



# Determination of phosphorus using high-resolution diphosphorus molecular absorption spectra produced in the graphite furnace

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## ABSTRACT

Molecular absorption of diphosphorus was produced in a graphite furnace and evaluated in view of its suitability for phosphorus determination. Measurements were performed with two different high-resolution continuum source absorption spectrometers. The first system is a newly in-house developed simultaneous broad-range spectrograph, which was mainly used for recording overview absorption spectra of  $P_2$  between 193 nm and 245 nm. The region covers the main part of the  $C^1\Sigma_u^+ \leftarrow X^1\Sigma_g^+$  electronic transition and shows a complex structure with many vibrational bands, each consisting of a multitude of sharp rotational lines. With the help of molecular data available for  $P_2$ , an assignment of the vibrational bands was possible and the rotational structure could be compared with simulated spectra. The second system is a commercial sequential continuum source spectrometer, which was used for the basic analytical measurements. The  $P_2$  rotational line at 204.205 nm was selected and systematically evaluated with regard to phosphorus determination. The conditions for  $P_2$  generation were optimized and it was found that the combination of a ZrC modified graphite tube and borate as a chemical modifier were essential for a good production of  $P_2$ . Serious interferences were found in the case of nitrate and sulfuric acid, although the nitrate interference can be eliminated by a higher pyrolysis temperature. The reliability of the method was proved by analysis of certified samples. Using standard tubes, a characteristic mass of 10 ng and a limit of detection of 7 ng were found. The values could further be improved by a factor of ten using a miniaturized tube with an internal diameter of 2 mm. Compared to the conventional method based on the phosphorus absorption line at 213.618 nm, the advantages of using  $P_2$  are the gentle temperature conditions and the potential of performing a simultaneous multi-line evaluation to further improve the limit of detection.

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## 1. Introduction

Phosphorus plays an essential role in living systems by providing a stable backbone for RNA and DNA, and by regulating catalytic reactions of protein. The colorimetric method for phosphorus determination was introduced ninety years ago [1] and became the key to the discovery of both phosphocreatine and ATP [2]. Nowadays, most classic elemental analytical techniques are replaced by modern ones, such as atomic absorption, atomic emission and atomic mass spectrometry. However, the classic method for phosphorus determination is still widespread in use in analytical praxis. Responsible for this situation are the technical limitation and interference problems faced with the above-mentioned instrumental techniques for the phosphorus determination.

Attempts to determine phosphorus directly by its resonance atomic absorption lines at 177.5 nm, 178.3 nm and 178.8 nm have been made more than forty years ago [3,4]. The method did not obtain acceptance as a routine analytical application because of the difficulties to perform absorption measurements in the vacuum-UV spectral region. Up to

now, atomic absorption methods for phosphorus determination are solely based on the utilization of its non-resonance doublet line situated at 213.547/213.618 nm, which was suggested by L'vov and Khartysyov in 1969 [5]. Due to the non-resonance nature, the sensitivity is very low and the population of excited phosphorus atoms is favored by using higher atomization temperatures, which makes the method susceptible to the temperature control of the graphite furnace and the condition of the graphite tube.

Furthermore, phosphorus tends to form small molecular species in the graphite furnace, which may lead to a considerable pre-atomization loss. Persson and Frech [6] investigated the atomization process of phosphorus in a graphite tube. They found that the phosphorus-containing species PO,  $PO_2$ ,  $P_2$  and P are generated, whose distribution is strongly influenced by the tube temperatures. The main process for the preparation of atomic phosphorus is the decomposition of the  $P_2$  molecule, because this species is the major phosphorus compound in the temperature range between 1500 and 2500 K.

A critical case might be the pre-atomization loss via the PO molecule. Due to higher thermal stability (the bond strength of PO is  $599.1 \pm 12.6 \text{ kJ mol}^{-1}$ , compared to  $489.5 \pm 10.5 \text{ kJ mol}^{-1}$  of  $P_2$  [7]), the atomization of phosphorus via the decomposition of PO needs a much higher

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temperature than in the case of  $P_2$ . In Ref. [8] it is shown that in the air-acetylene flame only a few PO molecular absorption bands but no atomic P absorptions arise. The latter could only be observed in the nitrous oxide-acetylene flame, indicating that the atomization (or partial atomization) of phosphorus via PO requires the higher flame temperature. Due to the limitation of the graphite material the working temperature of the graphite tube can normally not exceed the temperature of a nitrous oxide-acetylene flame. Therefore, the PO species formed in the graphite tube cannot be utilized as a pre-species for P atomization; it gets lost directly in this form.

Havezov and Russeva [9] pointed out some prerequisites for the phosphorus atomization, including the one of controlling oxygen concentration to avoid its loss in the form of PO. In order to control this sort of pre-atomization losses, the usage of special graphite materials and a chemical modifier were investigated thoroughly by Welz et al. [10,11]. A recent investigation using high-resolution continuum source absorption spectrometry [12] has even further revealed that without the addition of a chemical modifier essentially no atomic phosphorus is formed. Absorption measured by line source atomic absorption spectrometry in this case is due to PO molecular absorption.

As discussed above, the formation of volatile and stable species was the major problem for the determination of phosphorus by atomic absorption spectrometry. However, this problem could be avoided, if phosphorus was not determined by its atomic absorption, but by directly measuring the molecular absorption of phosphorus-containing species.

The introduction of high-resolution continuum source absorption spectrometry (HR-CS AS) let this idea come true, because it allows a random and gap-free access to any wavelength of analytical interest and enables the measurement of molecular absorption. Furthermore, the high-resolution nature and the ability of effective and flexible background correction make the technique very reliable and accurate. HR-CS AS has been used for the determination of a series of non-metallic elements such as P, S, F, Cl, Br, I and  $NO_3^-$  by utilizing molecular absorption of suitable diatomic species [8,13–16]. Phosphorus was determined by measuring PO molecular absorption produced both in the air-acetylene flame [8] and in the graphite furnace [14]. However, in both cases the efficiency of PO formation may strongly depend on the sample matrix. For example, the PO absorption of  $200 \text{ mg L}^{-1}$  P in the flame can almost completely be suppressed in the presence of  $1000 \text{ mg L}^{-1}$  Ca [17].

With HR-CS AS equipment it is possible to measure molecular absorption of  $P_2$  in the graphite furnace. The matrix effect on the  $P_2$  spectrum is expected to be significantly less serious than in the case of PO. If there is a deteriorating effect at all, it should not be stronger than the effect on the phosphorus atomization, because in the temporal progress molecular  $P_2$  is the pre-species [6]. Therefore, it is worth investigating the optimum conditions for  $P_2$  generation and testing the potential of phosphorus determination via this molecule. The intentions were supported by a newly developed simultaneous spectrograph with multi-element capabilities [18], which enabled the recording of high-resolution overview absorption spectra of  $P_2$ . On this basis, a new and reliable method for the determination of phosphorus via  $P_2$  at moderate temperature conditions should be established.

## 2. Experimental

### 2.1. Instrumentation

Two continuum source spectrometer systems were used for the absorption measurements. The first one was used to record overview absorption spectra of  $P_2$ . The system is a coupling of a modular simultaneous echelle spectrograph (MOSES) and a commercial HR-CS AS instrument contrAA 700 (Analytik Jena AG, Jena, Germany). After passing the graphite furnace of the contrAA 700, the xenon light-beam was divided by a 50% polka-dot mirror and distributed to both the MOSES and the contrAA 700 spectrometer. In this way, the absorption signal

could be synchronously recorded with different optical arrangements and detectors.

Detailed information about the in-house development MOSES can be found in a recent publication by the authors [18]. Briefly, this system features a large spectral coverage from 190 nm to 390 nm by utilizing four adjustable spectral segments (tiles). Simultaneous detection of each tile is achieved by using a CCD-array camera (ANDOR DU940P,  $2048 \times 512$  pixels, Andor Technology Ltd., Belfast, UK). The high spectral resolution, which is comparable to the commercial contrAA series, combined with the relatively high CCD frame rate makes the system particularly suitable for the investigation of complex molecular absorption spectra produced in the graphite furnace.

The second spectrometer is a sequential system, model contrAA 600 (Analytik Jena AG, Jena, Germany) with a transversely heated graphite furnace, which was used for  $P_2$  absorption measurements using  $P_2$  lines around 204.205 nm. The instrument is equipped with a 300 W xenon short-arc lamp operating in a hot-spot mode as a continuum source for wavelengths from 190 nm to 900 nm, a high-resolution double monochromator, consisting of a prism pre-monochromator and an echelle grating monochromator equipped with a linear CCD-array, providing a spectral bandwidth per pixel of about 1.3 pm at 204.205 nm, corresponding to a spectral resolution  $\lambda/\Delta\lambda = 50,000$  (3-pixel-criterion). Pyrolytically coated standard graphite tubes with Pin-platform (Analytik Jena, Part no. 407-A81.025) as well as miniaturized graphite tubes with 2 mm internal diameter (Schunk Graphite Technology, Heuchelheim, Germany) and a tailored autosampler for this graphite tube (specially manufactured by Analytik Jena AG, Jena, Germany) were used throughout [26]. The autosampler is able to provide an accurate dosage for small sample volumes down to 30 nL.

### 2.2. Standards, reagents and samples

Phosphorus standard solution ( $10,000 \text{ mg L}^{-1}$ ) was bought from Johnson Matthey (Karlsruhe, Germany). All other reagents used were bought from Merck (Darmstadt, Germany). The inorganic acids used, i.e., nitric (65%), hydrochloric (37%), sulfuric (98%) and phosphoric (85%) acids, were all of "pro analysi" quality. Zirconium ethanol solution made of zirconium oxide chloride octahydrate (Merck, Darmstadt) was used for modifying the standard and the miniaturized graphite tubes. Borate solution made of sodium tetra-borate (Merck) was used as a chemical modifier. Argon for spectrometry (99.998% vol.) was supplied by Air Liquid (Berlin, Germany).

The standard reference materials 1575 (pine needles) and 1570a (trace elements in spinach leaves) were provided by the National Institute of Standards and Technology (Gaithersburg, USA). Sero201405 and Sero203105 (trace elements in serum level 1 and level 2) were provided by SERO AS (1396 Billingstad, Norway).

### 2.3. Sample preparation and analysis

About 0.5 g of each sample (pine needles and spinach leaves) was weighed into a 50 mL beaker and decomposed using 3 mL  $HNO_3$  and 5 mL  $H_2O_2$  by gently heating on a plate. The digested samples were made up to 50 mL with water. A 1  $\mu\text{L}$  sample together with a 0.4  $\mu\text{L}$  modifier (sodium tetra-borate solution containing  $1000 \text{ mg L}^{-1}$  B) was pipetted into the mini-tube.

Peak volume selected absorbance (PVSA), i.e., time-integrated absorbance summated over five pixels has been used for signal evaluation. The calibration was performed using standard addition method with aqueous standard.  $P_2$  molecular absorption around 204.205 nm was used for the determination of phosphorus. The corresponding spectral bandwidth per pixel was 1.3 pm. In order to further improve the limits of detection, 10  $P_2$  absorption lines between 204.103 nm and 204.329 nm were simultaneously used for signal evaluation; the detailed wavelengths are given below. The optimized temperature program used for all measurements is given in Table 1. Prior to the

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