

## Determination of Trace Cadmium in Rice by Flow Injection On-Line Filterless Precipitation–Dissolution Preconcentration Coupled with Flame Atomic Absorption Spectrometry

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A simple, environmentally friendly, cost-effective, and sensitive method was developed for the determination of trace cadmium in rice by flow injection (FI) on-line precipitation preconcentration coupled with flame atomic absorption spectrometry (FAAS). The precipitation preconcentration of trace cadmium was achieved by on-line merging of the sample and ammonia solutions. The resultant precipitates were on-line collected by a knotted reactor (KR) without filtration. A solution of 1 mol L<sup>-1</sup> HNO<sub>3</sub> was employed to dissolve the collected precipitates and to deliver the analyte into the FAAS system for on-line detection. Preconcentration at a sample loading flow rate of 3.8 mL min<sup>-1</sup> for 35 s gave an enhancement factor of 44 and a detection limit (3σ) of 0.002 μg g<sup>-1</sup> for the solid sample with a sample throughput of 72 h<sup>-1</sup>. The precision (RSD, *n* = 11) was 2.0% at the 4.0 μg L<sup>-1</sup> level. The concentration of cadmium in a certified reference material (GBW 08511, rice flour) by the developed method using simple aqueous standards for calibration was in good agreement with the certified value. The proposed method was also successfully applied to the determination of trace cadmium in locally collected rice samples.

**KEYWORDS:** Cadmium; rice; flow injection; precipitation; preconcentration; flame atomic absorption spectrometry

### INTRODUCTION

Cadmium is one of the most toxic elements for animals and humans, even at low concentrations. In mammals, cadmium is known to accumulate exclusively in the kidneys. It has a long biological half-life in the human body, ranging from 10 to 33 years (1, 2). The amount of cadmium accumulated in the kidneys is a function of age and/or daily cadmium intake. The latter is mainly from food, beverage, and smoking (3). Cadmium occurs naturally in rocks and soils, generally associated with zinc and its compounds. Anthropogenic sources include smelter emissions, mainly related to the zinc industry, and application of fertilizers originating from incineration and purification stations (4) or sewage sludge to the land. All these practices produce an accumulation of cadmium in soils, allowing it to enter the food chain with the potential to cause serious health problems (5, 6).

Rice is a staple food in most Asian countries. Accurate determination of trace cadmium in rice is particularly important from a toxicological and environmental point of view. There are several techniques employed for the determination of cadmium in rice, e.g. flame atomic absorption spectrometry

(FAAS) (7–9), electrothermal atomic absorption spectrometry (ETAAS) (10), inductively coupled plasma atomic emission spectrometry (ICP-AES) (3), differential pulse anodic stripping voltammetry (DP-ASV) (11), and inductively coupled plasma mass spectrometry (ICP-MS) (12). One would expect to find ETAAS and ICP-MS as the most suitable techniques for the determination of trace cadmium in rice due to their high sensitivity. FAAS is also one of the choice of methods for trace Cd determination in light of the low operational and instrumental costs, easy operation, and high sample throughput. Because of the low levels of Cd or/and the complexity of the matrixes, a solvent extraction preconcentration and separation procedure employing DDTC/MIBK has been used before FAAS detection (7–9). Such a batch-mode solvent extraction preconcentration approach is time-consuming and labor-intensive, requires a large volume of sample and toxic solvent, and suffers great risks of contamination and analyte loss.

With on-line operation using flow injection (FI) techniques, the drawbacks of batchwise operation can be overcome to a great extent, while preconcentration and separation can be further enhanced (13). FI on-line preconcentration and separation coupled with FAAS has been shown to be a promising alternative to conventional ETAAS for the determination of trace elements in a variety of matrixes in view of the enhanced sensitivity, the efficient removal of matrix, the lower cost of the FAAS equipment, and the substantially higher sample

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**Table 1.** Operational Sequence for the FI On-line Filterless Precipitation–Dissolution System for FAAS Determination of Cadmium

step	function	time (s)	pumped medium	flow rate (mL min <sup>-1</sup> )		valve position
				pump 1	pump 2	
1 (Figure 1a)	precipitation	35	sample solution (pH 2) NH <sub>3</sub> ·H <sub>2</sub> O (0.5 mol L <sup>-1</sup> )	off	3.8	fill
2 (Figure 1b)	air segmentation	5	air	off	3.8	inject
3 (Figure 1b)	dissolution	10	HNO <sub>3</sub> (1 mol L <sup>-1</sup> )	2.9	off	inject

throughput achievable (13). Several FI on-line preconcentration techniques have been developed for FAAS determination of trace cadmium, including solid sorbent extraction (14–16), precipitation (17), coprecipitation (18), and sorption in knotted reactors (KRs) (19).

The application of the KR as sorption media in FI on-line sorption preconcentration for atomic spectrometric determination of cadmium in biological materials was reported by Fang et al. (19). In the system, cadmium complexed with diethyldithiocarbamate was sorbed on the inner wall of the KR and eluted on-line by isobutyl methyl ketone (IBMK) for FAAS detection. Thiourea and ascorbic acid/phenanthroline were used to overcome interference from copper and iron, respectively.

The purpose of the present work is to develop a simple, environmentally friendly, cost-effective, and sensitive method for the determination of trace cadmium in rice by FI on-line precipitation preconcentration coupled with FAAS. The determination of trace cadmium was achieved by on-line precipitation preconcentration via merging of the sample and ammonia solutions, collection of the resultant precipitates by a knotted reactor (KR) without filtration, dissolution of the precipitates with a solution of 1 mol L<sup>-1</sup> HNO<sub>3</sub>, and detection on-line by FAAS. The validity of the developed method was demonstrated by analyzing a certified rice flour reference material.

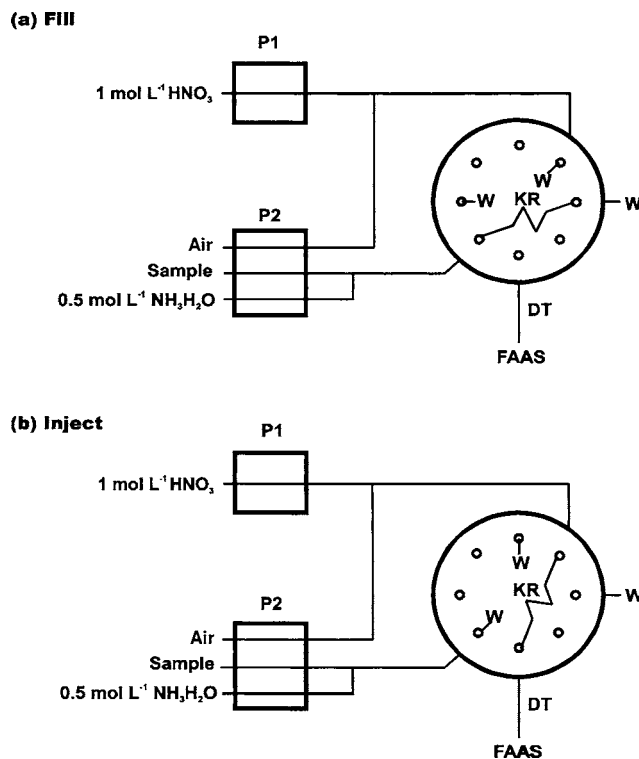
## EXPERIMENTAL SECTION

**Apparatus.** A Hitachi 180-80 atomic absorption spectrometer equipped with a hollow cathode cadmium lamp was used throughout this work. The instrument was set at a wavelength of 228.8 nm and a slit of 1.3 nm. The flame conditions (2.2 L min<sup>-1</sup> acetylene and 9.4 L min<sup>-1</sup> air) were employed according to standard recommendations. The peak height absorbance was used for quantitation.

A model FIA-3100 flow injection system (Vital Instruments Co. Ltd, Beijing, China), connected to the atomic absorption spectrometer with the shortest possible length of 0.35-mm i.d. PTFE tubing (ca. 20 cm), was employed for the preconcentration of trace cadmium. All samples and reagents were delivered with Tygon pump tubes. The FIA-3100 consists of two peristaltic pumps and a standard rotary injection valve (eight ports on the rotor and eight ports on the stator). The rotation speed of the two peristaltic pumps, their stop and go intervals, and the actuation of the injection valve were all programmed (Table 1). Small-bore (0.35-mm i.d.) PTFE tubing was used for all connections, which were kept as short as possible to minimize dead volumes. The KR used as the filterless collector was laboratory-made of 0.5-mm i.d. PTFE tubing by tying interlaced knots (20–22).

**Materials.** All other reagents used were of the highest available purity and at least of analytical grade. Doubly deionized water (DDW) was used throughout this work. All working Cd solutions were prepared from a stock standard solution of 1000 mg L<sup>-1</sup> Cd in 1% v/v HNO<sub>3</sub> (National Research Center for Standard Materials, Beijing, China). Perchloric acid, ammonia solution, and nitric acid were purchased from Tianjin Chemicals Co. (Tianjin, China).

**Sample Pretreatment.** Sampling was taken at random from seven commercial rice brands sold in the city of Tianjin, China. The rice samples were ground into powder for digestion. About 1 g of the rice flour was accurately weighed and thoroughly mixed with 3 mL of concentrated perchloric acid and 3 mL of concentrated nitric acid in a PTFE beaker. Then the mixture was gently heated on a hot plate until



**Figure 1.** FI manifold for the on-line precipitation preconcentration coupled with FAAS for determination of cadmium. For details see the text. P1 and P2, peristaltic pump; DT, delivery tubing; KR, knotted reactor (0.35-mm i.d. × 150-cm long PTFE tubing); W, waste. Valve position: (a) fill, (b) inject.

white fumes appeared. After cooling, the clear digests were transferred into a 10-mL calibrated flask and diluted to volume with DDW and diluted ammonia solution so that the final pH of the diluted digest is about pH 2.0. A certified reference material, GBW 08511 rice flour (National Research Center for Standard Materials), was used for validation of the developed method.

**Analytical Procedures.** The manifold for the FI on-line precipitation preconcentration is illustrated in Figure 1. Details of the FIA-3100 program and the operation sequence are given in Table 1. In step 1 (Figure 1a), pump 2 was active and the injection valve was in the fill position, so that the sample or standard solution and an ammonia solution were pumped and mixed on-line before passing through the KR. The resultant precipitates of the cadmium hydroxides were on-line collected by the KR. In step 2 (Figure 1b), pump 2 was still active, whereas the injection valve was turned into the inject position. As a result, a small air segment was introduced to avoid the penetration of the neighboring phases under fast elution rates. Finally, in step 3 (Figure 1b), the injection valve was still in the injection position, whereas pump 1 was turned on and pump 2 stopped. In this step, a solution of 1 mol L<sup>-1</sup> HNO<sub>3</sub> was introduced into the KR to dissolve the collected analyte precipitates and subsequently to deliver the analyte into the spectrometer. (**Caution:** The use of 1 mol L<sup>-1</sup> HNO<sub>3</sub> may cause some problems such as the corrosion of the injection valve or the nebulizer, so timely washing of the valve and nebulizer with DDW after experiments is highly recommended.) The total time for a single determination was 50 s including 35 s for sample loading.

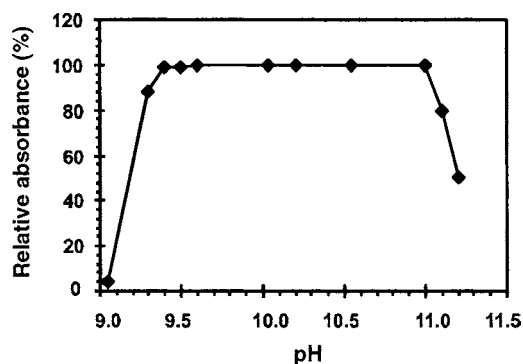


Figure 2. Effect of the pH of the effluent on the peak height absorbance of  $10 \mu\text{g L}^{-1}$  Cd. All other conditions as in Figure 1 and Table 1.

## RESULTS AND DISCUSSION

**Optimization of FI Variables.** To achieve good sensitivity and precision, the chemical and flow conditions were optimized for the FI on-line precipitation–dissolution system for FAAS determination of cadmium. These variables include the pH for on-line precipitation, sample loading flow rate, sample loading time, KR tubing length, the acid medium and its concentration, and flow rate for the precipitate dissolution. Considering the final pH (ca. 2) of the diluted sample digests obtained in the sample pretreatment section, the standard cadmium solutions were all adjusted to pH 2.0 with nitric acid so that the optimization of other parameters can be simplified.

To find the optimal conditions for the precipitation preconcentration of trace cadmium, a careful examination on pH effect was carried out. The on-line pH adjustment of the reaction mixture in step 1 was realized by adjusting the concentration of an ammonia solution while the pH of the sample solution was kept at 2. The pH of the effluent in step 1 was monitored as the indication of the pH of the system. As illustrated in Figure 2, the absorbance of  $10 \mu\text{g L}^{-1}$  Cd increased sharply upon increasing the pH of the effluent from 9.02 to 9.4 and then remained constant in the pH range of 9.4–11.0. Further increase in the pH from 11.0 to 11.2 resulted in a significant decrease in the absorbance, probably because the analyte precipitates were dissolved in excessive ammonia solution as the ammonia complexes. The above results indicate that the favorable pH of the effluent for the hydroxide precipitation ranged from 9.4 to 11.0, corresponding to a concentration range of 0.3–0.6 mol  $\text{L}^{-1}$  for ammonia solutions when the acidity of the sample solution was kept at pH 2.0. For further experiments, an ammonia solution of 0.5 mol  $\text{L}^{-1}$  was used.

For the sake of practical applications, we also checked the effect of the sample pH on the absorbance of  $10 \mu\text{g L}^{-1}$  Cd when the concentration of the ammonia solution was kept at 0.5 mol  $\text{L}^{-1}$ . The results showed that the use of an ammonia solution of 0.5 mol  $\text{L}^{-1}$  as the precipitating reagent permitted variation in the sample pH from 1.6 to 7 without changing the optimal absorbance.

The effect of sample loading time on the absorbance of  $10 \mu\text{g L}^{-1}$  Cd was tested at a sample flow rate of 3.8 mL  $\text{min}^{-1}$ . It was found that the absorbance increased almost linearly as sample loading time increased up to 35 s and then leveled off with further increase of sample loading time. The effect of sample flow rate on the absorbance of  $10 \mu\text{g L}^{-1}$  Cd for a sample loading time of 35 s revealed that the absorbance increased linearly up to a flow rate of 4.2 mL  $\text{min}^{-1}$  and then the slope gradually decreased as the flow rate further increased. On the basis of the above results, a sample loading time of 35

Table 2. Effect of Coexisting Ions on the Determination of  $10 \mu\text{g L}^{-1}$  Cd

ion	concn (mg $\text{L}^{-1}$ )	recovery (%)	ion	concn (mg $\text{L}^{-1}$ )	recovery (%)
K(I)	0.20	100	Zn(II)	0.01	100
	0.44	82		0.05	93
Na(I)	2.20	99	Cr(VI)	0.01	100
	6.80	90		0.05	96
Ca(II)	3.90	90	Ni(II)	0.01	86
	7.80	75		0.05	73
Mg(II)	1.10	98	Pb(II)	0.01	100
	2.20	88		0.05	90
Cu(II)	0.01	93	Cl <sup>-</sup>	0.10	85
	0.05	86		5.28	91
	0.10	79		SO <sub>4</sub> <sup>2-</sup>	3.50

s and a sample flow rate of 3.8 mL  $\text{min}^{-1}$  were employed in further work.

Diluted nitric acid was chosen for the on-line dissolution of the precipitates of cadmium hydroxides due to its high efficiency for precipitate dissolution. The concentration of nitric acid and the flow rate for dissolution are the two important factors affecting the dissolution process. The optimal concentration of HNO<sub>3</sub> was found to be 1.0 mol  $\text{L}^{-1}$ . Studies on the effect of the flow rate of 1.0 mol  $\text{L}^{-1}$  HNO<sub>3</sub> from 1.6 to 4.2 mL  $\text{min}^{-1}$  show that the absorbance of  $10 \mu\text{g L}^{-1}$  Cd increased linearly up to a flow rate of 2.5 mL  $\text{min}^{-1}$ , then the slope gradually decreased with further increase of the flow rate. However, high flow rates over 3.5 mL  $\text{min}^{-1}$  impaired the precision. Therefore, a flow rate of 2.9 mL  $\text{min}^{-1}$  was employed to achieve desired sensitivity but not to impair the precision.

The KR undertakes two important functions in the present on-line precipitation preconcentration system, providing reproducible conditions for the precipitation and serving as a collector of the precipitates. Because of changes in the flow direction caused by the knots, the KR creates a secondary flow with some centrifugal force in the stream carrying particles toward the tubing walls (20). Studies on the effect of KR tubing length on the absorbance of  $10 \mu\text{g L}^{-1}$  Cd show that the absorbance increased significantly with increases in the KR tubing length up to 150 cm, but the increase of the absorbance gradually slowed with a further increase in the KR tubing length. Accordingly, a KR tubing length of 150 cm was selected for the rest of this work.

**Evaluation of Interferences.** In this work, we investigated the interference effects of 11 foreign ions on the determination of cadmium. As shown in Table 2, 0.2 mg  $\text{L}^{-1}$  of K(I), 6.8 mg  $\text{L}^{-1}$  of Na(I), 3.9 mg  $\text{L}^{-1}$  of Ca(II), 1.1 mg  $\text{L}^{-1}$  of Mg(II), 0.01 mg  $\text{L}^{-1}$  of Cu(II), 0.05 mg  $\text{L}^{-1}$  of Zn(II), 0.05 mg  $\text{L}^{-1}$  of Cr(VI), 0.01 mg  $\text{L}^{-1}$  of Ni(II), 0.05 mg  $\text{L}^{-1}$  of Pb(II), 5.28 mg  $\text{L}^{-1}$  of Cl<sup>-</sup>, and 3.5 mg  $\text{L}^{-1}$  of SO<sub>4</sub><sup>2-</sup> caused no appreciable interferences in the determination of cadmium. As demonstrated later, the present system allowed the interference-free determination of trace cadmium in the rice samples studied.

**Figures of Merit.** The analytical characteristics data for the FI on-line precipitation–dissolution system for FAAS determination of trace cadmium are shown in Table 3. The detection limit was calculated on the basis of three times the standard deviation for 11 replicate determinations of the reagent blank. The precipitation preconcentration of 2.2 mL of the sample solution gave an enrichment factor of 44 and a detection limit ( $3\sigma$ ) of 0.2  $\mu\text{g L}^{-1}$  for the digest and 0.002  $\mu\text{g g}^{-1}$  for the solid sample with a sample throughput of 72 samples  $\text{h}^{-1}$ . The precision (RSD) for 11 replicate measurements of 4.0  $\mu\text{g L}^{-1}$  Cd was 2.0%.

**Table 3.** Analytical Characteristics Performance Data of the FI On-line Filterless Precipitation–Dissolution System for FAAS Determination of Cadmium under the Conditions Shown in Table 1

preconcentration time (s)	35
concentration range ( $\mu\text{g L}^{-1}$ )	1–64
enrichment factor	44
sample throughput (samples $\text{h}^{-1}$ )	72
sample consumption (mL)	2.2
reagent consumption (mL)	
0.4 mol $\text{L}^{-1}$ $\text{NH}_3 \cdot \text{H}_2\text{O}$	2.2
1 mol $\text{L}^{-1}$ $\text{HNO}_3$	0.5
precision (RSD, $n = 11$ ) (%)	2.0 ( $4 \mu\text{g L}^{-1}$ )
detection limit ( $3\sigma$ )	$0.2 \mu\text{g L}^{-1}$ for the digest
	$0.002 \mu\text{g g}^{-1}$ for the solid sample
calibration function	$A = 0.0044C + 0.0067$
( $A$ , peak height absorbance; $C$ , $\mu\text{g L}^{-1}$ ; six standards)	
correlation coefficient	0.999

**Table 4.** Analytical Results for the Determination of Trace Cadmium in Rice Samples

rice sample	determined concn (mean $\pm$ s, $n = 6$ ) ( $\mu\text{g g}^{-1}$ )	recovery of $5 \mu\text{g L}^{-1}$ Cd spike in the digest (%)
GBW 08511 <sup>a</sup>	$0.50 \pm 0.01$	–
1	n.d. <sup>b</sup>	95
2	$0.67 \pm 0.02$	101
3	nd	100
4	nd	94
5	nd	102
6	$0.45 \pm 0.01$	95
7	$0.91 \pm 0.006$	98

<sup>a</sup> This rice flour reference standard was certified to be  $0.504 \pm 0.018 \mu\text{g g}^{-1}$ .  
<sup>b</sup> nd, not detectable ( $<0.002 \mu\text{g g}^{-1}$ ).

To evaluate the accuracy of the proposed FI on-line filterless precipitation preconcentration coupled with FAAS for the determination of trace cadmium in rice, the certified reference material GBW 08511 (rice flour) was analyzed. As shown in Table 4, the determined concentration of cadmium in the rice flour by the present method using a simple aqueous standards for calibration was in good agreement with the certified value. The result demonstrates the applicability of the proposed method for interference-free determination of trace cadmium in rice flour.

**Application to Real Samples.** The developed method was applied to the determination of trace cadmium in seven commercial rice brands sold in the city of Tianjin, China. As shown in Table 4, the recoveries of  $5 \mu\text{g L}^{-1}$  Cd spiked in the digests of these rice samples ranged from 94 to 102%, indicating no interferences encountered from these rice matrixes. The analytical results obtained by the present method using a simple aqueous standard calibration technique are also given in Table 4. The concentrations of trace cadmium in these rice samples ranged from less than the detection limit ( $0.002 \mu\text{g g}^{-1}$ ) to  $0.91 \mu\text{g g}^{-1}$ . The difference in the content of Cd in these rice samples probably results from the soils in which the rice was planted. The exact reasons for the broad range of the content of Cd in these samples need further investigation from the toxicological point of view.

## CONCLUSIONS

The above results demonstrated the applicability of the developed FI on-line filterless precipitation preconcentration coupled with FAAS for the determination of trace cadmium in rice samples. The developed method is simple, sensitive, environmentally friendly, and cost-effective, being promising for routine determination of trace cadmium in rice samples.

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