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Short Communication

Simultaneous microdetermination of chlorine, bromine and phosphorus in organic compounds by ion chromatography

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ABSTRACT

A procedure for the simultaneous microdetermination of chlorine, bromine and phosphorus in organic compounds is described. It consists of ion chromatographic analysis, after suitable dilution, of the solution resulting from the collection in water containing hydrogen peroxide of the combustion products obtained by decomposition of the sample in a Schöniger flask. Before analysis, this solution undergoes a post-combustion procedure involving further hydrolysis of the combustion products which allows a nearly quantitative recovery of phosphorus to be achieved even in the presence of other heteroatoms such as chlorine and bromine. This post-combustion step avoids negative errors in the microdetermination of phosphorus by ion chromatography owing to the minor but not insignificant amounts of both pyrophosphate and a cyclic metaphosphate which are formed together with the predominant orthophosphate in the conventional Schöniger combustion of organophosphorus compounds. The accuracy and precision of the overall procedure were evaluated.

INTRODUCTION

A great deal of work conducted over many years has produced a number of procedures for the accurate determination of the chlorine, bromine and phosphorus contents of organic compounds. These procedures usually involve converting the organically bound heteroatoms into the corresponding chloride, bromide and phosphate ions by a suitable sample decomposition procedure and then determination of the amounts of these ions by volumetric or gravimetric procedures [1].

Because the ions mentioned can be readily detected by ion chromatography, the application of this instrumental technique to microanalysis appears to be particularly advantageous. Indeed, ion chromatography is an attractive alternative to classical volumetric or gravimetric procedures as it is a selective technique able both to provide the simultaneous determination of a series of heteroatoms by using the same instrumentation, procedure and sample, and to remove many known interferents that usually affect their de-

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termination. In addition, the chromatographic portion of the analysis can be readily automated and requires no extensive operator training. A further significant advantage of this approach over the traditional chemical methods is a decrease in the time required for analysis.

Several papers suggesting ion chromatographic determination following Schöniger combustion of heteroatoms (F, Cl, Br, P, S) frequently present in organic compounds have been published [2–10]. However, when this type of procedure is applied to the determination of phosphorus present in organic molecules together with other heteroatoms, problems are often encountered that arise from the complexity of phosphorus chemistry. In fact, speciation of combustion products obtained using a conventional hydrogen peroxide absorption solution (3–4% w/w) suggests the formation of at least three oxyanions of phosphorus. The desired product (orthophosphate) is formed predominantly, but significant amounts of pyrophosphate and a cyclic metaphosphate are also detected [10]. This is not a real problem when phosphorus determination is subsequently performed by volumetric or gravimetric procedures, as the equilibria between these species shift towards the orthophosphate form thanks to its sequestration occurring in the quantitative reaction involved. In contrast, the formation of the mentioned less oxygenated species leads to negative errors when the phosphorus determination is performed by an ion chromatographic separation of the combustion products which does not perturb substantially the slow, spontaneous solution equilibria, so that the phosphorus content turns out to refer only to the recorded orthophosphates. Consequently, the problem of avoiding the formation of the undesired oxyanions of phosphorus was practically ignored as no real alternative to volumetric or gravimetric determination methods was available. Such a problem is also the probable reason why the ion chromatographic determination of phosphorus following Schöniger combustion has been considered, to our knowledge, only in two [2,10] of the several papers reporting the application of this procedure to elemental microanalysis. In particular, only in the most recent of these papers [10] was the minimization of the relevant error tackled.

To overcome this drawback, we propose here a post-combustion procedure involving further hydrolysis of the combustion products which allows a nearly quantitative recovery of phosphorus to be achieved even in the presence of other heteroatoms. This procedure was evaluated in detail for the routine ion chromatographic microdetermination of chlorine, bromine and phosphorus in organic compounds following the Schöniger combustion procedure. This evaluation also included the determination of the accuracy and precision of the method.

EXPERIMENTAL

Chemicals

All the chemicals used were of analytical-reagent grade and were used as received. In all instances, water purified with a Millipore Milli-Q system ("Milli-Q water") was used as the solvent.

Stock standard solutions of chloride, bromide and phosphate ions ($1 \cdot 10^{-3}$ *M*) were prepared by dissolving suitable amounts of the corresponding salts (NaCl, NaBr and NaH_2PO_4, respectively) in Milli-Q water. They were standardized by titration using the conventional Volhard method for chlorides and bromides and by titration with NaOH after precipitation as quinoline–phosphomolybdate for phosphates [11]. These solutions were then diluted to the desired concentration with Milli-Q water containing 1.8 m*M* Na_2CO_3 and 1.7 m*M* $NaHCO_3$ and in which the absence of Cl^-, Br^- and phosphates at concentrations higher than 10^{-7} *M* was first checked by ion chromatography.

Procedure

The procedure adopted for organic compounds involves the decomposition of known amounts of pure organic samples (2–10 mg) in a 500-ml Schöniger flask by collecting the combustion products in 10 ml of Milli-Q water containing 0.8 ml of 30% (w/w) H_2O_2. The samples were weighed, wrapped in a piece of Schleicher and Schüll No. 589-2 paper and then placed in the platinum basket. Oxygen was blown into the flask and the samples were burned in the usual way. Following combustion, the solutions obtained were boiled gently for 10 min while their

TABLE I

ION CHROMATOGRAPHIC CONDITIONS ADOPTED

Column	5-cm Dionex AG4 guard column plus 25-cm Dionex AS-4A separation column
Mobile phase	0.0018 M Na_2CO_3 + 0.0017 M $NaHCO_3$ in Milli-Q water
Flow-rate	2 ml min^{-1}
Temperature	Ambient
Detection	Suppressed conductivity at 30 μS using 0.0125 M H_2SO_4 as regenerant
Injection volume	50 μl

initial volume was continuously restored by adding small drops of Milli-Q water as required.

This boiling step was added to the usual procedure with the aim of facilitating the hydrolysis reactions and allowing the conversion of the less oxygenated oxyanions of phosphorus to the desired ortophosphate product.

The solutions thus obtained were transferred into volumetric flasks where they were diluted with a solution of 1.8 mM Na_2CO_3 and 1.7 mM $NaHCO_3$ in milli-Q water, *i.e.*, the mobile phase adopted in the subsequent ion chromatographic analysis (see later). By this dilution step, solutions containing the analyte elements in the concentration range $5 \cdot 10^{-5}$–$3 \cdot 10^{-4}$ M were obtained.

Ion chromatography was carried out by injecting a 50-μl sample of these solutions into a Dionex Model 2000i chromatograph equipped with a Dionex AS-4A anion-exchange column at room temperature. All determinations were performed by using a Dionex AMMS-1 micro-membrane suppressor continuously regenerated with 0.0125 M H_2SO_4 and a conductance detector. The chromatographic conditions adopted are reported in Table I.

Calibration

A preliminary calibration of the instrumental responses was performed by using standard solutions of NaCl, NaBr and NaH_2PO_4. Table II gives the retention times, detection limits calculated for a signal-to-noise ratio of 3 and the dynamic ranges explored. In fact, linearity extends over a much wider range but it was intentionally limited to take into account the amount of organic sample usually applied in the Schöniger combustion step. All peak areas found were characterized by good reproducibility, the relative standard deviation being 1.3%.

RESULTS

The reliability of the proposed procedure, aimed at making nearly quantitative the hydrolysis of the combustion products obtained from phosphorus-containing organic compounds, was first tested by application to the analysis of different organic samples each containing only a single heteroatom. Such a test was designed to check not only if the extended boiling step was really advantageous for phosphorus but also

TABLE II

RESULTS OBTAINED IN THE CALIBRATION OF INSTRUMENTAL RESPONSES

Analyte	Retention time (min)[a]	Detection limit (M)	Dynamic range explored (M)
Cl^-	1.86 (±0.02)	$1.05 \cdot 10^{-7}$	$5 \cdot 10^{-6}$–$5 \cdot 10^{-4}$
Br^-	3.65 (±0.05)	$1.45 \cdot 10^{-7}$	$5 \cdot 10^{-6}$–$5 \cdot 10^{-4}$
HPO_4^{2-}	6.61 (±0.06)	$1.51 \cdot 10^{-7}$	$5 \cdot 10^{-6}$–$5 \cdot 10^{-4}$

[a] Standard deviations ($n = 5$) in parentheses.

whether it is able to interfere in the determination of other heteroatoms.

The results obtained in these preliminary tests are reported in Table III, where each value found was calculated as the average of five replicate measurements. The good agreement between the experimental and theoretical values indicates that the proposed modification of the conventional procedure leads to satisfactory results for phosphorus without affecting the results relating to other heteroatoms.

Subsequently, to evaluate the accuracy and precision attainable by the suggested procedure, multiple analyses were performed on high-purity, crystalline samples of known composition. For this purpose, suitably dosed mixtures of chemically stable and non-hygroscopic organic compounds, each containing a single heteroatom, were employed. This was because the use of commercially available organic compounds containing simultaneously chlorine, bromine and phosphorus is not advisable because they are almost always characterized by poor stability and purity.

A typical chromatogram obtained after combustion of these samples is reported in Fig. 1. Peaks 1, 3 and 5 relate to chlorides, bromides and phosphates, respectively, *i.e.*, the ions corresponding to the analyte heteroatoms. Peaks 2, 4 and 6 relate to nitrites, nitrates and sulphates, respectively, which are contaminants generated in the combustion step. In fact, as demonstrated by comparison with blanks of sample wrapper and absorption solution, which were analysed in the same way as the organic sample, nitrites and nitrates arise from combustion of atmospheric nitrogen whereas the combustion of the sample wrapper leads both to sulphates and to a rather small and reproducible chloride response, which was subtracted from the peak area due to chlorides from the samples (the same correction was also made to the chloride determinations summarized in Table III). In contrast, no peak due to the carbonate generated from the carbonaceous portion of the organic sample plus the sample wrapper was observed. This is because the concentration of carbonate coming from the

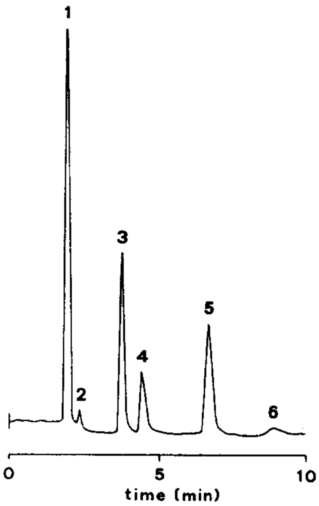

Fig. 1. Typical chromatogram obtained for organic samples containing simultaneously chlorine, bromine and phosphorus. Peaks: 1 = chloride; 2 = nitrite; 3 = bromide; 4 = nitrate; 5 = phosphate; 6 = sulphate.

TABLE III

COMPARISON BETWEEN EXPERIMENTAL AND THEORETICAL RESULTS FOR ORGANIC COMPOUNDS CONTAINING A SINGLE HETERO ATOM

Sample[a]	Chlorine (%)		Bromine (%)		Phosphorus (%)	
	Theoretical	Found[b]	Theoretical	Found[b]	Theoretical	Found[b]
PCBA	22.65	23.05 (0.36)	–	–	–	–
PBBA	–	–	39.75	39.92 (0.24)	–	–
TPP	–	–	–	–	11.81	11.72 (0.27)

[a] PCBA = *p*-Chlorobenzoic acid; PBBA = *p*-bromobenzoic acid; TPP = triphenylphosphine.
[b] Standard deviations ($n = 5$) in parentheses.

sample combustion does not exceed, under our experimental conditions, that present in the eluent, owing to the dilution of the combusted sample with the eluent which precedes the injection step. In fact, by simple calculations, such an additional concentration could be estimated to be typically *ca.* 20% of the background carbonate eluent.

Typical results obtained for the analysis of some of the mentioned sample mixtures, utilizing the peak areas for the various elements, are summarized in Table IV, which reports both accuracy and precision. Precision is expressed as the standard deviation calculated for five measurements relative to independent combustions of the same sample. These results appear to be satisfactory in that both their accuracy and precision compare fairly well with those expected by the classical methods.

CONCLUSIONS

The suggested procedure for the simultaneous microdetermination of chlorine, bromine and phosphorus in organic compounds is characterized by satisfactory accuracy. A maximum absolute difference with respect to the corresponding theoretical values of ±0.45% is observed, so that a relative error within 5% can in general be estimated. Good precision is also obtained, the relative standard deviation generally being within 4%. This performance is also comparable to (or only slightly worse than) that provided by gravimetric or volumetric methods for the same elements. However, the short analysis time and simplicity of the ion chromatographic analysis more than compensate for the slight difference.

The major advantages of this type of analysis are the selectivity, which eliminates possible

TABLE IV

COMPARISON BETWEEN EXPERIMENTAL AND THEORETICAL RESULTS FOR MULTIPLE HETEROATOM ORGANIC SAMPLES

Sample[a]	Chlorine (%)		Bromine (%)		Phosphorus (%)	
	Theoretical	Found[b]	Theoretical	Found[b]	Theoretical	Found[b]
2.892 mg PCBA 2.131 mg PBBA 4.327 mg TPP	7.00	7.39 (0.45)	9.06	9.15 (0.47)	4.86	4.78 (0.09)
1.991 mg PCBA 4.063 mg PBBA 3.851 mg TPP	4.55	4.80 (0.35)	16.30	16.48 (0.10)	4.63	4.60 (0.14)
4.099 mg PCBA 2.822 mg PBBA 2.813 mg TPP	9.54	9.46 (0.37)	11.52	11.96 (0.45)	3.41	3.25 (0.09)
2.847 mg CDEC 3.971 mg BAP 2.630 mg TPP	6.37	6.66 (0.45)	10.62	10.98 (0.28)	3.29	2.98 (0.28)
3.355 mg CDEC 3.073 mg BAP 2.730 mg TPP	7.74	7.75 (0.13)	8.48	8.67 (0.23)	3.52	3.24 (0.08)
2.840 mg CDEC 3.030 mg BAP 3.941 mg TPP	6.11	6.56 (0.42)	7.81	8.12 (0.05)	4.74	4.63 (0.38)

[a] PCBA = *p*-Chlorobenzoic acid; PBBA = *p*-bromobenzoic acid; TPP = triphenylphosphine; CDEC = chlordiazepoxide hydrochloride; BAP = bromazepan.

[b] Standard deviations ($n = 5$) in parentheses.

interferences without additional sample preparation, and the ability to perform simultaneous determinations using a single procedure which requires total analysis times of no longer than about 30 min.

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