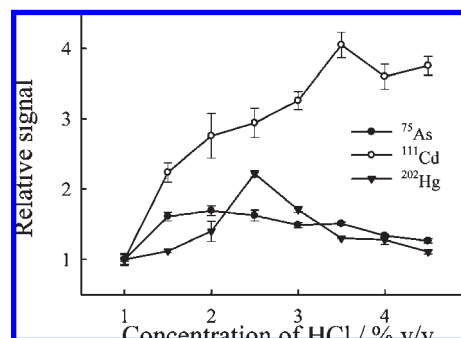


Figure 1. Dependence of ion signal on the concentration of HCl. The injected sample contained 4% m/v wheat flour slurry spiked with 1 ng mL⁻¹ of As, Cd, and Hg and various concentrations of HCl. The concentration of NaBH₄ was 2.5% m/v in 0.2% m/v NaOH. All of the data were measured relative to the first point (1.0% v/v HCl). Result was the mean of five determinations \pm standard deviation.

from TCI (Tokyo, Japan). NaBH₄ solution containing 0.2% m/v NaOH was freshly prepared just prior to analysis. Enriched isotopes of ¹¹¹CdO (96.4%) were purchased from the Oak Ridge National Laboratory (Oak Ridge, TN), and ²⁰¹HgO (82.3%) was obtained from Cambridge Isotope Laboratories (Andover, MA). The concentrations of the spike solutions were verified by reversed spike isotope dilution ICP-MS (20).

Sample and Slurry Preparation. The applicability of the method to real samples was demonstrated by analyzing NIST SRM 1567a Wheat Flour reference material and NIST SRM 1568a Rice Flour reference material and two cereal samples obtained locally. Because the sensitivities of As, Cd, and Hg in slurry solution and aqueous solution were quite different, the cereal samples were analyzed by standard addition and isotope dilution methods. The cereal slurry was prepared using the following procedure. A 0.6 g portion of the flour was transferred into a 10 mL flask, and 2.5 mL 10% v/v HCl was added. The slurry was heated at 85 °C for 10 min by using the water bath. After cooling, suitable amounts of thiourea and Co(II) were added to make the final solution containing 6% m/v flour, 0.7% m/v thiourea, 0.4 μ g mL⁻¹ Co(II), and 2.5% v/v HCl. A drop of antifoam Y-30 (Sigma Chemicals, St. Louis, MO) was added. After addition of suitable amounts of enriched isotopes or various amounts of As, Cd, and Hg element standard solutions, this slurry solution was diluted to the mark with pure water. The slurry was then sonicated for 5 min in an ultrasonic bath. A blank solution was also prepared, as outlined above, to correct any analyte in the reagents used for sample preparation. These slurries were analyzed for As, Cd, and Hg using ICP-MS by injecting 200 μ L of the slurry into the VG system. The concentrations of analytes in the sample were calculated by the equation described in a previous paper (21) and/or from the standard addition calibration curves. As arsenic has only one stable isotope, arsenic cannot be determined by the isotope dilution method. Owing to the mass bias effect, the sensitivity of the instrument at different *m/z* values might be different. The isotopic compositions of Cd and Hg in both natural elements and enriched isotopes were obtained by determining the intensities of all isotopes by ICP-MS with solution nebulization. The intensities of each isotope obtained during this measurement were used for the isotope ratio and atomic weight calculations of the elements studied. Because the mass bias effect could be eliminated during isotope dilution calculation, in this study, the measured isotope ratio was not corrected for mass bias effect.

RESULTS AND DISCUSSION

Selection of Vapor Generation Conditions. The concentration of acid is critical in the determination of As, Cd, and Hg by vapor generation. The effect of the concentration of HCl on the As, Cd, and Hg ion signals was investigated. **Figure 1** shows the area of the FI peak as a function of the concentration of HCl in the carrier and the injected slurry. A NaBH₄ concentration of 2.5% m/v in 0.2% m/v NaOH was employed for these experiments. As can be seen, as the HCl concentration increased, the peak areas of As, Hg, and Cd increased and reached a maximum at HCl

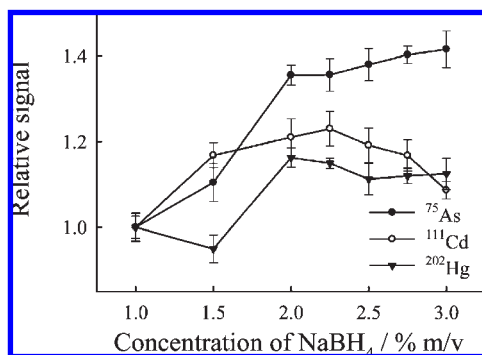


Figure 2. Dependence of ion signal on the concentration of NaBH₄. Carrier solutions contained 2.5% v/v HCl. The injected sample contained 4% m/v wheat flour slurry spiked with 1 ng mL⁻¹ of As, Cd, and Hg and 2.5% v/v HCl. All of the data were measured relative to the first point (1.0% m/v NaBH₄). Result was the mean of five determinations ± standard deviation.

concentrations of 2.0, 2.5, and 3.5% v/v, respectively. The background of Cd and Hg increased slightly with the increase of HCl concentration. To obtain better signal-to-noise ratios (S/N) for the elements studied, 2.5% v/v HCl was added to the carrier solution and slurry in the subsequent experiments. The efficiency of vapor generation is dependent on the concentration of NaBH₄. Thus, the effect of NaBH₄ concentration on the generation of As, Cd, and Hg vapor was also investigated. The results are shown in **Figure 2**. As the NaBH₄ concentration increased, the peak areas of Hg and Cd slowly increased and reached a maximum at NaBH₄ concentrations of 2 and 2.25% m/v, respectively. The signal of As increased with the increase of NaBH₄ concentration. A high concentration of NaBH₄ might generate too much of H₂, which would cause the plasma to become unstable, leading to poor reproducibility of the signal. To achieve better S/N for As, Cd, and Hg, in subsequent experiments, a NaBH₄ concentration of 2.25% m/v in 0.2% m/v NaOH was used.

Thiourea and cobalt have been used as catalysts for the cadmium vapor formation reaction with NaBH₄ in previous papers (22, 23). In the present work, a solution containing thiourea, Co(II), and HCl was used as the carrier. The effects of the concentrations of thiourea and cobalt in the carrier and injected slurry on As, Cd, and Hg vapor formation were also studied in this work. From the experiments, it was found that the peak area of As and Cd increased gradually with the increase of thiourea concentration. On the contrary, the signal of Hg decreased with the increase of thiourea concentration. For a compromise, for the subsequent experiments, 0.7% m/v thiourea was selected. The ion signals as a function of cobalt concentration are shown in **Figure 3**. The ion signals of As and Cd increased rapidly with increase in Co concentration and reached maxima when the Co concentration was about 0.8 μg mL⁻¹. However, the Hg signal decreased significantly when the cobalt concentration was > 0.4 μg mL⁻¹. This could be due to the interference caused in the solution phase of the vapor generation process (9). In the subsequent experiments, 0.4 μg mL⁻¹ Co(II) was used as the catalyst for the vapor formation reaction.

Figure S2 of the Supporting Information shows the effect of the flow rate of NaBH₄ and carrier solution on the peak height and peak area of the flow injection signal. As shown, the peak height and peak area of the flow injection signal revealed that the peak area and peak height increased with the increase of flow rate and reached maxima at 1.1 and about 1.5 mL min⁻¹, respectively. The peak area decreased gradually when the flow rate of NaBH₄ was > 1.1 mL min⁻¹. This could be due to the incomplete reaction

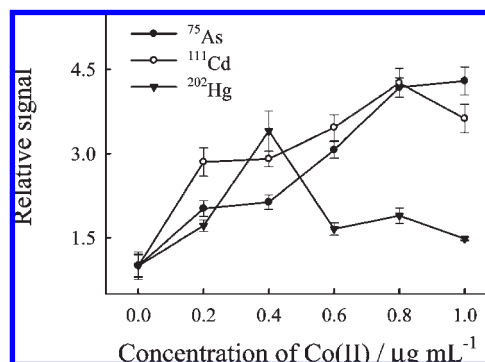


Figure 3. Dependence of ion signal on the concentration of Co. Carrier solutions contained 0.7% m/v thiourea, 2.5% v/v HCl, and various amounts of Co(II). The injected sample contained 4% m/v wheat flour slurry spiked with 1 ng mL⁻¹ of As, Cd, and Hg, 0.7% m/v thiourea, 2.5% v/v HCl, and various amounts of Co(II). The concentration of NaBH₄ was 2.25% m/v in 0.2% m/v NaOH. All of the data were measured relative to the first point (0 μg mL⁻¹ Co). Result was the mean of five determinations ± standard deviation.

when the flow rate was increased. The peak height of the flow injection peak will affect the calculation of the detection limit; on the other hand, the integrated area could affect the precision of the isotope ratio determination and also the quantification of As, Cd, and Hg. Therefore, for a compromise of detection limit and the repeatability of quantification, in the following experiments, a solution flow rate of 1.4 mL min⁻¹ was selected.

Another important factor in the slurry technique is the slurry concentration, that is, the dilution factor. As the dilution of the slurry can be carried out only within a limited range, the effect of the dilution factor on ion signals was also studied. From the experiments it was found that the sensitivity (counts per mass of analyte) of As, Cd, and Hg decreased with decrease in the dilution factor. To balance the homogeneity, the analyte sensitivity, and the method detection limit, a dilution factor of 16.7 (6% m/v) was selected. In a separate experiment, we found that the volume of the mixing coil did not affect the ion signal significantly. In the following experiments, except for the necessary connecting tubing (1.6 mm i.d. × 20 cm length), no extra mixing coil was used. All of the experiments were performed at room temperature. A summary of the optimum operating conditions of the FI vapor generation system is given in **Table 1**. Compared to conventional pneumatic nebulization, 54-, 16-, and 60-fold improvements in the As, Cd, and Hg ion signals, respectively, were obtained when the optimum vapor generation conditions were used.

Spectral Interference Studies. Because HCl was used in the vapor generation, ⁴⁰Ar³⁵Cl⁺ might be formed in the process and interfere in the determination of ⁷⁵As⁺. It was found that the background at *m/z* 75 was only about 700 counts s⁻¹ even when 2.5% v/v HCl was added to the carrier, demonstrating the value of vapor generation in alleviating ArCl⁺ interference. In this study, H₂ was also tested as reaction gas in the DRC system to alleviate this interference. From the experimental results, it was found that the detection limits of As, Cd, and Hg did not improve. Hence, the ICP-MS was operated in the standard mode (no reaction gas) for the real sample analysis.

A sample with a high concentration of Mo gives rise to the molecular ions MoO⁺, which interfere with the determination of all cadmium isotopes. The extent of the interference is such that the direct determination of Cd in samples with high Mo is difficult. The concentration of Mo was 67 times higher than that of Cd in NIST SRM 1568a Rice Flour. The effect of increasing Mo concentration on ¹¹¹Cd/¹¹³Cd ratio was studied. It was found

that the ratio of $^{111}\text{Cd}/^{113}\text{Cd}$ remained constant when a $50 \mu\text{g mL}^{-1}$ spike of Mo was added, which demonstrated that MoO interference is insignificant when vapor generation sample introduction is used (8).

The repeatability of the peak area, peak height, and isotope ratio was determined by five consecutive injections of 0.5 ng mL^{-1} of As and Cd and 0.2 ng mL^{-1} of Hg in 6% m/v wheat flour slurry. As shown in Table S1 of the Supporting Information, the relative standard deviations of the peak area, peak height, and isotope ratio determination were better than 3.5, 5.5, and 1.7%, respectively, for five consecutive injections.

Determination of As, Cd, and Hg in Flour by Slurry Sampling FI-VG-ICP-MS. From the preliminary experiments, it was found that the determined results of As, Cd, and Hg were lower than the expected values when the cereal slurry was injected into the VG-ICP-MS system without further treatment, which could be due to the incomplete extraction of As, Cd, and Hg from the powder sample. Different methods, including microwave-assisted leaching (24) and ultrasound-assisted extraction (25), have been used in published papers to improve the determined results. In this study a simple water bath heating was tested. To study the effect of heating of the prepared slurry on the ion signals, slurries containing 10% v/v HCl were heated at 60 and 85 °C in a water bath for 10 min. From the experiment it was found that better recoveries of 99, 99, and 104% could be obtained for As, Cd, and Hg, respectively, when the slurry was heated at 85 °C. Hence, heating at 85 °C for 10 min was selected.

Cereals contain certain amounts of As(III), As(V), and organic arsenic compounds and inorganic Hg(II) and methylmercury compounds (26–28). As As(III), As(V), and organic arsenic compounds and inorganic mercury and methylmercury compounds show different sensitivities in the vapor generation process (28, 29), it is necessary to decompose the organic compounds to a single inorganic ion to generate accurate results. It is preferred to reduce arsenic to the lower oxidation state to increase hydride generation efficiency. To compare the difference in the hydride generation efficiency of various arsenic and mercury species in the slurry, calibration curves obtained by standard addition method using 6% m/v slurry solution and As(III), As(V), DMA, Hg(II) and methylmercury standard solutions have been plotted. The results are shown in Table S2 of the Supporting Information. As shown, the sensitivities of As and Hg were similar when the slurry was spiked with different standards. The mixture of the hot concentrated HCl and thiourea solution used for vapor generation is believed to act as an effective method for the decomposition of organic compounds and reduction of As(V) to lower oxidation state. These results indicated that As and Hg in the slurry could be readily quantified by FI-VG-ICP-MS using As(III) and Hg(II) as the calibration standard.

The FI-VG-ICP-MS method has been applied for the determination of As, Cd, and Hg in four cereal samples. To evaluate the possibility of using an external calibration method, calibration curves obtained by standard addition method of 6% m/v slurry solution and external calibration of aqueous standard were compared. The calibration data of different methods are shown in Table S3 of the Supporting Information. As shown, the calibration slopes of As, Cd, and Hg obtained by standard addition method were 41, 24, and 43% higher than those of external calibration. This could be due to the difference in the vapor generation efficiency between slurry matrix and aqueous solution. Hence, standard addition and isotope dilution methods were used for the quantification of As, Cd, and Hg in cereal samples. Aliquots of $200 \mu\text{L}$ of the slurry were injected for the determination of As, Cd, and Hg using the FI vapor generation system. Typical element-selective flow injection signals (ICP-MS

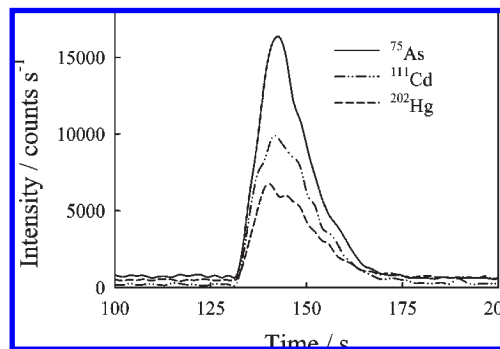


Figure 4. Typical element-selective flow injection peaks of 6% m/v flour slurry. The injected sample contained 6% m/v Taiwan wheat flour slurry, 0.7% m/v thiourea, 2.5% v/v HCl, and various amounts of Co(II). The concentrations of As, Cd, and Hg in the injected slurry solution are about 0.47, 1.1, and 0.09 ng mL^{-1} , respectively. Operating conditions of FI vapor generation are given in **Table 1**.

Table 2. Determination of As, Cd, and Hg in Cereal by Slurry Sampling FI-VG-ICP-MS^a ($n = 3$)

sample	method ^b	concentration/ ng g^{-1}		
		As	Cd	Hg
NIST SRM 1568a Rice Flour	1	289 ± 6	20.9 ± 0.4	6.0 ± 0.4
	2 certified	290 ± 30	21.3 ± 1.6 22 ± 2	5.6 ± 0.3 5.8 ± 0.5
NIST SRM 1567a Wheat Flour	1	5.7 ± 0.2	25.4 ± 0.3	0.53 ± 0.22
	2 certified	6	25.5 ± 0.4 26 ± 2	0.53 ± 0.12 0.5
Taiwan rice	1	109 ± 4	36.6 ± 1.2	6.7 ± 0.3
	2		35.2 ± 0.7	6.4 ± 0.2
	3	102 ± 10	34.8 ± 0.7	6.6 ± 0.9
Taiwan wheat flour	1	7.9 ± 0.2	18.4 ± 0.4	1.5 ± 0.2
	2		17.0 ± 0.5	1.5 ± 0.1
	3	7.4 ± 0.9	17.6 ± 0.3	1.8 ± 0.3

^a Values are means of three measurements \pm standard deviation. ^b Method 1, standard addition method. Method 2, isotope dilution method. Method 3, obtained by pneumatic nebulization ICP-MS. The total dilution factor was 50 times. Certified, NIST certified and/or information value.

detection) for a solution containing 6% m/v wheat flour slurry are shown in **Figure 4**. The concentrations of As, Cd, and Hg in the injected solution were about 0.47, 1.1, and 0.09 ng mL^{-1} , respectively. Peak areas of the flow injection signals were used for quantification. Because another isotope of the same element represents the ideal internal standard for that element, isotope dilution results are expected to be highly accurate even when the sample contains high concentrations of concomitant elements and/or losses occur during sample preparation or during sample introduction into the ICP. In this work, the concentrations of Cd and Hg were also determined by isotope dilution method. Analysis results are shown in **Table 2**. As shown, the quantification results of standard reference materials agreed with the certified values. The analytical results of local cereal samples determined by standard addition and isotope dilution methods were in good agreement with those of digested samples using microwaves and analyzed by pneumatic nebulization ICP-MS. All of the determined results, except the Cd result of the Taiwan wheat flour, were in good agreement in accordance with

Student's *t* test for a confidence level of 95%. The relative standard deviation obtained by the reported procedure was 1.1–7.5% (41% for Hg in wheat flour) for all determinations. The higher value obtained for Hg in wheat flour is due to its extremely low concentration. According to the regulations of the Taiwan government, the maximum allowable concentrations of Cd and Hg in rice are 0.4 and 0.05 $\mu\text{g g}^{-1}$, respectively. The concentrations of Cd and Hg in the analyzed cereal samples are far below the maximum allowable concentration. These experimental results indicate that As, Cd, and Hg in cereals could be readily quantified by slurry sampling inductively coupled plasma mass spectrometry with vapor generation sample introduction.

Under the selected FI-VG-ICP-MS operating conditions, standard addition calibration plots (0.01–2 ng mL⁻¹) for As, Cd, and Hg were linear with calibration coefficients (*r*²) of >0.999. The detection limits were estimated from the standard addition curves based on the concentration necessary to yield a net peak height equal to 3 times the standard deviation of the blank. The detection limits of As, Cd, and Hg were 0.006, 0.01, and 0.004 ng mL⁻¹, respectively, in prepared slurry solution, corresponding to 0.10, 0.16, and 0.07 ng g⁻¹ for As, Cd, and Hg, respectively, in the original cereal sample. The detection limits obtained for As, Cd, and Hg with this system are low enough for the determination of As, Cd, and Hg in many cereal samples.

ABBREVIATIONS USED

ICP-MS, inductively coupled plasma mass spectrometry; VG, vapor generation; FI, flow injection; DMA, dimethylarsinic acid.

Supporting Information Available: Additional tables and figures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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