

Research Article

Minimizing Chloride Interferences Produced by Calcium Chloride in the Determination of Cd by Graphite Furnace Atomic Absorption Spectrometry

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Cadmium concentrations in CaCl_2 extracting solutions at various concentrations were determined by graphite furnace atomic absorption using two background correctors: the deuterium and the high-speed self-reversal background correction systems. Under- and overestimation of the Cd absorbance signals in CaCl_2 solutions were observed for concentrations greater than 0.005 M using the deuterium lamp while no important effect was observed using the other background correction system. The analytical performance of the spectrometer for the determination of Cd was studied in 0.01 M CaCl_2 solution and single extractions were performed using reference materials and contaminated soil samples. Cadmium was determined using the two background correction systems and a third method, which consists of the use of the deuterium lamp without any chemical modifier, was added to the study. The results showed that the third method was unable to determine Cd concentrations in the CaCl_2 solution due to the presence of extractable arsenic and iron. For solutions without any dilution or diluted with a very low dilution factor, the CaCl_2 -extractable Cd concentrations measured using the deuterium lamp were systematically below those found using the high-speed self-reversal method. These differences were explained by the presence of chloride ions in the atomization step.

1. Introduction

Cadmium uptake by organisms is poorly related to the total Cd concentrations in contaminated soils [1]. Many studies pointed out that the chemical behavior and the potential toxicity of metals (often related to their environmental availability to organisms) depended on the binding of metals with ligands [2–6]. Depending on the physicochemical parameters of the soils, the soluble metals usually react with organic (humic and fulvic acids) as well as inorganic (sulfate, sulfide, phosphate, carbonate, oxide and hydroxide, and chloride) ligands. The most-studied ligand is probably the chloride ion because salinity increases Cd-uptake by plants by forming environmentally available Cd-chloro complexes as CdCl^+ and CdCl_2 [5, 7–13].

The prediction of metal bioavailability is of crucial importance for the assessment of environmental quality of contaminated soils. Thus, to understand the processes involved in metal uptake by plants (phytoavailability), the use of extracting solutions rather than the total metal contents is so recommended [13–16]. Among salt solutions used in single extractions, calcium chloride (CaCl_2) appears as the most widely used extractant to assess plant-available Cd concentrations in soils [15–18]. Compared to the other salts, CaCl_2 does not interfere with the natural pH of the soil [19]. On the other hand, the CaCl_2 extracting solution improves the metal desorption within the soils due to the complexation of free ions by Cl^- [19, 20]. Molar (M), decimolar, 0.05 M, and centimolar concentrations are widely used by various authors to study the metal behaviors and

particularly to estimate the phytoavailable Cd in soils [16, 21, 22]. However, high concentrations of CaCl_2 produce many problems in terms of chemical analysis of Cd at trace levels using GFAAS. With this technique and at the most sensitive line for Cd (228.802 nm), spectral interferences have been reported for the use of ammonium phosphate as a chemical modifier, especially when determining very low concentrations of Cd in matrices with iron (Fe) and arsenic (As) contents and especially with high chloride concentrations, one of the main causes of background noise in GFAAS [23]. These interferences cannot be eliminated using the deuterium background correction (D_2 -BGC), or Zeeman-effect background correction system, but they can be minimized using palladium-magnesium, palladium-ammonium, ammonium salt of EDTA, nickel, or hydrofluoric acid as chemical modifiers [23–27].

In recent years, the high-speed self-reversal background correction (HSSR-BGC) system has been presented as a powerful background corrector to avoid background interferences between Pb and some anionic species (SO_4^{2-} , SiO_3^- , PO_4^{3-} , and NO_3^-) [28] and spectral interferences between Cd and As/Fe species [29, 30]. Based on the Smith-Hieftje (S-H method) background corrector [31], the specificity of the HSSR-method is the high frequency applied during measurements which permits a rapid modulation between currents at low and high levels through the Cd hollow-cathode lamp. In this work, the development of an analytical method to measure Cd in CaCl_2 extracting solution by GFAAS associated to the HSSR-BGC is presented and compared with the D_2 -BGC for which a deuterium lamp was used as a continuum light source in combination with a chemical modifier. The effects of CaCl_2 on the Cd absorbance were carefully studied and optimized. The accuracy of the proposed method was verified by means of four reference materials. The analytical technique was successfully applied to the determination of CaCl_2 -extractable Cd in soils contaminated with various metals collected in the north of France.

2. Materials and Methods

2.1. Standard Solutions and Reagents. All CaCl_2 solutions were prepared from calcium chloride dihydrate reagent for analysis (Acrös Organics, Noisy-le-Grand, France) and doubly distilled water (Carlo Erba, Val de Reuil, France) with a specific conductivity of $0.1 \mu\text{S cm}^{-1}$. The Cd metal stock solutions, 1, 2, and 5 mg L^{-1} in 2% HNO_3 (Chemical Products for Analysis, Association Corporation Standard Distribution, C.P.A. groupe A.C.S.D., Voisins le Bretonneux, France), were used for the preparation of standard solutions.

All glassware and polypropylene materials were cleaned by soaking for 1 day in 0.5 M nitric acid (J.T. Baker for metal trace analysis, Deventer, Netherlands), rinsed with doubly distilled water and stored in closed plastic bags.

2.2. Instrumentation. Measurements of Cd in CaCl_2 extracting solutions were carried out by means of a Shimadzu Model AA-6800 atomic absorption spectrometer (GFAAS, Tokyo,

Japan) fitted with a digital control technology graphite furnace atomizer (GFA-EX7), an ASC-6100 autosampler, and an ASK-6100 autodiluter (Shimadzu, Tokyo, Japan). Pyrolytic graphite-coated tubes with pyrolytic L'vov platforms from Shimadzu were used throughout this work. Firstly, a conventional Cd hollow-cathode lamp (Hamamatsu, Photonics K.K., Tokyo, Japan) was used as the spectral radiation source at a 228.802 nm analytical line, and was operated at 10 mA in combination with a deuterium lamp for the background correction (D_2 -BGC). A Cd high-intensity boosted discharge hollow-cathode lamp from Hamamatsu was also used. This lamp was operated with two different discharges within the lamp, a low-current value (10 mA) and then, a high-current value (300 mA) in order to increase the emission intensity and was pulsed with a frequency of 100 Hz (HSSR-BGC). Both Cd lamps were used with spectral bandpass value of 1.0 nm. The iron concentration in CaCl_2 solutions was determined by flame atomic absorption spectrometer with an ASC-6100 autosampler (Shimadzu) at 248.3 nm with a lamp current of 12 mA and a deuterium lamp (Hamamatsu) for the background correction. Arsenic concentrations were measured by GFAAS following the procedure described by Oppermann et al. [29].

2.3. Soil Sampling and Pretreatment Procedure. The contaminated soils were collected in an area highly affected by the past atmospheric emissions of two lead and zinc smelters located in the north of France. For each site, a composite sample was constituted in the ploughed layer (0–25 cm) and was prepared following the NF ISO 11464 procedure. The samples were then sieved to less than $250\text{-}\mu\text{m}$ particle size using an ultracentrifugal mill (Retsch type ZM 200, Hann, Germany) to obtain contaminated soil samples named CS1 to CS9 for subsequent analyses. Moreover, the validation of the proposed method was carried out using four reference materials:

- (i) CRM BCR-483: certified reference material composed of sewage-sludge-amended soil from Great Billings Sewage Farm (Northampton, England) with indicative CaCl_2 -extractable Cd.
- (ii) CRM BCR-141R: certified reference material composed of calcareous loam soil.
- (iii) CRM BCR-701: certified reference material composed of sediment from Lake Orta (Piemonte, Italy).
- (iv) SRM 2710a (NIST): Standard reference material (Montana I soil) from Montana, USA.

2.4. Extraction Procedures. Triplicate subsamples of each soil and replicate six samples of reference materials were weighed (3 g) in a polyethylene tube and 30 mL of 0.01 M CaCl_2 solution was added. After shaking the suspension with a rotor disc for 2 h at 10 rpm, the extract was separated from the solid residue by centrifugation at 4530 rpm (Rotanta 460 Hettich, Tuttlingen, Germany) for 20 min at room temperature. Afterwards, the solution was filtered over an acetate Millipore membrane (Millipore, $0.45\text{-}\mu\text{m}$ porosity, Minisart) and was transferred into a polypropylene container

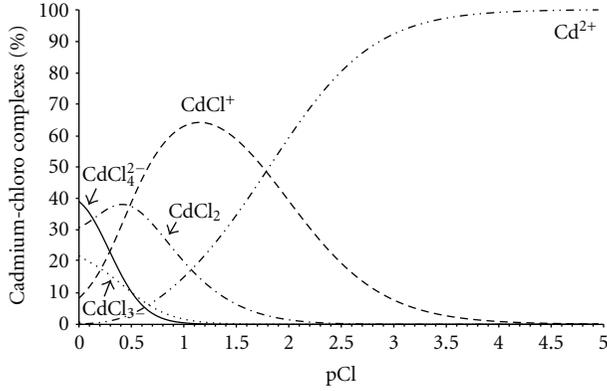


FIGURE 1: Distribution graph of Cd-chloro complexes.

[30]. The concentrations of Cd in the 0.01 M CaCl₂ solutions were expressed as $\mu\text{g kg}^{-1}$ dry weight (DW).

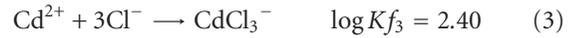
2.5. Soil Moisture Content. The residual moisture contents were measured by weighing three replicates of each soil samples before and after drying at 105°C in an oven (Binder, Tuttlingen, Germany) until it reached a constant mass according to the NF ISO 11465 standard.

2.6. Statistical Analyses. For each soil, Bonferroni, a Tuckey, and Fischer post hoc tests were conducted to determine significant differences among Cd concentrations according to the analytical techniques and the background compensations. All statistical tests were performed using Statistica

6.0 (Statsoft, Tulsa, OK, USA) for Windows. The level of significance was set at $P < 0.05$.

3. Theory and Calculation

Cadmium-free ions can react to chloride according to a molar ratio Cd:Cl up to 1:4 to form the complex CdCl_n^{2-n} ($0 \leq n \leq 4$) [32]. The mechanism, stepwise, is described as follow:



For each equation, equilibrium constant (Kf_n) is expressed as the following general equation:

$$Kf_n = \frac{[\text{CdCl}_n^{2-n}]}{[\text{Cd}^{2+}][\text{Cl}^-]^n}, \quad (5)$$

where n is the number of Cl^- added to the Cd^{2+} ion; CdCl_n^{2-n} , Cd^{2+} and Cl^- are expressed in concentrations. The use of the principle of the matter conservation permitted to defined the total dissolved Cd ($[\text{Cd}]_T$) as the sum of the soluble Cd-chloro complexes. The concentration of each of them can be denoted by the three terms $[\text{Cd}]_T$, $[\text{Cl}^-]$ and Kf_n and expressed as follows.

$$[\text{Cd}^{2+}] = \frac{[\text{Cd}]_T}{1 + Kf_1[\text{Cl}^-] + Kf_2[\text{Cl}^-]^2 + Kf_3[\text{Cl}^-]^3 + Kf_4[\text{Cl}^-]^4}, \quad (6)$$

$$[\text{CdCl}^+] = \frac{Kf_1[\text{Cd}]_T}{Kf_1 + 1/[\text{Cl}^-] + Kf_2[\text{Cl}^-] + Kf_3[\text{Cl}^-]^2 + Kf_4[\text{Cl}^-]^3}, \quad (7)$$

$$[\text{CdCl}_2] = \frac{Kf_2[\text{Cd}]_T}{Kf_2 + 1/[\text{Cl}^-]^2 + Kf_1/[\text{Cl}^-] + Kf_3[\text{Cl}^-] + Kf_4[\text{Cl}^-]^2}, \quad (8)$$

$$[\text{CdCl}_3^-] = \frac{Kf_3[\text{Cd}]_T}{Kf_3 + 1/[\text{Cl}^-]^3 + Kf_1/[\text{Cl}^-]^2 + Kf_2/[\text{Cl}^-] + Kf_4[\text{Cl}^-]}, \quad (9)$$

$$[\text{CdCl}_4^{2-}] = \frac{Kf_4[\text{Cl}^-]^4[\text{Cd}]_T}{1 + Kf_1[\text{Cl}^-] + Kf_2[\text{Cl}^-]^2 + Kf_3[\text{Cl}^-]^3 + Kf_4[\text{Cl}^-]^4}. \quad (10)$$

These equations indicate that the concentration of Cl^- affects the concentration as well as the activity of each Cd-chloro complex. Therefore, the ionic strength in CaCl₂ solutions was calculated using (11):

$$I = \frac{1}{2} \sum_{i=1}^n c_i z_i^2, \quad (11)$$

in which c is the molarity of the ions i and z_i is the charge number of the ion i . The summation includes all ion concentrations in the solution. Ion activities were calculated using the Davies equation [33]:

$$\log a_i = -0.509 z_i^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.30I \right), \quad (12)$$

where a is the activity of the ion i .

Various forms of the equation were optimized in Microsoft Excel 2010. The distribution diagram of Cd-chloro complexes was given as a distribution graph in which the Y -axis indicates the percentage of each complex and the X -axis represents $pCl = -\log[Cl^-]$ (Figure 1). If $[CaCl_2] < 0.008$ M, Cd is almost in the form of Cd^{2+} . When the $CaCl_2$ concentration ranges from 0.008 to 0.177 M, the major Cd species is $CdCl^+$ and the remaining Cd is in the form of Cd^{2+} and $CdCl_2$. The concentrations of both species are similar for $[CaCl_2] = 0.045$ M.

4. Results and Discussion

4.1. Temperature Program. In the absence of a chemical modifier, the GFAAS temperature program was optimized in terms of temperature and time of drying, pyrolysis, and atomization steps. In all tests, the drying step was carried out in two stages, 120 and 250°C, with the aim of achieving a complete removal of the liquid present in the sample and avoiding any sputtering of sample (Table 1). The charring temperature was 300°C [34, 35] and the furnace temperature on atomization step was 1800°C to obtain a maximum-peak absorbance value [34, 36].

4.2. Interference from the Sample Solutions. The peak profiles of Cd absorption in $CaCl_2$ solutions at various concentrations using the D_2 -BGC and the HSSR-BGC were shown in Figures 2 and 3, respectively. Decreases of Cd absorbance were found in the presence of $CaCl_2$ at 0.005, 0.01 and 0.05 M while an increase was observed in the 0.1 M $CaCl_2$ solution despite the use of deuterium lamp and chemical modifier. In contrast, Cd signal recorded in the 0.001 M $CaCl_2$ solution was similar to Cd in water. As shown in Figure 2, the Cd absorbance in $CaCl_2$ solutions was unchanged up to 0.01 M concentration compared with the absorbance from Cd alone in water. A very small enhancement of Cd absorbance was found in the presence of 0.05 and 0.1 M $CaCl_2$ from which Cd concentrations were 1.2 and 1.4 $\mu g L^{-1}$. Even if it was demonstrated that the principal causes for loss of precision could be the variation in the heating characteristics of the furnace, the performance of the technique used for processing the signals is very important [38]. Regarding the peak profiles (Figure 2), the signal processing was so carried out on the basis of peak height (at 24 s; Figure 3) rather than peak area measurements.

Based on the previous consideration, a Cd solution at 0.66 $\mu g L^{-1}$ in 0.1 M $CaCl_2$ was prepared and 2-, 5-, and 10-fold serial dilutions were made. Despite the use of the deuterium lamp as a continuum light source for the background correction, the signal processing was impossible (Figure 4; the first solution was not shown). As can be seen in Figure 5, no signal overlapping was obtained using the HSSR-BGC. A first approach of this background correction has been proposed in 1983 by Smith-Hieftje [31] but was rapidly criticized due to its low modulation frequencies (maximum 10 Hz which were not compatible with the rapid transient signals common to GFAAS experiments. The modulation cycle used in the HSSR-method was 10 times

TABLE 1: Furnace temperature program for Cd determination.

Furnace program step	Temperature (°C) ^a	Hold time (s)	Ramp rate (°C s ⁻¹)	Argon gas flow rate (L min ⁻¹)
Drying-1	120 (150) ^b	5	24	1
Drying-2	250 (250) ^b	5	26	1
Pyrolysis-1	300 (500) ^b	5	10	1
Pyrolysis-2	300 (500) ^b	3*	0	0
Atomisation	1800 (2200) ^b	6*	3400	0 (read)
Cleaning	2300 (2400) ^b	3	3400	1

^aTemperature program used in absence of chemical modifier.

^bTemperature program used in presence of chemical modifier.

*The high-sensitivity mode was applied and the argon flow was stopped.

higher than in the original Smith-Hieftje background correction system). Therefore, the rapid modulation generated by the high frequency (100 Hz) between currents at low and high levels (from 10 to 100 mA) applied to the Cd high-intensity boosted discharge hollow-cathode lamp may be of importance in interpolation of transient time-dependent signal fluctuations. On the other hand, whereas D_2 corrects for an average background over the full spectral band width, the HSSR-BGC, like the S-H method, corrects at the center of the resonance line. Two distinct signals have been obtained under the analytical conditions, the first being attributed to Cd (at 24 s as in Figure 3). It is worth noting that the variation of the Cd absorbance corresponded well to the dilution factor, reflecting the efficiency of the HSSR-BGC.

4.3. Analytical Figures of Merit. Over the last decade, single extraction of metals in contaminated soils with 0.01 M $CaCl_2$ has become an international method [37, 39, 40]. Calibration curves were so obtained from Cd stock solution after dilution with 0.01 M $CaCl_2$ solution and the analytical characteristics of the GFAAS were determined in 0.01 M $CaCl_2$ solution. The curve was obtained from 10 calibration plots, ranging from 0.01 to 3.33 $\mu g L^{-1}$. As shown in Table 2, Cd absorbance correlated well with concentrations. The limits of detection (LOD) and quantification (LOQ), based on three and ten times the standard deviation of the blank values ($n = 10$) were 10.7 and 35.6 $ng L^{-1}$, respectively. These values were in the same order of magnitude than those obtained using doubly distilled water (LOD = 10.9 and LOQ = 36.4 $ng L^{-1}$). The characteristic mass (m_0) was defined as the mass of analyte to an integrated absorbance of 0.0044 s following the relation, $m_0 = (0.0044CV)/(A_1 - A_2)$ in which C is the analyte concentration, V is the introduced volume, and A_1 and A_2 are the integrated absorbance of the sample and blank, respectively [41]. The characteristic mass found in 0.01 M $CaCl_2$ solution was $m_0 = 0.34$ pg. The reproducibility of the analytical method was investigated for the determination of 0.66 $\mu g L^{-1}$ Cd in 0.01 M $CaCl_2$ solution (Figure 6). The relative standard deviation (RSD) was 4.8% ($n = 10$).

It is well known that the high temperature applied for the Cd pyrolysis decreases the lifetime of graphite tubes as

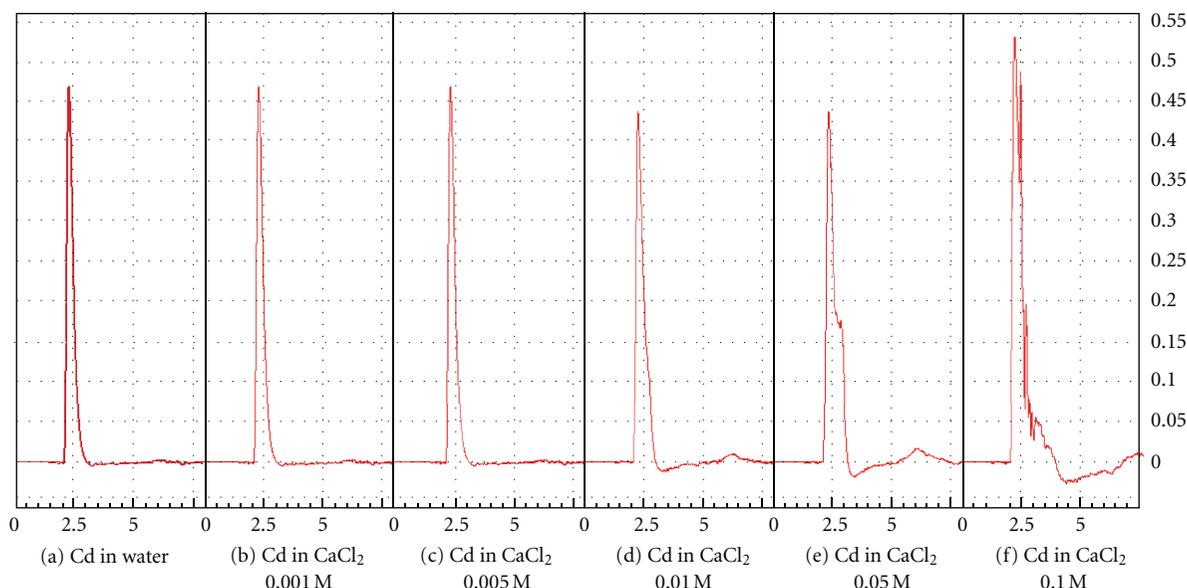


FIGURE 2: Absorption-time profiles of Cd at $1 \mu\text{g L}^{-1}$ resulting from atomization of CaCl_2 solution at various concentrations using the D_2 -BGC.

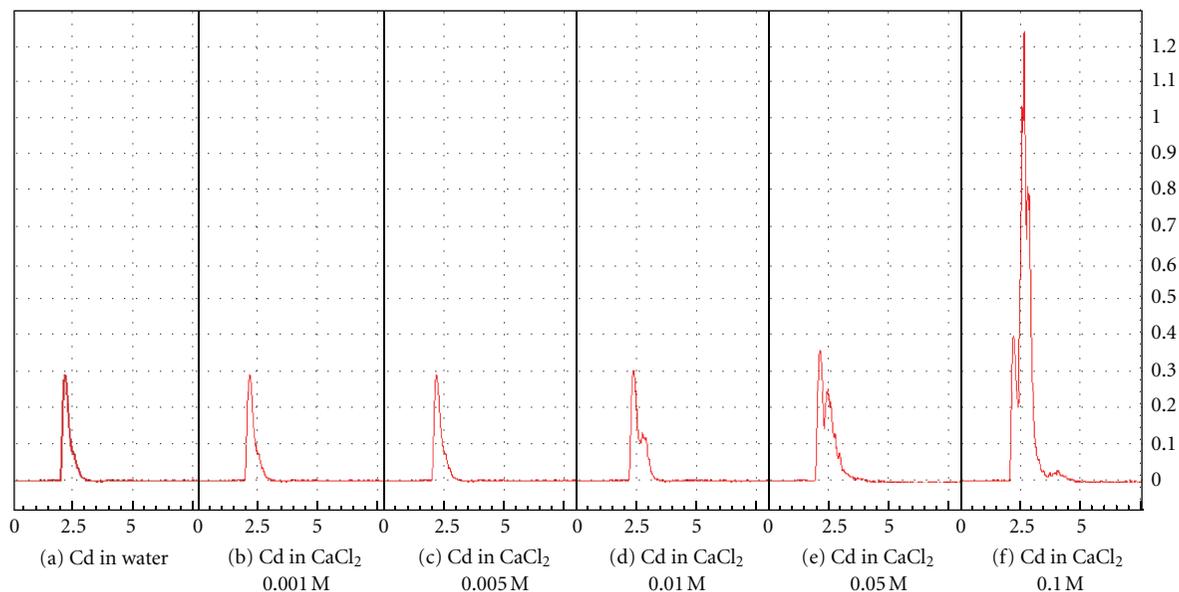


FIGURE 3: Absorption-time profiles of Cd at $1 \mu\text{g L}^{-1}$ resulting from atomization of CaCl_2 solution at various concentrations using the HSSR-BGC.

well as the corrosive action of some modifiers [42]. The lifetime of the graphite tube using the chemical modifier and the high temperature conditions was around 650 firings. Without any chemical modifiers, the lifetime of the graphite tube was up to 1600 firings. If the HSSR method appears as an efficient method to avoid interferences in the Cd determination using GFAAS without any chemical modifier in the experimental conditions, this method also improves the life time of graphite tubes.

4.4. Quality Control of Analytical Data. Calcium chloride at 0.01 M is widely used to evaluate the environmental availability of Cd in contaminated soils [21, 39, 43–45] and to monitor the changes in CaCl_2 -extractable Cd generated by a soil remediation technique [46–48]. It is so very important to obtain a good determination of CaCl_2 -extractable Cd concentrations in contaminated soils.

The quality of the combined single extraction and analytical technique was evaluated using certified and standard

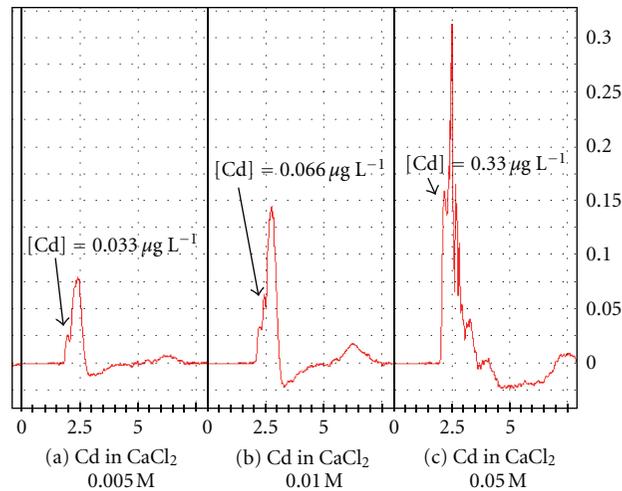


FIGURE 4: Absorbance of Cd in CaCl₂ solution after successive dilutions using the D₂-BGC.

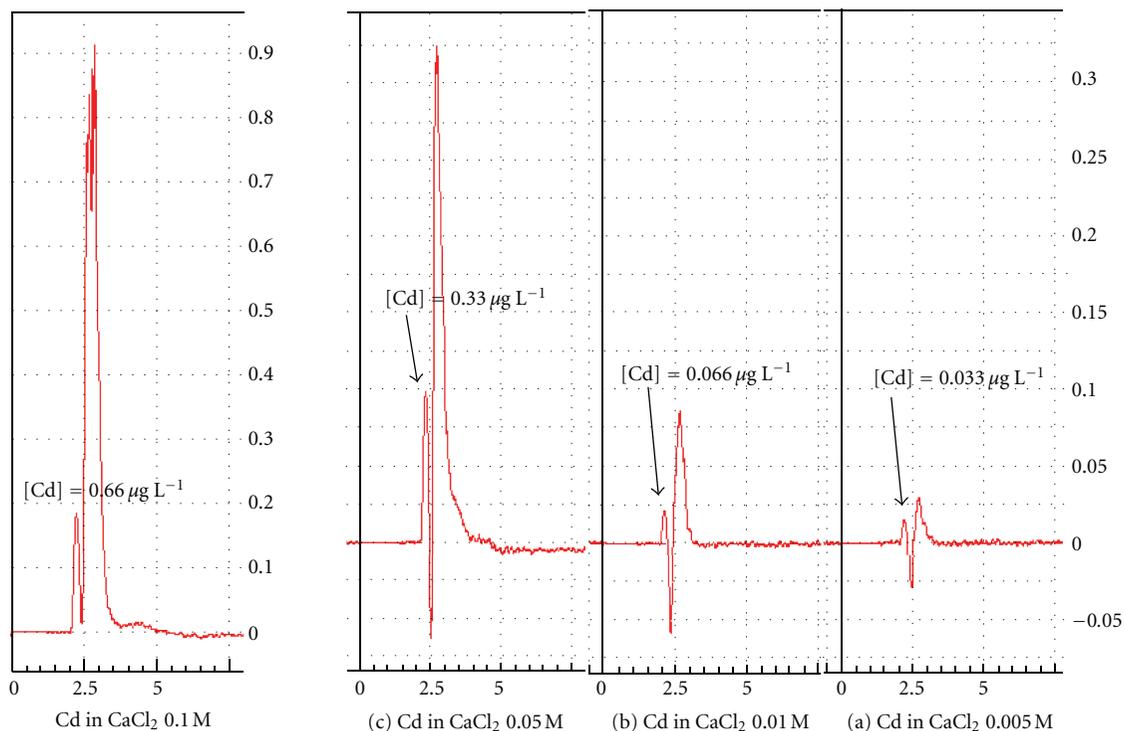


FIGURE 5: Absorbance of Cd in CaCl₂ solution after successive dilutions using the HSSR-BGC.

reference materials (BCR-483, BCR-701, BCR-141R, and NIST 2710a). No significant difference between the mean extractable Cd measured in reference materials and the certified, or indicative Cd values was found (Table 3). The ratio As/Cd and Fe/Cd ranged from 0.11 to 1.83 and 1.76 to 3.77, respectively. Therefore, the presence of As and Fe in CaCl₂ extracting solution cannot lead to a substantial modification in the Cd concentrations [29, 30]. The lowest Cd concentrations measured in the CaCl₂ extracting solution were provided by the BCR-141R material. Very high standard

deviation (SD) value was obtained using the deuterium lamp and chemical modifier. This value explains the low precision defined as the relative standard deviation (RSD = 40.7%) and the fact that the two mean Cd values obtained using the two analytical methods were not significantly different. Regarding the results for the BCR-141R material, an underestimation of the mean extractable Cd concentration using the deuterium lamp combined to the chemical modifier was suspected. As a consequence, to prevent the increase of the ratio Cl/Cd when the Cd concentration is too high to

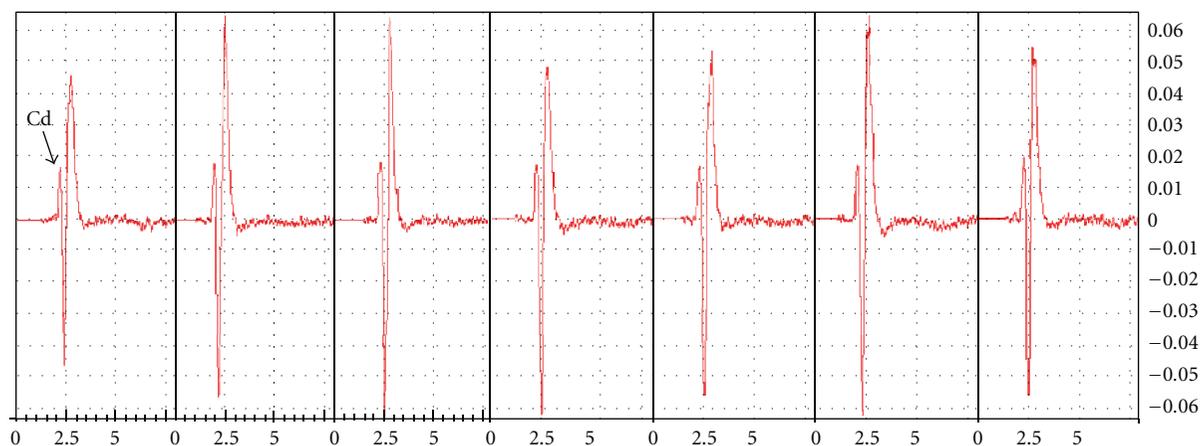


FIGURE 6: Reproducibility of the Cd signal (at $0.66 \mu\text{g L}^{-1}$) in 0.01 M CaCl_2 solution using the HSSR-BGC.

be determined by GFAAS, dilutions were carried out with doubly distilled water in the following experiments instead of the 0.01 M CaCl_2 solution.

4.5. Calcium-Chloride-Extractable Cd in Contaminated Soils.

For each contaminated soil, the 0.01 M CaCl_2 -extractable concentration of Cd was determined by means of GFAAS combined with three modes: HSSR-BGC without any modifier, D_2 -BGC with palladium as chemical modifier [24], and D_2 -BGC without any modifier. With the last mode, Cd concentrations were much higher than those measured using the two other modes. The ANCOVA (Bonferroni, Fischer and Tuckey post-hoc tests) statistical analyses showed significant differences between the two first datasets and the third. These differences can be explained by the presence of As and Fe in the extracting solution rather than CaCl_2 . The absorption lines of As at 228.812 nm and Fe at 228.763 and 228.725 may cause highly structured spectral interferences that the deuterium lamp is not able to correct [26, 27]. For contaminated soil samples (CS1 to CS9), statistical tests showed no significant differences between the average Cd concentrations measured using the HSSR-BGC method and the D_2 -BGC method combined with the chemical modifier. This result attests that the HSSR-BGC mode is an efficient background compensation technique to minimize the spectral interferences caused by concomitant species during the Cd measurements in GFAAS. Because all samples were diluted with doubly distilled water (from 1:4 to 1:100), the concentration of CaCl_2 ranged from 0.0025 to 0.0001 M ($2.3 < \text{pCl} < 4$). Therefore, more than 73% of Cd in CaCl_2 solution was found as Cd^{2+} (Figure 1) and no decrease of the Cd absorbance was recorded using the D_2 method. The real problem was the determination of Cd in extracts from soil samples CS10 to CS22 for which statistical differences were found between the two modes. The 0.01 M CaCl_2 -extractable concentrations of Cd were the lowest and the Cd concentration measured using the deuterium lamp combined with the chemical modifier were systematically below those measured using the HSSR method (Table 3). Taking into account the ratio solid:liquid (1:10), these concentrations were obtained after

low dilution with doubly distilled water (1:1.25 for CS10, CS11, and CS12) and without any dilution for the other (CS13–CS22). Thus, the concentration of CaCl_2 ranged from 0.01 to 0.008 M . With regards to Figure 1, the speciation of Cd in the CaCl_2 extracting solution is in the form of Cd^{2+} (43–50%) and in the form of CdCl^+ (50–52%, resp.). The presence of this Cd-chloro complex in the graphite tube probably caused chloride interferences during the atomization step. These interferences could explain the decrease of the absorbance of the Cd signal as observed in Figure 2 using the deuterium lamp combined with the chemical modifier whereas no loss of Cd absorbance was observed in the experimental conditions. This subject is of major concern in the determination of Cd in plants grown on soils with high sodium chloride concentration and in the determination of Cd speciation using the DGT (diffusion gradients thin films) technique. Indeed, in each case, the formation of Cd-chloro complex was demonstrated and the determination of Cd using GFAAS can be a real problem [7, 9].

5. Conclusions

The measurements of Cd in CaCl_2 solutions at various concentrations were performed using GFAAS with two background correction systems. The first was based on the well-known deuterium background correction and the second involved the use of a single Cd hollow-cathode lamp pulsed with currents ranging from 10 to 100 mA with a frequency of 100 Hz . Depending on the CaCl_2 concentrations, decrease and increase of the Cd absorbance signal occurred with the conventional background corrector. In contrast, the HSSR-BGC appeared to be a more versatile technique for the compensation of interferences caused by the presence of CaCl_2 over the course of the determination of Cd. The high frequency applied to pass from low to high current intensities generated more than one peak profile, the first being attributed to the Cd absorbance signal. Very low detection limit and characteristic mass values of the analyte in 0.01 M CaCl_2 solution were found using the HSSR-BGC,

TABLE 2: Equation of calibration range, limits of detection (LOD) and quantification (LOQ), and characteristic mass (m_0) for peak absorption.

Calibration range ($\mu\text{g L}^{-1}$)	Equation of calibration curves	LOD (ng L^{-1})	LOQ (ng L^{-1})	m_0 (μg)
0.01–2	Abs = 0.2579[Cd] + 0.0039 $R^2 = 0.9998$	10.7	35.6	0.34
0.01–3.33	Abs = $-2.8 \cdot 10^{-2}$ [Cd] ² + 0.3125[Cd] + 0.0123 $R^2 = 0.9993$	10.7	35.6	0.31

Abs means integrated absorbance and [Cd] is in $\mu\text{g L}^{-1}$. Units for slopes are in $\text{L } \mu\text{g}^{-1}$.

TABLE 3: Extractable Cd in 0.01 M CaCl_2 soil extracts (mean \pm standard deviation (SD); $n = 6$).

Samples	Fe in this work (mg kg^{-1})	As in this work ($\mu\text{g kg}^{-1}$)	Cd HSSR-BGC ^a ($\mu\text{g kg}^{-1}$)	Cd D ₂ -BGC ($\mu\text{g kg}^{-1}$)	Cd D ₂ -BGC ^a ($\mu\text{g kg}^{-1}$)
BCR-483	0.98 \pm 0.15	883 \pm 30	482 \pm 19 ^{b,c}	473 \pm 19	ND
BCR-701	0.62 \pm 0.07	65 \pm 5	352 \pm 6	349 \pm 15	ND
BCR-141R	0.55 \pm 0.03	18 \pm 1	146 \pm 5	113 \pm 46	ND
NIST 2710a	14.10 \pm 0.67	455 \pm 46	3979 \pm 58	4015 \pm 60	ND
CS1	1.42 \pm 0.16	1336 \pm 157	2220 \pm 9	2217 \pm 6	2332 \pm 10
CS2	0.12 \pm 0.03	1467 \pm 158	444 \pm 9	443 \pm 9	556 \pm 18
CS3	2.91 \pm 1.75	83 \pm 9	145 \pm 4	132 \pm 10	447 \pm 19
CS4	0.39 \pm 0.04	1582 \pm 57	139 \pm 6	138 \pm 9	147 \pm 6
CS5	3.90 \pm 0.38	192 \pm 7	125 \pm 9	120 \pm 19	342 \pm 10
CS6	3.94 \pm 0.96	334 \pm 35	114 \pm 9	122 \pm 9	287 \pm 32
CS7	3.03 \pm 0.26	77 \pm 10	85 \pm 10	73 \pm 6	184 \pm 10
CS8	0.39 \pm 0.13	1515 \pm 170	64 \pm 6	66 \pm 6	120 \pm 19
CS9	4.27 \pm 1.29	335 \pm 24	54 \pm 3	55 \pm 3	161 \pm 6
CS10	0.16 \pm 0.03	1630 \pm 89	39 \pm 10	25 \pm 12	289 \pm 9
CS11	3.40 \pm 0.80	64 \pm 3	38 \pm 3	20 \pm 3	94 \pm 9
CS12	5.30 \pm 1.05	168 \pm 7	32 \pm 1	24 \pm 5	67 \pm 6
CS13	2.25 \pm 0.33	111 \pm 3	26.3 \pm 0.7	20.2 \pm 3.5	ND
CS14	3.56 \pm 0.18	208 \pm 5	23.6 \pm 0.3	17.9 \pm 3.1	ND
CS15	1.44 \pm 0.26	151 \pm 7	18.3 \pm 0.5	13.2 \pm 3.3	ND
CS16	1.92 \pm 0.12	186 \pm 6	16.7 \pm 0.7	11.1 \pm 2.9	ND
CS17	0.22 \pm 0.08	81 \pm 6	14.0 \pm 0.7	9.3 \pm 2.9	ND
CS18	0.53 \pm 0.15	78 \pm 4	13.3 \pm 0.4	8.9 \pm 1.8	ND
CS19	2.16 \pm 0.30	62 \pm 3	10.2 \pm 0.2	6.3 \pm 0.2	ND
CS20	0.81 \pm 0.21	35 \pm 3	7.4 \pm 0.5	No value	ND
CS21	0.24 \pm 0.08	12 \pm 1	5.7 \pm 0.3	No value	ND
CS22	0.12 \pm 0.04	15 \pm 1	3.3 \pm 0.2	No value	ND

^aIn absence of chemical modifier.

^bIndicative value: [Cd] = 450 \pm 50 $\mu\text{g kg}^{-1}$.

^cFrom Pueyo et al. (2004), [Cd] = 480 \pm 10 $\mu\text{g kg}^{-1}$ (ICP-MS) [37].

ND: not determined.

10.9 $\mu\text{g L}^{-1}$ and 0.34 pg, respectively. With regards to the results, dilution of solutions with water is recommended to avoid the increase of the ratio Cl/Cd when the Cd concentration is too high to be determined by GFAAS. The HSSR-BGC and the D₂-BGC (combined with a chemical modifier) can be used to prevent the As and Fe interferences. In contrast, for a very low-factor dilution, large decreases of the Cd absorbance signal were observed using the D₂-BGC due to the presence of CdCl⁺ species. In this case, the HSSR-method is highly recommended.

Appendix

Standard

NF ISO 11464. Soil Quality: Pretreatment of samples for physicochemical analyses. AFNOR, 1994, 9 p.

NF ISO 11465. Soil Quality: Determination of dry matter and water content on a mass basis: gravimetric method. AFNOR, 1994, 4 p.

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