

Investigation of phosphorus atomization using high-resolution continuum source electrothermal atomic absorption spectrometry

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Abstract

The atomization of phosphorus in electrothermal atomic absorption spectrometry has been investigated using a high-resolution continuum source atomic absorption spectrometer and atomization from a graphite platform as well as from a tantalum boat inserted in a graphite tube. A two-step atomization mechanism is proposed for phosphorus, where the first step is a thermal dissociation, resulting in a fast atomization signal early in the atomization stage, and the second step is a slow release of phosphorus atoms from the graphite tube surface following the adsorption of molecular phosphorus at active sites of the graphite surface. Depending on experimental conditions only one of the mechanisms or both might be active. In the absence of a modifier and with atomization from a graphite or tantalum platform the second mechanism appears to be dominant, whereas in the presence of sodium fluoride as a modifier both mechanisms are observed. Intercalation of phosphorus into the graphite platform in the condensed phase has also been observed; this phosphorus, however, appears to be permanently trapped in the structure of the graphite and does not contribute to the absorption signal.

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1. Introduction

In a recent article Lepri et al. [1], using high-resolution continuum source atomic absorption spectrometry (HR-CS AAS) [2], investigated the atomization of phosphorus in a graphite furnace at the 213.618 nm non-resonance line, which has been proposed by L'vov and Khartsyzov [3] back in 1969. Lepri et al. [1] discovered that without the use of a modifier very little atomic phosphorus is formed in a conventional transversely heated graphite tube atomizer, even at 2700 °C. The absorption measured with a hollow cathode lamp is mostly due to the PO molecule, which exhibits pronounced rotational fine structure in the vicinity of the phosphorus line at 213.618 nm. An absorption signal can be measured with conventional line source AAS (LS AAS) only because one of the molecular 'lines' is overlapping with the

emission profile of the radiation source. However, using HR-CS AAS kind of a tailing was observed that obviously was due to atomic phosphorus and that extended over several seconds in the atomization stage until it was interrupted by the purge gas flow in the cleaning stage. In our previous work [1] this observation has been explained with a penetration of phosphorus into the graphite structure, forming an intercalation compound and/or metallic carbide, such as P₂C₆ [4], from which it is released only very slowly in atomic form.

Due to the very low sensitivity that is obtained for phosphorus without a chemical modifier in conventional equipment, a variety of modifiers have been proposed in the literature, which have been reviewed in Ref. [1]. Among the most frequently used and best investigated modifiers for phosphorus are lanthanum [5], a mixture of palladium and calcium [6] and sodium fluoride [7]. Lepri et al. [1] found that lanthanum and sodium fluoride produced a mixture of atomic phosphorus and PO molecules, the ratio of which was strongly dependent on the atomization temperature. Only the palladium and calcium mixed modifier was

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capable of producing almost exclusively atomic phosphorus. A much sharper absorption signal for atomic phosphorus was obtained in the presence of all these modifiers and no significant tailing was observed. This was explained by a competition for intercalation between the modifier and phosphorus. At least for lanthanum [8] and palladium [9] this intercalation is well documented and could prevent the penetration of phosphorus into the graphite structure in the condensed phase.

The goal of the present work was to investigate in more detail this supposed penetration of phosphorus into the graphite structure as well as the tailing of the phosphorus atomic absorption signal in the absence of a modifier. Among other things atomization from a tantalum surface was investigated in order to exclude any contact between phosphorus and graphite in the condensed phase.

2. Experimental

2.1. Instrumentation

All measurements were carried out using a prototype high-resolution continuum source atomic absorption spectrometer, built at ISAS, Department Berlin. The prototype is based on a Model AAS 6 Vario (Analytik Jena AG, Jena, Germany), from which the entire optical compartment including detector and associated controls had been removed and replaced by a high-resolution double monochromator (DEMON), similar to the system described by Heitmann et al. [10]. The instrument, which utilizes a high-intensity xenon short-arc lamp as a continuum source, and a linear CCD array detector with 512 pixels, has been described in detail in previous publications [2,11,12]. At 213.617 nm, the analytical line for phosphorus used in this work, the spectral bandwidth per pixel was 1.9 pm. An intermediate slit width of about 400 μm was used, making possible the simultaneous evaluation of 200 pixels, corresponding to about ± 0.2 nm around the analytical wavelength.

One of the features of the software used in this equipment is the possibility to measure and store reference spectra, which may be subtracted from the spectrum measured for the actual sample, using a least-squares algorithm [1,2]. Using this procedure, specifically that part of the structured background will be eliminated that corresponds to the fine structure of the reference spectrum.

The original transversely heated graphite tube atomizer of the AAS 6 Vario (Analytik Jena) was used and sample and modifier solutions were introduced using an MPE 5 furnace autosampler (Analytik Jena). Argon with a purity of 99.996% (White Martins, São Paulo, Brazil) was used as the purge gas. Most of the experiments were carried out using pyrolytic graphite-coated graphite tubes with PIN platform (Analytik Jena, Part No. 407-A81.025); a pyrolytic graphite-coated graphite tube without platform (Analytik Jena, Part No. 407-A81.011) was used for the experiments with the tantalum platform. The tantalum platform was taken from a solid sampling accessory built in the 1970s ("Tantalum Boat", Part No. 114 430, Bodenseewerk Perkin Elmer, Überlingen, Germany). Integrated absorbance (peak area) was used exclusively for signal evaluation. The optimized graph-

ite furnace temperature program used for all measurements is given in Table 1.

2.2. Reagents and solutions

Water was purified in a Milli-Q system (Millipore, Bedford, MA, USA), resulting in water with a resistivity of 18 M Ω cm. A phosphorus standard solution containing 10.0 g L⁻¹ P was prepared by dissolving the appropriate amount of NH₄H₂PO₄, 99% m/m (Merck) in water. The solution was not acidified; the working standards were prepared by serial dilutions of the stock solution with water, depending on the specific application. Ten or 20 μL of solution were introduced into the graphite tube for measurement.

A 2.0 g L⁻¹ NaF modifier solution was prepared by dissolving sodium fluoride, 99% m/m (Riedel-de-Haen) in water; the solution was not acidified. A 10 μL volume of the modifier solution was introduced into the graphite tube, corresponding to a mass of 20 μg NaF in the graphite tube.

3. Results and discussion

3.1. Atomization from a graphite platform

It has been shown that in the absence of a modifier mostly PO is formed, even at an atomization temperature of 2700 °C, which exhibits pronounced rotational fine structure in the vicinity of the phosphorus non-resonance line at 213.618 nm. Phosphorus atomic absorption only appeared as kind of a tailing that extended over several seconds until it was interrupted by the cleaning stage [1]. This phenomenon is shown in Fig. 1 for 3 pixels, the center pixel (No. 250) at 213.618 nm and 1 pixel on each side (No. 248 and No. 252). It is obvious that the first sharp absorbance signal that appears at about 1.2 s (recording starts with Auto Zero, i.e., 1 s prior to the atomization stage) and returns to the baseline at 2 s is due to a molecular PO 'line' that has its maximum at pixel No. 248 and falls off rapidly towards higher wavelengths. The 'tail', in contrast, has its maximum at pixel 250 and falls off symmetrically to both sides, i.e. it is due to atomic phosphorus.

This observation has been explained with a penetration of phosphorus into the graphite structure in the condensed phase, forming an intercalation compound and/or metallic carbide, such as P₂C₆ [4], from which it is released only very slowly in

Table 1
Graphite furnace temperature program for phosphorus without modifier and with NaF as a modifier

Stage	Temperature / °C	Ramp / °C s ⁻¹	Hold time / s	Ar flow rate / L min ⁻¹
Drying 1	110	5	20	2.0
Drying 2	140	5	15	2.0
Pyrolysis	400 ^a 1000 ^b	100	15	2.0
Auto Zero	400 ^a 1000 ^b	0	1	0
Atomization	2700	3000	3	0
Cleaning	2700	0	3	2.0

^a Without modifier.

^b With NaF as chemical modifier.

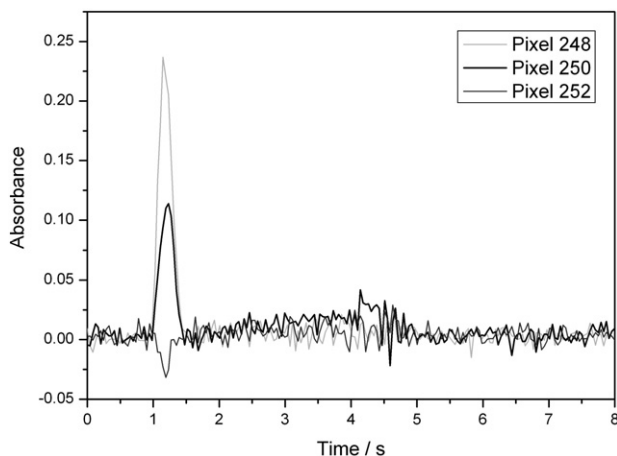


Fig. 1. Absorbance over time for 20 μg phosphorus without a modifier measured at 3 pixels in the vicinity of the phosphorus non-resonance line at 213.617 nm (Pixel 250); transversely heated graphite tube with graphite platform; atomization temperature 2700 $^{\circ}\text{C}$; recording starts with Auto Zero, i.e., 1 s prior to the atomization stage.

atomic form [1]. This theory has actually been supported by recent findings, where we deliberately began our experiments making a calibration curve with a virgin graphite tube (open symbols in Fig. 2). Starting with low masses of phosphorus (1.0–3.5 μg P), initially we got only very low absorbance signals until we reached 4 μg P, from where on we got ‘normal’ sensitivity, as is shown in Fig. 2. These two calibration curves with significantly different inclination led us to the assumption that the graphite platform has to be ‘saturated’ with a certain amount of phosphorus before the final sensitivity is obtained. As all measurements were carried out in duplicate, this means that a total of 24 μg P has been deposited on the platform before normal sensitivity has been obtained. Obviously, part of this phosphorus has been volatilized in molecular or atomic form, but a significant percentage has been retained on the platform. This theory was confirmed by repeating the same calibration

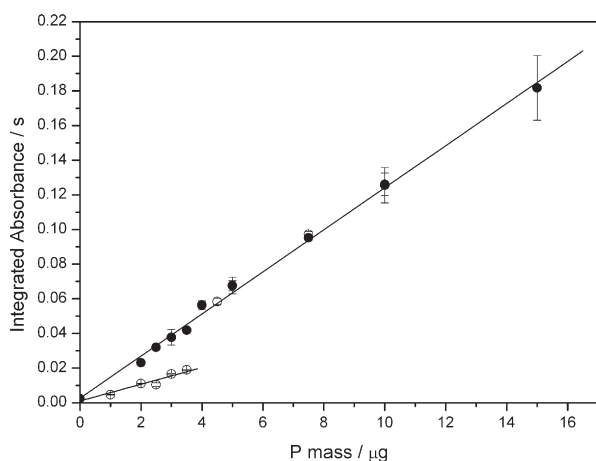


Fig. 2. Calibration curve for phosphorus without a modifier at 213.617 nm measured in a ‘virgin’ graphite tube with graphite platform, first going from low to high masses (open symbols) and then from high to low masses (full symbols); $\text{CP} \pm 1$; $n = 2$; atomization temperature 2700 $^{\circ}\text{C}$.

curve in the same tube (now saturated with phosphorus) going from high to low masses of phosphorus (full symbols). As can also be seen in Fig. 2, essentially identical absorbance values have been obtained between 15 μg P and 4 μg P, and the integrated absorbance values for lower masses of phosphorus were now on the same calibration curve, i.e., exhibited ‘normal’ sensitivity. From this experiment it appears as if a certain amount of phosphorus would penetrate into the graphite structure, being trapped there irreversibly, before ‘normal’ behavior of the atomizer could be expected. This experiment has been repeated several times with fresh tubes and it has been perfectly reproducible.

3.2. Atomization from a tantalum platform

In order to further investigate this penetration phenomenon we changed from the platform tube to a graphite tube without platform and inserted a boat-type platform made of tantalum foil. This boat holds at least 20 μL of solution and hence avoids any contact of the phosphorus solution with graphite prior to the atomization stage. The time- and wavelength-resolved absorbance spectrum for 4 μg of phosphorus obtained under these conditions is shown in Fig. 3. At a first glance, the result is quite surprising, as the overall appearance of this absorbance spectrum is not different from that obtained by atomization from a graphite platform, except for a significantly higher sensitivity obtained with the Ta boat. The main product of the ‘atomization’ was still the PO molecule and, most surprisingly, the ‘tail’ was still there and appeared to be even more pronounced than in the case of the graphite platform. This means that the slowly appearing phosphorus atomization signal cannot be due to a penetration of phosphorus into the graphite structure in the condensed phase and a subsequent slow release of phosphorus atoms from the bulk of graphite.

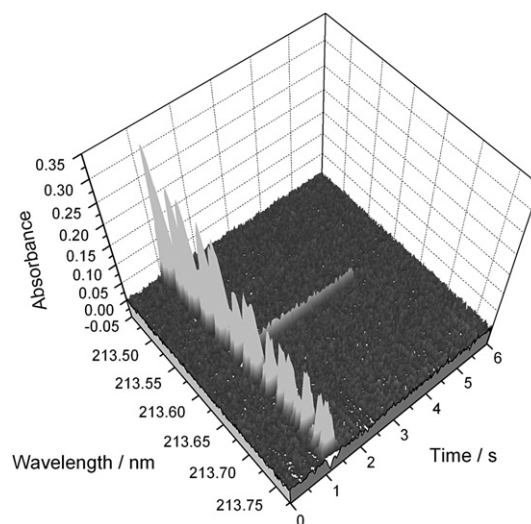


Fig. 3. Time and wavelength resolved absorbance spectrum for 4 μg phosphorus without a modifier using a tantalum platform in a transversely heated graphite tube, recorded in the vicinity of the phosphorus non-resonance line at 213.617 nm; atomization temperature 2700 $^{\circ}\text{C}$; recording starts with Auto Zero, i.e., 1 s prior to the atomization stage.

The obvious next step was to establish a calibration curve for phosphorus with atomization from the Ta boat under the same conditions that have been used for the graphite platform. The first and most important finding was that there was no ‘run-in-effect’, i.e., starting with low concentrations of phosphorus gave the full sensitivity from the very beginning. This means that no phosphorus was penetrating into the tantalum and/or the graphite substrate in the condensed phase, which was according to our expectations. The linear regression equations obtained for both surfaces without and with least-squares background correction (LSBC) are given in Table 2. A comparison of the data shows that the sensitivity obtained for the Ta boat after LSBC, i.e., for atomic phosphorus only is about a factor of 3.5 higher than that with the graphite platform. In addition, the contribution of molecular PO absorption to the uncorrected signal was only about 20% in case of the Ta boat compared to about 40% in the case of the graphite platform. All this confirms the more efficient atomization of phosphorus from a Ta surface.

However, for a quantitative comparison of the above data it has to be taken into consideration that the atomic phosphorus tail always has to be cut – in this case after 3 s of atomization under gas stop conditions – in order to avoid excessive consumption of graphite tubes. This means that the contribution of atomic phosphorus to the total absorbance measured depends on the atomization and integration time chosen for measurement. The absorbance signal in Fig. 4 clearly demonstrates this problem and there appears to be no easy solution. Fig. 4 shows the net phosphorus absorption at three pixels after subtraction of the PO absorption using LSBC. Firstly, this figure shows that there is essentially no atomic phosphorus signal hidden under the PO absorption spectrum of Fig. 3, and secondly it shows that there is practically no phosphorus atomic absorption at a distance of about ± 4 pm from the line center. The relatively high noise level results from the low absorbance values of only $A=0.05$, and also from the fact that these signals are obtained from the difference of two signals using LSBC, i.e., total absorbance (atomic plus structured molecular absorption after correction for continuous background) and the reference spectrum for PO.

3.3. Discussion

From the experiments described in Section 3.1 it is obvious that some phosphorus is intercalated into the graphite structure when the solution is introduced directly onto a graphite platform. This intercalation appears to be limited to a certain quantity of phosphorus, and no additional phosphorus is apparently penetrating into the graphite structure after ‘saturation’ has

Table 2

Linear regression equations and correlation coefficients for phosphorus atomization from a graphite platform and from a tantalum surface in a pyrolytic graphite coated tube without and with LSBC

Platform	LSBC	Linear regression equation	R
Graphite	No	$A=0.0101+0.0325 m$	0.9946
Graphite	Yes	$A=-0.0125+0.0203 m$	0.9964
Tantalum	No	$A=-0.0197+0.0860 m$	0.9959
Tantalum	Yes	$A=-0.0267+0.0688 m$	0.9917

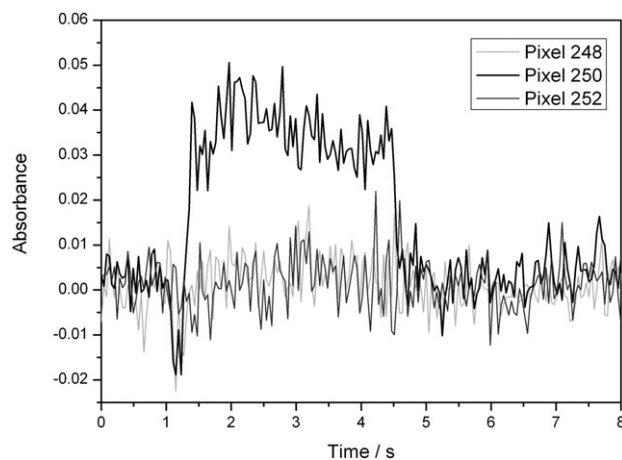


Fig. 4. Absorbance over time for 4 µg phosphorus without a modifier measured at 3 pixels in the vicinity of the phosphorus non-resonance line at 213.617 nm (Pixel 250); transversely heated graphite tube with tantalum platform; atomization temperature 2700 °C; the PO absorbance visible in Fig. 3 has been removed using LSBC; recording starts with Auto Zero, i.e., 1 s prior to the atomization stage.

been achieved, as is demonstrated by the calibration curve in Fig. 2. In addition, this quantity of phosphorus appears to be permanently trapped within the graphite structure, or there is kind of a dynamic exchange of phosphorus that keeps the total quantity trapped in the platform constant.

However, it is obvious from the experiments described in Section 3.2 that the ‘tail’, i.e., the atomic phosphorus cannot be due to phosphorus intercalated in the graphite structure. Hence, the only other plausible explanation is that it results from a gas phase reaction of phosphorus molecules, such as PO and/or P₂ with the graphite tube surface. This kind of ‘second-surface atomization’ or ‘inverse atomization’ has already been described in the literature for several elements, such as arsenic [13], aluminum, gallium, indium and thallium [14] and is most likely also valid for phosphorus. This means that molecular phosphorus, after it has been released into the gas phase, is

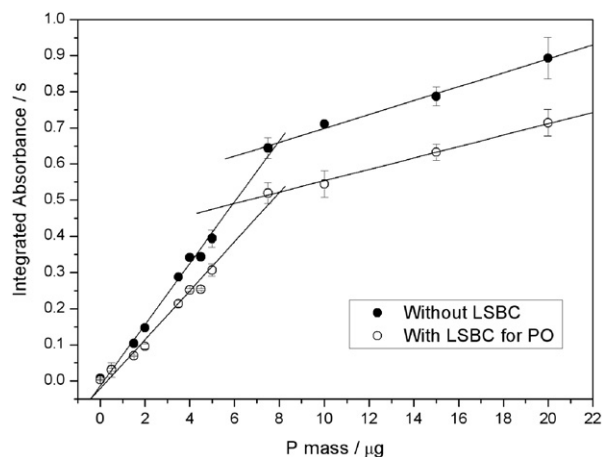


Fig. 5. Calibration curves for phosphorus without a modifier at 213.617 nm measured in a transversely heated graphite tube with a tantalum platform, without and with correction for the PO absorbance using LSBC; CP±1; n=2; atomization temperature 2700 °C.

adsorbed at the graphite tube surface, possibly forming a metallic carbide such as P_2C_6 , and from there it is released very slowly as atomic phosphorus, resulting in the ‘tail’.

The calibration curves for phosphorus atomized from the Ta platform shown in Fig. 5 are considered another proof of this theory. Although a quadratic equation could be applied, two linear relations with significantly different slopes appear to fit the experimental data much better, as indicated in Fig. 5. This fact supports the adsorption theory, as there are sites of significantly different reactivity available on the graphite surface. Once the most reactive sites (edge carbons) are occupied, less reactive sites have to be used, such as the zig–zag carbon [15], which perfectly explains the break in the calibration curve above a certain mass of phosphorus. This relatively sudden change in the slope of the calibration curve has been observed already in earlier, unpublished work, but no explanation could be given for this effect.

3.4. Atomization in the presence of a modifier

A relatively sharp phosphorus atomic absorption signal was obtained in the presence of lanthanum and palladium-based modifiers in earlier work [1] and no tailing could be observed. These experiments have not been repeated here. One reason for that observation is the high reactivity of both modifiers with graphite [8,9], i.e., active sites are preferentially covered by the modifier and not by the analyte; another reason is the relatively small amount of molecular phosphorus generated, particularly in the presence of palladium-based modifiers, i.e., palladium alone or mixed with calcium or ascorbic acid [1]. In contrast, some tailing was observed in the presence of sodium fluoride in this work, as is shown in Fig. 6, which could not be detected in earlier work [1]. This finding fits with the above theory, as neither sodium fluoride itself nor its thermal dissociation products generated in the atomization stage are likely to block the active sites of the graphite tube surface. In addition, sodium fluoride is

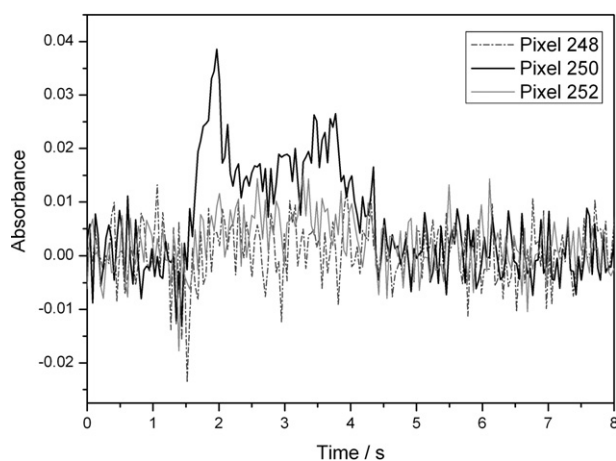


Fig. 6. Absorbance over time for 3 μg phosphorus with 20 μg sodium fluoride as a chemical modifier measured at 3 pixels in the vicinity of the phosphorus non-resonance line at 213.617 nm (Pixel 250); transversely heated graphite tube with graphite platform; atomization temperature 2700 $^{\circ}\text{C}$; the PO absorbance has been removed using LSBC; recording starts with Auto Zero, i.e., 1 s prior to the atomization stage.

the modifier producing the highest amount of PO that can be atomized later in part after adsorption at the tube wall. The ‘double peak’ shown in Fig. 6 clearly indicates two distinctly different atomization mechanisms. The first, rapid absorbance signal is obviously due to direct atomization of phosphorus by thermal dissociation, whereas the second, broad absorbance signal is due to the above-described atomization from the graphite tube wall. The reason for the high noise level is the same as discussed for Fig. 4. Very similar double peaks have also been observed for other elements, such as aluminum [14] and silicon [16] without the use of a modifier, and have been associated with two distinctly different atomization mechanisms.

4. Conclusion

Using HR-CS ET AAS, and particularly atomization from a refractory metal surface in addition to a conventional graphite platform, made it possible to get more insight into the mechanisms that are involved in the atomization of phosphorus. Particularly the possibility to ‘remove’ reliably the molecular absorption due to PO using LSBC is of fundamental importance. None of the background correction systems available for conventional LS AAS, including Zeeman-effect background correction, is capable of dealing with this kind of background, as the PO molecular absorption is affected by the magnetic field [2], resulting in erroneous correction.

A two-step atomization mechanism has been proposed for phosphorus, where the first step is a thermal dissociation, resulting in a fast atomization signal early in the atomization stage, and the second step is a slow release of phosphorus atoms from the graphite tube surface following the adsorption of molecular phosphorus at active sites of the graphite surface. Depending on experimental conditions only one of the mechanisms or both might be active. In the absence of a modifier and with atomization from a graphite or tantalum platform only the second mechanism appears to be active, whereas in the presence of lanthanum or palladium based modifiers – which have been investigated in earlier work [1] – the first mechanism is clearly dominant. Intercalation of phosphorus into the structure of the graphite platform has also been observed; this phosphorus, however, appears to be permanently trapped and does not contribute to the absorption signal.

It might be expected that HR-CS AAS could be an extremely useful tool to elucidate mechanistic details regarding atomization and interferences also for other analytes due to the visibility of the vicinity of the analytical line at high resolution and the unsurpassed background correction capabilities.

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References

- [1] F.G. Lepri, M.B. Dessuy, M.G.R. Vale, D.L.G. Borges, B. Welz, U. Heitmann, Investigation of chemical modifiers for phosphorus in a graphite furnace using high-resolution continuum source atomic absorption spectrometry, *Spectrochim. Acta Part B* 61 (2006) 934–944.
- [2] B. Welz, H. Becker-Ross, S. Florek, U. Heitmann, *High-Resolution Continuum Source AAS*, Wiley-VCH, Weinheim3-527-30736-2, 2005.
- [3] B.V. L'vov, A.D. Khartsyzov, Atomic absorption determination of phosphorus in a graphite cuvette, *Z. Prikl. Spektrosk.* 11 (1969) 9–12 (in Russian).
- [4] F. Benesovsky, 4th edn., *Ullmanns Encyklopädie der Technischen Chemie*, vol. 9, Verlag Chemie, Weinheim, 1975, p. 122.
- [5] R.D. Ediger, A.R. Knott, G.E. Peterson, R.D. Beaty, The determination of phosphorus by atomic absorption using the graphite furnace, *At. Absorpt. Newsl.* 17 (1978) 28–32.
- [6] A.J. Curtius, G. Schlemmer, B. Welz, Determination of phosphorus by graphite furnace atomic absorption spectrometry: Part 2. Comparison of different modifiers, *J. Anal. At. Spectrom.* 2 (1987) 115–124.
- [7] J. Alvarado, A.R. Cristiano, A.J. Curtius, Fluoride as a chemical modifier for the determination of phosphorus by electrothermal atomic absorption spectrometry, *J. Anal. At. Spectrom.* 10 (1995) 483–486.
- [8] B. Welz, A.J. Curtius, G. Schlemmer, H.M. Ortner, W. Birzer, Scanning electron microscopy studies on surfaces from electrothermal atomic absorption spectrometry: III. The lanthanum modifier and the determination of phosphorus, *Spectrochim. Acta Part B* 41 (1986) 1175–1201.
- [9] H.M. Ortner, E. Bulska, U. Rohr, G. Schlemmer, S. Weinbruch, B. Welz, Modifiers and coatings in graphite furnace atomic absorption spectrometry — mechanisms of action (a tutorial review), *Spectrochim. Acta Part B* 57 (2002) 1835–1853.
- [10] U. Heitmann, M. Schütz, H. Becker-Ross, S. Florek, Measurements of Zeeman-splitting of analytical lines by means of a continuum source graphite furnace atomic absorption spectrometer with a linear charge coupled device array, *Spectrochim. Acta Part B* 51 (1996) 1095–1105.
- [11] A.F. Silva, D.L.G. Borges, B. Welz, M.G.R. Vale, M.M. Silva, A. Klassen, U. Heitmann, Method development for the determination of thallium in coal using solid sampling graphite furnace atomic absorption spectrometry with continuum source, high-resolution monochromator and CCD array detector, *Spectrochim. Acta Part B* 59 (2004) 841–850.
- [12] M.G.R. Vale, I.C.F. Damin, A. Klassen, M.M. Silva, B. Welz, A.F. Silva, F.G. Lepri, D.L.G. Borges, U. Heitmann, Method development for the determination of nickel in petroleum using line source and high-resolution continuum source graphite furnace atomic absorption spectrometry, *Microchem. J.* 77 (2004) 131–140.
- [13] D.L. Styris, L.J. Prell, D.A. Redfield, Mechanisms of palladium-induced stabilization of arsenic in electrothermal atomization atomic absorption spectrometry, *Anal. Chem.* 63 (1991) 503–507.
- [14] A.Kh. Gilmudinov, Yu.A. Zakharov, V.P. Ivanov, A.V. Voloshin, Shadow spectral filming: A method of investigating electrothermal atomization, Part I. Dynamics of formation and structure of the absorption layer of thallium, indium, gallium and aluminium atoms, *J. Anal. At. Spectrom.* 6 (1991) 505–519.
- [15] J.C. Bokros, *Chemistry and Physics of Carbon*, vol. 9, Marcel Dekker, New York, 1972.
- [16] C.J. Rademeyer, I. Vermaak, Atomization mechanisms of silicon in a graphite furnace atomizer, *J. Anal. At. Spectrom.* 7 (1992) 347–351.