Background Corrections in the Determination of Cd and Pb by Flame AAS in Plant and Soil Samples with High Fe Levels

J. J. VAN DER LEE,* E. TEMMINGHOFF, V. J. G. HOUBA, and I. NOVOZAMSKY

Department of Soil Science and Plant Nutrition, Agricultural University, De Dreijen 3, 6703 BC Wageningen, The Netherlands

Plant leaf digests and soil extracts were analyzed for Cd and Pb by flame AAS in three ways: with deuterium background correction, with the Smith-Hieftje background correction system, and without any background correction. Background correction proved to be necessary for both elements and for both types of material. The two background correction systems gave equal results, provided that Fe concentrations were low. High Fe concentrations caused spectral interference (i.e., structured background), which was overcompensated by the deuterium system. The Smith-Hieftje system, however, produced correct results.

Index Headings: Background correction, Smith-Hieftje system, deuterium system, Cd and Pb determination, flame AAS.

INTRODUCTION

Since the recognition of Cd and Pb as physiologically and environmentally toxic metals, much attention has been paid to their determination in various matrices, such as blood, tissue, plant leaves, soil, etc. Both elements can be determined by a variety of methods, of which voltammetry and atomic absorption spectrometry (AAS) are most frequently applied. In the latter technique, a flame atomizer is preferred with respect to a graphite furnace—if concentrations are high enough—since flame AAS is more rapid and less prone to interferences.

Among many other elements, Cd and Pb are determined in the course of an annual Dutch interlaboratory analysis program for soils and plant material. Within this framework, it was noticed that the results for Cd in a Dutch river clay soil showed remarkably large variations. The same was true for Pb, although to less extent. All laboratories used flame AAS for the final determination, but with different apparatus and different pretreatment procedures. The only relevant common factor appeared to be the extremely high HCl-extractable Fe content of this soil (25 g per kg). It was assumed that such an amount of Fe could cause line and/or background interference. Therefore, the participants took measurements with and without background correction on standard Cd solutions to which a large amount of Fe had been added. Without background correction, the results were higher than the nominal Cd concentrations.

Application of deuterium arc background correction, on the contrary, resulted in lower figures, which indicates overcompensation. This gave cause for testing a double-pulsed hollow-cathode-lamp system (the so-called Smith-Hieftje background correction system[1]) in flame AAS measurements of Cd and Pb in the above-mentioned synthetic solutions, in plant material, and in soil samples.

EXPERIMENTAL

Apparatus. Measurements were taken on an S-11 atomic absorption spectrophotometer (Instrumentation Laboratory, Andover, MA), equipped with both a deuterium background corrector (D_2) and a Smith-Hieftje background correction system (SH). A stoichiometric air/acetylene flame was used. For Cd the wavelength 228.8 nm was chosen; and for Pb, 217.0 nm. The slit width was adjusted so as to give a bandpass of 1 nm.

For reference purposes, some measurements were taken on a PE 460 atomic absorption spectrophotometer (Perkin-Elmer, Norwalk, CT), equipped with an HGA 76 graphite furnace, an AS-1 autosampler, and a deuterium background corrector.

Reagents. Standard solutions for Cd and Pb were prepared from Titrisol ampoules (Merck, Darmstadt, GFR; Nos. 9961 and 9969, respectively) and diluted appropriately. We prepared standard Fe solutions by dissolving $FeSO_4 \cdot 6H_2O$ in 0.12-M HCl at appropriate dilution. All reagents were analytical grade, and "demi-dest" (i.e., distilled after demineralization) water was used throughout.

Pretreatment Procedures. *Plant Material.* Leaf samples of different plant species were air-dried, ground, and dry-ashed in duplicate according to a procedure adopted from the Comité Inter-Instituts d'Etudes des Techniques Analytiques du Diagnostic Foliaire (C.I.I.).[2] In this method, 2 g of sample is heated at 450°C for 2 h, then taken up in HCl and filtered. The filter is heated for 0.5 h at 550°C, and the remainder is treated with HF, evaporated to dryness so as to volatilize the silicates present, and taken up in HCl. The combined solutions are made up to 100 mL with water. Because of the low Cd levels, 5 g was weighed out in the present procedure.

TABLE I. Interference of iron on the cadmium signal in flame AAS (0.1 mg L⁻¹ Cd in 0.12-M HCl; Fe added as $FeSO_4 \cdot 6H_2O$; IL S-11; 228.8 nm; air/acetylene; mean of 5 readings; no background correction).

Fe added (mg L⁻¹)	0	10	20	50	100	200	500	1000	2000	2500
Absorbance × 10³ (stoichiometric)	102	101	102	103	101	100	106	109	119	122
Absorbance × 10³ (reducing)	104									122
Absorbance × 10³ (oxidizing)	100									130

TABLE II. Influence of iron on cadmium measurements by flame AAS with different background correction systems (Fe added as $FeCl_3 \cdot 6H_2O$; IL S-11; 228.8 nm; stoichiometric air/acetylene; mean of 5 readings).

Solution			Apparent Cd concentration (μg L^{-1}) (mean ± standard deviation)		
Code no.	Cd (μg L^{-1})	Fe (mg L^{-1})	Without BG	With D_2	With SH
A	40	2500	56 ± 1	22 ± 1	41 ± 1
B	0	2500	11 ± 1	-17 ± 1	-1 ± 1
C	70	2500	80 ± 2	56 ± 1	71 ± 2
D	200	0	198 ± 9	201 ± 2	202 ± 3

TABLE III. Influence of iron on Cd and Pb measurements in plant material with and without background correction (Cd: 228.8 nm, sample: tobacco leaves; Pb: 217.0 nm, sample: apple leaves).

Added Fe concentration (mg L^{-1})	Cd (mg kg^{-1})			Pb (mg kg^{-1})		
	Without	D_2	SH	Without	D_2	SH
0	3.9	3.3	3.3	23.1	21.2	20.9
55	3.8	3.3	3.4	23.4	20.8	21.0
110	3.8	3.3	3.4	23.1	20.5	20.8
165	3.7	3.2	3.4	22.5	20.3	20.6
220	3.8	3.2	3.4	22.6	20.4	21.0
320	3.7	3.2	3.4	22.8	19.7	21.0
420	3.7	3.2	3.4	23.5	20.1	20.9
620	3.7	3.0	3.4	24.0	19.5	20.7
820	3.8	3.1	3.4	24.4	19.4	20.5
1000	3.7	3.1	3.4	24.4	19.5	20.4

Soils. The soils were treated as follows:

1. Digestion: different soil samples were digested according to a standard procedure in use in the authors' laboratory. In this method, 3 g of soil is repeatedly heated in Teflon® beakers with concentrated HNO_3 and H_2O_2 at 170°C and taken to dryness. Thereafter, the soil cake is heated several times with an HNO_3-HF mixture until the major part of the silicates has disappeared. The remainder is suspended in HCl, diluted with water to 100 mL, and filtered.
2. Extraction: 5 g of soil is shaken with 50 mL of 0.43-M HNO_3 and filtered.

RESULTS AND DISCUSSION

The Cd absorbance signal, measured in a stoichiometric air/acetylene flame without background correction, was not affected by Fe concentrations up to 200 mg L^{-1}. From 500 to 2500 mg L^{-1}, the apparent Cd signal increased gradually (Table I). The upper value was chosen on the basis of the Fe content of the Dutch river clay soil mentioned in the introduction. It also appears that variations in the air/acetylene ratio do not have much influence on the signal.

For the highest Fe concentration, measurements were taken with some Cd-containing solutions for different background correction conditions (Table II). The results without background correction show the same tendency, as indicated in Table I. The D_2 background correction

gave values that were too low; this result can be interpreted as overcompensation of the interfering effect. In the literature, the problem of overcompensation and negative values because of the occurrence of atomic lines within the spectral bandpass has already been recognized.[3-5] The degree of overcompensation is roughly equal to the value found for solution B, which supports the assumption that the interference is due to Fe. The Smith-Hieftje system turned out to be able to compensate for this interference to the right degree. This may very well indicate a structured background, of which the average absorbance as measured by the D_2 lamp is higher than the actual background just under the Cd absorption peak. Measurements at 228.8 nm with an Fe hollow cathode lamp on a 2500 mg/L Fe solution gave an appreciable absorbance, whether D_2 correction was applied or not, and zero absorbance when SH correction was applied. With the use of the same Fe lamp at the same wavelength and no background correction, a 1000 mg/L Cd solution gave essentially no absorption signal. Thus, in the 228.3–229.3-nm region there must be one or more resonance lines of Fe. Scanning of the emission spectrum from the used Fe hollow cathode lamp revealed one line at 228.72 nm. This is in accordance with the table of Zaidel, quoted by Michaud and Mermet,[6] who

TABLE IV. Determination of Cd and Pb in plant material (leaves) with and without background correction (mean of duplicate 5 g weighings).

Plant material type	Fe content (mg kg^{-1})	Cd content (mg kg^{-1})					Pb content (mg kg^{-1})				
		Without BG	D_2	SH	GFAAS 1.1. extr.	Mean of int. coll. study, or certified value	Without BG	D_2	SH	GFAAS 1.1. extr.	Mean of int. coll. study, or certified value
Tobacco	740	3.7	3.2	3.1	3.3	3.0	8.2	4.5	4.3	3.9	4
Apple (Golden Delicious)	260	0.40	0.25	0.25	0.25	0.20	13.8	12.8	13.9	13.6	16
Apple (Cox)	1055	1.2	1.0	0.9	0.61	0.50	23.1	20.4	20.7	24.3	22
Vine	256	0.5	0.3	0.2	0.28	0.20	19.0	16.0	15.7	16.0	18
Lettuce	510	1.5	1.1	1.1	0.87	0.95	8.8	6.4	6.2	5.4	6
Grass	200	0.30	0.24	0.22	0.25	0.20	3.0	3.6	4.3	2.9	4.5
CRM 060 Lagarosiphon mj	1189	4.0	3.2	3.2	n.d.[a]	2.20[b] ±0.10	60	56	58	n.d.[a]	63.8[b] ±3.2
CRM 061 Platihypnidium riparioides	4650	1.7	0.7	1.0	n.d.	1.07[b] ±0.08	62	57	59	n.d.	64.4 ±3.5
CRM 062 Olea europaea	140	0.2	0.2	0.2	n.d.	0.10[b] ±0.02	27.2	28.3	27.9	n.d.	25.0[b] ±1.5

[a] n.d. = Not determined.
[b] Certified value ± 95% conf. int.

TABLE V. Influence of background correction on Cd measurements in iron-rich clay soils (air/acetylene flame; IL S-11; Cd 228.8 nm; Pb 217.0 nm; Fe 248.3 nm; mean of duplicate weighings).

Soil			Fe	Cd (mg kg^{-1})			Pb (mg kg^{-1})		
Code	Type	Pretreatment	(g kg^{-1})	Without BG	D$_2$	SH	Without BG	D$_2$	SH
OMC-2	River clay	Digestion	26.0	1.87	0.52	0.74	38.5	27.7	31.2
OMC-202	River clay	Digestion	41.9	1.97	0.36	0.64	46.0	34.4	39.3
OMC-203	River clay	Digestion	23.4	1.32	0.14	0.34	29.0	20.4	23.8
OMC-204	Sea clay	Digestion	30.0	1.40	0.47	0.68	66.4	58.7	62.4
OMC-205	Sea clay	Digestion	28.0	1.27	<0.02	0.28	30.6	21.6	24.4
OMC-2	River clay	Extraction	1.73	0.50	0.50	0.50	18.3	18.0	18.2
OMC-202	River clay	Extraction	2.83	0.63	0.52	0.58	23.8	23.0	23.5
OMC-203	River clay	Extraction	1.71	0.49	0.36	0.32	15.8	15.0	15.4
OMC-204	Sea clay	Extraction	6.64	0.95	0.63	0.62	56.3	54.0	54.5
OMC-205	Sea clay	Extraction	2.67	0.35	0.32	0.29	18.8	19.5	18.5

give several ground-state transitions for Fe around the wavelength of 228.8 nm. Similar results were found for the Pb line at 217.0 nm.

Addition of Fe to plant leaf digests gave similar results: (too) high values without any background correction, low values with D$_2$ correction, and intermediate values with SH correction, for Cd as well as for Pb (Table III). Note, however, that both background correction systems give equal results as long as the Fe concentration is not higher than about 100 mg L^{-1}.

In addition to these fortified digests, Cd and Pb were determined in several plant materials with different intrinsic Fe levels. For this purpose, the plant materials of Table IV were purchased either from C.I.I. or from the European Community Bureau of Reference (CRM 060, 061, and 062) because of their known levels of Cd and Fe. Although the Fe concentrations in the digests were far too low to have any influence on Cd or Pb, as in the foregoing experiments, the results with background correction were, for both systems, significantly lower than without background correction (Table IV). It should be noticed that this effect is more pronounced for Cd than for Pb, and that both types of background correction give the same results. The only exception is CRM 061, which behaves just like the pattern that appeared from Table III, and for which material the certified Cd value shows a remarkably good agreement with the value obtained by SH correction. It is certainly more than pure coincidence that this is also the only sample with an extremely high Fe content. For the other samples, the Fe content indeed seems to be too low (concentrations in the digests, 7–60 mg/L) to play a role; presumably the plant material matrix causes a smooth continuous background absorption profile, to which both correction systems respond to the same degree.

For reasons of comparison, Table IV shows the average Cd and Pb values of some leaf samples from an international collaborative study on plant material analysis. Statistical analysis revealed that the difference with "no BG" is significant, the difference with D$_2$ is not significant, and the difference with SH is not significant at the 5% level.

Table IV also shows results for Cd and Pb determinations by graphite furnace AAS after matrix elimination by a liquid-liquid extraction procedure with diethylammonium-N,N-diethyldithiocarbamate in xylene. These values are closer to the D$_2$ and SH results than to the uncorrected ones. All differences were found to be insignificant at the 5% level, including the differences with the results of the international collaborative study.

Finally, some Dutch clay soils with high iron content were analyzed for Cd and Pb after digestion with $HNO_3 + H_2O_2 + HF$ and after extraction with 0.43-M HNO_3 (Table V). After digestion, the Cd as well as the Pb content consistently showed the same trend as described for the fortified synthetic solutions. After extraction, however, the results showed a tendency similar to that for plant material. This is evidently due to the lower apparent Fe content, since 0.43-M HNO_3 does not extract so much iron from the soil.

Thus, background correction is always necessary in the flame AAS determination of Cd and Pb in plant and soil material. A double-pulsed hollow-cathode-lamp background correction system gives more accurate results than does a deuterium arc background corrector in the case of a structured background due to spectral interference of high concentrations of iron. At normal Fe concentrations, the D$_2$ system is to be preferred because of the inherent loss of sensitivity of the SH system.

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