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Determination of phosphorus by sample combustion followed by non-suppressed ion chromatography

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Abstract

The determination of phosphorus using sample combustion in oxygen followed by quantification of orthophosphate using non-suppressed ion chromatography (IC) was studied using phenylphosphonic acid as a model sample compound. Even under optimal conditions, the recovery of phosphorus (measured as orthophosphate) was <70% when dilute aqueous hydrogen peroxide was used as the absorbing solution employed to collect the combustion products. However, use of inductively coupled plasma atomic emission spectroscopy and spectrophotometry using heteropoly blue formation showed that all of the phosphorus in the original sample was in fact also present in the absorbing solution, but suggested that some of this phosphorus was present as forms other than orthophosphate. ³¹P Nuclear magnetic resonance was used to study the composition of the combustion solution and confirmed the presence of orthophosphate, pyrophosphate and trimetaphosphate. Hydrolysis of the combustion sample solution by boiling for at least 20 min at pH < 3 was shown to convert all of these forms of phosphorus to orthophosphate, thereby enabling their determination by IC. Quantitative recoveries of phosphorus were achieved when this post-combustion hydrolysis step was incorporated into the analytical procedure.

1. Introduction

Combustion by the oxygen flask technique has been used extensively for the determination of species such as halogens, sulfur, nitrogen and phosphorus. In this technique, the sample is combusted in oxygen and the desired species are released from the sample matrix in the form of oxides which are then absorbed in an appropriate absorbing solution. This procedure has greatly simplified the sample treatment required for the analysis of phosphorus in organophosphorus compounds, and the combustion solution thus produced contains phosphates in their inor-

ganic form. A number of analytical techniques for the analysis of inorganic phosphates have been reported. These methods include both gravimetric and titrimetric analyses [1,2], electrochemical methods such as polarography [3], and other instrumental methods such as atomic absorption spectrometry [4], UV spectrophotometry [5], inductively coupled plasma atomic emission spectroscopy (ICP-AES) [6], ³¹P nuclear magnetic resonance (NMR) [7] and ion chromatography (IC) [8,9].

Gravimetric and titrimetric methods are often unsuitable for ultramicro analysis due to losses during sample manipulation, and these methods are subject to interferences from other elements produced during combustion. UV spectropho-

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tometry involving reaction of oxidised phosphates with a molybdate reagent, Mo(V)–Mo(VI), with subsequent formation of a phosphomolybdate complex (commonly known as heteropolyblue) is used widely. This technique is relatively free from interferences but requires a lengthy sample preparation time and takes at least 1 h for the reaction to be complete [10]. ^{31}P NMR may be employed in the analysis of phosphates [7] and has the advantage of specificity of defined chemical shifts of phosphorus nuclei. Its limitations, however, include inherent low sensitivity, which necessitates the use of a large amount of sample, and the complexity of spectra for polyphosphates higher than tripolyphosphate [11]. ICP-AES provides the total phosphorus content without structural information but has the advantage of detection of numerous other elements in a simultaneous determination. IC is used routinely for the determination of orthophosphate in the presence of other anions by both the suppressed and non-suppressed approaches. When orthophosphate is present together with the other lower oxides of P such as phosphite (H_3PO_2^-) and hypophosphite (H_2PO_2^-) speciation may be achieved using conductivity detection in suppressed IC [12].

Anomalous chromatographic behaviour of pyrophosphate in classical ion-exchange chromatography was observed by Fukuda et al. [13] who found that hydrolysis of pyrophosphate occurred during the chromatographic run causing the appearance of an orthophosphate peak in the elution chromatogram. They attributed this observation to the action of multivalent metals which promoted the hydrolysis of pyrophosphate at pH values above 4. Addition of ethylenediaminetetraacetic acid (EDTA) secured the normal chromatographic behaviour of pyrophosphate by masking the heavy metals present in the solution. Nakamura et al. [14] applied the same approach in the separation of linear oligophosphates.

The problem of low recovery of phosphorus (as orthophosphate) following the combustion of an organophosphorus compound has been encountered by several workers. Binkowski and Rutkowski [15] attributed this difficulty to the

use of platinum wire as the sample holder because this wire absorbed too much heat and therefore the combustion temperature was insufficient to cause complete combustion of the organic compound. For a high combustion temperature to be attained, they used a very thin fused-silica hook and in so doing obtained quantitative recoveries for phosphorus by titrating the absorbed orthophosphate with standard lanthanum solution. Busman et al. [16] encountered the same difficulty in suppressed IC and associated the problem with the formation during combustion of either some polyphosphates that were not detectable by IC or some insoluble metal phosphates. Senior [17,18] also suggested the formation of some polyphosphates, such as pyrophosphate and cyclic metaphosphate, but did not report the methods employed.

The chemical instability of polyphosphates is well known, and under appropriate conditions all P–O–P linkages in a structure can be ruptured [19]. The ultimate products of hydrolysis are discrete orthophosphate ions, although the route and rate of hydrolysis are characteristic of the particular polyphosphate anion and of the conditions employed. The principal factors influencing the rate of hydrolysis of a polyphosphate solution are the number of corners shared by the PO_4 tetrahedra in the structure, the temperature, the pH and the concentration of the polyphosphates. The hydrolysis rate is accelerated by either raising or lowering the pH from neutral and by increasing the temperature. The hydrolysis rate may also be influenced to some degree by the type of cations present. Watanabe et al. [20] demonstrated the effect of cations on the rate of hydrolysis of pyro- and tripolyphosphates. They found that alkali metal, alkaline earth metal, aluminium and some transition metals such as Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) cations retard the hydrolysis of the phosphates in acidic media. Pyrophosphates are almost completely stable in alkaline or neutral solutions at normal temperatures. They are hydrolysed under acid conditions although over the whole pH range they are the most stable of the polyphosphates.

In this paper we examine in detail the nature

of the combustion products formed when an organophosphorus test compound, phenylphosphonic acid, is combusted in oxygen. The aim of this work was to develop a sample treatment procedure which would permit the reliable determination of phosphorus in organophosphorus compounds by non-suppressed IC.

2. Experimental

2.1. Combustion apparatus and procedure

The oxygen combustion flask used throughout the work is shown in Fig. 1 and consisted of a modified 500-ml Erlenmeyer flask, fitted with inlet and outlet tubes. Inserted into this tube and held in place by elastic bands affixed to glass hooks was a glass stopper assembly, through which were passed two platinum wires. These wires were supported mechanically by a PTFE disc inside the stopper and by encasing them in glass extensions attached to the underside of the stopper. One of the platinum wires was coiled to form a sample basket. The two platinum wires were then joined with a short length of nichrome wire using stainless-steel connectors. The above design gave sufficient rigidity to the electrode assembly to enable the flask to be swirled during operation without risk of breakage.

Phenylphosphonic acid, $C_6H_5P(O)(OH)_2$ (Aldrich, Milwaukee, WI, USA) was used as the

model phosphorus-containing compound. The purity of this reagent was determined by microanalysis. The required amount of the sample was weighed in an ashless filter paper (Whatman No. 41) and folded in such a way to provide a paper protrusion which served as a wick. Absorbing solution (usually 10 ml) was added to the flask. The sample was positioned in the sample holder which was then placed inside the flask, sealed with silicone grease and held securely by two elastic bands wrapped around the hooks provided. After passing a suitable amount of oxygen (CIG, Grade 020) into the flask, the oxygen inlet and outlet were both closed simultaneously. Ignition of the sample was initiated inside the flask using an electrical igniter connected to a variable-voltage regulator. After the combustion of the sample was complete, the flask was shaken to allow rapid absorption of gaseous products. The solution was allowed to stand for a few minutes, after which it was transferred quantitatively to a 25-ml volumetric flask and diluted to the mark with distilled water. After each combustion, the sample holder was removed from the flask and heated on a Bunsen burner to eliminate any uncombusted residues.

2.2. Analysis of combustion solutions

IC was performed using a Waters (Milford, MA, USA) Model 510 pump, U6K injector and Model 430 conductivity detector interfaced to an Omniscrite (Houston, TX, USA) Model 5000 dual-pen strip-chart recorder. The chromatographic column was a Waters IC-PAK A anion column, 50×4.6 mm I.D., packed with polymethacrylate-based resin of $10 \mu\text{m}$ particle size and an exchange capacity of $30 \mu\text{equiv./g}$. A stock gluconate–borate eluent solution was prepared by mixing 12.5 g of sodium tetraborate decahydrate, 9.0 g of boric acid and 8.0 g of sodium D-gluconate in 1 l of Milli-Q (Millipore, Bedford, MA, USA) water. A 20-ml aliquot of this stock solution was mixed with 120 ml of acetonitrile and 10 ml of 25% glycerol and diluted to 1 l with Milli-Q water. The resulting eluent was then filtered through a $0.45\text{-}\mu\text{m}$ filter and degassed in an ultrasonic bath prior to use.

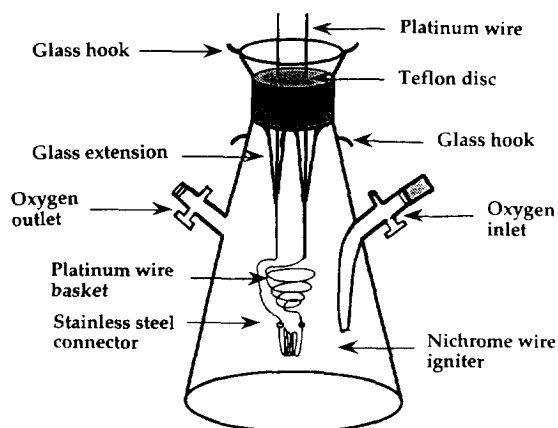


Fig. 1. Construction of the oxygen combustion flask.

Analysis by ICP-AES was performed using a Plasmalab instrument manufactured by Labtam International (Melbourne, Australia), which employed a 27.12-MHz plasma operating at a power of 1.4 kW. Spectrophotometric determinations of phosphorus as orthophosphate were performed using the procedure of Yoza and Ohashi [10] by reacting the sample solution with a mixture of 1 ml of 1 M sodium hydrogensulphite solution and 2 ml of the Mo(V)–Mo(VI) reagent for 1 h at 98–100°C.

^{31}P NMR spectra were acquired on a Bruker AC300P spectrometer with a multinuclear probe tuned to 121.49 MHz for ^{31}P . Free induction decays were routinely acquired with a spectral width of 12 kHz (100 ppm), $\sim 45^\circ$ pulse width (10 μs), using 8K data points and a relaxation delay of 2 s. Chemical shifts, δ_{p} , were reported with respect to 85% H_3PO_4 ($\delta_{\text{p}} = 0$ ppm) as an external reference. Positive shifts were downfield to higher frequency. No ^1H decoupling was used. Between 400 and 1600 scans were collected for each sample and spectra were acquired at 300 K.

3. Results and discussion

3.1. Optimisation of the combustion–absorption process

Using the chromatographic conditions described in the experimental section, non-suppressed IC was used to determine the recovery of phosphorus (as orthophosphate) from combusted phenylphosphonic acid. The effects on recovery of varying the composition and volume of the absorbing solution, the time and conditions used for absorption of the combustion gases, and the sample size were studied. Changes to the volume of the absorbing solution and the conditions used for absorption produced only minor alterations in recovery and it is worth noting that the water produced as a by-product of combustion plays an important role in the absorption of the combustion gases. A number of different absorbing solutions were examined, including water, dilute hydrogen peroxide and gluconate–borate eluent. The results obtained

showed that solutions containing hydrogen peroxide at or above a concentration of 0.15% (v/v) gave the best results. Some problems were encountered with the use of the gluconate–borate eluent as the absorbing solution in that a nitrate peak was produced, presumably from oxidation of the acetonitrile which forms part of this eluent. It should also be noted that all chromatograms showed a large carbonate peak resulting from absorption of the carbon dioxide produced in the combustion and a chloride peak resulting from the residual chloride in the filter paper used to contain the sample. A dilute solution of hydrogen peroxide (0.15%, v/v) was selected as the optimal absorbing solution and was used to study the effect of sample size on recovery (Fig. 2a). It can be seen that recovery decreased steadily as the sample size increased.

In all of the above experiments, the recovery fell in the range 40–70%. The precision of combustion, as determined by eight successive replicates performed under uniform conditions and with careful attention to the performance of the flask, was found to be 6.56% R.S.D. These analytical performance values are unsatisfactory and suggested that the combustion process and/

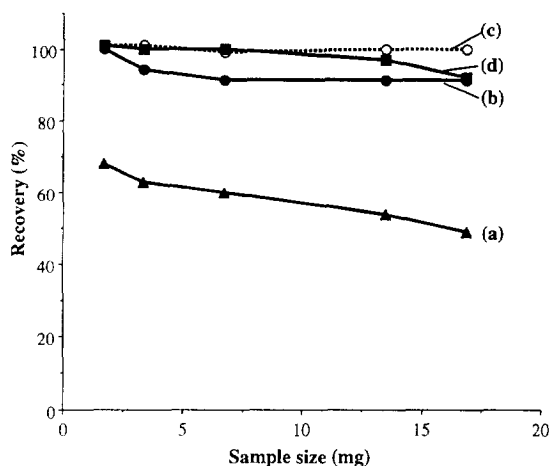


Fig. 2. Recovery of phosphorus from combusted samples of phenylphosphonic acid under optimal combustion conditions (see text) and with 0.15% (v/v) H_2O_2 as absorbing solution, as determined using (a) IC without post-combustion hydrolysis, (b) ICPAES, (c) spectrophotometry and (d) ion chromatography with post-combustion hydrolysis.

or the absorption process was incomplete and variable, or that the chromatographic analysis method used was not measuring all of the phosphorus species present in the absorbing solution.

3.2. Analysis of combustion solutions by ICP-AES and spectrophotometry

The second of the above possibilities was examined using ICP-AES to determine the recovery values under the same combustion conditions used for the IC determinations. These results, plotted in Fig. 2b, show that recovery was >90% for all sample sizes, despite the fact that the IC results showed decreasing recoveries.

ICP-AES provides a measure of total phosphorus and does not give information about the identity of the species present. One method which has been frequently used in the identification of polyphosphates is the formation of the heteropolyblue complex followed by UV spectrophotometric determination. Yoza and Ohashi [10] used this method to investigate the oxidation products of thirteen P-acids and showed that the absorption spectrum of the heteropolyblue reaction product could be used to indicate the type of phosphate species that had reacted.

Application of the derivatization procedure of Yoza and Ohashi (summarized under Experimental) gave the results shown in Fig. 2c. It can be seen that quantitative recoveries of phosphorus were obtained. Moreover, the visible spectrum of the heteropolyblue product gave only a single maximum at 810 nm, which suggested only the presence of the heteropolyblue complex of orthophosphate. Such a complex can be produced from reaction of those phosphate species that contain either a single P atom or multiple P atoms that are not adjacent to each other. Phosphate species of this type which can be expected to show resistance to hydrolysis include hypophosphite, phosphite, orthophosphate and trimetaphosphate (Fig. 3). A further phosphate species that was not included in the study of Yoza and Ohashi [10] and which was possibly formed during combustion is pyrophosphate (Fig. 3). The reaction of pyrophosphate with Mo(V)–Mo(VI) was investigated by treat-

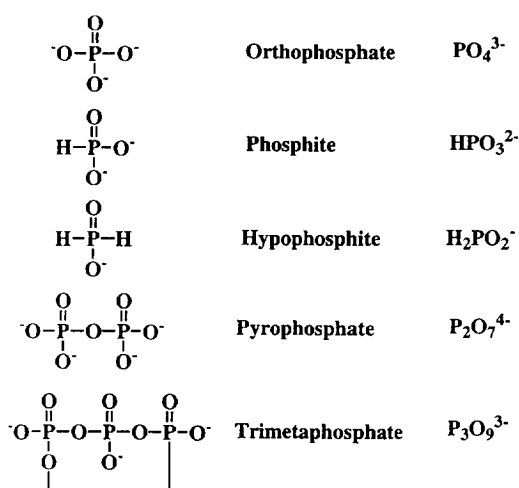


Fig. 3. Structures of inorganic phosphates likely to be present in the combustion solution.

ing a standard solution of this species according to the procedure described in the Experimental section. The product of this reaction exhibited an absorption spectrum with a single λ_{max} at 810 nm which again indicated the sole formation of orthophosphate in the heteropolyblue complex.

3.3. Identification of combustion products by IC and NMR

The results obtained above suggested that the phosphate species likely to be present in the solution would include hypophosphite, phosphite, orthophosphate and pyrophosphate. The formation of the first two of these species was indicated in the early work of Belcher and MacDonald [21] and Gedansky et al. [22]. Non-suppressed IC using a tartrate eluent at pH 3.2 has been used previously to separate orthophosphate, hypophosphite and phosphite, all of which were weakly retained on a strong-base anion-exchange material [23]. However, we have found it necessary to raise the eluent pH to a value in excess of $\text{p}K_{\text{a}2}$ for tartaric acid (4.91) in order to eliminate interference from system peaks produced by the presence of undissociated tartaric acid [24–26]. At a pH of approximately 5, there should be no non-ionised tartaric acid present. Using an eluent comprising 2 mM

sodium tartrate at pH 4.98, hypophosphite could be resolved from orthophosphate, but no peaks attributable to phosphite or pyrophosphate could be identified, perhaps due to hydrolysis of these species at the eluent pH used. These chromatographic conditions were then employed to analyse the combustion products from phenylphosphonic acid, absorbed in aqueous hydrogen peroxide. No peak for hypophosphite was detected.

^{31}P NMR has been used to identify different forms of phosphorus in mixtures of inorganic phosphates [27,28]. Gard et al. [29] employed this method in the simultaneous determination of lower oxo acids of phosphates including orthophosphate, pyrophosphate, trimetaphosphate and tripolyphosphate in a commercial tripolyphosphate sample. In their work, samples were maintained at pH near 9 in order to optimise the signal separation. Yoza et al. [30] showed the effect of pH changes on chemical shifts for a series of eleven inorganic phosphates. ^{31}P Chemical shifts of the phosphates in the combustion

solution were obtained at pH 8.56 and the chemical shifts were reported relative to the signal of 85% orthophosphoric acid as an external reference. A small amount of EDTA was used, the purpose of which was to sequester any trace of multiply charged metal ions that may be present in solution.

The ^{31}P NMR spectrum of the combustion solution is shown in Fig. 4. The peak identities, assigned using published chemical shift data [29,30], were a singlet at $\delta_{\text{p}} = 3.2$ ppm due to orthophosphate and a singlet at $\delta_{\text{p}} = -6.9$ ppm due to pyrophosphate. The absence of a doublet at $\delta_{\text{p}} = 5.5$ ppm ruled out the presence of tripolyphosphate in the solution, but the presence of a small peak at $\delta_{\text{p}} = -20.74$ ppm suggested the presence of trimetaphosphate. The formation of a cyclic metaphosphate during combustion of an organophosphorus compound was mentioned in the early work of Cohen and Chezch [31] and more recently by Senior [17]. However, no positive identification of the type of cyclic metaphosphate has been given. The sole product

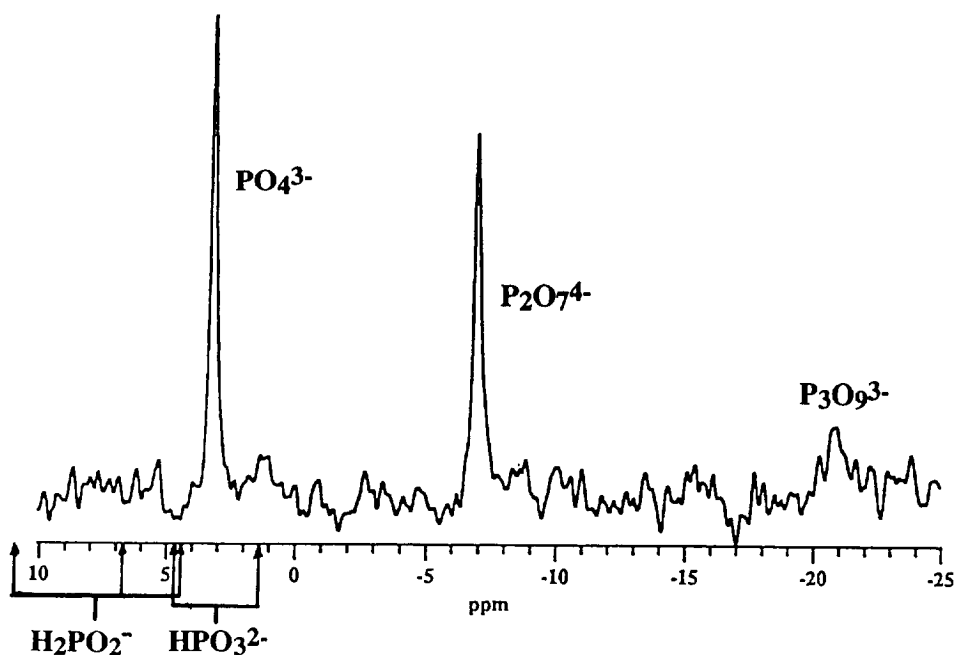


Fig. 4. ^{31}P NMR spectrum of a combustion solution obtained from phenylphosphonic acid. The chemical shifts for hypophosphite (triplet) and phosphite (doublet) are indicated.

of the reaction of trimetaphosphate with Mo(V)–Mo(VI) can be expected to be the orthophosphate heteropolyblue complex. The spectrophotometric results described earlier are therefore consistent with the presence of trimetaphosphate in the combustion solution.

The influence of pH on the chemical shifts of phosphate species was studied and downfield shifts were observed on going from acidic to alkaline pH, in accordance with similar findings in the literature [32]. The third weak peak, which was present in all solutions analysed and which was assigned as trimetaphosphate, also shifted downfield at alkaline pH. This change in chemical shift toward the deshielded portion of the spectrum with increasing pH has been attributed to a decreasing degree of protonation of the phosphate tetrahedra as the solution becomes alkaline [33].

3.4. Post-combustion hydrolysis

Having identified the higher phosphates present in the combustion solution, a post-combustion reaction which would convert these species to orthophosphate was sought in order to simplify the use of the combustion–IC analysis approach. Methods published for the hydrolysis of phosphates usually require the use of a high concentration of acid, such as sulfuric, hydrochloric, nitric or perchloric acid, because polyphosphates are rather stable under alkaline conditions but are more easily hydrolysed in an acidic medium. The use of these acids, however, must be avoided where possible in IC due to the probable interference of large amounts of the acid anion in the detection of orthophosphate. This is, of course, aside from the fact that the very low pH of the hydrolysis solution is not suitable for use with chromatographic columns having limited tolerance to low pH values. While this limitation can be overcome by neutralising the solution to an appropriate pH this is not recommended since interferences and contamination are easily introduced by further sample manipulation. Based on the above-mentioned limitations, the best alternative was to use an oxidising agent which will not introduce any

anion in the determination. In this case H_2O_2 was again the best choice. Since it was essential that the reaction take place at a low pH, tartaric acid was used and attention was focussed on the hydrolysis of pyrophosphate because it was present at much higher concentrations than trimetaphosphate in the combustion solutions.

The optimal conditions for hydrolysis of pyrophosphate were determined by performing the hydrolysis using a range of concentrations of H_2O_2 at varying pH, and by adjusting the boiling time. Best results were obtained using 0.6% (w/v) H_2O_2 at pH < 3 (using tartaric acid for pH adjustment) and boiling for at least 20 min. The presence of alkali metal cations in the solution should be avoided since these are known to retard the hydrolysis of pyrophosphate [34]. Fig. 2d shows the phosphorus recovery (as orthophosphate) obtained when this hydrolysis procedure was applied to a series of combustion solutions prepared using varying weights of phenylphosphonic acid as sample. Quantitative recovery was obtained for sample sizes less than 10 mg.

3.5. Analysis of a vegetation sample

The developed method was applied to the analysis of a vegetation sample. Two combustions of 0.06 g each were performed using water as the absorbing solution. The solution from the first combustion was injected directly onto the ion chromatograph after filtration, while into the second ten drops of 30% H_2O_2 were added. The introduction of tartaric acid was not necessary because the pH was measured to be 2.75 which was sufficiently acidic to allow the hydrolysis to take place. Hydrolysis was performed by boiling the solution for 45 min to ensure complete conversion of pyrophosphate to orthophosphate.

The chromatograms produced by the two combustion solutions are shown in Fig. 5. Important features of the chromatogram for the unhydrolysed sample (Fig. 5a) are a large peak for nitrite and a very small peak for orthophosphate. After hydrolysis (Fig. 5b), increased peak areas for nitrate, orthophosphate and sulfate are evident as a result of hydrolysis of

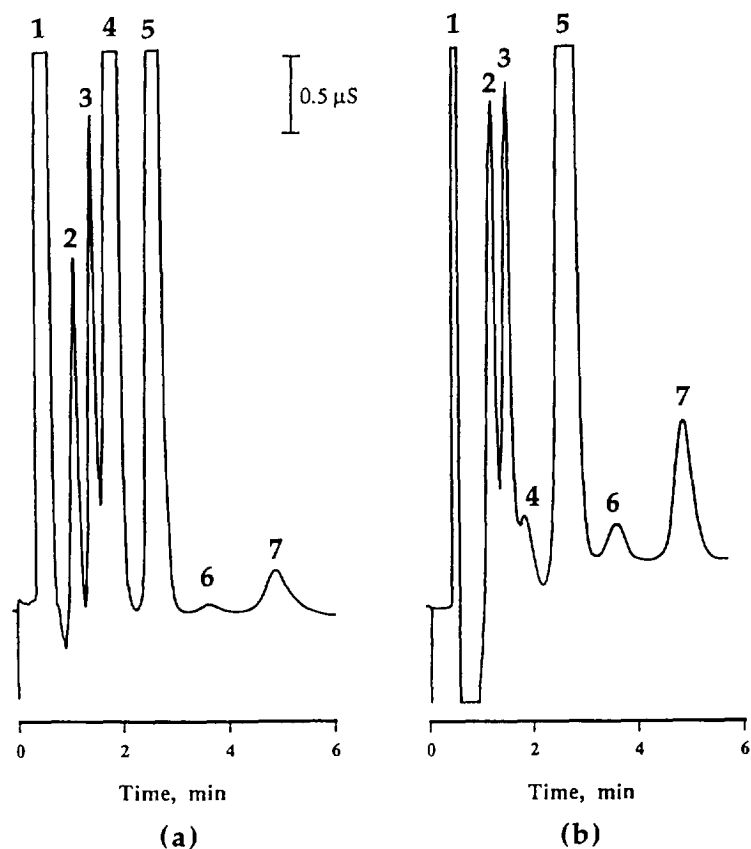


Fig. 5. Chromatograms of the combustion solution obtained from a vegetation sample (a) before hydrolysis and (b) after hydrolysis by boiling for 45 min. A gluconate–borate eluent was used with an IC-PAK A anion-exchange column. Peaks: 1 = injection peak; 2 = HCO_3^- ; 3 = Cl^- ; 4 = NO_2^- ; 5 = NO_3^- ; 6 = HPO_4^{2-} ; 7 = SO_4^{2-} .

polyphosphates and the oxidation of nitrite and sulfite to nitrate and sulfate, respectively.

4. Conclusions

It has been shown that more than one phosphorus species is produced upon combustion of an organophosphorus compound. The presence (as well as the confirmed absence) of several P species was demonstrated by IC in combination with ICP-AES, spectrophotometry and ^{31}P NMR measurements performed on combustion samples. The latter technique identified the phosphates as orthophosphate, pyrophosphate and trimetaphosphate. Post-combustion hydrolysis using tartaric acid and H_2O_2 converted the

pyrophosphate and trimetaphosphate to orthophosphate. Application of the hydrolysis method to a combusted vegetation sample illustrated the utility of the technique.

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References

- [1] G.F. Anisimova and V.A. Kilmova, *Zh. Anal. Khim.*, 37 (1982) 1100.

- [2] R.L. Grob and M.E.P. McNally, *Anal. Lett. A*, 13 (1980) 219.
- [3] S.W. Rishara and F.M. El-Samman, *Microchem. J.*, 27 (1982) 44.
- [4] F.J. Langmyr and I.M. Dahl, *Anal. Chim. Acta*, 131 (1981) 303.
- [5] W.A. Dick and M.A. Tabaitabai, *Agron. J.*, 74 (1982) 59.
- [6] M. Siroki, G. Vujicic, V. Milun, Z. Hudovsky and L. Marie, *Anal. Chim. Acta*, 192 (1987) 175.
- [7] T.W. Gurley and W.M. Ritchey, *Anal. Chem.*, 47 (1975) 1444.
- [8] A. Quinn, K.W.M. Sui, G.J. Gardner and S.S. Berman, *J. Chromatogr.*, 370 (1986) 203.
- [9] J.F. Colaroutolo, *Anal. Chem.*, 49 (1977) 884.
- [10] N. Yoza and S. Ohashi, *Chem. Soc. Jpn.*, 37 (1964) 37.
- [11] D.R. Gard, J.C. Burquin and J.K. Gard, *Anal. Chem.*, 64 (1992) 557.
- [12] T. Tanaka, K. Hiroyo, A. Kawahara and S. Wakida, *Bunseki Kagaku*, 32 (1983) 771.
- [13] F. Fukuda, T. Nakamura and S. Ohashi, *J. Chromatogr.*, 128 (1976) 212.
- [14] T. Nakamura, T. Yano, A. Fujita and S. Ohashi, *J. Chromatogr.*, 130 (1977) 384.
- [15] J. Binkowski and P. Rutkowski, *Mikrochim. Acta (Wien)*, 1 (1986) 245.
- [16] L.M. Busman, R.P. Dick and M.A. Tabatabai, *Soil Sci. Soc. Am. J.*, 47 (1983) 1167.
- [17] J.P. Senior, *Anal. Proc.*, 27 (1990) 116.
- [18] J. Senior, in P.A. Anthony, M.J. Hudson (Editors), *Proc. Int. Conf. Ion Exchange Processes*, 2 (1990) 17.
- [19] N.W. Alcock and K.A. Raspin, *J. Chem. Soc. A*, (1968) 2108.
- [20] M. Watanabe, M. Matsuura and T. Yamada, *Bull. Chem. Soc. Jpn.*, 54 (1981) 738.
- [21] R. Belcher and A.M.G. Macdonald, *Talanta*, 1 (1958) 408.
- [22] S.J. Gedansky, J.E. Bowen and O.I. Milner, *Anal. Chem.*, 32 (1960) 1447.
- [23] *Waters IC Lab.*, Report No. 354.
- [24] P.E. Jackson and P.R. Haddad, *J. Chromatogr.*, 346 (1985) 125.
- [25] P.E. Jackson and P.R. Haddad, *J. Chromatogr.*, 355 (1986) 87.
- [26] P.R. Haddad and P.E. Jackson, *Ion Chromatography: Principles and Applications*, Elsevier, Amsterdam, 1990, p. 124.
- [27] S.A. Sojka and R.A. Wolfe, *Anal. Chem.*, 50 (1978) 585.
- [28] D.A. Stanislawski and J.R. Van Wazer, *Anal. Chem.*, 52 (1980) 96.
- [29] J.K. Gard, D.R. Gard and C.F. Callis, *Am. Chem. Soc. Symp. Series*, 486 (1992) 41.
- [30] N. Yoza, N. Ueda and S. Nakashima, *Fresenius J. Anal. Chem.*, 348 (1994) 633.
- [31] L.E. Cohen and F.W. Chezech., *Chem. Anal.*, 47 (1958) 86.
- [32] I.B. Rubin, *Anal. Lett.*, 17 (1984) 1259.
- [33] R.K. Osterheld, in E.J. Griffith and M. Grayson (eds), *Topics in Phosphorus Chemistry*, Vol. 7, Interscience, New York, 1972, p. 103.
- [34] P.S. Belton, K.J. Packer and T.E. Southon, *J. Sci. Food Agric.*, 40 (1987) 283.