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Investigation of spectral interferences in the determination of lead in fertilizers and limestone samples using high-resolution continuum source graphite furnace atomic absorption spectrometry ☆

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ABSTRACT

In the present work, spectral interferences on the determination of lead in fertilizer and limestone samples were investigated using high-resolution continuum source graphite furnace atomic absorption spectrometry at the main analytical lines: 217.001 and 283.306 nm. For these investigations, samples were introduced into the furnace as slurry together with a mixture of Pd and Mg as chemical modifier. Spectral interferences were observed for some samples at both analytical lines. In order to verify whether a wet digestion procedure would avoid these interferences, a reference method for wet digestion of fertilizers was employed as an alternative sample preparation procedure. However, the same interferences were also observed in the digested samples. In order to identify and eliminate the fine-structured background using a least-squares background correction, reference spectra were generated using the combination of different species. The use of the latter technique allowed the elimination of spectral interferences for most of the investigated samples, making possible the determination of lead in fertilizer and limestone samples free of interferences. The best results were found using a reference spectrum of $NH_4H_2PO_4$ at 217.001 nm, and a mixture of H_2SO_4 + Ca and HNO_3 + Ca at the 283.306 nm line. The accuracy of the method was evaluated using a certified reference material "Trace Elements in Multi-Nutrient Fertilizer". Similar results were obtained using line source graphite furnace atomic absorption spectrometry with Zeeman-effect background correction, indicating that the latter technique was also capable to correct the spectral interferences, at least in part.

1. Introduction

In a previous work [1] about the determination of lead in fertilizer samples with slurry sampling using line source graphite furnace atomic absorption spectrometry (LS GF AAS) with Zeeman-effect background correction a high background signal was observed, indicating the presence of a spectral interference and it was not possible to determine lead at the 217.0 nm line due to the presence of this interference. The determination of some elements in samples with high phosphorus content, such as fertilizers, might be susceptible to errors when Zeeman-effect background correction is used due to the splitting of the rotational lines of the molecular spectrum of the gaseous phosphorus monoxide (PO) under the influence of the magnetic field [2–6]. In this case, the background absorption without and with magnetic field is not the same, resulting in background correction errors. The overcorrection for the determination of lead using the absorption lines at 217.0 nm and 283.3 nm was already reported in the literature [3]. High-resolution continuum source atomic absorption spectrometry (HR-CS AAS) is an extremely valuable tool for investigating such interference due to the visibility of the spectral environment of the analytical line at high resolution and other features [7–9]. One of the advantages of the software employed in this equipment is the possibility to measure and store reference spectra of diatomic molecules with rotational fine structure that coincide temporally and spectrally with the analyte absorption. To eliminate the fine-structured background using least-squares background correction (LSBC) it is mandatory to identify the molecule which is responsible for the spectral interference. Then the reference spectrum of the interfering molecule is recorded and subtracted from the sample spectrum using LSBC and a spectrum of the pure analyte is obtained [9–11]. It is important to highlight that the fine-structured background depends on the chemical composition of each sample.

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The use of LSBC has already been reported in the literature several times. Becker-Ross et al. [12] reported the presence of fine-structured background absorption in the determination of arsenic and selenium in human urine. In the case of arsenic the spectral interferences were corrected using a reference spectrum obtained from NaCl and PO, while in the case of selenium NO and PO reference spectra were used to correct the interferences. In both cases, it was possible to obtain accurate results after LSBC for the analysis of a reference material. In another study, Welz et al. [10] reported the presence of fine structured background of a sulfur containing molecule in the determination of thallium in a marine sediment reference material. The fine structured molecular background was completely removed by subtracting a reference spectrum of $KHSO_4$ from the sample spectrum using LSBC.

Araujo et al. [13] found significant background absorption with pronounced rotational fine structure coinciding with the antimony atomic absorption signal in sediment certified reference materials using direct solid sample analysis. This background was found to be due to the electron excitation spectra of mostly SiO and PO molecules, which could be eliminated by LSBC using a reference spectrum of pure silica (SiO_2) and another one of $NH_4H_2PO_4$, for PO.

The aim of the current contribution was to investigate the potential spectral interferences in the determination of lead in fertilizer and limestone samples using slurry sampling and HR-CS GF AAS. For this purpose, the main analytical lines of lead at 217.001 and 283.306 nm, were evaluated, employing the conditions (slurry preparation procedure, modifier composition and mass and furnace temperature program) optimized in our previous work [1].

2. Experimental

2.1. Instrumentation

A high-resolution continuum source atomic absorption spectrometer Model contrAA 700 (Analytik Jena, Germany) was employed in this study. This instrument is equipped with a flame and a graphite furnace atomizer in two separate compartments, and a xenon short-arc lamp with a nominal power of 300 W, operating in a hot-spot mode. The high-resolution double monochromator with a linear charge-coupled device (CCD) array detector with 588 pixels has a spectral resolution of 1.2 pm per pixel at 200 nm. The integrated absorbance of three pixels, the center pixel (CP) and the two adjacent pixels, i.e. CP ± 1, was summed and used for signal evaluation at both analytical lines.

Transversely heated and pyrolytically coated graphite tubes with PIN platform (Analytik Jena, Part No. 407-A81.025) were used for all measurements. An MPE 60 furnace autosampler (Analytik Jena) was used for the introduction of slurry samples, standard and modifier solutions. Argon with a purity of 99.996% (White Martins, São Paulo, Brazil), with a flow-rate of 2 L min^{-1}, was used as the purge and protective gas during all stages, except during atomization, when the flow was stopped. The previously optimized graphite furnace temperature program [1] used for all the determinations is shown in Table 1.

Table 1
Graphite furnace temperature program for the determination of lead by HR-CS GF AAS using 10 μg Pd + 6 μg Mg as a modifier in solution.

Stage	Temperature/°C	Ramp/°C s^{-1}	Hold time/s
Drying	90	5	20
Drying	120	5	10
Drying	150	5	20
Pyrolysis	900	500	30
Atomization	2100	3000	4
Cleaning	2200	1000	4

2.2. Reagents

All reagents were of analytical grade or higher purity. Ultrapure water with a specific resistivity of 18.2 MΩ cm from a Milli-Q water purification system (Millipore, Bedford, MA) was used. The nitric acid (Merck, Darmstadt, Germany), used for the preparation of the slurry samples and standard solutions, was further purified by sub-boiling distillation in a quartz apparatus (Kürner Analysentechnik, Rosenheim, Germany). The working standards were prepared by serial dilution of the 1000 mg L^{-1} Pb stock solution (SpecSol, São Paulo, Brazil) in 0.014 mol L^{-1} HNO_3. The chemical modifier solution, a mixture of Pd and Mg, was prepared from Pd modifier stock solution, 10.0 ± 0.2 g L^{-1} Pd in 15% (v/v) HNO_3 and Mg modifier stock solution, 10.0 ± 0.2 g L^{-1} $Mg(NO_3)_2$ in 15% (v/v) HNO_3 (Merck). Ethanol and Triton X-100 (both from Merck) were used for the preparation of the slurry. For the digestion of the samples distilled HNO_3 and H_2O_2 30% (Merck) were used. The certified reference material NIST SRM 695, Trace Elements in Multi-Nutrient Fertilizer (National Institute of Standards and Technology, Gaithersburg, MD, USA) was used to evaluate the trueness of the results.

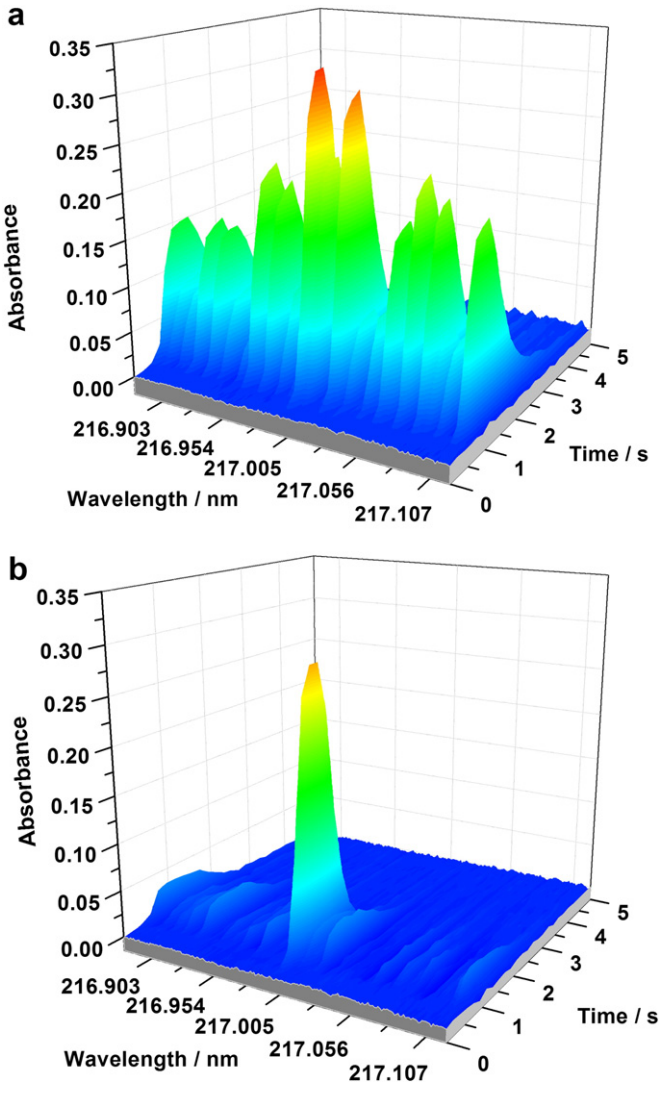

Fig. 1. Time-resolved absorbance spectra in the vicinity of the 217.001 nm analytical line recorded for the sample 46% P_2O_5 + 15% Ca using 10 μg Pd + 6 μg Mg as modifier in solution: a) without correction; b) after correction with 1% $NH_4H_2PO_4$. T_{pyr} = 900 °C; T_{at} = 2100 °C.

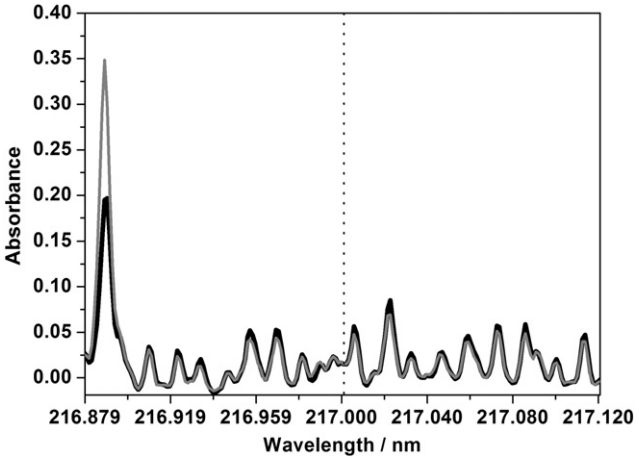

Fig. 2. Absorbance spectra obtained in the vicinity of the 217.001 nm analytical line for the fertilizer samples (gray line) N:P:K 4:14:8 and (black line) N:P:K 10:10:10 using 10 μg Pd + 6 μg Mg as modifier in solution, after correction with 1% $NH_4H_2PO_4$. Dotted line indicates the analytical line position. T_{pyr} = 900 °C; T_{at} = 2100 °C.

2.3. Sample preparation

All samples were acquired at local agricultural stores in Rio Grande do Sul, Brazil and are identified according to their label. The investigated samples were fertilizers N:P:K 10:10:10, N:P:K 4:14:8, 23.1% K_2O + 11.3% Mg + 22.5% S and 46% P_2O_5 + 15% Ca and limestone. The sample pre-treatment was performed according to the procedure described in previous publications [1,14]; it consisted of a grinding step in a ball mill and a sieving step to control the sample particle size (<45 μm) using a polyester sieve. The samples were placed into an oven at 50 °C until they reached constant weight. The diluent solution consisted of 5% (v/v) HNO_3, 0.05% (v/v) Triton X-100 and 10% (v/v) ethanol. The slurries were prepared with concentrations of about 2% (w/v); however, due to the high concentration of lead in the NIST SRM 695, the slurry of this material was prepared in a concentration of 0.01% (w/v). The slurries were homogenized for 30 min in an ultrasonic bath and placed into the autosampler cups of the instrument. Prior to sample injection, the slurry was homogenized manually. The determination of lead was carried out using slurry volumes between 5 and 30 μL, according to the analyte concentration in the samples. The slurries were prepared in triplicate and six aliquots of each one were analyzed.

In order to compare the results obtained using direct slurry sampling, a wet digestion was employed as an alternative sample preparation method. This method was based on EPA Method 3050B [15], established by the United States Environmental Protection Agency and recommended as reference method by the Brazilian Ministry of Agriculture.

3. Results and discussion

3.1. Investigation of spectral interferences

In a previous study about the determination of lead by LS GF AAS using Zeeman-effect background correction [1], the use of Pd/Mg as chemical modifier allowed employing pyrolysis temperatures of up to 900 °C, but it was not sufficient to eliminate completely the background signal for some fertilizer samples at 283.3 nm. Using the analytical line at 217.0 nm it was not possible to determine lead in the samples due to strong spectral interferences. In contrast to line source atomic absorption spectrometry (LS AAS), where the 217.0 nm line exhibits a poor signal-to-noise ratio and a pronounced non-linearity, it can be used without problems in HR-CS AAS because of the much higher radiation intensity available from the xenon short-arc lamp [9].

Considering the visibility of the background in the vicinity of the analytical line and the superior background correction possibilities, measurements were performed using HR-CS GF AAS at both analytical lines and using the previously optimized conditions with Pd/Mg modifier. The limestone could be analyzed at both analytical lines without spectral interference. However, using the 217.001 nm line, the fertilizers N:P:K 4:14:8, N:P:K 10:10:10 and 46% P_2O_5 + 15% Ca exhibited strong spectral interferences.

As discussed earlier, at 217.001 nm, it could be expected that this spectral interference is due to the PO molecule [4,6]. Then, a reference spectrum of PO was recorded using 10 μL of 1% (w/v) $NH_4H_2PO_4$ solution, the same amount of modifier and the same pyrolysis and atomization temperatures as employed for the sample. This spectrum was subtracted from the sample spectra using LSBC. The spectral interference of the 46% P_2O_5 + 15% Ca fertilizer sample was corrected, as shown in Fig. 1. Some structures remained, however, these did not overlap with the three pixels (CP ± 1) used for the evaluation of the signal, allowing the quantification of lead in this sample.

However, for the N:P:K 4:14:8 and N:P:K 10:10:10 fertilizer samples, the spectral interferences were not completely eliminated using the PO reference spectrum. Taking into account the profiles of the resulting spectra obtained for both samples at 217.001 nm, it can be noticed, in Fig. 2, that they are completely overlapped, suggesting that both samples are suffering from the same interference, as expected since both are N:P:K fertilizers. Moreover, analyzing the signal profile of CP ± 1, it was observed that the interference coincided in time and wavelength with the analytical signal of lead, in the three pixels. This spectral interference is caused by some unknown molecule and, for this reason,

Table 2
Solutions investigated for producing reference spectra.

	Spectrum	
Solution (10 μL)	217.001 nm	283.306 nm
5% H_2SO_4	Not observed	Not observed
1% HNO_3	Not observed	Not observed
5% H_2SO_4 + 0.05% $CaCl_2$	Different from the samples	Similar to samples 23.1% K_2O + 11.3% Mg + 22.5% S and N:P:K 4:14:8
1% HNO_3 + 0.05% $CaCl_2$	Similar to samples N:P:K 4:14:8 and 10:10:10	Similar to samples 23.1% K_2O + 11.3% Mg + 22.5% S and N:P:K 4:14:8
1% $NH_4H_2PO_4$	Similar to sample 46% P_2O_5 + 15% Ca	n.i.
1% $NH_4H_2PO_4$ + 0.05% $CaCl_2$	Different from the samples	n.i.
1% $NH_4H_2PO_4$ + 0.05% KCl	Different from the samples	n.i.
5% H_2SO_4 + 0.05% KCl	Different from the samples	n.i.
1% HNO_3 + 0.05% KCl	Not observed	n.i.
1% NaOH + 0.05% $CaCl_2$	Different from the samples	n.i.
1% NaOH + 0.05% $SnCl_2$	Different from the samples	n.i.
1% HNO_3 + 0.05% $SnCl_2$	Different from the samples	n.i.

n.i. = not investigated.

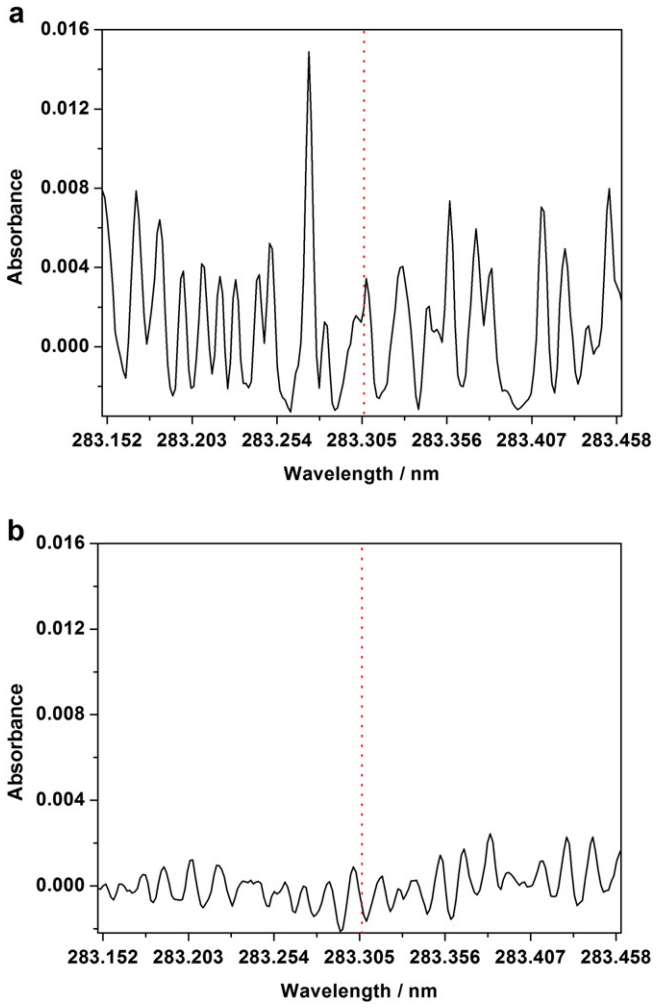

Fig. 3. Absorbance spectra obtained in the vicinity of 283.306 nm: a) mixture of 5% H_2SO_4 + 0.05% $CaCl_2$; b) mixture of 1% HNO_3 + 0.05% $CaCl_2$. Dotted line indicates the analytical line position. T_{pyr} = 900 °C; T_{at} = 2100 °C.

it was not possible to generate a reference spectrum for the adequate elimination of this interference using LSBC.

On the other hand, at 283.306 nm, only N:P:K 4:14:8 and 23.1% K_2O + 11.3% Mg + 22.5% S fertilizer samples exhibited fine-structured background. In order to find which molecules were responsible for the observed spectral interferences, at 217.001 and 283.306 nm, different solutions were used to record reference spectra for both wavelengths, as shown in Table 2. These solutions were chosen based in the sample composition in an attempt to reproduce these interferences.

H_2SO_4, HNO_3 and $NH_4H_2PO_4$ were studied in combination or not with Ca, K and Sn salts. Although the presence of Ca and/or K are not stated in the composition of the analyzed samples, they were employed because previous works reported that calcium in combination with nitric acid produces a structured background absorption in the vicinity of the analytical line of P, at 213.681 nm, which is due to the formation of the NO molecule [16]. Although only one of the investigated samples has sulfur in their composition, the influence of S-containing molecules has been investigated in the present study using H_2SO_4, since the literature reports the interference of sulfur molecules in the vicinity of the analytical line of thallium at 276.787 nm [10]. The mixture of tin chloride and sodium hydroxide was studied due to a possible interference caused by SnO at 217.001 nm indicated by the software of the instrument.

As can be seen in Table 2, the results indicate that solutions of 5% H_2SO_4 + 0.05% $CaCl_2$ and 1% HNO_3 + 0.05% $CaCl_2$ generated reference spectra similar to the structures observed in the spectra of samples N:P:K 4:14:8 and 23.1% K_2O + 11.3% Mg + 22.5% S for 283.306 nm. On the other hand, at 217.001 nm, the spectrum of the mixture of 1% HNO_3 + 0.05% $CaCl_2$ was similar to the structures observed for the N:P:K 4:14:8 and 10:10:10 samples. These observations suggest that the presence of calcium affects the thermal behavior of interfering molecules since the measurement of $CaCl_2$ alone did not present any absorbance signal. Therefore, the presence of calcium was required to reproduce the matrix and generate the correct reference spectrum. Thus, it is important not only to find the molecule responsible for the interferences, but it is also necessary to consider how the other components of the sample can affect the thermal behavior of this molecule and consequently, its absorption profile.

The other solutions studied (5% H_2SO_4 + 0.05% $CaCl_2$; 1% $NH_4H_2PO_4$ + 0.05% $CaCl_2$; 1% $NH_4H_2PO_4$ + 0.05% KCl; 5% H_2SO_4 + 0.05% KCl; 1% NaOH + 0.05% $CaCl_2$; 1% NaOH + 0.05% $SnCl_2$; 1% HNO_3 + 0.05% $SnCl_2$), generated spectra around 217.001 nm, but the profiles were different from those structures obtained for the samples. The spectra of these mixtures were not generated at 283.306 nm, because the interference at this analytical line has already been found.

Fig. 3a shows the spectrum generated, at 283.306 nm, from the mixture 5% H_2SO_4 + 0.05% $CaCl_2$, and Fig. 3b the spectrum generated from the mixture of 1% HNO_3 + 0.05% $CaCl_2$. When these solutions were

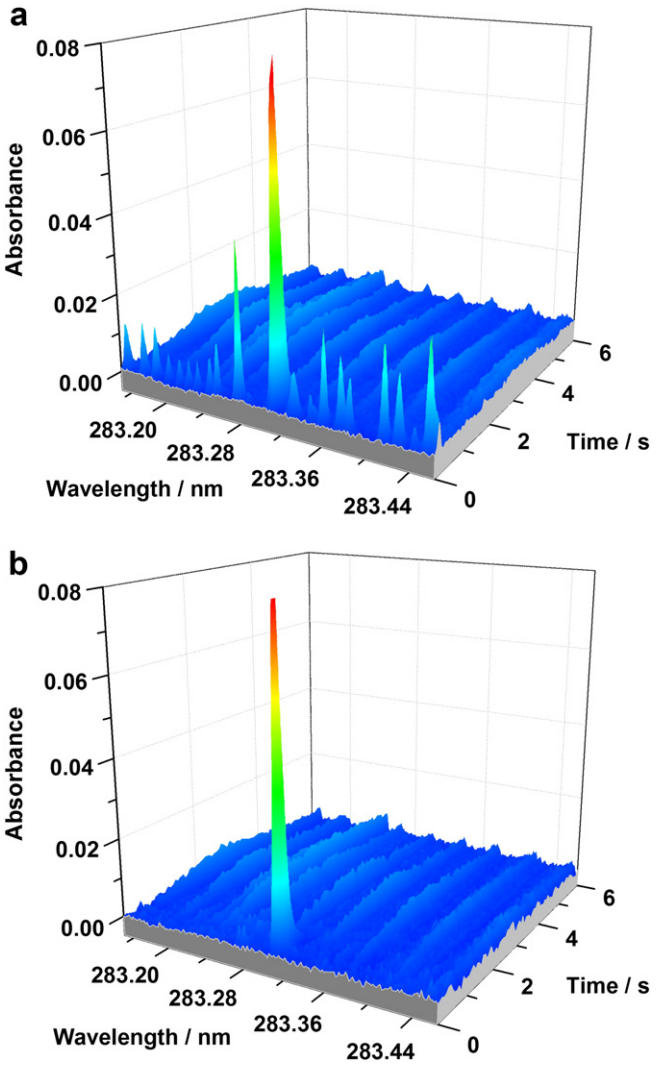

Fig. 4. Time-resolved absorbance spectra in the vicinity of the 283.306 nm analytical line recorded for the sample N:P:K 4:14:8 using 10 μg Pd + 6 μg Mg as modifier in solution: a) without correction; b) after correction with the mixture of 5% H_2SO_4 + 0.05% $CaCl_2$ and 1% HNO_3 + 0.05% $CaCl_2$. T_{pyr} = 900 °C; T_{at} = 2100 °C.

employed separately, i.e., H_2SO_4 + Ca or HNO_3 + Ca, the spectrum obtained after LSBC was not well corrected. However, when they were used together, it was possible to eliminate properly the spectral interference at the analytical line at 283.306 nm for the samples N:P:K 4:14:8 and 23.1% K_2O + 11.3% Mg + 22.5% S.

Fig. 4 shows the time-resolved absorbance spectra of lead without correction (Fig. 4a) and after correction by LSBC (Fig. 4b), using the mixture of 5% H_2SO_4 + 0.05% $CaCl_2$ and 1% HNO_3 + 0.05% $CaCl_2$ for the sample N:P:K 4:14:8 at 283.306 nm. It can be seen that the fine-structured background cannot be completely eliminated using LSBC. However, the background does not overlap the pixels used for the evaluation of the signal, CP ± 1, thus allowing the quantification of lead in this sample.

Fig. 5 shows spectra for the sample 23.1% K_2O + 11.3% Mg + 22.5% S without correction (Fig. 5a) and with correction (Fig. 5b) at 283.306 nm. The obtained spectrum, after applying the LSBC using the reference spectra generated by the mixture 5% H_2SO_4 + 0.05% $CaCl_2$ and 1% HNO_3 + 0.05% $CaCl_2$, is free of spectral interference. Figs. 4 and 5 indicate the possibility of using the same reference spectrum to eliminate spectral interferences in samples of different composition.

In order to identify any spectral interference which remained at 217.001 nm for N:P:K 10:10:10 and 4:14:8 samples, the reference spectrum obtained from the mixture of 1% HNO_3 + 0.05% $CaCl_2$ was

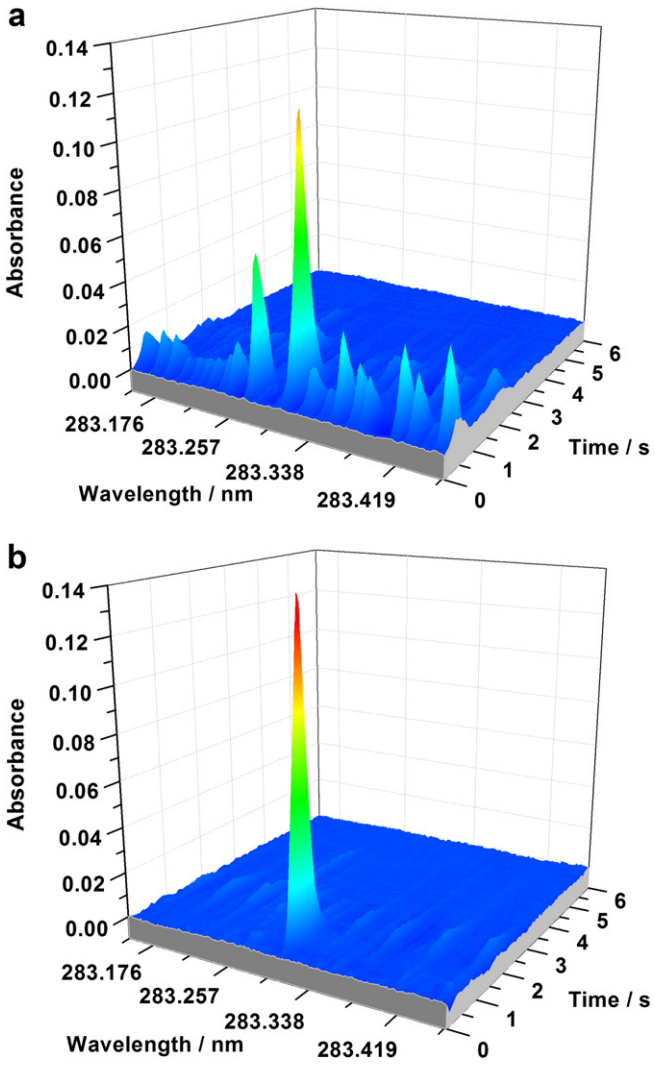

Fig. 5. Time-resolved absorbance spectra in the vicinity of the 283.306 nm analytical line recorded for the sample 23.1% K_2O + 11.3% Mg + 22.5% S using 10 μg Pd + 6 μg Mg as modifier in solution: a) without correction; b) after correction with the mixture of 5% H_2SO_4 + 0.05% $CaCl_2$ and 1% HNO_3 + 0.05% $CaCl_2$. T_{pyr} = 900 °C; T_{at} = 2100 °C.

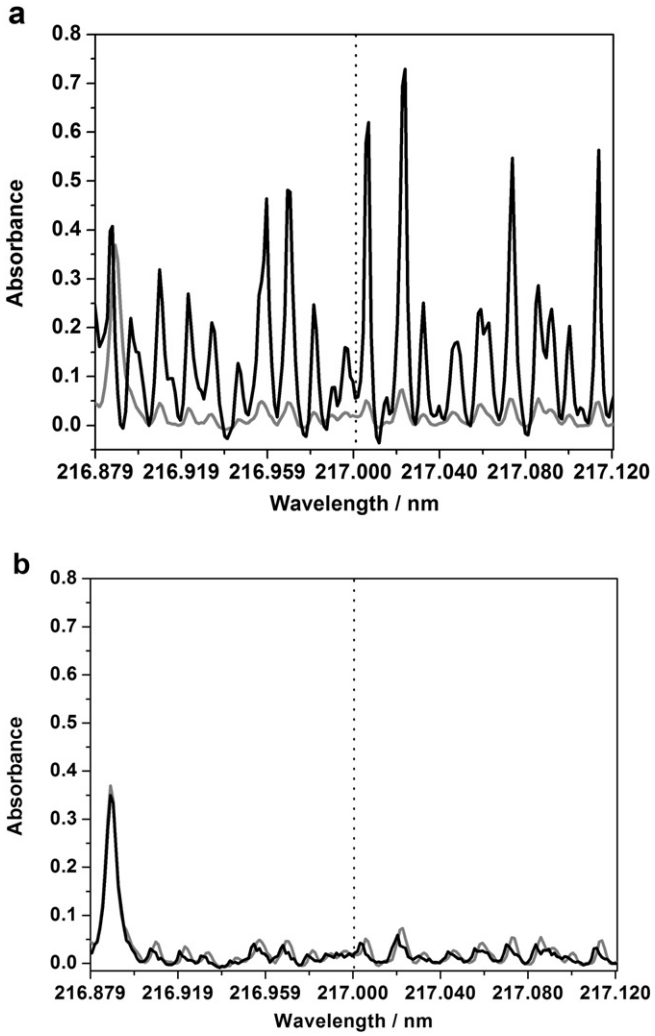

Fig. 6. Absorbance spectra in the vicinity of the 217.001 nm analytical line using 10 μg Pd + 6 μg Mg as modifier in solution; a) (gray line) fertilizer N:P:K 4:14:8 and (black line) mixture of 1% HNO_3 + 0.05% $CaCl_2$; b) (gray line) fertilizer N:P:K 4:14:8 and (black line) fertilizer N:P:K 4:14:8 after correction with a mixture of 1% HNO_3 + 0.05% $CaCl_2$. Dotted line indicates the analytical line position. T_{pyr} = 900 °C; T_{at} = 2100 °C.

subtracted from the spectra of these samples, since their spectra (sample and solution) showed similar structures (Table 2). The spectrum of the mixture 5% H_2SO_4 + 0.05% $CaCl_2$ is different from that found for the samples, consequently this mixture was not used to correct the spectral interference at this wavelength. Fig. 6a shows two spectra, the black line corresponds to the reference spectrum generated from the mixture of 1% HNO_3 + 0.05% $CaCl_2$ and the gray line corresponds to the spectrum from the sample N:P:K 4:14:8, previously corrected with PO. Fig. 6b shows the spectrum of the sample previously corrected with PO (gray line) and after the correction using the reference spectrum from Fig. 6a (black line). Analyzing the resulting spectrum after the application of LSBC, it is partially corrected, suggesting that in this case, even after two spectral corrections have been applied ($NH_4H_2PO_4$ and HNO_3 + $CaCl_2$), another unknown molecule still

Table 3
Figures of merit for the lead determination in fertilizer and limestone samples using 10 μg Pd + 6 μg Mg as modifier in solution. LOD and LOQ were calculated for 0.6 mg of sample; R = correlation coefficient.

Analytical line/ nm	Linear regression equation	R	LOD/ ng g^{-1}	LOQ/ ng g^{-1}	m_0/ pg
217.001	A_{int} = 0.0238 + 0.4247ng_{Pb}	0.9947	15	49	8
283.306	A_{int} = 0.0133 + 0.2011ng_{Pb}	0.9983	20	66	19

remains causing some spectral interference in the determination of lead in the N:P:K samples, at the 217.001 nm line.

Summarizing, using the analytical line at 217.001 nm, the N:P:K 4:14:8 and 10:10:10 samples could not be analyzed due to the presence of spectral interferences which were not completely eliminated even using LSBC; the unknown fine-structured background coincides in time and wavelength with the analytical signal of lead. At this analytical line, the sample 46% P_2O_5 + 15% Ca could be analyzed after subtracting the PO contribution. On the other hand, using the analytical line at 283.306 nm, the samples N:P:K 4:14:8 and 23.1% K_2O + 11.3% Mg + 22.5% S could be analyzed after eliminating the interference caused by S- and N-containing molecules. The sample N:P:K 10:10:10 could be analyzed without any interference at 283.306 nm and the measurements of limestone sample were completely free of interference at both analytical lines.

3.2. Analytical characteristics and figures of merit

After the elimination of spectral interferences from the investigated samples using LSBC, the figures of merit were established and are presented in Table 3. The linear range was from 0.03 to 1.0 ng at 217.001 nm and from 0.04 to 1.4 ng at 283.306 nm. The limits of detection (LOD) and quantification (LOQ) were calculated as three and ten times, respectively, the standard deviation of the blank solution divided by the slope of the calibration curve. They were calculated based on the injection of 30 μL of slurry, which corresponds to 0.6 mg of sample — the maximum sample mass introduced into the furnace.

Comparing the slopes of the calibration curves, as expected, the analytical line of 217.001 nm presented two times higher sensitivity when compared to the line at 283.306 nm; this behavior was reflected in the characteristic mass (m_0) values. However, the values of LOD and LOQ were only 25% lower using the 217.001 nm line and not 50%, as expected. This fact can be attributed to the higher standard deviation values obtained for the blank measurements at this line. Nevertheless, these values are comparable to those reported in literature [17].

The trueness of the results was evaluated using the certified reference material (CRM) NIST SRM 695, prepared as slurry. The concentration of lead in the reference material was 270 ± 9 and 264 ± 10 μg g^{-1} for the 217.001 and the 283.306 nm line, respectively. These results were in agreement with the certified value, 273 ± 17 μg g^{-1}. It is important to notice that the dilution factor (0.1% w/v) of the SRM NIST 695 slurry was much higher compared to that used for the samples (2% w/v), which was necessary due to the very high lead content in this CRM, as discussed in our previous work [1]. This procedure could explain the observed results that the CRM did not present any spectral interference at both analytical lines.

Table 4 presents the lead concentration in samples at both analytical lines for slurry sampling and digestion. Using slurry sampling, limestone, 23.1% K_2O + 11.3% Mg + 22.5% S and 46% P_2O_5 + 15% Ca samples could be analyzed using both analytical lines. Comparing these results, just for the 46% P_2O_5 + 15% Ca sample the concentration of lead was not in agreement using the *t-test* at 95% confidence level. The N:P:K samples could not be analyzed using the 217.001 nm line, as discussed above.

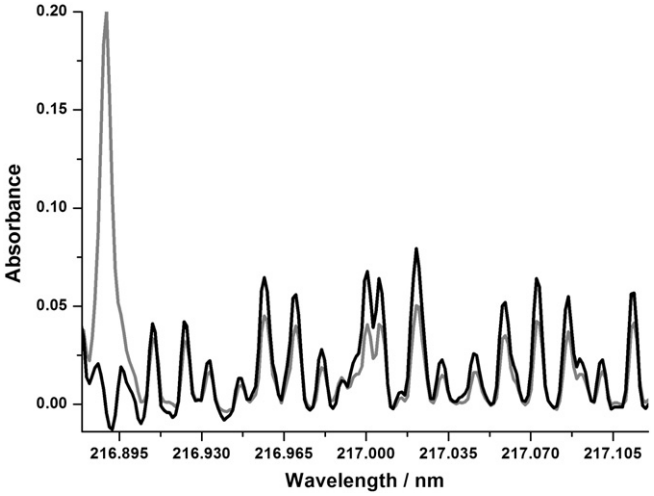

Fig. 7. Absorbance spectra of the sample 46% P_2O_5 + 15% Ca in the vicinity of the 217.001 nm analytical line using 10 μg Pd + 6 μg Mg as modifier in solution (gray line) digested and (black line) slurry. T_{pyr} = 900 °C; T_{at} = 2100 °C.

In order to verify whether a wet digestion procedure would avoid spectral interferences observed in direct analysis, an alternative procedure for sample preparation was employed; the procedure used was the Method 3050B from the United States Environmental Protection Agency [15]. Four samples with different compositions were investigated and the results are listed in Table 4. Fine structures similar to those observed in the slurries were also present in the digested samples at both analytical lines. This can be seen in Fig. 7 for the 46% P_2O_5 + 15% Ca sample at 217.001 nm and using an average of absorbance values for CP ± 1. Then, the same reference spectra employed for slurry samples were used to correct fine structures from digested samples. Regarding the lead content in the investigated samples, the results obtained with digestion procedure are similar to those found by slurry sampling.

The present results were compared with the results from a previous work [1], using LS GF AAS with Zeeman-effect background correction and slurry sampling, which are also shown in Table 4. For most investigated samples prepared as slurry, the concentration of lead obtained by HR-CS GF AAS at 283.306 nm was between 10% and 40% higher than the ones obtained by LS GF AAS, therefore, these results are not statistically in agreement for most of the samples. Taking into account the very small mass of sample used to prepare each aliquot of slurry and the low concentration of lead in the samples as well as the sample heterogeneity (Table 4), the results obtained in both techniques might be considered similar; this indicates that LS GF AAS with Zeeman-effect background correction corrects the background from samples to an acceptable extent.

Table 4
Lead content in fertilizer and limestone samples using slurry sampling and wet digestion (n = 3); all values are in μg g^{-1} Pb.

Samples	HR-CS GF AAS				LS GF AAS[a]
	Slurry		Digestion		Slurry
	217.001 nm	283.306 nm	217.001 nm	283.306 nm	283.3 nm
N:P:K 4:14:8	Interference	1.31 ± 0.05[b]	Interference	1.11 ± 0.10[b]	1.17 ± 0.03
Limestone	2.53 ± 0.04	2.76 ± 0.35	2.47 ± 0.21	2.49 ± 0.05	2.05 ± 0.23
N:P:K 10:10:10	Interference	1.44 ± 0.14	–	–	1.12 ± 0.04
23.1% K_2O + 11.3% Mg + 22.5% S	4.72 ± 0.44	5.11 ± 0.27[b]	4.56 ± 0.28	4.92 ± 0.17[b]	5.21 ± 0.26
46% P_2O_5 + 15% Ca	31.4 ± 0.9[c]	36.7 ± 1.3	26.0 ± 1.8[c]	33.5 ± 2.1	32.0 ± 0.4

[a] Borges et al. [7].
[b] Corrected by H_2SO_4 + $CaCl_2$ and HNO_3 + $CaCl_2$.
[c] Corrected by $NH_4H_2PO_4$.

4. Conclusions

Using HR-CS GF AAS, it was possible to detect the presence of spectral interferences in the determination of lead in fertilizer and limestone samples, using both analytical lines. At 283.306 nm, S and N containing molecules were responsible for the fine-structured background, which was completely corrected using LSBC. On the other hand, using the most sensitive line, at 217.001 nm, there are some unknown spectral interferences, which were not completely eliminated. Moreover, using HR-CS GF AAS it was possible to verify that the digestion of samples did not avoid the presence of spectral interferences, since digested samples presented fine-structured background similar to the samples prepared as slurry. Once the NIST SRM 695 material was diluted 20 times more than the samples, the matrix has been equally diluted and did not represent the investigated samples any more. Comparing HR-CS GF AAS and LS GF AAS with Zeeman-effect background correction, the results can be considered similar, indicating that the latter technique was able to correct the herein found spectral interferences to a reasonable extent.

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