Sequential and simultaneous determination of four elements in soil samples using high-resolution continuum source graphite furnace atomic and molecular absorption spectrometry

W. Boschetti, M. Orlando, M. Dullius, M. B. Dessuy, M. G. R. Vale, B. Welz and J. B. de Andrade

An analytical method has been developed for the sequential and simultaneous determination of Cd, Cr, Fe and Al (via the AlH molecule) in soil samples using high-resolution continuum source graphite furnace atomic and molecular absorption spectrometry and direct solid sample analysis. First, Cd (228.802 nm) was determined using 800 °C and 1700 °C as the pyrolysis and atomization temperatures, respectively. Subsequently, after changing the wavelength, Cr (425.433 nm), Fe (425.076 nm) and Al (425.315 nm) were determined simultaneously from the same sample aliquot using 2600 °C as the atomization (Cr and Fe) or vaporization (AlH) temperature. Al determination was carried out using the diatomic molecule AlH without adding a molecule-forming reagent. The interference caused by Al in Cd determination was minimized by using 10 μL of a 10% v/v H2SO4 solution in all measurements. Aqueous standard solutions were used for calibration and the limits of detection and quantification obtained were 7.3 and 24 pg mg⁻¹ for Cd, 0.13 and 0.45 ng mg⁻¹ for Cr, 0.07 and 0.23 μg mg⁻¹ for Fe and 0.42 and 1.4 μg mg⁻¹ for Al, respectively. The concentration values for Cd, Cr, Fe and Al obtained from the soil certified reference material (CRM) Montana Soil I (NIST SRM 2710a) analysis were in agreement with the reported ones. The precision of the measurements, expressed as the relative standard deviation, was better than 10%. Six soil samples from a vineyard field were investigated and the results are in accordance with the Brazilian legislation.

1. Introduction

Soils are essential for life in the sense that they provide the medium for the growth of plants, which are the base for a complete food chain, and a habitat for many insects and other organisms. Soils act as a filtration system for surface water and as a carbon storage reservoir and maintain other environmental systems.¹,² The preservation and improvement of soil quality is critical to sustain agricultural productivity and environmental quality for future generations.² This goal can be achieved with the proper use of soil amendments; however, this procedure may also lead to soil contamination by potentially toxic elements.³,⁴ In this context, soil analysis plays an important role in the determination of the presence of nutrients and contaminants in soil samples.²,³,⁶

Cadmium, chromium and aluminum are known as potentially toxic elements for plants, being directly related to growth problems in roots, stems and leaves.⁷–¹¹ Aluminum may also compete with the absorption of K, Ca, Mg, Cu, Zn and Fe, which are essential for plant development, affecting their metabolic activities.¹¹,¹² Iron is known to be a micronutrient for plants; it is related to metabolic activities and enzyme formation and it is essential for the photosynthesis process.¹³,¹⁴ On the other hand, the accumulation of iron has been associated with foliar and root diseases in some plant species.¹⁵

In this context, regulations regarding the amount of Cd, Cr, Al and Fe present in soils must be followed. The Brazilian legislation establishes that a soil is apt for agriculture if it presents Cd and Cr concentrations below 1.0 and 100 mg kg⁻¹, respectively;¹⁶,¹⁷ however, nothing is mentioned about Fe and Al concentrations. Several studies in the literature discuss the effects of Al and Fe on plant development.⁹–¹⁵ The authors report that the problems caused by Al and Fe are related to their amount and bioavailability in the soil composition and to the plant species. For example, according to the United States
Environmental Protection Agency, some plants, such as tobacco, might tolerate Fe and Al concentrations up to 1000 mg kg⁻¹. This information provides to the soil analysis a vital function in order to control and maintain the soil quality.

Literature reports several techniques to determine Cd, Cr, Fe and Al in soil samples. The most commonly used ones are flame atomic absorption spectrometry (FAAS), graphite furnace atomic absorption spectrometry (GF AAS), inductively coupled plasma optical emission spectrometry (ICP OES) and inductively coupled plasma mass spectrometry (ICP-MS). However, sample pretreatment procedures, which are time consuming and costly and involve the use of hazardous reagents, are required for most of these techniques. Depending on the selected procedure and the type of soil, satisfactory results are not always guaranteed due to the possibility of analyte losses, sample contamination or incomplete analyte recovery.

Direct solid sample (SS) analysis is an attractive alternative in order to minimize sample preparation. Moreover, the combination of high-resolution continuum source graphite furnace atomic absorption spectrometry (HR-CS GF AAS) and SS analysis (HR-CS SS-GF AAS) can be considered as a powerful analytical tool, making possible multi-element determination with a minimum sample pretreatment.

Multi-element determination is one of the substantial innovations of the HR-CS AAS technique. Fast sequential determination from the same sample aliquot, as reported by Duarte et al. for Cd and Cr determination in biomass samples, can be carried out if the elements present different thermal behaviors and distant analytical lines, i.e., the wavelengths do not appear in the same spectral interval covered by the Charge Coupled Device (CCD) detector. The simultaneous determination of elements as reported by several authors is possible if the analytes present similar thermal behaviors and analytical lines in the same spectral interval covered by the CCD detector. An additional possibility for simultaneous analysis, reported by some authors, takes into account analytes with different thermal behaviors and wavelengths in the same spectral interval covered by the CCD detector.

Another improvement achieved by the HR-CS AAS technique is the possibility to determine different elements, including non-metals via molecular absorption spectrometry (MAS) using the rotational fine structure of the electron excitation spectra of diatomic molecules. This can be accomplished due to the association of a continuum source, a high-resolution monochromator and a CCD detector. Thus, any rotational line or a combination of lines of the spectrum of a diatomic molecule can be used for analytical purposes. Several studies report the application of HR-CS AAS instrumentation for the determination of non-metals via diatomic molecules; this alternate technique is denoted as HR-CS MAS.

The main goal of this work was to develop an analytical method for the sequential and simultaneous determination of Al (via the AlH molecule), Cd, Cr and Fe in soil samples. This method for the sequential and simultaneous determination of non-metals.

2. Experimental

2.1. Instrumentation

All measurements were carried out using a model contrAA 700 high-resolution continuum source atomic absorption spectrometer (Analytik Jena AG, Jena, Germany). This instrument is equipped with a flame and a transversely heated graphite tube atomizer in two different sample compartments and a high-intensity xenon short-arc lamp operating in a hot-spot mode. The high-resolution is achieved by combining a double monochromator (prism and echelle grating) with a linear CCD array detector with 588 pixels. The primary analytical line at 228.802 nm was used for Cd and secondary lines for Cr at 245.433 nm and Fe at 245.076 nm. For the determination of Al via the AlH molecule, the 425.315 nm wavelength was chosen. The integrated absorbance values for each analyte were obtained using the peak area of the center pixel (CP) only, for Cd and Cr, three pixels (CP ± 1) for Al and five pixels (CP ± 2) for Fe. All four analytical lines were directly selected in the software supplied by the manufacturer, which automatically provides the analyte recovery.

All experiments were carried out using pyrolytically coated solid sampling (SS) graphite tubes without a dosing hole (Analytik Jena, Part no. 407-A81.303) and SS graphite platforms (Analytik Jena, Part no. 407–152.023). A microbalance model MA65.65-000-DM (Sartorius, Göttingen, Germany) was used for weighing the samples directly onto the SS platform. A model SSA 5 manual solid sampling accessory (Analytik Jena) with a pre-adjusted pair of tweezers was used to transfer the SS platforms to the GF.

Argon with a purity of 99.999% (White Martins, São Paulo, Brazil) was used as purge gas with a flow rate of 2.0 L min⁻¹ during all stages, except during the atomization of Cr and Fe and vaporization of AlH, where the flow was stopped. For Cd, an internal flow rate of 0.1 L min⁻¹ was kept during the atomization stage in order to reduce the sensitivity. The optimized graphite furnace temperature program used for all determinations is shown in Table 1.

2.2. Reagents

High-purity deionized water supplied by a Milli-Q water purification system (Millipore, Bedford, MA, USA) was used to prepare analytical solutions and dilutions. Standard stock solutions of 1000 mg L⁻¹ Cd, Cr and Fe (SpecSol, São Paulo, Brazil) and 1000 mg L⁻¹ Al (Sigma-Aldrich, St. Louis, MO, USA) were used, all of them in HNO₃ to avoid chloride interference, as AlCl might be formed under similar thermal conditions. Adequate dilutions of 97% (m/v) H₂SO₄, 35% (m/v) H₂O₂, 65% (m/v) HNO₃ and NH₄H₂PO₄ salt (all from Merck, Darmstadt, Germany) were used as chemical modifiers. All flasks were cleaned by soaking in a 1.4 mol L⁻¹ HNO₃ solution for at least 24 h and rinsed abundantly with high-purity deionized water before use. The aqueous standard solutions were prepared by adequate dilutions of the Cd, Cr, Fe and Al stock solutions in a 10% (v/v) solution of H₂SO₄.

2.3. Samples and sample preparation

Six soil samples were collected from a vineyard field with 10 000 m² in Pinto Bandeira (Rio Grande do Sul, Brazil). Approximately...
500 g of each soil sample was collected from different points of the vineyard and then transferred to plastic bags. After collection, the samples were dried in a dark room, protected from the wind and stored in plastic bags. The soil samples were subjected to a grinding process in a mortar and then sieved through a 200 μm polyester sieve and kept in sealed plastic vials until further analysis.

A certified reference material (CRM), NIST SRM 2710a – Montana I Soil, (National Institute of Standards and Technology, Gaithersburg, MD, USA), was employed for method optimization and validation. The sample mass, weighed onto the SS platforms and introduced into the graphite furnace, was between 0.02 mg and 0.25 mg. Since the sample mass was different for each measurement, the $A_{\text{int}}$ was normalized for an appropriate sample mass for comparison.

### 3. Results and discussion

#### 3.1. Preliminary studies

Due to the high concentration of Cd and Cr in the samples, two different measures were taken to adjust the sensitivity to the linear range: for Cd determination, a gas flow rate of 0.1 L min$^{-1}$ was used in the atomization stage and for Cr determination, an alternate line at 425.433 nm was chosen. This secondary line of Cr has 33% of relative sensitivity in comparison with the most sensitive line at 357.869 nm. Within the spectral window of this secondary Cr line appear also an absorption line of Fe at 425.076 nm and some rotational lines of the AlH molecule. Fig. 1 shows the time-resolved absorbance spectrum of the soil CRM; the analytical lines of Cd (Fig. 1a), Cr, Fe and AlH (Fig. 1b) are identified. The proximity of these lines was explored in order to develop an analytical method for determining first Cd, and after changing the wavelength, for determining simultaneously Cr, Fe and Al from the same sample aliquot. As can be seen in Fig. 1b, Cr shows some minor tailing, which is typical for this element. To overcome Cr tail formation, Dobrowolski et al. investigated the use of different chemical modifiers. In the present work, the tail did not influence the results as the standard and samples showed the same behavior and RSD values were lower than 10% for all measurements. No memory effect was observed; to verify this,
after a few soil samples, a measurement of the blank solution (10 μL of H2SO4 10%) was regularly carried out (Aint values lower than 0.008 s). In this context, the use of chemical modifiers was not investigated.

Initially, the effect of the minimum gas flow rate, used during the atomization of Cd, on the simultaneously evaluated elements Cr, Fe and Al was investigated in order to ensure that there were no losses of these elements during this stage. A multi-element aqueous standard solution and the soil CRM were measured several times, and the Aint values for Cr, Fe and Al were not affected by the minimum gas flow during Cd atomization.

3.2. Investigation of AlH formation and interference

Identical peak profiles of AlH were obtained for evaluating the soil CRM, the soil samples and an aqueous standard solution; these analytical signals were in agreement with the reference spectrum found in the equipment library for AlH. As stated by Resano et al.,47 to analyze a diatomic molecule by HR-CS SS-GF AAS it is in most cases necessary to add an adequate molecule-forming reagent. In this context, different compounds were investigated as AlH forming reagents: (i) 1 and 10% (v/v) H2SO4; (ii) 1 and 10% (v/v) HNO3; (iii) 1 and 10% (v/v) H2O2; (iv) H2O and (v) 10% (m/v) NH4H2PO4. This investigation was carried out with the CRM and a multi-element aqueous standard solution; ten microliters of each molecule-forming reagent solution was pipetted over the standard or CRM. No significant improvement in the Aint values was observed with any of the molecule-forming reagents. This means that both the CRM and aqueous standard solution have sufficient hydrogen in their composition to guarantee the AlH molecule formation. It was also observed that the analytical signals of Fe and Cr were not affected by the investigated molecule-forming reagents.

For the Cd signal, significant differences in the peak profile could be observed for an aqueous standard solution with and without Al, as shown in Fig. 2. Literature reports that Al can be considered an interferent for Cd determination by electrothermal AAS, using a molybdenum tube atomizer.51 Interestingly, Al was recently used as a chemical modifier added into solution52 or as a permanent modifier53 for Cd determination by GF AAS. This need not be considered a contradiction, as Al in fact delays the appearance time and the peak maximum of Cd significantly, as can be seen in Fig. 2. At the same time, however, Aint is reduced significantly due to the faster diffusion of Cd atoms at the higher effective gas phase temperature, which is a well-known effect. Obviously, the use of Al as a modifier could not be considered here, as Al had to be determined as well. In order to minimize the effects of Al on the analytical signal of Cd, observed in the molybdenum atomizer, Ohta et al.51 reported the use of 1 μL of 1.0% (v/v) H2SO4 solution, which completely eliminated the interference if the Cd concentration was not too high.

In the present study, a similar behavior was observed for the addition of H2SO4; the use of 10 μL of 10% (v/v) H2SO4 resulted in a similar appearance time with and without Al, improved the Cd peak symmetry and increased the Aint values of Cd for an aqueous standard solution, as can be seen in Fig. 2. For comparison, a mono elemental aqueous standard solution of Cd was measured with and without H2SO4.

However, for the samples and the CRM, no significant difference was observed in the peak shape of Cd with and without the addition of H2SO4 solution (Fig. 3). Moreover, comparing Fig. 2 and 3, the peak shapes of Cd obtained from the soil CRM and Cd standard solution, both with 10% (v/v) H2SO4, are similar. This indicates that the interaction between Cd and Al in the samples and the CRM is much lower than that in the standard solution, which may be attributed to the chemical form in which Cd and Al are present in the sample.

The evaluation of the amount of H2SO4 necessary to reduce the Al interference on the Cd signal is shown in Fig. 4. This figure compares the Aint values for the CRM and a Cd standard solution (with 5 μg Al) without the addition of H2SO4 and using 10 μL of four H2SO4 solutions of different concentrations. The peaks obtained without H2SO4 and with 5% H2SO4 solution were broader and more asymmetrical than those obtained with higher H2SO4 concentration. Therefore, 10 μL of 10% (v/v)
H₂SO₄ was chosen as the best condition. The Aᵢₙ values of aqueous standard solutions prepared in H₂SO₄ were compared with those obtained by adding the acid over the standard solution (on the platform) and no difference between them was observed. Thus, in order to simplify the experimental procedure, all standard solutions were prepared in 10% H₂SO₄. It should be mentioned that the use of sulfuric acid decreased the life time of the SS graphite tube and platform to approximately 180 cycles.

3.3. Graphite furnace temperature program

The temperature program was optimized using the soil CRM and an aqueous standard solution with 50 µg L⁻¹ Cd, 40 µg L⁻¹ Cr, 200 mg L⁻¹ Fe and 500 mg L⁻¹ Al in the presence of H₂SO₄. Taking into account that a sequential determination will be performed, the pyrolysis (Tpyr) and atomization (Tatom) temperatures of the most volatile element (Cd) were optimized first. Fig. 5 shows the Cd pyrolysis and atomization curves.

In Fig. 5, a plateau is observed up to a pyrolysis temperature of 900 °C for the standard solution and for the soil CRM, which is very high for Cd in the absence of any of the typically used chemical modifiers. This high thermal stability of Cd may be attributed to the Al effect and the presence of H₂SO₄, performing as chemical modifiers. Moreover, at 800 °C, the volatile matrix components were eliminated and the relative standard deviation (RSD) values were lower than those for the other Tpyr investigated; thus, a temperature of 800 °C was used in all further experiments.

During this study, the Aᵢₙ values of Cr, Fe and AlH were also monitored, using a second Tatom/vap of 2600 °C, with the Tatom of Cd as a second Tpyr for these elements. Fig. 6 shows that the analytical signal for Cr remained stable up to 2000 °C; however, for Fe and AlH, the Aᵢₙ values decreased using temperatures higher than 1800 °C. This effect was more significant for the analytical signal of AlH, probably due to the increasing dissociation of the AlH molecule at higher temperatures. For this reason, a Tatom of 1700 °C was chosen for Cd according to the most symmetric and reproducible peaks and highest Aᵢₙ values (Fig. 5). This Tatom can also be considered a second Tpyr for the more stable elements Al, Cr and Fe. The Tpyr and Tatom for Cd in the following measurements were fixed at 800 °C and 1700 °C, respectively.

After establishing the Tpyr and Tatom for Cd, the Tatom values for Cr and Fe and Tvap for AlH were optimized. The results are shown in Fig. 7. It is important to highlight that these three species were monitored simultaneously. A temperature of 2600 °C presented the best results for Cr and Fe, with high Aᵢₙ values and the most reproducible peaks. For AlH, symmetric analytical signals were observed above 2400 °C. Although the Aᵢₙ values for the AlH molecule decreased slightly for higher Tvap, the Tatom/vap was fixed at 2600 °C in order to guarantee the complete atomization of Cr and Fe. This condition does not influence the Al quantification, via the AlH molecule, since the standard solution and the CRM experienced the same moderate reduction of sensitivity at a temperature of 2600 °C.

Fig. 4 Investigation of different H₂SO₄ concentrations to minimize the Al interference in Cd determination by HR-CS SS-GF AAS; ■ 500 pg Cd and 5 µg Al, ▲ soil CRM (Aᵢₙ values normalized to a mass of 0.05 mg). A volume of 10 µL of H₂SO₄ solution was used. Tpyr = 800 °C and Tatom = 1700 °C using a gas flow rate of 0.1 L min⁻¹ in the atomization stage.

Fig. 5 Pyrolysis and atomization curves of Cd using 10 µL of 10% (v/v) H₂SO₄ as the chemical modifier; ■ 500 pg Cd aqueous standard solution (with 400 pg Cr, 2 µg Fe and 5 µg Al) and ▲ soil CRM (Aᵢₙ values normalized to a mass of 0.05 mg). Tpyr for pyrolysis curves = 1700 °C. Tpyr for atomization curves = 800 °C. A gas flow rate of 0.1 L min⁻¹ was used in the atomization stage.

Fig. 6 Integrated absorbance values for ■ Cr, ▲ Fe and ● AlH; ... in a multi-element aqueous standard solution, and — in a soil CRM, monitored during the optimization of the Cd atomization temperature, using 10 µL of 10% (v/v) H₂SO₄ as the chemical modifier, and a Tatom/vap of 2600 °C for the less volatile elements. The Tatom of Cd might be considered a second Tpyr for Cr, Fe and Al. The CRM Aᵢₙ values were normalized to a mass of 0.05 mg.
After the optimization of the temperature program, the influence of the mass of the CRM and soil samples, inserted into the furnace, on the $A_{int}$ values was investigated. For all analytes, Cd, Cr, Fe and Al, acceptable correlation coefficients, higher than 0.955, were obtained, evaluating masses from 0.02 to 0.25 mg of the CRM and sample. For higher CRM and soil masses (above 0.25 mg), the $A_{int}$ and the repeatability for Cd and Cr decreased as well as the correlation coefficient. Hence, the maximum sample mass that could be inserted into the furnace, considering the investigated soil samples, was 0.25 mg.

3.4. Figures of merit

Calibration curves were established with a blank and six calibration solutions within the ranges of 0.05–0.8 ng Cd, 0.2–4.0 ng Cr, 1.0–16 µg Fe and 2.5–40 µg Al. The limit of detection (LOD) was calculated as three times the standard deviation of 10 measurements of a blank, divided by the sensitivity (slope of the calibration curve), and the limit of quantification (LOQ) as ten times the standard deviation of the same 10 measurements. Blank measurements were carried out according to the “zero mass response” principle using only the modifier (10 µL of 10% (v/v) H$_2$SO$_4$) on the SS platform. The characteristic mass ($m_0$) is defined as the mass of the analyte corresponding to an integrated absorbance of 0.0044 s. The figures of merit of the developed method are summarized in Table 2; the LOD and LOQ were calculated for the maximum sample mass weighed onto the SS platform, i.e., 0.25 mg.

Due to the high content of Cd, Cr, Fe and Al present in the soil samples, several measures were taken to reduce the sensitivity of the results: a gas flow rate of 0.1 L min$^{-1}$ in the atomization stage for Cd, and secondary analytical lines for Cr (425.433 nm), Fe (425.076 nm) and AlH (425.315 nm). In addition, only the center pixel was used to measure the $A_{int}$ values for Cd and Cr, which reduced the sensitivity to about 40–50% compared to the use of three pixels. In this context, the LOD and LOQ presented in this work cannot be directly compared with those reported in the literature. Moreover, the LOD and LOQ presented in Table 2 are comfortably lower than the maximum limits established for Cd and Cr by Brazilian legislation.

### 3.5. Analysis of the CRM and the soil samples

The soil CRM was evaluated in order to check the trueness of the developed method. The concentration values obtained for Cd, Cr, Fe and Al were in agreement with the certified ones. Table 3 shows the certified and the found concentrations and $t$-Student calculated values ($t_{calc}$). The comparison of the found

<table>
<thead>
<tr>
<th>Analyte</th>
<th>LOD</th>
<th>LOQ</th>
<th>$m_0$</th>
</tr>
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<tbody>
<tr>
<td>Cd</td>
<td>7.3 pg mg$^{-1}$</td>
<td>24 pg mg$^{-1}$</td>
<td>3.9 pg</td>
</tr>
<tr>
<td>Cr</td>
<td>0.13 ng mg$^{-1}$</td>
<td>0.45 ng mg$^{-1}$</td>
<td>27 pg</td>
</tr>
<tr>
<td>Fe</td>
<td>0.07 µg mg$^{-1}$</td>
<td>0.23 µg mg$^{-1}$</td>
<td>0.09 µg</td>
</tr>
<tr>
<td>Al</td>
<td>0.42 µg mg$^{-1}$</td>
<td>1.4 µg mg$^{-1}$</td>
<td>0.18 µg</td>
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</table>

$^a$ LOD and LOQ calculated for 0.25 mg of sample.

Table 3. Figures of merit for Cd, Cr, Fe and Al determination in soil samples by HR-CS SS-GF AAS/MAS using 10 µL of 10% (v/v) H$_2$SO$_4$ as the chemical modifier. $T_{pyr} = 800$ °C, $T_{atom} = 1700$ °C (Cd) and $T_{atom/vap} = 2600$ °C (Cr, Fe, and Al)$^a$

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Certified (conc. ± sd)</th>
<th>Found (conc. ± sd)</th>
<th>$t_{calc}$</th>
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<tbody>
<tr>
<td>Cd/µg mg$^{-1}$</td>
<td>$12.3 ± 0.3$</td>
<td>$11 ± 1$</td>
<td>$1.9$</td>
</tr>
<tr>
<td>Cr/µg mg$^{-1}$</td>
<td>$23 ± 6$</td>
<td>$22 ± 3$</td>
<td>$0.57$</td>
</tr>
<tr>
<td>Fe/µg mg$^{-1}$</td>
<td>$4.32 ± 0.08$</td>
<td>$4.6 ± 0.4$</td>
<td>$1.4$</td>
</tr>
<tr>
<td>Al/µg mg$^{-1}$</td>
<td>$5.95 ± 0.05$</td>
<td>$5.9 ± 0.5$</td>
<td>$0.36$</td>
</tr>
</tbody>
</table>

Note: HR-CS SS-GF AAS/MAS using 10 µL of 10% (v/v) H$_2$SO$_4$. $T_{pyr} = 800$ °C, $T_{atom} = 1700$ °C (Cd) and $T_{atom/vap} = 2600$ °C (Cr, Fe, and Al)
and certified concentrations for each element was performed through a Student t-test with 95% confidence level ($t_{\text{calc}} < t_{\text{crit}}$; $t_{\text{crit}} = 2.7$). The good agreement of the results confirms that the developed method is trustworthy and can be used to determine Cd, Cr, Fe and Al in soil samples. Considering all measurements, the RSD values were around or lower than 10%, proving that the developed method provides precise results. The total analysis time per sample for five replicates, including weighing the sample aliquot, is around 30 min, which is clearly less than the time required for techniques that require sample digestion. However, a direct and fair comparison of various techniques is almost impossible, as the total analysis time depends on many more factors, including the number of elements that have to be determined.

On evaluating the results for the vineyard field soil samples (Table 4), the concentrations found for Cd and Cr are in agreement with the Brazilian legislation, providing to this soil the status of apt for agriculture. Great amounts of Fe and Al were observed in these soil samples. The Fe concentration values suggest that this might be a nutritive soil for plants. However, considering the high Al content, special care must be taken in order to minimize its absorption by plants.

<table>
<thead>
<tr>
<th>Soil samples</th>
<th>Cd/ng mg$^{-1}$</th>
<th>Cr/ng mg$^{-1}$</th>
<th>Fe/μg mg$^{-1}$</th>
<th>Al/μg mg$^{-1}$</th>
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<tr>
<td>Site 1</td>
<td>0.47 ± 0.05</td>
<td>19 ± 2</td>
<td>58 ± 5</td>
<td>69 ± 7</td>
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<tr>
<td>Site 2</td>
<td>0.20 ± 0.02</td>
<td>16 ± 1</td>
<td>68 ± 8</td>
<td>95 ± 11</td>
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<tr>
<td>Site 3</td>
<td>0.28 ± 0.03</td>
<td>18 ± 1</td>
<td>68 ± 5</td>
<td>70 ± 9</td>
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<tr>
<td>Site 4</td>
<td>0.16 ± 0.01</td>
<td>14 ± 2</td>
<td>101 ± 13</td>
<td>93 ± 3</td>
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<tr>
<td>Site 5</td>
<td>0.28 ± 0.03</td>
<td>20 ± 1</td>
<td>64 ± 2</td>
<td>102 ± 10</td>
</tr>
<tr>
<td>Site 6</td>
<td>0.17 ± 0.01</td>
<td>15 ± 1</td>
<td>69 ± 6</td>
<td>105 ± 10</td>
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</table>

### Acknowledgements

The authors are grateful to the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), the Instituto Nacional de Ciência e Tecnologia do CNPq – INCT de Energia e Ambiente, Salvador, BA, Brazil, and Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) for financial support and scholarships.

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