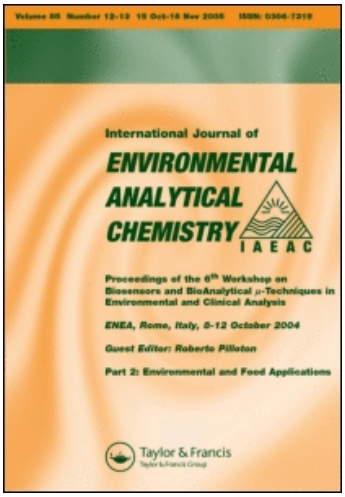

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Electrothermal atomic absorption spectrometric determination of cadmium in bangladeshi vegetables with a metal tube atomizer and slurry sampling technique

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ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRIC DETERMINATION OF CADMIUM IN BANGLADESHI VEGETABLES WITH A METAL TUBE ATOMIZER AND SLURRY SAMPLING TECHNIQUE

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Ultrasonic slurry sampling electrothermal atomic absorption spectrometry with a molybdenum tube atomizer has been applied for the determination of cadmium in vegetable samples in Bangladesh. The suspension-stabilizing medium was 10% glycerol solution. The optimum pyrolysis temperature was 300°C. The detection limit was 13 fg ($3S/N$). Matrix element interference was studied and it was found that thiourea as a chemical modifier eliminated the interference. The results for the determination of cadmium in vegetable samples by the proposed method were in good agreement with those measured in dissolved acid-digested samples. The method enables rapid calibration, and simple and rapid analysis of cadmium in vegetable samples at low cost.

Keywords: Electrothermal atomic absorption spectrometry; Metal tube atomizer; Slurry sampling technique; Cadmium; Bangladeshi vegetables

INTRODUCTION

Cadmium toxicity is well known and the health effects of cadmium exposure have been reviewed [1]. Among these, renal tubular damage appears to be one of the critical health effects of cadmium exposure in the general population. The International Agency for Research on Cancer concluded in 1993 that there was sufficient evidence to classify cadmium as a human carcinogen. Sources of human and environmental cadmium exposure have been reviewed by the World Health Organization (WHO) [2,3]. Food is the major source of cadmium exposure in the general non-smoking population. Natural and anthropogenic sources such as industrial emissions, applications of fertilizers and sewage sludge from farming have led to the contamination of soils. As a result,

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an increased cadmium uptake occurs by crops and vegetables grown for human consumption. Additionally, airborne cadmium will contribute to the cadmium content of vegetables and grain. The provisional tolerable weekly intake (PTWI) proposed by FAO/WHO was 7 μg/(kg_{bw} week) [4]. From the viewpoint of public health, consumable products such as foods and vegetable should be regularly monitored in order to reduce the risks of health hazard. Therefore, it is necessary to develop a rapid and simple method for the determination of cadmium at low levels in human consumable products.

In Bangladesh, vegetables make up approximately 16% of the total diet. The average per capita consumption of leafy and non-leafy vegetables was 130 g (wet weight)/(person day) for males and females of all ages [5]. Hence, the exact content of cadmium in common vegetables in Bangladesh has received some attention.

Electrothermal atomization AAS (ETA-AAS) with a metal tube atomizer, which is similar to GFAAS, is known to enable better sensitivity for most metal elements, and better reproducibility at relatively low power and low cost [6–8]. On the other hand, the slurry-sampling methods have many benefits such as timesaving, no contamination from added chemicals, no separation/preconcentration steps, less loss of volatile elements caused by digestion, and less chemical treatment [9]. Despite these advantages, there is still little information on the combination of the metal tube atomizer in ETA-AAS with slurry-sampling techniques [10–16]. Although we investigated the determination of cadmium in biological materials [10] and drug samples [13] by slurry-sampling ETA-AAS with the metal tube atomizer, the sedimentation of the suspension material occurred quickly because of the absence of suspension-stabilizing agents.

In the present work, we report the determination of cadmium in Bangladeshi vegetable samples by slurry sampling ETA-AAS with a molybdenum tube atomizer. Moreover, the measured data of this study were compared with PTWI proposed by the FAO/WHO.

EXPERIMENTAL

Apparatus

A molybdenum tube atomizer (20 mm × 1.8 mm i.d., wall thickness 0.05 mm), made from pure molybdenum sheet (99.95% purity, Rembar Co.), was used for slurry sampling ETA-AAS. The samples were injected by means of a glass micropipette through a 0.3-mm diameter hole at the mid point of the tube.

Cadmium determinations were performed with a Nippon Jarrell–Ash 0.5 m Ebert-type monochromator atomic absorption spectrometer equipped with an R928 photomultiplier tube (Hamamatsu Photonics Co.), a fast response amplifier, a storage oscilloscope (Kenwood CS–8010), and a microcomputer (PC 9801 FA, NEC Corporation). All determinations were performed at the resonance line of 228.80 nm (Cd hollow-cathode lamp, Hamamatsu Photonics Co.), and with a deuterium lamp (Original Hanau D200F) to compensate background absorption, a step-down transformer and a transformer (Yamabishi volt–slider, S–130–30, capacity 3 kVA) to supply electric power for heating the atomizer, and two pinhole apertures (1.0-mm diameter) placed in front and at the rear end of the atomizer to collimate the light beam and eliminate radiation from the atomizer surface. The absorption signal from

the amplifier and the output signal from a photodiode for the measurement of atomizer temperature were simultaneously fed into a microprocessor. Calibration of the temperature of the atomizer using the photodiode voltage was achieved by means of an optical pyrometer (Minolta TR–630) and microcomputer software. The baseline was measured by heating without the sample. The time constant was 4 ms. The atomic absorption signal was evaluated from the peak height.

The mass of chemicals was determined by use of a Mettler H20 semi-micro analytical balance with a precision of ± 0.01 mg. Herbal medicine powder samples were ground to different particle diameters by use of an agate mortar and a filter (Nippon Rikagaku Kikai, ISO 38). An optical microscope (Kenko, KL–1200) was used to determine the particle diameters of ground vegetable samples. A Uni-seal decomposition vessel was used for digestion of vegetable samples. An ultrasonic washing apparatus (B–12, 40 W, Branson Cleaning Equipment Co., USA) was used to homogenize slurried vegetable powder immediately before sample injection. Ultrapure water was prepared using an Advantec CW–102 ultrapure water system.

Sample and Reagents

Vegetable samples were bind weed (*Ipomoea aquatica*), celery (*Amaranthus gangeticus*) and basil (*Basella rubra*), which are daily taken in Bangladesh. The vegetables, which were grown near the tannery industry area in Hazaribag, Dhaka, Bangladesh, were collected in June 2002. The collected vegetable samples were cleaned with distilled water. The samples were air-dried in a dust-free room and then oven-dried at 65°C for 48 h. The detailed procedures are described in Ref. [16].

A standard cadmium solution (1 mg/mL in 0.1 M nitric acid solution) and pure glycerol used as slurry medium were obtained from Nacalai Tesque (Kyoto, Japan). Thiourea solution (5 mg/mL) was prepared by diluting in pure water. Working standard solutions of appropriate concentration were prepared by dilution of stock standard solutions with pure water immediately before use. All reagents and chemicals used were of analytical grade or spectroscopic purity.

Procedures

A powdered vegetable sample was ground to a very fine mesh, filtered, and material with a particle size range of 26–38 μm was collected. An accurately weighed sample of the vegetable samples (approximately 50 mg) was transferred into a 100-mL volumetric flask and diluted to the desired volume with 10% glycerol solution. Immediately before injection, ultrasonic agitation was performed for 5 min to homogenize the slurries. A 1-μL aliquot of the slurry was injected into the Mo tube atomizer by means of a glass pipette. After drying at 100°C for 10 s, a 1-μL portion of thiourea matrix modifier was injected into the tube. The sample was then pyrolyzed at 300°C for 20 s and atomized at 2100°C (using a heating rate of 3.4°C/ms) for 3 s in Ar 480 mL/min + H_2 20 mL/min purge gas.

For the interference study, a 1-μL portion of 10% glycerol solution containing cadmium (3 ng/mL) and interferent (30 μg/mL) was pipetted into the molybdenum tube atomizer. The solution was measured under the same conditions as were used for the slurry sample.

RESULTS AND DISCUSSION

Ultrasonic agitation has been considered as an effective system of homogenizing slurries for GFAAS [9]. It can be used in combination with both manual and automated introduction of the slurry. This sample preparation is more thorough than magnetic agitation and vortex mixing, so in this study ultrasonic agitation was used for slurry preparation.

It has been reported previously [6] that the optimal purge gas on ETA-AAS with a molybdenum tube atomizer was Ar 480 mL/min + H_2 20 mL/min and the optimal atomization temperature was 2100°C for obtaining a sensitive AA signal and protecting the metal atomizer from oxidation by residual traces of oxygen in the atomizer chamber. Hence, the subsequent experiments for slurry sampling ETA-AAS were carried out under these experimental conditions.

Slurry Medium

Because most powdered materials undergo rapid sedimentation, slurry preparation in water sample is not suitable. The sedimentation of the suspension material usually occurs after mixing the slurry and its rate depends on the densities of the diluent and solid material, the viscosity of the diluent medium, and the radius of the sample particles. The slurried sample can be stabilized by use of a highly viscous liquid medium. Until now, viscalex [18–21], glycerol [22,23], non-ionic surfactants [24], and organic solvents of high viscosity [25] have been used as suspension-stabilizing agents. Hoening and Hoeyweghen [23] stated that the viscosity of glycerol kept different types of particles in suspension for a sufficient time. Therefore, glycerol was selected as the slurry-stabilizing agent and the effect of its concentration on Cd absorption was studied. The results are shown in Fig. 1. The highest signal was observed using

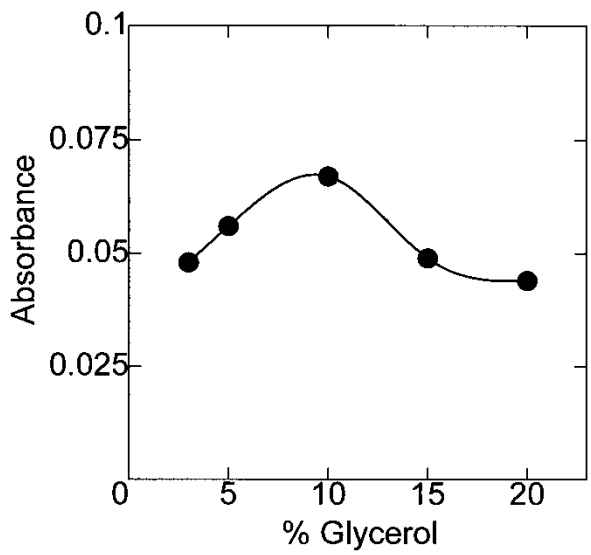

FIGURE 1 Effect of glycerol concentration on the Cd signal using vegetable sample (Bind weed). Purge gas, Ar 480 mL/min + H_2 20 mL/min; pyrolysis temperature, 300°C; atomization temperature, 2100°C.

10% glycerol as the slurry medium. During the pyrolysis stage, despite heavy smoke as a result of decomposition of the glycerol, no significant background signals were found in the atomization. Consequently, 10% glycerol solution was selected as the optimum concentration for the slurry medium.

Slurry Concentration

The slurry concentration is one of the important factors in the slurry technique. Because the slurry can be easily suspended, samples of high analytes content can be analyzed more readily by the slurry technique than by direct solid sampling. On the contrary, when the analyte content of the original sample is very low, the concentration of the slurry can be increased accordingly, though the pipetting efficiency can decrease if slurries are more concentrated. Lynch and Littlejohn [26] investigated an optimal slurry concentration range for the analysis of food. The accuracy deteriorated when the slurry concentration was >5% m/v, as a result of the excess of matrix. Slurry concentrations >5% also resulted in inefficient deposition of the slurry. Because ETA-AAS with the molybdenum tube atomizer is highly sensitive for cadmium, a slurry concentration of 0.05% was sufficient for evaluation of the cadmium content in the vegetable samples in this study.

Effect of Agitation Time

The effect of ultrasonic agitation time on a vegetable powder slurry sample was investigated. The results are shown in Fig. 2. Data for zero agitation time were observed from the slurry sample that was manually stirred for 2–3 s. The peak absorption

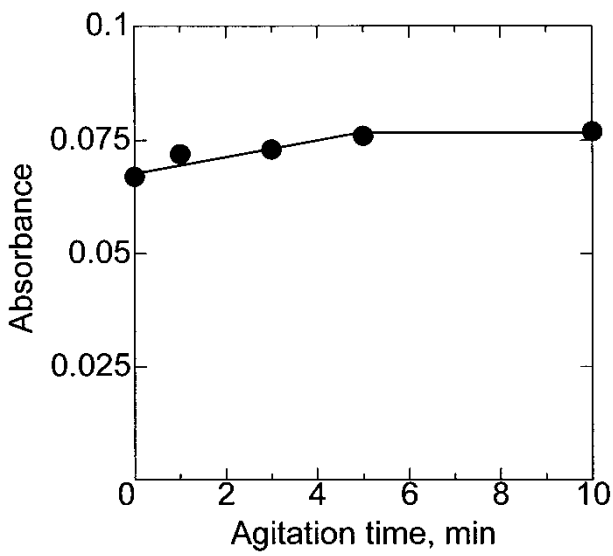

FIGURE 2 Effect of ultrasonic agitation time on the Cd signal using vegetable sample (Bind weed). Purge gas, Ar 480 mL/min + H_2 20 mL/min; pyrolysis temperature, 300°C; atomization temperature, 2100°C; slurry medium; 10% glycerol.

TABLE I Effect of the particle size of the vegetable samples on cadmium absorbance and the RSD of the absorbance

Particle size, μm		*Absorbance*	*RSD*, %
Range	*Average*		
150 ~ 300	225	0.010 ± 0.002	20
75 ~ 150	112	0.030 ± 0.003	10
38 ~ 75	56	0.049 ± 0.008	16
26 ~ 38	32	0.067 ± 0.005	7
< 26	–	0.060 ± 0.006	10

The number of replicate measurements >5.

increased for agitation times up to 5 min, and then reached a plateau. Therefore, an agitation time of 5 min was selected for the vegetable powder samples.

Effect of Particle Size

In general, the particle size of the solid material used to make a slurry can affect the stabilization, deposition and atomization efficiency of the slurry, and so can influence both accuracy and precision [9]. Nakamura *et al.* demonstrated that smaller particle diameter of tooth sample [27], silicate rocks [28] and quartz [29] gave better reproducibility. The effect of five different particle sizes of powdered vegetables was studied. The results are shown in Table I. Significant changes in absorption were observed with variation in particle size. The absorption signal gradually increased with decrease in particle size, down to the range 26–38 μm. This might be attributed to the good dispersion and homogeneity of relatively small suspended particles. For particle sizes < 26 μm, however, absorption signals were lower and RSD higher than for the 26–38 μm range. The reason for this is not clear, but it may be due to coagulation of the particles. Therefore, the best particle size was 26–38 μm for the slurry sampling technique.

Effect of Pyrolysis Temperature

The effect of the pyrolysis temperature on the atomic absorption signal of cadmium was investigated with the slurried vegetable sample in order to achieve sensitive absorption. The results are shown in Fig. 3. Though the trend in the presence of thiourea was very similar to that without thiourea, the curve shifted slightly to the higher temperature region in the former case. It was noted in previous papers [6,7] that thiourea reacts with many elements to form complexes, which mainly decompose into metal sulfides on heating. Sulfide formation in the pyrolysis process for slurry-sampling ETA-AAS may serve to eliminate the interference of matrix elements, because interferences from many elements in the aqueous solution were suppressed by the addition of thiourea. The shift to higher temperature range in the presence of thiourea may be due to the difference in the bond dissociation energies between CdO (280 kJ/mol) and CdS (201 kJ/mol) [30]. The absorbance of cadmium decreased gradually until 300°C, and abruptly thereafter. Consequently, in view of background absorption and reproducibility, 300°C was selected as the optimum pyrolysis temperature for the determination of cadmium in vegetable samples. This temperature was the same as those in

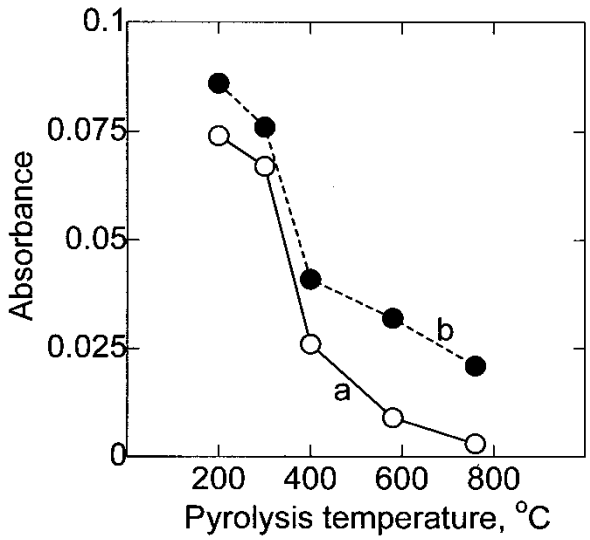

FIGURE 3 Effect of pyrolysis temperature on the Cd signal using vegetable sample (Bind weed). a, only vegetable sample; b, vegetable sample with thiourea. Purge gas, Ar 480 mL/min + H_2 20 mL/min; atomization temperature, 2100°C; slurry medium, 10% glycerol.

TABLE II Interferences on the atomic absorption signal of cadmium in 10% glycerol solution and the effect of thiourea

Interfering element	*Amount*, ng	*Absorbance*	
		Without thiourea	*With thiourea*
Cd	3×10^{-3}	0.233 ± 0.011	0.250 ± 0.014
Al	30	0.126 ± 0.012	0.256 ± 0.011
Ca	30	0.131 ± 0.006	0.246 ± 0.015
Fe	30	0.277 ± 0.008	0.220 ± 0.011
K	30	0.116 ± 0.013	0.282 ± 0.010
Mg	30	0.173 ± 0.006	0.236 ± 0.007
Na	30	0.174 ± 0.007	0.287 ± 0.023
Zn	30	0.089 ± 0.006	0.223 ± 0.011

The number of replicate measurements > 5.

the determination of cadmium using slurry-sampling ETA-AAS with the metal tube atomizer in biological materials [10] and drug samples [13].

Matrix Interferences

Generally, vegetables contain large amounts of Ca, Mg, Na and K. Although the interferences from matrix elements containing these elements were assessed for the atomization of Cd from aqueous solution [6], there is little information on the interferences in 10% glycerol solution. Therefore, using the molybdenum tube atomizer, the effects of Al, Ca, Fe, K, Mg, Na and Zn on the cadmium absorption signal were investigated for 10% glycerol solution. Most of the elements in the 10% glycerol solution interfered with the cadmium signal, as shown in Table II. These phenomena were different from the results obtained when glycerol was used as

a chemical modifier in the determination of lead [12], manganese [15] and copper [16] when using the molybdenum tube atomizer. In a previous work [8], the effect of thiourea as the matrix modifier on the elimination of interferences from coexisting elements has been reported. Hence, thiourea was tried as the matrix modifier for the atomization of Cd in 10% glycerol solution. In the presence of thiourea, the cadmium signal was little affected by the matrix elements in 10% glycerol solution. The interference-reducing effect of thiourea may result from sulfide formation of cadmium and the coexisting elements.

Detection Limit, Characteristic Mass and Reproducibility

The detection limit of cadmium by slurry sampling ETA-AAS with the molybdenum tube atomizer was 13 fg ($3S/N$, corresponding to 2.6 ng/g, 10-μL sample). The characteristic mass of cadmium, defined as the mass of analyte giving a peak height absorbance of 0.0044, with the molybdenum tube atomizer was 53 fg. These values were better than the detection limit (0.12 pg) and characteristic mass (0.85 pg) obtained for direct determination of solid biological sample by slurry sampling ETA-AAS [31].

The reproducibility of the cadmium atomic absorption signal by slurry sampling ETA-AAS with the molybdenum tube atomizer was investigated. The RSD with vegetable samples was 9% for seven measurements.

Determination of Cadmium in Vegetable Samples

The proposed method of slurry sampling ETA-AAS with the molybdenum tube atomizer was applied to the determination of cadmium in vegetable samples in Bangladesh. The dynamic range of the calibration curve was up to 50 ng/mL (100 μg/g in dry weight). When a deuterium lamp was used as the light source, insignificant background absorption signals were observed for the vegetable samples. The cadmium content of the vegetable samples is shown in Table III. The results from slurry sampling ETA-AAS were in good agreement with those obtained after acid digestion. The RSD for determination of cadmium in vegetable samples by the proposed method was better than 11%. The recovery of spiked cadmium from vegetable samples was in the range of 97–103%. This indicates excellent recovery of cadmium. The measured

TABLE III Results from determination of cadmium in vegetable samples (dry weight)

Sample	*Average particle size*, μm	*Amount of cadmium*			
		Added, μg/g	*Found*, μg/g	*Recovery*, %	*Acid digestion*, μg/g
Bind weed	32	–	1.82 ± 0.20	–	2.06 ± 0.11
		6	8.01 ± 0.30	103	–
Celery	32	–	1.58 ± 0.12	–	1.73 ± 0.07
		6	7.37 ± 0.22	97	–
Basil	32	–	1.75 ± 0.16	–	1.73 ± 0.09
		6	7.61 ± 0.39	98	–

The number of replicate measurements = 3.

data of cadmium content in vegetable samples in Bangladesh seems to be reasonable, considering that these vegetables were grown near the tannery industrial area. Here, we tried to roughly estimate the dietary intake of cadmium from vegetables for Bangladeshi people. The dry/wet conversion factor for Bangladeshi vegetables was approximately 0.11. Provided that the average per capita consumption of vegetables in Bangladesh is 130 g (wet weight)/(person day) [5], the dietary intake of cadmium from vegetables will be 23–26 μg/(person day). Compared to the PTWI of 7 μg/(kg_{bw} week) proposed by FAO/WHO, the estimated value will constitute 38–43% of the PTWI in the case of adults with 60-kg body weight. Therefore, since vegetables make up about 16% of the total diet in Bangladesh, the Cd content in common vegetables needs to be regularly and continuously monitored in order to minimize the risk of adverse health effects due to cadmium.

CONCLUSION

Slurry sampling ETA-AAS with a molybdenum tube atomizer has been shown to be a feasible means of determination of cadmium in vegetable samples. The best pyrolysis temperature was 300°C. Matrix element interference was investigated and using thiourea as a chemical modifier eliminated the interference caused by various elements. The analytical results for vegetable samples by the proposed method were in good agreement with those measured in acid-digested samples. Use of the metal tube atomizer with an argon–hydrogen atmosphere has the benefit of higher sensitivity and longer metal tube lifetime (more than 5000 firings) [11–14] compared with use of a graphite atomizer (200–250 firings) [32]. Thus the recommended method will be useful for reliable measurements of trace and ultra-trace levels of cadmium, with high accuracy, in various types of vegetable samples.

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