

Simultaneous Determination of Cd and Fe in Beans and Soil of Different Regions of Brazil Using High-Resolution Continuum Source Graphite Furnace Atomic Absorption Spectrometry and Direct Solid Sampling

LISIA M. G. DOS SANTOS,^{†,‡} BERNHARD WELZ,^{*,†,¶} RENNAN G. O. ARAUJO,^{†,§}
 SILVANA DO C. JACOB,[‡] MARIA GORETI R. VALE,^{||,¶} ANDREAS MARTENS,[⊥]
 IRLAND B. GONZAGA MARTENS,[#] AND HELMUT BECKER-ROSS[∇]

[†]Departamento de Química, Universidade Federal de Santa Catarina, 88040-900 Florianópolis-SC, Brazil, [‡]Instituto Nacional de Controle de Qualidade em Saúde—INCQS-Fiocruz, Av. Brazil, 4365, 21040-900 Rio de Janeiro-RJ, Brazil, [¶]Instituto Nacional de Ciência e Tecnologia—INCT de Energia e Ambiente do CNPq, Universidade Federal da Bahia, 40170-115 Salvador-BA, Brazil, [§]Departamento de Química, Universidade Federal de Sergipe, Aracaju-SE, Brazil, ^{||}Instituto de Química, Universidade Federal do Rio Grande do Sul, Porto Alegre-RS, Brazil, [⊥]Institute of Inorganic and Analytical Chemistry, Technical University Braunschweig, Germany, [#]Instituto de Ciências da Saúde, Universidade Federal do Pará, Belem-PA, Brazil, and [∇]ISAS—Institute for Analytical Sciences, Department of Interface Spectroscopy, Berlin, Germany

A fast routine screening method for the simultaneous determination of cadmium and iron in bean and soil samples is proposed, using high-resolution continuum source graphite furnace atomic absorption spectrometry and direct solid sampling. The primary absorption line at 228.802 nm has been used for the determination of cadmium, and an adjacent secondary line, at 228.726 nm, for iron. Fourteen bean samples and 10 soil samples from nine states all over Brazil have been analyzed. The limits of detection (3σ , $n = 10$) were $2.0\ \mu\text{g kg}^{-1}$ for Cd and $4.5\ \text{mg kg}^{-1}$ for Fe. The relative standard deviation ranged from 4 to 7% for Cd and from 5 to 28% for Fe, which is usually acceptable for a screening method. The accuracy of the method has been confirmed by the analysis of two certified reference materials; the results were in agreement with the certified values at a 95% confidence interval.

KEYWORDS: Bean and soil samples; simultaneous determination of Cd and Fe; high-resolution continuum source AAS; graphite furnace atomization; direct solid sample analysis

1. INTRODUCTION

Since soil contamination by anthropogenic sources has increased significantly in many parts of the world, soil pollution has become an important environmental issue in industrialized countries. Heavy metals might influence the soil quality, the agricultural production and the groundwater quality, affecting human health through the water supply and foods (1). The content of metallic elements in foods depends on their concentration in the soil, their availability, and their capacity to be incorporated by the plants.

Cadmium is extremely toxic even at low concentration levels; it was classified as carcinogenic of group 1 (2) by the International Agency for Research on Cancer (IARC), and set in the seventh position in the list of the substances most aggressive to health and to the environment by the Program for Answers Reparations and Environmental Responsibilities (Cercla) of the ATSDR-EPA (3). Concern has therefore been expressed in several recent publications about pollution in environmental and health areas, because humans and animals are constantly exposed to such risks through air, soil, water and food (4).

The retention of cadmium in soil is positively correlated to cation exchange capacity, organic matter and pH, and appears to be negatively correlated to the amount of free iron oxide (5). Some studies show that foods contaminated with cadmium affect the absorption of important elements such as zinc, calcium and iron, essential in combating anemia (6), and that the iron depletion results in an increased intestinal absorption of Cd, and its subsequent transfer to the body circulation and tissues, particularly liver and kidneys (7, 8).

In developing countries, anemia affects predominantly the low-income group of the population, and it has in general a great impact on the quality of life in so-called Third World Countries. The increased risk for various infectious diseases is directly related to the reduction of immune resistance generated by anemia (9). Legumes, such as beans, constitute the main source of proteins and are a good source of mineral elements, such as iron, for large groups of population in Latin America and Africa. However, soil contamination affects the iron absorption and could cause damage to public health (10).

Recently a method for the simultaneous determination of cadmium and iron in grain products has been developed by our group (11) using high-resolution continuum source graphite furnace atomic absorption spectrometry (HR-CS GF AAS) (12)

*Corresponding author. E-mail: Welz@qmc.ufsc.br. Fax: +55-48-3721-6850.

and direct solid sampling (SS) analysis. The latter technique is particularly suited for fast screening analyses, as essentially no sample preparation is necessary, avoiding in addition all potential sources of error associated with this stage of an analysis. Direct SS analysis also provides the highest possible sensitivity, as no dilution at all is involved in this technique. In addition, HR-CS GF AAS has been shown to be an extremely rugged technique that makes possible direct SS analysis of complex samples using aqueous standards for calibration (13).

The purpose of this work was to investigate the possibility of extending the simultaneous determination of Cd and Fe to bean and soil samples coming from different regions of Brazil, in order to establish a fast routine screening procedure for this kind of analysis. While no major difficulties were expected for the bean samples, the soil samples have been a real challenge, first, because the matrix is obviously very much different, and second, because the iron content in soils is typically in the g kg^{-1} range, whereas it is in the mg kg^{-1} range in the beans, and the cadmium content is in the $\mu\text{g kg}^{-1}$ range in both types of samples. Possibilities to reduce the sensitivity of this technique, which usually offers the highest sensitivity, had therefore to be investigated in order to reach the goal.

2. EXPERIMENTAL PROCEDURES

2.1. Instrumentation. All the experiments were carried out using a prototype high-resolution continuum source atomic absorption spectrometer, based on a model AAS 6 Vario (Analytik Jena, Jena, Germany), from which all optical components, including the detector and controls, had been removed and replaced by a spectrometer built at ISAS (Berlin, Germany). This spectrometer consists of a high-intensity xenon short-arc lamp operating in a hot-spot mode, a high-resolution double monochromator and a CCD array detector. The double monochromator consists of a predispersing prism and a high-resolution echelle grating monochromator, resulting in a resolution of $\lambda/\Delta\lambda \approx 140,000$, corresponding to a resolution of ~ 1.6 pm per pixel at the cadmium line. The system is controlled by a Pentium III personal computer (100 MHz), running a data acquisition program developed at ISAS Berlin. Details of this equipment were described in previous publications of our group (12, 14, 15). The primary resonance line for Cd at 228.802 nm and the adjacent secondary line for Fe at 228.726 nm have been used for the simultaneous determination of the two elements. The atomic absorption for cadmium has been measured using peak volume selected absorbance (PVSA) (16) using three pixels ($A_{\Sigma 3, \text{int}}$), corresponding to a spectral interval of ~ 5 pm, as the best signal-to-noise ratio was obtained under these conditions. Iron in bean samples has been determined using the same measurement principle; however, the concentration of iron in the soil samples was too high, so that measurement at the line wings ($A_{\Sigma \pm 2, \text{int}}$) had to be used in order to reduce sensitivity and increase the working range.

The transversely heated graphite tube atomizer system supplied by Analytik Jena together with the model AAS 6 Vario has been used throughout. All experiments were carried out using pyrolytically coated SS graphite tubes without dosing hole (Analytik Jena Part No. 407-A81.303) and SS platforms (Analytik Jena Part No. 407-152.023). The samples were weighed directly onto the SS platforms using an M2P microbalance (Sartorius, Göttingen, Germany) and inserted into the graphite tube using a preadjusted pair of tweezers, which is part of the SSA 5 manual solid sampling accessory (Analytik Jena). For the measurement of solid samples the PVSA was normalized for a sample mass of 1 mg, as it is impossible (and unnecessary) to weigh and introduce always the same sample mass into the graphite furnace. Aqueous standards and modifier solutions were injected manually onto the SS platform using micropipets with disposable tips. Argon (99.996%, White Martins, São Paulo, Brazil) was used as purge and protective gas throughout. The optimized graphite furnace temperature program used for the simultaneous determination of Cd and Fe is shown in Table 1. The typical time required for one measurement including weighing and introducing the sample is about 2 min, so that five replicate measurements could be made within 10 min.

2.2. Reagents and Standard Solutions. A standard solution containing 1000 mg L^{-1} Cd was prepared from a Spex standard (Spex,

Table 1. Graphite Furnace Temperature Program for the Simultaneous Determination of Cadmium and Iron in Bean and Soil Samples by SS–HR–CS AAS Using W–Ir as the Permanent Modifier

stage	temp/°C	ramp/°C s ⁻¹	hold time/s	Ar flow rate/L min ⁻¹
drying	90	10	10	2.0
drying	130	5	5	2.0
pyrolysis	700	50	15	2.0
auto zero ^a	700	100	1	0
atomization ^a	1700	2000	3	0
atomization ^a	2600	3000	12	0
cleaning	2600	1000	3	2.0

^a Signal registration in these stages.

Table 2. Temperature Program for the Thermal Deposition of the Permanent Modifier on the SS Graphite Platform^a

stage	temp/°C	ramp/°C s ⁻¹	hold time/s
1	130	30	20
2	400	30	20
3	1000	100	10
4	2000	100	5

^a The gas flow was 2 L min^{-1} in all stages.

Eddison, NJ), and a 1000 mg L^{-1} Fe solution was obtained by diluting a Titrisol concentrate (Merck, Darmstadt, Germany) to volume. The calibration solutions were prepared daily through serial dilution of the stock solutions with the addition of 0.5% (v/v) nitric acid. Deionized water from a Milli-Q system (Millipore, Bedford, MA) with a resistivity of $18 \text{ M}\Omega \text{ cm}$ was used throughout. Atomic absorption standard solutions of 1000 mg L^{-1} Ir and 1000 mg L^{-1} W (both from Fluka, Buchs, Switzerland) have been used for the permanent modifiers. In order to coat the platform with the W–Ir mixed permanent modifier, five aliquots of $40 \mu\text{L}$ of the W modifier solution were applied first, each one followed by the temperature program shown in Table 2, and then five aliquots of $40 \mu\text{L}$ of the Ir modifier solution were applied, also followed by the same temperature program, resulting in a coating with $200 \mu\text{g}$ each of W and Ir.

The following certified reference materials (CRM) have been used in this work: BCR No. 191 Brown Bread and BCR No. 142 Light Sandy Soil (Community Bureau of Reference, Brussels, Belgium).

2.3. Collection and Preparation of the Samples. Fourteen bean samples and ten soil samples, collected in nine states of Brazil, have been investigated in this study. Most of the samples have been collected at experimental farms of Embrapa (Brazilian enterprise for research in agronomy and cattle breeding) or similar institutions. The soil samples were always taken close to the area where the beans (mostly *Faseolus vulgaris* L.) were grown. Ten soil samples were collected from each field, using a gauge auger (Eijkelcamp Agrisearch Equipment, The Netherlands) or a custom-made hand auger. The samples were collected in polyethylene bags and kept in an ice chest during transportation; then all bags were sealed and stored at $-18 \text{ }^\circ\text{C}$. In the laboratory the samples were allowed to warm to room temperature, and dried at $50 \text{ }^\circ\text{C}$ in an air-ventilated oven for 24 h. The samples were allowed to cool over silica gel and stored in closed polyethylene cups. All samples were first ground manually in an agate mortar until the material passed a mesh of 0.5 mm ; roots and plant material were removed during this procedure. Further grinding was done using a planetary ball mill (Fritsch Pulverisette model 05.102) with agate cups, lids and balls. The cups were rotated at 300 rpm for 20 min; the final fineness was $< 100 \mu\text{m}$. The analysis by SS–HR–CS GF AAS has been carried out without further sample treatment. The sample mass weighed onto the SS platforms was typically between 0.09 mg and 0.15 mg of soil.

A total amount of 1–2 kg of beans without pod was collected at each location in sealed plastic bags; the samples were transported in an ice chest and later stored at $-18 \text{ }^\circ\text{C}$ until further treatment. The frozen beans were allowed to warm up to room temperature slowly; shells and damaged beans were removed. The samples were weighed and dried at $50 \text{ }^\circ\text{C}$ in an air-ventilated oven for at least 24 h and treated in a laboratory mixer with stainless steel blades until a fine powder was obtained. Before the analysis by SS–HR–CS GF AAS, the samples were ground one more time in a vibration ball mill (model MM 200, Retsch, Düsseldorf, Germany) with

agate balls at a frequency of 30 s^{-1} for 30 min; the samples were not sieved, as a very fine powder was obtained after the treatment in the mill. The sample mass weighed onto the SS platforms was typically between 1.0 mg and 1.5 mg of beans.

3. RESULTS AND DISCUSSION

3.1. Method Development. The currently available spectrometers for HR-CS AAS are not designed for simultaneous multielement determination. Nevertheless, it is possible to determine more than one element at a time if the absorption line of a second element is located within the spectral interval that reaches the detector, which is about 0.3 nm at 200 nm and about 0.6 nm at 400 nm. This is of only minor interest in flame AAS, where fast sequential determination of several analytes under optimized conditions is clearly the better choice (17). In GF AAS, however, where fast sequential determination is not feasible because of the transient nature of the absorbance signals, simultaneous determination of more than one analyte is of great interest, as it reduces analysis time proportionally. However, several requirements have to be met in order to make this approach feasible, and conditions have to be optimized, as any simultaneous determination implies compromises.

One of the requirements is that a compromised graphite furnace temperature program can be established that makes possible the simultaneous determination of the analytes of interest without too many sacrifices in sensitivity and overall performance. This condition could be fulfilled in the simultaneous determination of Cd and Fe in grain products using W–Ir as permanent chemical modifier and a two-step atomization, as shown in Table 1 (11). Another requirement is that the sensitivity ratio between the elements to be determined at the available analytical lines corresponds roughly to the concentration ratio of the analytes in the samples to be analyzed. This was for example the case for the simultaneous determination of Cr and Fe (18), and Co and V (19) in crude oil. This condition was also fulfilled in the analysis of grain products (11), as the iron line 228.726 nm is about 2 orders of magnitude less sensitive than the primary line 248.327 nm, and about 3 orders of magnitude less sensitive than cadmium at the 228.802 nm line. This situation is shown in Figure 1 for the CRM Brown Bread, and it has been anticipated that the same could apply for the bean samples. However, it could also be expected that the developed method could not be transferred directly to soil samples, which are usually rich in iron, particularly in many regions of Brazil.

Fortunately HR-CS AAS offers various possibilities to decrease sensitivity and increase linearity by choosing appropriate pixels for measurement (12, 16). Maximum sensitivity and the best S/N ratio are usually obtained when the integrated absorbance measured at three or five pixels at the line core is summated, a procedure called peak volume selected absorbance, PVSA (16). On the other hand, sensitivity can be reduced and the linear working range extended significantly when measurement is made at the line wings; this becomes obvious from Figure 2, where the absorbance signals recorded at different pixels in the vicinity of the iron line at 228.726 nm are shown for BCR CRM 142 (Light Sandy Soil). A careful study has been carried out recently about the possibility to extend the linear working range for the determination of iron using measurement at the line wings (20), and the results of this study have been used in this work for the simultaneous determination of Cd and Fe in soil samples.

3.2. Calibration and Validation. Several calibration approaches were proposed in the literature to compensate for potential matrix effects in direct SS–GF AAS, such as calibration against solid standards (usually CRM) with a matrix composition and analyte concentration similar to those of the sample to be

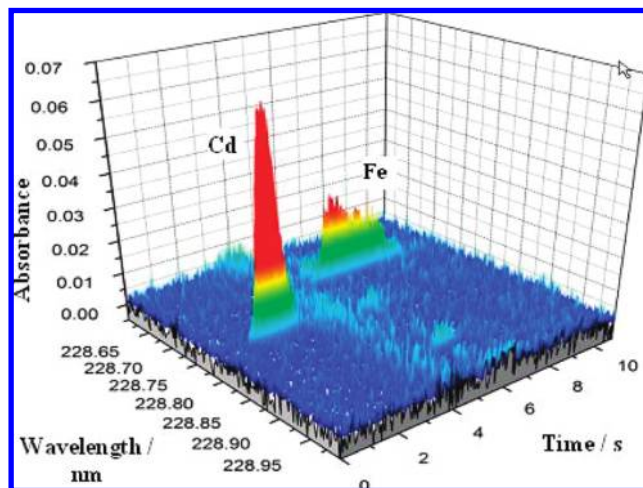


Figure 1. Time- and wavelength-resolved absorbance spectrum for the BCR CRM 191 (Brown Bread) in the vicinity of the cadmium resonance line at 228.802 nm; pyrolysis temperature, 700 °C; atomization temperature, 1700 °C for Cd and 2600 °C for Fe; W–Ir mixed permanent modifier.

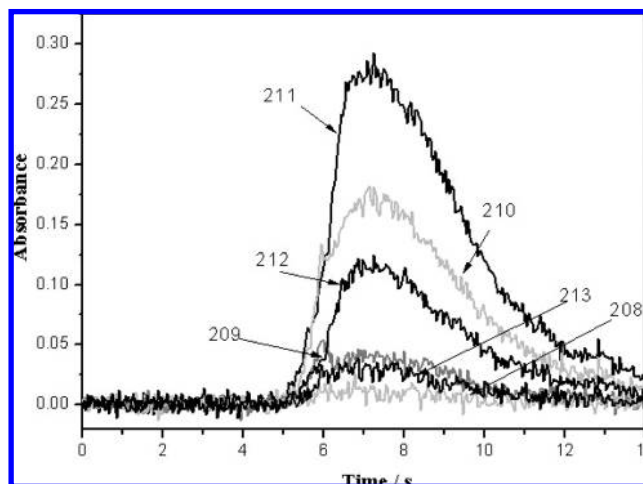


Figure 2. Transient absorbance signals measured for BCR CRM 142 (Light Sandy Soil) at pixels 208–213 in the vicinity of the secondary iron line at 228.725 nm (pixel 211); pyrolysis temperature, 700 °C; atomization temperature, 2600 °C; W–Ir mixed permanent modifier; sample mass, 0.043 mg.

analyzed, and a three-dimensional analyte addition technique (21). However, if the literature about SS–GF AAS of the last 15–20 years is consulted, the vast majority of determinations have actually been carried out using aqueous standards for calibration (13, 21), which is mostly due to the uncompromising use of the stabilized temperature platform furnace concept (22). The main components of this concept are (i) atomization from a L'vov platform, (ii) integration over the peak area, (iii) the use of a chemical modifier and (iv) efficient background correction. The latter one was always the weak link in conventional AAS, a problem that has been finally solved with the introduction of HR-CS GF AAS, which also reflects in the publications about direct solid sampling using aqueous standards for calibration (13).

Calibration against aqueous standards has therefore been investigated in this work as well, as it is without doubt the most convenient approach for a screening procedure. The linearity assessment was based on the methodology described by Souza et al. (23) The calibration curves have been prepared, with concentration levels of 1, 3, 5, and $7\ \mu\text{g L}^{-1}$ Cd (corresponding to 10, 30,

50, 70 pg of Cd), and 1, 2, 4, and 6 mg L⁻¹ Fe (corresponding to 10, 20, 40, and 60 ng of Fe) for the determination of Cd in beans and soil and the determination of Fe in bean samples; for the determination of Fe in soil samples, calibration curves have been prepared with concentrations of 20, 50, 100, 200, and 400 mg L⁻¹ Fe (corresponding to 200, 500, 1000, 2000, and 4000 ng of Fe). The linearity has been tested by examining a plot of residuals produced by linear regression of the response on the concentration in an appropriate calibration set. The statistic test (Ryan–Joiner, Levene, Durbin–Watson) has been carried out by comparing the lack-of-fit variance with that due to pure error, which confirmed the linearity of the calibration curves for Cd and Fe (24).

Two CRM have been used to validate the method, BCR CRM 191, Brown Bread, and BCR CRM 142, Light Sandy Soil. The results, which are shown in **Table 3**, clearly confirm that aqueous standards can be used for this kind of analysis, giving results that are within the 95% confidence interval of the certified values. The only concern might be the precision of the iron determination in soil, which exhibits high uncertainty. This is without doubt due to the very small sample size of typically <0.1 mg used for these determinations and to the natural inhomogeneity of the iron distribution in soil samples.

3.3. Figures of Merit. The figures of merit of the method have been established using aqueous calibration standards and are summarized in **Table 4**. The data are in part different for bean and soil samples, at least in concentration, as the data for beans have been based on an average sample mass of 0.5 mg, whereas those for soil are calculated for 0.07 mg of sample. For the analysis of real samples, however, lower or higher masses have been used, depending on the actual analyte concentrations. All measurements of Cd and Fe in the bean samples are based on the PVSA of three pixels ($A_{\Sigma 3, \text{int}}$) around the line core. The measurements of Cd in soil samples are based on the same principle, whereas those for Fe in soil samples are based on the summation of the integrated absorbance measured at two side pixels (209 + 213; refer to **Figure 2**) that are located at the two line wings ($A_{\Sigma \pm 2, \text{int}}$) symmetrically to the line center. Two calibration curves of significantly different inclination have been obtained in this case for low and high iron concentrations, respectively, as has been described previously (20).

Table 3. Results Obtained for the Determination of Cd and Fe in BCR CRM 191 (Brown Bread) and BCR CRM 142 (Light Sandy Soil) Using the Proposed Procedure and Aqueous Standards for Calibration ($n = 5$)

CRM	Cd/mg kg ⁻¹		Fe/g kg ⁻¹	
	certified	found	certified	found
BCR 191	0.028 ± 0.002	0.025 ± 0.002	0.0407 ± 0.0024	0.0410 ± 0.0086
BCR 142	0.25 ± 0.09	0.24 ± 0.07	28.0 ^a	27.9 ± 5.9

^a Expressed as Fe₂O₃

The limit of detection (LOD) was calculated according to the 'zero mass response' (25) as three times the standard deviation of the signal obtained for 10 repetitive atomization cycles with an empty SS platform, only containing the modifier. The LOD was 2.0 μg kg⁻¹ for Cd and 4.5 mg kg⁻¹ for Fe in the bean samples, and 14 μg kg⁻¹ for Cd and 170 mg kg⁻¹ for Fe in the soil samples, respectively. The limit of quantification (LOQ) is defined as ten times the standard deviation, using the same measurements as for the LOD.

The characteristic mass (m_0), which is defined as the analyte mass that gives a PVSA of 0.0044 s, has been determined in this work as 0.7 pg for Cd, which is in agreement with literature data; the characteristic mass found for Fe was 1.0 ng using the PVSA of three pixels and 2.0 ng for sum of the pixel 209 and 213; no values could be found in the literature for this line for comparison.

The precision is defined as the closeness of agreement between independent test results under stipulated conditions (26). In this work precision is expressed as relative standard deviation (% RSD) of five replicate measurements of a CRM (refer to **Table 3**). The RSD values were between 4% and 7% for Cd and between 5% for Fe in the bread CRM and 28% in soil CRM. The significantly higher RSD for Fe in soil is most likely due to the very small sample mass used for this determination and the inhomogeneous distribution of iron in the investigated CRM.

3.4. Analysis of Real Samples. The proposed method has been used for the simultaneous determination of cadmium and iron in bean and soil samples from different regions of Brazil; the results of the investigation, using aqueous standards for calibration, are shown in **Table 5**. The concentration of cadmium in most of the bean samples, except for two, was below 2 μg kg⁻¹, a value that is

Table 5. Results Obtained for the Determination of Cadmium and Iron in Bean and Soil Samples Using SS–HR–CS GF AAS and Aqueous Standards for Calibration^a

state	type	beans		soil	
		Cd/μg kg ⁻¹	Fe/mg kg ⁻¹	Cd/μg kg ⁻¹	Fe/g kg ⁻¹
Amazonas	brown	10 ± 1	57 ± 10	315 ± 54	67 ± 22
	black	24 ± 6	80 ± 6		
Pará	brown	<2	57 ± 6	<14	4.7 ± 1.6
Ceará	brown	<2	61 ± 6	30 ± 6	78 ± 16
Goiás	white	<2	99 ± 16	57 ± 8	>200
Mato Grosso do Sul	brown	<2	127 ± 28	24 ± 1	47 ± 10
Minas Gerais	brown	<2	104 ± 13	<14	133 ± 63
	brown	<2	117 ± 19		
Paraná	black	<2	103 ± 12	28 ± 1	87 ± 36
Santa Catarina	black	<2	111 ± 21	62 ± 4	11 ± 2
	brown	<2	69 ± 13	14 ± 5	<0.5
Rio Grande do Sul	black	<2	161 ± 21	40 ± 6	118 ± 44
	brown	<2	159 ± 16		

^a For details refer to the text.

Table 4. Figures of Merit for the Simultaneous Determination of Cd and Fe by SS–HR–CS ET AAS at 228.802 and 228.726 nm, Respectively^a

parameter	beans ^b		soil ^c		
	Cd	Fe	Cd	Fe	
calibration range	10–70 pg/1–7 μg L ⁻¹	10–60 ng/1–6 mg L ⁻¹	10–70 pg/1–7 μg L ⁻¹	20–200 ng/2–20 mg L ⁻¹	200–4000 ng/20–400 mg L ⁻¹
analytical curve	$A_{\Sigma 3, \text{int}} = 0.0058m_{\text{Cd}} + 0.0092$	$A_{\Sigma 3, \text{int}} = 0.0046m_{\text{Fe}} + 0.0019$	$A_{\Sigma 3, \text{int}} = 0.0058m_{\text{Cd}} + 0.0092$	$A_{\Sigma \pm 2, \text{int}} = 0.0021m_{\text{Fe}} + 0.0353$	$A_{\Sigma \pm 2, \text{int}} = 0.0008m_{\text{Fe}} + 0.2451$
R	0.9998	0.9998	0.9998	0.9991	0.9985
m_0	0.7 pg	1.0 ng	0.7 pg	2.0 ng	6 ng
LOD	1.0 pg/2.0 μg kg ⁻¹	2.2 ng/4.5 mg kg ⁻¹	1.0 pg/14 μg kg ⁻¹	12 ng/170 mg kg ⁻¹	nd ^d
LOQ	3.0 pg/6.0 μg kg ⁻¹	7.5 ng/15 mg kg ⁻¹	3.0 pg/43 μg kg ⁻¹	40 ng/570 mg kg ⁻¹	nd ^d

^a For details refer to the text. ^b Calculated for an average sample mass of 0.5 mg. ^c Calculated for an average sample mass of 0.07 mg. ^d nd = not determined; conditions used for high analyte concentrations only.

well below the limits established by the *Codex Alimentarius* (0.2 mg kg^{-1}) and the Brazilian National Health Surveillance Agency—ANVISA (1.0 mg kg^{-1}) (27). It is interesting to note that the only cadmium concentrations above the LOQ were found in beans that had been grown on a soil the cadmium content of which was about an order of magnitude above the average for all the other soils. This suggests a direct correlation between the cadmium content in soil and in beans, although the number of samples analyzed here is clearly too small to allow any statistical comparison. The values obtained for cadmium in soil samples were between < 14 and $315 \mu\text{g kg}^{-1}$, with an average around $31 \mu\text{g kg}^{-1}$, not considering the soil from Amazonas. These values are well below those found ($< 1.0 \text{ mg kg}^{-1}$), and the limits established (3.0 mg kg^{-1}) for agricultural soils in Europe (28). The cadmium concentration in Brazilian soil is related to various factors, such as organic matter, pH, CaCO_3 , that influence absorption and retention of this element (5).

The content of iron in beans ranged from 57 mg kg^{-1} to 159 mg kg^{-1} . According to Embrapa the amount of iron in beans should be approximately 76 mg kg^{-1} , which corresponds to 29% of women's daily needs and 55% of men's needs (29). Hence, we can say that the beans produced in Brazil do have a sufficiently high iron content, which is in contrast to many grain products, which do not provide a sufficient iron supply (11). The iron content in the investigated soils ranged from $< 0.5 \text{ g kg}^{-1}$ to 133 g kg^{-1} . The high concentration of iron, in the soil samples, has been according to expectation because of the reddish color of most of the samples, characteristic of the iron oxide. There appears to be no correlation between the iron content in the soil that varied by more than 2 orders of magnitude, and that in the beans grown on that soil, which varied by less than a factor of 3. This means that the iron uptake by the plants is regulated by a mechanism that is independent of the iron content in the soil and that also assures sufficient iron content in the beans in case the soil is low in iron.

LITERATURE CITED

- Beach, J.; Tume, P.; Longan, L.; Revert, F.; Bech, J.; Tume, L.; Tempio, M. Concentration of Cd, Cu, Pb, Zn, Al, and Fe in soils of Manresa, NE Spain. *Environ. Monit. Assess.* **2008**, *14*, 257–266.
- World Health Organization. *Safety evaluation of certain food additives and contaminants. WHO food additives Series: 59*; IPCS-International Programme on Chemical Safety: Geneva, 2008. <http://www.codexalimentarius.net>.
- Agency for Toxic Substances and Disease Registry. Top 20 Hazardous Substances from the CERCLA Priority List of Hazardous Substances for 2005. <http://www.atsdr.cdc.gov/>.
- Mirlean, N.; Roisenberg, A. The effect of emissions of fertilizer production on the environment contamination by cadmium and arsenic in southern Brazil. *Environ. Pollut.* **2006**, *143*, 335–340.
- De Matos, A. T.; Fontes, M. P. F.; Da Costa, L. M.; Martinez, M. A. Mobility of heavy metals as related to soil chemical and mineralogical characteristic of Brazilian soils. *Environ. Pollut.* **2001**, *111*, 429–435.
- Reeves, P. G.; Chaney, R. L. Bioavailability as an issue in risk assessment and management of food cadmium: A review. *Sci. Total Environ.* **2008**, *398*, 13–19.
- Min, K. S.; Iwata, N.; Tetsutikawahara, N.; Onosaka, S.; Tanaka, K. *Toxicol. Lett.* **2008**, *179*, 48–52.
- Min, K. S.; Ueda, H.; Kihara, T.; Tanaka, K. Increased hepatic accumulation of ingested Cd is associated with up regulation of several intestinal transporters in mice fed diets deficient in essential metals. *Toxicol. Sci.* **2008**, *106*, 284–289.
- Moura, N. C.; Canniatti-Brazaca, S. G. Avaliação da disponibilidade de ferro de feijão comum (*Phaseolus vulgaris* L.) em comparação com carne bovina. *Cienc. Tecnol. Aliment.* **2006**, *26*, 270–276.
- Laparra, J. M.; Glahn, R. P.; Miller, D. D. Bioaccessibility of phenols in common beans (*Phaseolus vulgaris* L.) and iron (Fe) availability to Caco-2 cells. *J. Agric. Food Chem.* **2008**, *56*, 10999–11005.
- Dos Santos, L. M. G.; Araujo, R. G. O.; Welz, B.; Jacob, S. C.; Vale, M. G. R.; Becker-Ross, H. Simultaneous determination of Cd and Fe in grain products using direct solid sampling and high-resolution continuum source electrothermal atomic absorption spectrometry. *Talanta* **2009**, *78*, 577–583.
- Welz, B.; Becker-Ross, H.; Florek, S.; Heitmann, U. *High-Resolution Continuum Source AAS - The Better Way to do Atomic Absorption Spectrometry*; Wiley-VCH: Weinheim, Germany, 2005.
- Welz, B.; Vale, M. G. R.; Borges, D. L. G.; Heitmann, U. Progress in direct solid sampling analysis using line source and high-resolution continuum source electrothermal atomic absorption spectrometry. *Anal. Bioanal. Chem.* **2007**, *389*, 2085–2095.
- Vale, M. G. R.; Damin, I. C. F.; Klassen, A.; Silva, M. M.; Welz, B.; Silva, A. F.; Lepri, F. G.; Borges, D. L. G.; Heitmann, U. Method development for the determination of nickel in petroleum using line-source and high-resolution continuum-source graphite furnace atomic absorption spectrometry. *Microchem. J.* **2004**, *77*, 131–140.
- Silva, A. F.; Borges, D. L. G.; Welz, B.; Vale, M. G. R.; Silva, M. M.; Klassen, A.; Heitmann, U. Method development for the determination of thallium in coal using solid sampling graphite furnace atomic absorption spectrometry with continuum source high-resolution monochromator and CCD array detector. *Spectrochim. Acta, Part B* **2004**, *59*, 841–850.
- Heitmann, U.; Welz, B.; Borges, D. L. G.; Lepri, F. G. Feasibility of peak volume, side pixel and multiple peak registration in high-resolution continuum source graphite furnace atomic absorption spectrometry. *Spectrochim. Acta, Part B* **2007**, *62*, 1222–1230.
- Raposo Júnior, J. L.; De Oliveira, S. R.; Caldas, N. M.; Gomes Neto, J. A. Evaluation of alternate lines of Fe for sequential multi-element determination of Cu, Fe, Mn and Zn in soil extracts by high-resolution continuum source flame atomic absorption spectrometry. *Anal. Chim. Acta* **2008**, *627*, 198–202.
- Dittert, I. M.; Silva, J. S. A.; Araujo, R. G. O.; Curtius, A. J.; Welz, B.; Becker-Ross, H. Direct and simultaneous determination of Cr and Fe in crude oil using high-resolution continuum source graphite furnace atomic absorption spectrometry. *Spectrochim. Acta, Part B* **2009**, *64*, 537–543.
- Dittert, I. M.; Silva, J. S. A.; Araujo, R. G. O.; Curtius, A. J.; Welz, B.; Becker-Ross, H. Simultaneous determination of cobalt and vanadium and their volatile fractions in crude oil using direct analysis by high-resolution continuum source graphite furnace atomic absorption spectrometry. *J. Anal. At. Spectrom.*, accepted for publication September 30, 2009.
- Welz, B.; Santos, L. M. G.; Araujo, R. G. O.; Jacob, S. C.; Vale, M. G. R.; Becker-Ross, H. Unusual calibration curves observed for iron using high-resolution continuum source graphite furnace atomic absorption spectrometry. *Spectrochim. Acta, Part B*, accepted for publication September 28, 2009.
- Vale, M. G. R.; Oleszczuk, N.; Dos Santos, W. N. L. Current status of direct sampling for electrothermal atomic absorption Spectrometry - A critical review of the development between 1995 and 2005. *Appl. Spectrosc. Rev.* **2006**, *41*, 377–400.
- Slavin, W.; Manning, D. C.; Carnrick, G. R. The stabilized temperature platform furnace. *At. Spectrosc.* **1981**, 137–145.
- Souza, S. V. C.; Lima, J. A.; Teodoro, J. C.; Junqueira, R. G. In-house validation of a multi-residue method for determining residual avermectin in cow's milk by HPLC coupled with fluorescence detection. *Cienc. Tecnol. Aliment.* **2007**, *27*, 823–836.
- Miller, J. C.; Miller, J. N. *Statistics for Analytical Chemistry*, 2nd ed.; Ellis Harwood Ltd: England, 1998.

- (25) Kurfürst, U. In *Solid sample analysis – Direct and slurry sampling using GF AAS and ETV-ICP*; Springer: Berlin, Heidelberg, New York, 1998; pp 115-116.
- (26) Welz, B.; Sperling, M. *Atomic Absorption Spectrometry*; Wiley-VCH: Weinheim, Germany, 1999.
- (27) BRASIL. Decreto n° 55871, de 26 de março do 1965. Modifica o Decreto n° 50040, de 24 de Janeiro de 1961, referente a normas reguladoras do emprego de aditivos para alimento, alterado pelo Decreto n° 691 de 13 de Abril de 1962. Diário Oficial [da] República Federativa do Brasil, Poder Executivo, Brasília, DF, 09 abr. 1965.
- (28) Gonzaga, B. I. *Avaliação nutricional relativa ao selênio em crianças com dieta enriquecida de castanha-do-brasil*; Universidade de São Paulo, Brazil, 2002.
- (29) <http://www.cnpaf.embrapa.br/parperfeito/feijao/composicao.htm>, accessed in April 2009.

Received July 20, 2009. Revised manuscript received September 9, 2009. Accepted September 14, 2009. The authors are grateful to Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) for financial support. L.M.G.d.S. has a scholarship from CAPES, and R.G.O.A., B.W. and M.G.R.V. have research scholarships from CNPq. The authors are also grateful to Analytik Jena AG for the donation of the prototype HR-CS GF AAS equipment.