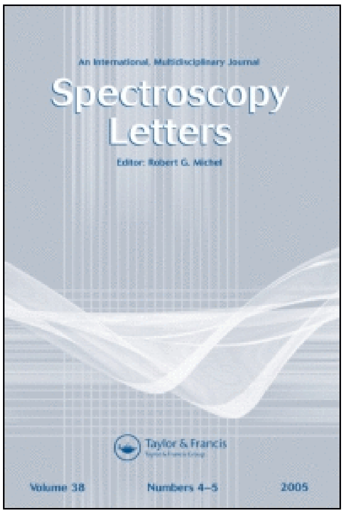

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Determination of Trace Cadmium and Zinc in Corn Kernels and Related Soil Samples by Atomic Absorption and Chemical Vapor Generation Atomic Fluorescence After Microwave-Assisted Digestion

Yongpei Ke[a]; Qun Sun[a]; Zhirong Yang[a]; Juanjuan Xin[b]; Li Chen[b]; Xiandeng Hou[b]
[a] College of Life Sciences, Sichuan University, Chengdu, Sichuan, China [b] College of Chemistry, Sichuan University, Chengdu, Sichuan, China

To cite this Article Ke, Yongpei , Sun, Qun , Yang, Zhirong , Xin, Juanjuan , Chen, Li and Hou, Xiandeng(2006) 'Determination of Trace Cadmium and Zinc in Corn Kernels and Related Soil Samples by Atomic Absorption and Chemical Vapor Generation Atomic Fluorescence After Microwave-Assisted Digestion', Spectroscopy Letters, 39: 1, 29 — 43

To link to this Article: DOI: 10.1080/00387010500434396

URL: http://dx.doi.org/10.1080/00387010500434396

Spectroscopy Letters, 39: 29–43, 2006

ISSN 0038-7010 print/1532-2289 online
DOI: 10.1080/00387010500434396

Determination of Trace Cadmium and Zinc in Corn Kernels and Related Soil Samples by Atomic Absorption and Chemical Vapor Generation Atomic Fluorescence After Microwave-Assisted Digestion

Yongpei Ke, Qun Sun, and Zhirong Yang
College of Life Sciences, Sichuan University, Chengdu, Sichuan, China

Juanjuan Xin, Li Chen, and Xiandeng Hou
College of Chemistry, Sichuan University, Chengdu, Sichuan, China

Abstract: Various hybrids or inbred lines of corn kernels and their corresponding soils were sampled from Sichuan, China, for the investigation of cadmium and zinc transfer from soil to corn. A new analytical procedure based on closed-vessel microwave-assisted digestion and chemical vapor generation atomic fluorescence spectrometry (CVG-AFS) was investigated for the determination of total trace cadmium in the corn samples, with accuracy confirmation by inductively coupled plasma atomic emission spectrometry (ICP-AES). Flame atomic absorption spectrometry (FAAS), also with accuracy confirmation by ICP-AES, was used for the determination of total Zn in the corn, also after the microwave digestion. For the corresponding soil samples, an incomplete digestion procedure (leaching or extraction) by 3 mL HNO_3 and 3 mL H_2O_2 proved to be adequate for the determination of zinc by FAAS, whereas a complete decomposition of the samples by the combination of 4 mL HNO_3, 3 mL HF, and 2 mL H_2O_2 was needed for the determination of cadmium by ICP-AES. A linear correlation was found between zinc content in corn kernels and that in the corresponding soil samples.

Keywords: Atomic absorption, atomic emission, atomic fluorescence, cadmium, chemical vapor generation, corn, inductively coupled plasma, microwave digestion, soil

Received 15 January 2005, Accepted 16 May 2005

Yongpei Ke is on leave from Agronomy College, Sichuan Agricultural University, Ya'an, Sichuan, China.

Address correspondence to Xiandeng Hou, College of Chemistry, Sichuan University, Chengdu, Sichuan, China. Fax: +86-28-85412907; E-mail: houxd@scu.edu.cn; houxiandeng@yahoo.com.cn

INTRODUCTION

Most heavy metals including cadmium and zinc transfer from soil to various plant seeds and accumulate in human and animal bodies through the consumption of food.[1–3] Cadmium is a nonessential element for human beings and animals and toxic beyond a certain concentration. Moreover, cadmium is not only toxic to human beings but also persistent in the environment once discharged; when absorbed, it stays in the human body with a very long half-life of more than a year.[4,5] Thus, the determination of cadmium in crop plants is of major importance due to its effects on the health of human beings and animals. Zinc, on the other hand, is a nutritional element for human beings, and zinc deficiency is found to be the cause of dwarfism and hypogonadism among adolescents, but zinc is also toxic at high concentration.[6] Therefore, the concentration levels of the two elements are among the important factors for corn quality.

There are many studies on the contamination of heavy metals in soil and their transfer within the soil-crop system.[7,8] Nan et al.[9] studied the cadmium and zinc interactions and their transfer in the soil-crop system under field conditions. It was found that increasing cadmium and zinc contents in soil could increase their accumulations in the crops. Pinto et al.[10] found that organic matter promoted the translocation of cadmium to plant shoots and decreased the uptake of copper, zinc, and iron. Cui et al.[8] evaluated the contamination levels in soil and vegetables with cadmium, lead, zinc, and copper and their transfer factors from soil to vegetable plants with their health risks calculated accordingly. Jung and Thornton[11] investigated the heavy metal contamination of soil and plants in the vicinity of a lead-zinc mine in Korea and found that the concentrations of heavy metals in soil decreased exponentially with distance from the mine source.

The most common methods for the determination of cadmium and zinc include FAAS,[1] electrothermal atomic absorption spectrometry (ETAAS),[12] ICP-AES,[13] and inductively coupled plasma mass spectrometry (ICP-MS).[14–16] Among these methods, ICP techniques and ETAAS are most sensitive, although somewhat expensive for the instrument and running costs. Chemical vapor generation atomic fluorescence spectrometry (CVG-AFS) is another very sensitive method for the determination of ultratrace cadmium, with much lower analytical cost than that of ETAAS or ICP techniques. By CVG-AFS, LODs of 8–10 ppt ($\mathrm{ng\,L^{-1}}$) can be obtained for the determination of cadmium.[17,18] To date, only samples with a relatively simple matrix, such as water,[12,17] and urine[19] have been analyzed by CVG atomic spectrometry for cadmium.

As for the sample digestion, a conventional scheme is mainly a fusion or a wet procedure based on an acidic digestion with a heated mixture of mineral acids. There are different heating systems that can be used for digestion such as a sand-bath,[20] an electric hot plate,[1,14] and a microwave oven.[21,22] Digestion procedures such as wet digestion or dry ashing are often the most time-consuming step of the analysis. These methods are laborious and tedious, often accompanied with a high tendency for contamination. With closed-vessel microwave digestion, analysis time, the amounts of reagents, and risk of contamination or volatile analyte loss can be greatly reduced.[13,21,22]

The goal of the current work was to establish convenient and accurate atomic spectrometric procedures for the determination of cadmium and zinc in soil samples and corn kernels, in order to investigate cadmium and zinc transfer from soil to corn. For fast and efficient sample digestion, a closed-vessel microwave digestion procedure with HNO_3-H_2O_2 was proposed for the digestion of the corn kernels. The concentrations of cadmium and zinc in the corn kernels were then determined by CVG-AFS (cadmium) and FAAS (zinc), respectively. The related soil samples were also analyzed for cadmium by ICP-AES and zinc by FAAS.

MATERIALS AND METHODS

Atomic Spectrometric Instruments

A commercial atomic fluorescence spectrometer (Model AFS-2202, Beijing Haiguang Instrument Co., Beijing, China) was used for the determination of cadmium in the corn samples. Details about the instrument can be found in previous publications.[18,21] The chemical vapor generation (CVG) reactor is shown in Fig. 1, with its optimal working program listed in Table 1.

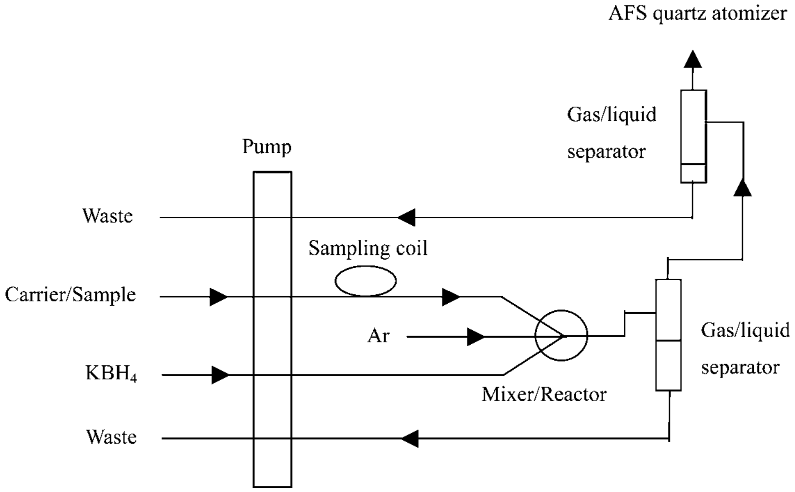

Figure 1. The schematic diagram of the intermittent CVG reactor for the AFS spectrometer.

Table 1. Optimal working-program for the intermittent-flow CVG reactor

Step	Flow rate[a] (mL min^{-1})	Time (s)	Reading
1	Sample, 7.1; reductant, 4.6	10	N
2	0	5	N
3	Carrier, 8.2; reductant, 5.3	16	Y
4	0	5	N

[a] Sample: cadmium in 3% HCl solution containing 1% thiourea and 2 μg mL^{-1} cobalt; reductant: 100 g L^{-1} KBH_4 in the medium of 8 g L^{-1} KOH solution; carrier: 3% HCl solution.

An FAAS instrument with Zeeman background correction (Model GGX-6, Beijing Haiguang Instrument Co.) was used for the determination of zinc in the corn and soil samples. The optimized FAAS instrumental parameters for the determination of zinc were lamp current, 4 mA; the height of the burner, 3 mm; the flow rate of C_2H_2, 1.3 L min^{-1}; and the flow rate of air, 7 L min^{-1}.

For comparison of the analytical results, an ICP-AES instrument (Iris Advantage, Thermo Jarrell Ash Corporation, Franklin, Massachusetts, USA) was used for the determination of cadmium (in both corn and soil) and zinc (in corn). The major instrumental parameters for the ICP-AES are power, 1150 W; sampling rate, 2.0 mL min^{-1}; nebulizer pressure, 27 PSI; integration time, 16 s; analytical lines, Cd 226.8 nm and Zn 213.9 nm; and the two-line (the closest baselines of the spectral profile of the analytical lines at each side) scheme was used for the background correction.

A common household cooking microwave oven (Model PJ17C-M, Midea Corporation, Guangdong, China) with five shifts, 17% power, 33% power, 55% power, 77% power, and 100% power, was used for the closed-vessel (70 mL Teflon containers) microwave sample digestion. The full power is 700 W. An electric hot plate (Model EH20A, LabTech Corporation, Beijing, China) with a controllable temperature range of 40°C to 250°C was used for the evaporation of the digests. The heating programs are described later in the analytical procedures.

Reagents and Standard Solutions

All solutions were prepared using distilled deionized water (denoted with sub-boiled deionized water) made with a quartz sub-boiler (Guoqiang Glass Instrument Corporation, Jintan, China). The purity of all the concentrated acids used for the experiments were analytical grade or better, the hydrogen peroxide

(30%, v/v), thiourea, KBH_4, $CoCl_2 \cdot 6H_2O$, and KOH were analytical grade and all purchased from Xilong Chemical Factory (Shantou, China).

Standard stock solution of cadmium, $1\,g\,L^{-1}$ in 5% HCl; working standard solution, $10\,ng\,Cd\,mL^{-1}$ prepared from step dilutions of the standard stock solution; and solution of KBH_4, $100\,g\,L^{-1}$ in the medium of $8\,g\,L^{-1}$ KOH. Five grams of thiourea was dissolved in 100 mL distilled water to obtain 5% thiourea solution. To obtain $1\,g\,L^{-1}$ cobalt solution, 0.4039 g $CoCl_2 \cdot 6H_2O$ was accurately weighted and dissolved in 100 mL distilled water. A solution containing $50\,\mu g\,Co\,mL^{-1}$ was prepared from step dilution of the $1\,g\,L^{-1}$ cobalt solution. Standard stock solution of zinc, $1\,g\,L^{-1}$ in 5% HNO_3; working standard solution, $5\,\mu g\,Zn\,mL^{-1}$ prepared from step dilutions of the zinc standard stock solution.

Procedures

Standard Calibration Series

To obtain the calibration curve of cadmium by CVG-AFS, we pipetted 5 mL of 5% thiourea solution, 1 mL of $50\,\mu g\,mL^{-1}$ cobalt solution, and 2.5 mL of 30% HCl solution into each of six 25-mL volumetric flasks, and then added 0, 0.25, 0.5, 1, 2, and 4 mL of $10\,ng\,mL^{-1}$ cadmium standard solution to the six volumetric flasks. Finally, we diluted the six volumetric flasks to the 25-mL mark with sub-boiled deionized water, then capped and shook them to mix well. The standard series obtained, with concentrations of 0, 0.1, 0.2, 0.4, 0.8, and $1.6\,ng\,mL^{-1}$, was measured under the optimized experimental conditions and used for the construction of the calibration curve of cadmium by CVG-AFS.

We pipetted 5 mL of 25% HNO_3 solution to each of five 25-mL volumetric flasks, and then added 0, 0.25, 0.5, 1, and 2 mL of $5\,\mu g\,mL^{-1}$ zinc standard solution to the five volumetric flasks. After dilution with sub-boiled deionized water to the 25-mL mark, and capping and shaking to mix well, the standard series with concentrations of 0, 0.05, 0.1, 0.2, and $0.4\,\mu g\,Zn\,mL^{-1}$ was obtained and used for the construction of the calibration curve by FAAS for the determination of zinc in corn. The standard series used for the determination of zinc by FAAS and cadmium by ICP-AES in the soil samples was 0.1, 0.2, 0.5, and $1\,\mu g\,Zn\,mL^{-1}$ and 1, 5, 10, and $50\,ng\,Cd\,mL^{-1}$, respectively. The standard series for the determination of cadmium by ICP-AES in the corn grain samples was 1, 2, 5, and $10\,ng\,Cd\,mL^{-1}$. The medium of the standard series for ICP-AES was all 5% HNO_3.

Analytical Procedure for Corn Samples

The corn samples were cleaned with sub-boiled deionized water and dried in an oven at 105°C for 24 hr, then the grains were ground into powder.

We accurately weighed around 0.2 g of the corn powder with an analytical balance to Teflon vessels, added 2 mL HNO_3 and 2 mL H_2O_2 to each of them, and then shoot the vessels slightly in order to mix well the solid and liquid. Then the Teflon vessels were closed tightly and put into a microwave oven for digestion. The heating program was 33% power for 3 min, 55% power for 5 min, 100% power (700 W) for 3 min, and 77% power for 3 min. After heating, they were taken out of the microwave oven and cooled to the ambient temperature before being opened under a laboratory hood. The digests were then quantitatively transferred into Teflon crucibles and heated to near dry on an electric hot plate at 200°C. The residues obtained were dissolved and transferred to 25-mL volumetric flasks with a mixture of 3% HCl, 1% thiourea, and 2 $\mu g\,mL^{-1}$ Co for the determination of cadmium by CVG-AFS. For the determination of zinc by FAAS, the digests were directly transferred to 25-mL volumetric flasks by sub-boiled deionized water. Because of the extremely low content of cadmium in corn grain and the relatively high limit of detection (LOD) for cadmium by ICP-AES, much larger amount of sample should be used for the ICP-AES determination. Therefore, digests of five trials were combined and quantitatively transferred to the Teflon crucibles and concentrated to nearly 3 mL on an electric hot plate and then transferred to 10 mL test tubes and diluted to the mark with sub-boiled deionized water for the determination of cadmium and zinc in corn grains by ICP-AES.

Analytical Procedure for Soil Samples

The soil samples were ground into powder (particle size: 76 μm) and dried in an oven at 105°C for 24 hr. We accurately weighed around 0.2 g of the sample to the Teflon vessels. For the determination of cadmium by ICP-AES, 4 mL HNO_3, 3 mL HF, and 2 mL H_2O_2 were added into the Teflon vessels. The heating program was 55% power for 5 min, 100% power for 10 min, and 77% power for 10 min. The digests were then quantitatively transferred into Teflon crucibles with sub-boiled deionized water, and 1 mL $HClO_4$ was subsequently added. The Teflon crucibles were then heated on the electric hot plate at 200°C until the white smoke nearly disappeared. The residues were dissolved and transferred to 25-mL volumetric flasks with 5% HNO_3. For the determination of zinc in soil samples by FAAS, 3 mL HNO_3 and 3 mL H_2O_2 were used as the digesting reagents. The heating program of the microwave oven remained unchanged. The samples were not completely decomposed in this case, and the digests obtained were mixtures of liquid and solid. After quantitatively transferred into 50-mL volumetric flasks with sub-boiled deionized water and shaken up, the mixtures were filtered and the filtrates obtained were analyzed by FAAS for zinc.

RESULTS AND DISCUSSION

Determination of Cadmium and Zinc in Corn Samples

Optimization of Instrumental Parameters of CVG-AFS for Cadmium

Considering the complication of the matrix, the CVG system with thiourea and cobalt was used for the determination of cadmium in corn by CVG-AFS. Still, the matrix of the soil is too complicated to be tolerated by the CVG approach, and the determination of cadmium in the soil samples was performed by ICP-AES. As expected, the higher value of the negative voltage of the photomultiplier tube or the higher the lamp current, the larger the fluorescence signal. However, the noise of the instrument also became more significant at the same time, and this meant that a higher negative voltage or lamp current would not always improve the signal-to-noise ratio (SNR). In this experiment, considering both the signal-to-background ratio and the SNR of the determination, a negative voltage of 310 V and a lamp current of 70 mA were chosen for use. Similarly, an observation height of 13 mm and an argon flow rate at 800 mL min^{-1} were selected for use.

Reaction Conditions for the Generation of Volatile Cd Species

For the CVG of cadmium, the significant factors are the concentrations of potassium tetrahydroborate, thiourea, cobalt, and acidity. As shown in Fig. 2 and Fig. 3, the concentrations of potassium tetrahydroborate and

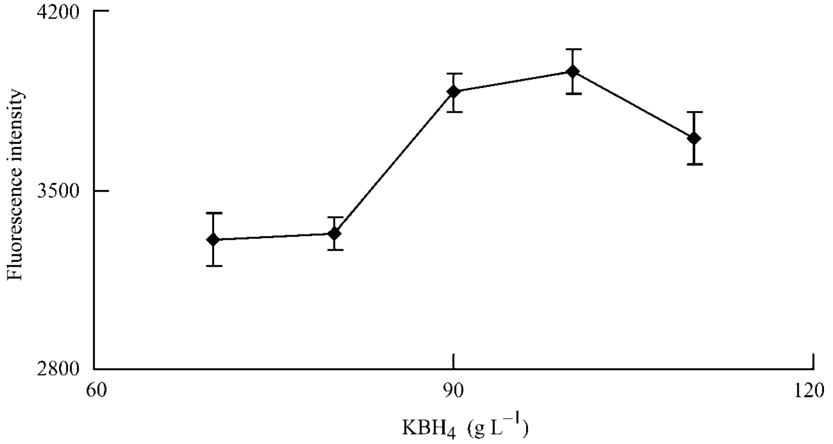

Figure 2. The influence of the concentration of KBH_4 on the intensity of fluorescence of cadmium. The error bars represent ± one standard deviation of fluorescence intensities of five parallel measurements. Cadmium standard, 2 ng mL^{-1}; thiourea, 10 g L^{-1}; cobalt, 2 μg mL^{-1}; KOH, 8 g L^{-1}; and hydrochloric acid, 3%.

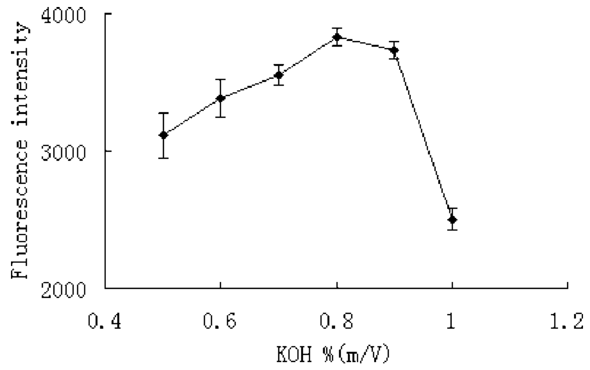

Figure 3. The influence of the concentration of KOH on the intensity of fluorescence of cadmium. The error bars represent ± one standard deviation of fluorescence intensities of five parallel measurements. Cadmium standard, 2 ng mL^{-1}; thiourea, 10 g L^{-1}; cobalt, 2 μg mL^{-1}; KBH_4, 100 g L^{-1}; and hydrochloric acid, 3%.

potassium hydroxide were chosen for 100 g L^{-1} and 8 g L^{-1}, respectively. Thiourea and cobalt act as catalysts for the CVG of cadmium, and the sensitivity of the determination is greatly increased with the presence of the two reagents.[17] In this experiment, it was found that the concentration of thiourea between 5 g L^{-1} and 10 g L^{-1} and cobalt between 1.5 μg mL^{-1} and 3 μg mL^{-1} did not significantly affect the stability of the fluorescence intensity of cadmium. A concentration of 10 g L^{-1} of thiourea and 2 μg mL^{-1} of cobalt in the final test solution was recommended for the determination for the best SNR.

Sample Preparation for the Determination of Cadmium

There is about 80% or more starch and cellulose in the corn powder;[23] so oxidants such as HNO_3, H_2O_2, or $HClO_4$ are needed for the digestion of corn samples. In this experiment, three acidic systems involving HNO_3-H_2O_2, aqua regia, and H_2O_2 only, respectively, were tested for the microwave-assisted digestion of the samples. When 4 mL H_2O_2 was used as a digesting reagent to avoid the influence of the acid remaining after the digestion, the heating time at 100% power must be prolonged to 10 min for complete decomposition of the corn samples. In addition, the fluorescence intensity was too low to be detected. One of the reasons for this phenomenon could be that the remnant H_2O_2 would consume KBH_4. For the aqua regia system, somehow the corn powder could not be completely decomposed. Finally, an acid combination of 2 mL HNO_3 and 2 mL H_2O_2 was recommended for the digestion, because the corn powder can be completely decomposed for a clear digest.

If the digests obtained were directly transferred into volumetric flasks with sub-boiled deionized water with calculated amounts of hydrochloric acid, thiourea, and cobalt added, there would be white precipitates generated, and the fluorescence intensity detected was very low. Because thiourea was a reducing reagent and there was N_xO_y remaining in the digests, the white precipitates might be something generated by the redox reaction of thoiurea and N_xO_y. Thus, the thiourea was consumed, and this (together with the excess remained acid) resulted in the low fluorescence intensity. Therefore, the N_xO_y or acid remaining in the digests must be removed before determination. Teflon crucibles were directly used as the containers for the evaporation of the digests to avoid high blank from glass containers and to simplify the procedure.[24]

Analytical Results of Cadmium and Zinc in the Corn Samples

The analytical results of cadmium and zinc in the corn samples by CVG-AFS and FAAS, respectively, in comparison with those by ICP-AES, are listed in Table 2. It can be seen that the analytical results for cadmium by both methods are in good agreement with each other. The recoveries of cadmium by CVG-AFS from corn samples ranged from 95% to about 110%. The precision and recoveries were satisfactory for trace element analysis. The corn grains are not contaminated with cadmium for all samples except Sample 178, of which the cadmium concentration is slightly larger than the threshold value ($<0.05\,\mu g\,g^{-1}$) of Chinese Standard GB 15201-1994. The concentrations of zinc in corn samples are relatively high and easy to measure by FAAS, thus the details are not discussed here. The contents of zinc in corn grains ranged from 14 to $35\,\mu g\,g^{-1}$, and the analytical results obtained by FAAS and ICP-AES were also in good agreement. Therefore, the corn grains are not contaminated with zinc, according to Chinese Standard GB 13106-1991 (Zn content $< 50\,\mu g\,g^{-1}$).

Determination of Zinc and Cadmium in Soil Samples

Sample Preparation

The determination of trace metals in soil is complicated by the diversity of the chemical and physical structure of soil. High concentrations of various poorly soluble silicates demand alternative methods for sample dissolution and the subsequent determination. Problems arising from the determination of metals in soil by FAAS or ICP-AES are mainly associated with the need to dissolve the sample.[1] Various acids have been used for the digestion of soil, such as HNO_3, $HClO_4$, HF, and HCl,[1,13,14] and the time for complete digestion is usually long, up to 30 hr at some extreme occasion.[14]

Table 2. The analytical results of cadmium and zinc in the corn samples (μg g^{-1})[a]

Corn samples	CVG-AFS (Cd ± 3SD)	ICP-AES (Cd ± 3SD)	FAAS (Zn ± 3SD)	ICP-AES (Zn ± 3SD)
Zhenghong 2	0.010 ± 0.004	0.012 ± 0.001	23.0 ± 1.3	19.8 ± 3.0
Zhenghong 6	0.011 ± 0.010	≤0.001 (calculated from LOD)	21.7 ± 0.5	17.7 ± 2.0
Zhenghong 115	0.013 ± 0.004	0.013 ± 0.003	25.6 ± 1.8	19.5 ± 2.3
Zhenghong 311	0.040 ± 0.025	0.020 ± 0.010	21.4 ± 1.7	18.2 ± 2.7
Chengdan 14	0.029 ± 0.016	0.027 ± 0.05	23.9 ± 0.7	19.9 ± 3.0
Fuyou 1	0.042 ± 0.015	0.031 ± 0.013	18.4 ± 0.6	20.5 ± 3.0
Danyu 56	0.029 ± 0.014	0.020 ± 0.010	19.0 ± 0.7	20.4 ± 2.4
E'yu 16	0.019 ± 0.002	0.016 ± 0.008	17.9 ± 3.9	16.1 ± 0.5
Yayu 10	0.017 ± 0.015	≤0.001 (calculated from LOD)	23.0 ± 2.7	23.3 ± 1.4
K169	0.008 ± 0.002	0.007 ± 0.003	14.3 ± 1.7	16.5 ± 0.5
200B	0.015 ± 0.004	0.012 ± 0.002	33.4 ± 3.0	35.1 ± 3.5
178	0.065 ± 0.033	0.051 ± 0.021	21.5 ± 3.9	21.2 ± 2.5
18-599	0.038 ± 0.013	0.033 ± 0.008	22.8 ± 2.7	23.1 ± 2.8

[a] Number of measurements = 3; SD = standard deviation. The limit of detection (LOD), all based on 11 measurements of a blank solution for standard deviation, was calculated as 3 standard deviation/slope of calibration curve. The LODs of Cd by CVG-AFS and ICP-AES were 0.01 ng mL^{-1} and 0.1 ng mL^{-1}, respectively, and those of Zn by FAAS and ICP-AES are 0.40 ng mL^{-1} and 0.076 ng mL^{-1}, respectively.

Table 3. Comparison of the analytical results of zinc in soils by the two digestion procedures ($\mu g\,g^{-1}$)[a]

Sample name	K169 (Zn ± 3SD)	Zhenghong 115 (Zn ± 3SD)	Zhenghong 311
(Zn ± 3SD)			
Complete digestion (ICP-AES)	94.1 ± 2.6	116 ± 1.9	102 ± 2.8
Incomplete digestion (FAAS)	93.0 ± 1.4	115 ± 3.0	105 ± 2.1

[a] Number of measurements = 3; SD = standard deviation.

Fortunately, many elements (such as zinc, lead, and manganese) in soil are unbound or weakly bound to silicates, and acids without HF are strong enough to dissolve/extract these metals from the soil sample. Usually, the extraction procedure is assisted by ultrasonic[25–28] or microwave.[25,29] In this work, a combination of HNO_3 and H_2O_2 was used for the microwave-assisted extraction. The analytical results for zinc in soil samples by this approach agreed very well with those by the complete digestion procedure, as shown in Table 3. However, a complete digestion, by use of HF, was needed for the ICP-AES determination of cadmium in these same soil samples. This means that some of cadmium is included inside or as a part of the crystal lattices of certain silicates.[15,30] It should be pointed out that the use of HF leads to a long, dangerous, and cumbersome procedure, and usually its use is not recommended for routine analysis. In this work, it was found that a leaching/extraction procedure with HNO_3-H_2O_2 in closed vessel by microwave heating was adequate for the determination of zinc in the soil samples.

Analytical Results of Cadmium and Zinc in Soil Samples

Soils with cadmium in excess of 1 $\mu g\,g^{-1}$ are considered to be evidence of anthropgenic pollution.[7,9] The mean level of cadmium in soil in Sichuan province is 0.079 $\mu g\,g^{-1}$.[23] Table 4 shows that the soils are contaminated with cadmium according to Chinese Standard GB15618-1995 (Cd content $<0.2\,\mu g\,g^{-1}$), because the concentration of cadmium is in the range 2∼3.6 $\mu g\,g^{-1}$. Recoveries of cadmium for the soil samples by ICP-AES ranged from 90% to 110%. Table 4 also shows that the analytical results of zinc in the soil samples ranged from 93 to 142 $\mu g\,g^{-1}$, so the soils are not contaminated with zinc according to Chinese Standard GB15618-1995 (Zn content $<200\,\mu g\,g^{-1}$).

Table 4. The analytical results of cadmium and zinc in soil ($\mu g\,g^{-1}$)[a]

Soil samples	Zn by FAAS (Zn ± 3SD)	Cd by ICP-AES (Cd ± 3SD)
Zhenghong 2-S	109 ± 3.3	3.3 ± 0.92
Zhenghong 6-S	101 ± 2.5	3.5 ± 0.54
Zhenghong 115-S	115 ± 3.0	2.8 ± 0.69
Zhenghong 311-S	105 ± 2.1	3.2 ± 0.084
Chengdan 14-S	111 ± 3.6	2.9 ± 0.96
Fuyou 1-S	94.6 ± 0.93	3.6 ± 0.023
Danyu 56-S	97.5 ± 3.3	3.5 ± 0.81
E'yu 16-S	97.8 ± 4.2	3.1 ± 0.45
Yayu 10-S	111 ± 4.5	3.0 ± 0.51
K169-S	93.0 ± 1.4	2.9 ± 0.15
200B-S	142 ± 2.8	2.3 ± 0.66
178-S	102 ± 2.3	2.0 ± 0.042
18-599-S	116 ± 2.7	2.5 ± 0.51

[a] Number of measurements = 3; SD = standard deviation.

Relationship of Zinc and Cadmium Contents in Corn Samples to Those in Soil Samples

It was reported that the transfer factors of the two metals from soil to crop parts were relatively low, and the order of the element transfer in different plant tissues was root > stem > grain. In this work, it was found that the zinc

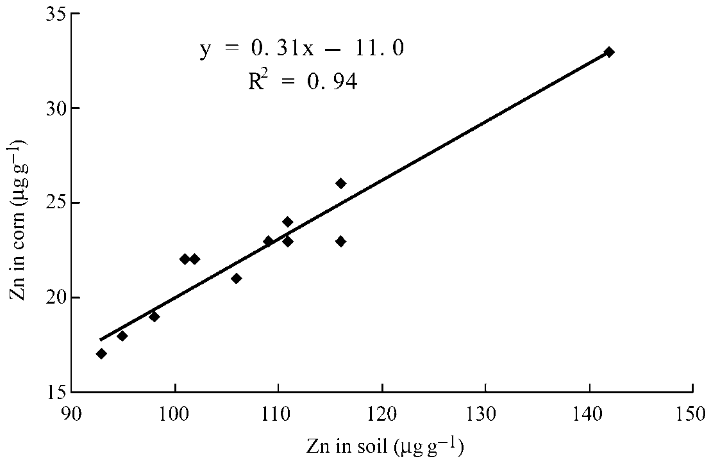

Figure 4. The relationship of Zn concentration in corn with zinc concentration in soil.

concentrations in the corn samples corresponded fairly linearly with those in the soil samples, with a correlation coefficient of 0.94, as shown in Fig. 4. There was no significant difference between hybrids and inbred lines, in terms of the corn's ability for accumulating zinc from soil. However, no statistical model could be found between the cadmium concentrations in the corn samples and those in the soil samples. The reason could be that the concentrations of cadmium in the soil samples are so close to each other, and the concentration of cadmium in corn samples are so low.

CONCLUSIONS

With closed-vessel microwave-assisted digestion, atomic spectrometric methods (CVG-AFS, FAAS, and ICP-AES) were successfully used for the determination of trace cadmium and zinc in corn and soil samples. This investigation showed that the zinc contents of the corn kernels correlated very well with those of the soils where they grew. According to Chinese National Standard and the analytical results of zinc in this work, there was no zinc contamination problem for the soil or the corn samples. However, it was found that the soil samples were contaminated with cadmium. Fortunately, the corn kernels (with one exception) were not contaminated with cadmium. The proposed analytical procedures can also be used for providing useful information for other agricultural studies, such as zinc and cadmium transfer from environmental soils to other plants.

ACKNOWLEDGMENTS

The authors are grateful to the Department of Science and Technology of Sichuan Province of China for the financial support for this project through grant no. JS02SQ02.

REFERENCES

1. HYongpei Ke is on leave from Agronomy College, Sichuan Agricultural University, Ya'an, Sichuan, China.ödrejYongpei Ke is on leave from Agronomy College, Sichuan Agricultural University, Ya'an, Sichuan, China.ärv, H.; Vaarmann, A. Pseudo-total analysis for metallic elements in siliceous soil by acid digestion and flame atomic absorption spectrometry. *Anal. Chim. Acta* **1999**, *396* (2–3), 293–301.
2. Stefanov, K.; Seizova, K.; Yanishlieva, N.; Marinova, E.; Popov, S. Accumulation of lead, zinc and cadmium in plant seeds growing in metalliferous habitats in Bulgaria. *Food Chem.* **1995**, *54*, 311–313.

3. Dudka, S.; Piotrowska, M.; Terelak, H. Transfer of cadmium, lead and zinc from industrially contaminated soil to crop plants: a field study. *Environ. Pollut.* **1996**, *94* (2), 181–188.
4. Zhang, Z. W.; Subida, R. D.; Agetano, M. G.; Nakatsuka, H.; Inoguchi, N.; Watanabe, T.; Shimbo, S.; Higashikawa, K.; Ikeda, M. Non-occupational exposure of adult women in Manila, the Philippines, to lead and cadmium. *Sci. Total Environ.* **1998**, *215* (1–2), 157–165.
5. Watanabe, T.; Zhang, Z.-W.; Qu, J.-B.; Xu, G.-F.; Song, L.-H.; Wang, J.-J.; Shimbo, S.; Nakatsuka, H.; Higashikawa, K.; Ikeda, M. Urban–rural comparison on cadmium exposure among general populations in Shandong Province, China. *Sci. Total Environ.* **1998**, *217* (1–2), 1–8.
6. Hussein, L.; Bruggeman, J. Zinc analysis of Egyptian foods and estimated daily intakes among an urban population group. *Food Chem.* **1997**, *58* (4), 391–398.
7. Abollino, O.; Aceto, M.; Malandrino, M.; Mentasti, E.; Sarzanini, C.; Petrella, F. Heavy metals in agricultural soil from Piedmont, Italy. Distribution, speciation and chemometric data treatment. *Chemosphere* **2002**, *49*, 545–557.
8. Cui, Y. J.; Zhu, Y. G.; Zhai, R. H.; Chen, D. Y.; Huang, Y. Z.; Qiu, Y.; Liang, J. Z. Transfer of metals from soil to vegetables in an area near a smelter in Nanning, China. *Environ. Int.* **2004**, *30*, 785–791.
9. Nan, Z. R.; Li, J. J.; Zhang, J. M.; Cheng, G. D. Cadmium and zinc interactions and their transfer in soil-crop system under actual field conditions. *Sci. Total Environ.* **2002**, *285* (1–3), 187–195.
10. Pinto, A. P.; Mota, A. M.; de Varennes, A.; Pinto, F. C. Influence of organic matter on the uptake of cadmium, zinc, copper and iron by sorghum plants. *Sci. Total Environ.* **2004**, *326* (1–3), 239–247.
11. Jung, M. C.; Thornton, I. Heavy metal contamination of soil and plants in the vicinity of a lead-zinc mine, Korea. *Appl. Geochem.* **1996**, *11*, 53–59.
12. PiYongpei Ke is on leave from Agronomy College, Sichuan Agricultural University, Ya'an, Sichuan, China.ñeiro, J. M.; PYongpei Ke is on leave from Agronomy College, Sichuan Agricultural University, Ya'an, Sichuan, China.érez, C. M.; Mahía, P. L.; Lorenzo, S. M.; FernYongpei Ke is on leave from Agronomy College, Sichuan Agricultural University, Ya'an, Sichuan, China.ández, E. F.; Rodríguez, D. P. Multivariate optimisation of hydride generation procedures for single element determinations of As, Cd, Sb and Se in natural waters by electrothermal atomic absorption spectrometry. *Talanta* **2001**, *53* (4), 871–883.
13. Sandroni, V.; Smith, C. M. M. Microwave digestion of sludge, soil and sediment samples for metal analysis by inductively coupled plasma-atomic emission spectrometry. *Anal. Chim. Acta* **2002**, *468* (2), 335–344.
14. Goossens, J.; Moens, L.; Dams, R. Inductively coupled plasma mass spectrometric determination of heavy metals in soil and sludge candidate reference materials. *Anal. Chim. Acta* **1995**, *304* (3), 307–315.
15. Ivanova, J.; Djinggova, R.; Korhammer, S.; Markert, B. On the microwave digestion of soil and sediments for determination of lanthanides and some toxic and essential elements by inductively coupled plasma source mass spectrometry. *Talanta* **2001**, *54* (4), 567–574.
16. Becker, J. S. Determination of trace elements in small amounts of environmental samples by ICP-MS: A review. *Can. J. Anal. Sci. Spectrosc.* **2002**, *47* (4), 98–108.
17. Guo, X. W.; Guo, X. M. Studies on the reaction between cadmium and potassium tetrahydroborate in aqueous solution and its application in atomic fluorescence spectrometry. *Anal. Chim. Acta* **1995**, *310* (2), 377–385.

18. Li, G.; Wu, L.; Xin, J. J.; Hou, X. D. Chemical vapor generation by reaction of cadmium with potassium tetrahydroborate and sodium iodate in acidic aqueous solution for atomic fluorescence spectrometric application. *J. Anal. At. Spectrom.* **2004**, *19* (9), 1010–1013.
19. Lampugnani, L.; Salvetti, C.; Tsalev, D. L. Hydride generation atomic absorption spectrometry with different flow systems and in-atomizer trapping for determination of cadmium in water and urine/overview of existing data on cadmium vapour generation and evaluation of critical parameters. *Talanta* **2003**, *61* (5), 683–698.
20. Wang, J. Y.; Dang, X. F.; Ding, D. M.; Wang, Z. Q. Reasons for increased zinc concentrations by complete digestion of soil samples. *Nongye Huanjing yu Fazhan* **2001** (4), 40–41.
21. Long, Z.; Xin, J. J.; Hou, X. D. Determination of arsenic and mercury in Chinese medicinal herbs by atomic fluorescence spectrometry with closed-vessel microwave digestion. *Spectrosc. Lett.* **2004**, *37* (3), 263–274.
22. Lamble, K. J.; Hill, S. J. Microwave digestion procedures for environmental matrices. *Analyst* **1998**, *123* (7), 103R–133R.
23. Liao, Z. J. *Huanjing zhong Weiliang Zhongjinshu Yuansu de Wuran Weihai yu Qianyi Zhuanhua*; Science Press: Beijing, 1989; pp. 43–75.
24. Bock, R. *A Handbook of Decomposition Methods in Analytical Chemistry*; International Textbook Co.: Edinburgh, UK, 1979; pp. 6–12.
25. Filgueiras, A. V.; Capelo, J. L.; Lavilla, I.; Bendicho, C. Comparison of ultrasound-assisted extraction and microwave-assisted digestion for determination of magnesium, manganese and zinc in plant samples by flame atomic absorption spectrometry. *Talanta* **2000**, *53* (2), 433–441.
26. Alvarez, J.; Marco, L. M.; Arroyo, J.; Greaves, E. D.; Rivas, R. Determination of calcium, potassium, manganese, iron, copper and zinc levels in representative samples of two onion cultivars using total reflection X-ray fluorescence and ultrasound extraction procedure. *Spectrochim. Acta Part B* **2003**, *58* (12), 2183–2189.
27. Barrera, P. B.; Naveiro, O. M.; PiYongpei Ke is on leave from Agronomy College, Sichuan Agricultural University, Ya'an, Sichuan, China.ñeiro, A. M.; Barrera, A. B. Experimental designs in the optimisation of ultrasonic bath-acid-leaching procedures for the determination of trace elements in human hair samples by atomic absorption spectrometry. *Forensic Sci. International* **2000**, *107*, 105–120.
28. Barrera, P. B.; Naveiro, Yongpei Ke is on leave from Agronomy College, Sichuan Agricultural University, Ya'an, Sichuan, China.Ó. M.; PiYongpei Ke is on leave from Agronomy College, Sichuan Agricultural University, Ya'an, Sichuan, China.ñeiro, A. M.; Barrera, A. B. The multivariate optimisation of ultrasonic bath-induced acid leaching for the determination of trace elements in seafood products by atomic absorption spectrometry. *Anal. Chim. Acta* **2001**, *439* (2), 211–227.
29. Sandroni, V.; Smith, C. M.M.; Donovan, A. Microwave digestion of sediment, soil and urban particulate matter for trace metal analysis. *Talanta* **2003**, *60* (4), 715–723.
30. Hoenig, M.; de Kersabiec, A. M. Sample preparation steps for analysis by atomic spectrometry methods: present status. *Spectrochim. Acta Part B* **1996**, *51* (11), 1297–1307.