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Short communication

Determination of chlorine, sulphur and phosphorus in organic materials by ion chromatography using electro dialysis sample pretreatment[☆]

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Abstract

Wet decomposition of an organic material results in a residue of strong acid or alkali which should be neutralized before ion chromatographic (IC) analysis. Oxidative sample decomposition by sodium peroxide fusion in a Parr bomb and subsequent chloride, phosphate and sulphate determination by IC are described. Residual NaOH, formed during the decomposition procedure, was neutralized in an electro dialysis sample pretreatment step. Samples were neutralized in a commercially available electro dialysis cell. Using the described procedure, real samples were analysed and the results compared with those obtained by other analytical procedures. Detection limits of 0.005% for chlorine and 0.008% for sulphur and phosphorus were achieved when 0.1–0.3 g of sample was analysed.

1. Introduction

To employ ion chromatography (IC) for the determination of elements such as chlorine, sulphur and phosphorus in organic materials, these materials should be previously decomposed by an appropriate procedure in order to convert the mentioned elements into chloride, sulphate and orthophosphate, respectively. Classical wet chemical decomposition procedures often result

in a very acidic or alkaline decomposition mixture, very rich in ions, which makes IC analysis impossible. Decomposition in a Schöniger oxygen flask with an absorbing solution composed of dilute H₂O₂ or NaOH [1–4] or combustion of organic material in a flow of oxygen and consequent trapping of the component of interest in dilute H₂O₂ [5] allows the IC determination of the mentioned elements. Several workers [1–4] have reported a high efficiency of these decomposition procedures. Recent results report by Umali et al. [6] confirm the quantitative conversion of chlorine and sulphur into chloride and sulphate using the Schöniger oxygen flask decomposition procedure. When phosphorus is also to be determined, an additional hydrolysis

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step, following the decomposition procedure, was necessary to ensure the complete conversion of different forms of phosphorus into orthophosphate [6].

The number of decomposition procedures compatible with IC analysis became much broader after the introduction of Donnan dialysis as a sample pretreatment step. Cox and co-workers [7,8] reported the determination of some anions in carbonate- and NaOH-based samples after carbonate fusion or oxygen combustion. Instead of Donnan dialysis, a dual ion-exchange method was used [7,8] to prevent sample contamination by the anion of the acid used as the source of H_3O^+ ions. Further improvement in the selectivity of the Donnan dialysis sample pretreatment was achieved with the introduction of electro dialysis Donnan pretreatment [9–14]. In the work cited, different electro dialysis devices were constructed and tested. The electro dialysis cell described by Siriraks and Stillian [11] allows the in-cell generation of hydronium ions by electrolysis of pure demineralized water (of 18 $\text{M}\Omega/\text{cm}$ resistance). In that way contamination of the sample by acid co-ions is completely prevented.

Sodium peroxide fusion decomposition results in complete mineralization of organic materials [15], quantitatively converting halogens into halides, sulphur into sulphate and phosphorus into orthophosphate. This method is often used as the sample preparation procedure in the classical, usually titrimetric, determination of chlorine and sulphur contents in organic material. Owing to the formation of an equivalent amount of NaOH from Na_2O_2 , this method was avoided as a decomposition procedure for IC analysis. With the introduction of Donnan or electro dialysis sample neutralization before IC analysis, the drawback of Na_2O_2 fusion decomposition (strongly alkaline solution after the decomposition), can be easily overcome. The described analytical procedure has not previously been published and is the main objective of this paper. The proposed method was optimized and the accuracy and precision of the results obtained were validated by the analysis of some certified reference materials.

2. Experimental

2.1. Reagents

All reagents were of analytical-reagent grade. A sodium hydrogencarbonate–carbonate-based eluent was prepared according to Dionex [16]. Stock standard solutions of inorganic anions (Cl^- , HPO_4^{2-} , SO_4^{2-}) were prepared by dissolving appropriate amounts of their sodium salts in water purified with a Milli-Q system (Millipore). The accuracy of the procedure was tested by the analysis of some certified standard reference materials (SRMs) provided by NIST (Washington, DC, USA) (SRM 1084 Wear-Metals in Lubricating Oil, SRM 1085 Wear-Metals in Lubricating Oil, SRM 1548 Total Diet and SRM 1577b Bovine Liver).

2.2. Instrumentation

All chromatographic measurements were done with a Dionex 4000i chromatographic system. The electro dialysis system that was used for the off-line neutralization of alkaline samples is presented schematically in Fig. 1.

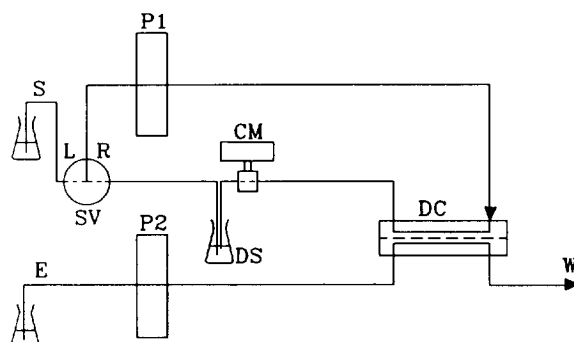


Fig. 1. Scheme of the Donnan dialysis system for the neutralization of alkaline samples after oxidative sample decomposition by sodium peroxide fusion in a Parr bomb. S = Sample; E = donor of H_3O^+ ions (H_2SO_4 or electrolysed 18 $\text{M}\Omega/\text{cm}$ water); P1 = peristaltic pump; P2 = pneumatic donor delivery system; SV = selection valve; DC = dialysis cell; CM = conductivity meter; DS = dialysed sample; W = waste.

2.3. Chromatographic conditions

The following conditions were used: sample loop volume, 50 μ l; guard column, HPIC-AG4A SC (4 mm) (Dionex); separation column, HPIC-AS4A SC (4 mm) (Dionex); eluent, 180 mM Na_2CO_3 -1.7 mM NaHCO_3 ; eluent flow-rate, 2.0 ml/min; suppressor, ASRS-1, Dionex (4 mm), current setting 1; regenerant, electrolysed 18 M Ω /cm water; and regenerant flow-rate, 3.0 ml/min.

2.4. Dialysis conditions

The conditions were as follows: dialysis cell, ASRS-1, Dionex (4 mm), current setting 2 or 3; sample flow-rate, ca. 1 ml/min; donor of H_3O^+ ; electrolysed 18 M Ω /cm water; and donor flow-rate, 3.0 ml/min.

2.5. Analytical procedure

A 150–300-mg amount of a sample was decomposed by 7.0 g of Na_2O_2 according to the standard procedure for organic material decomposition by sodium peroxide fusion in a Parr bomb [15]. After the decomposition, the reaction mixture was dissolved in 250 ml of 18 M Ω /cm water (obtained with a Milli-Q system). The

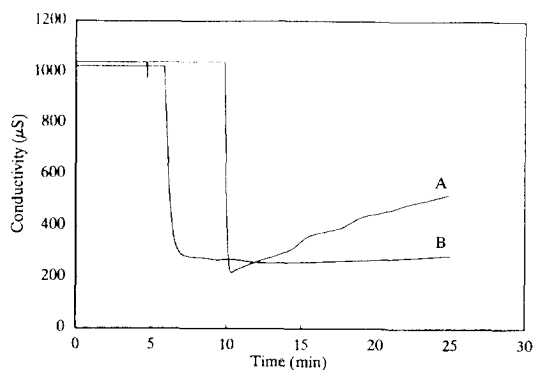


Fig. 2. Effect of (A) Donnan dialysis and (B) electro dialysis neutralization on the integral sample conductivity. The sample contained 2 mg/l F^- , 3 mg/l Cl^- , 8 mg/l NO_2^- , 10 mg/l Br^- , 10 mg/l NO_3^- , 15 mg/l HPO_4^{2-} and 15 mg/l SO_4^{2-} in 1.0 mol/l NaOH. Dialysis cell, ASRS-1; donor of hydronium ions (A) 12 mM H_2SO_4 and (B) electrolysed 18 M Ω /cm water.

concentration of the residual NaOH was between 0.7 and 0.8 mol/l. An aliquot (20 ml) was filtered through a 0.45- μ m pore size membrane filter. The whole dialysis system was rinsed with the filtered sample. On selecting valve position L (load) (Fig. 1), about 5 ml of the sample were collected in a volumetric flask, whereas on selecting valve position R (recycle), sample from the volumetric flask was dialysed until the neutralization was finished (constant conductivity, usually achieved in about 30 min). The concentrations of individual anions in the dialysed sample were determined by subsequent IC analysis using the standard addition method.

3. Results and discussion

3.1. Selection of the source of H_3O^+ ions

To ascertain the influence of the source of hydronium ions on the sample contamination for the tested electro dialysis cell, an experiment was carried out in which the overall conductivity of the sample was monitored during its dialysis neutralization. Because a commercially available electro dialysis cell was used, only the sources of hydronium ions suggested by the manufacturer were tested. Two series of experiments were performed; in first 12 mM H_2SO_4 and in the second electrolysed 18 M Ω /cm water were used as the source of H_3O^+ ions. The results of these experiments are demonstrated in Fig. 2. The minimum values of the overall conductivity on both curves (A and B) represent neutralization of NaOH present in the sample. In the experiment, in which H_2SO_4 was used as the donor of H_3O^+ ions (curve A), the conductivity increased slowly after the minimum had been reached. This effect can be attributed to the non-ideal permselectivity of the cation-exchange membrane incorporated in the dialysis cell, which allows SO_4^{2-} ions to permeate into the sample. Permeation of the SO_4^{2-} ions was proved by IC analysis of the dialysed sample. The concentration of sulphate increased almost linearly with the time of dialysis, whereas the concentrations of other anions of interest (chloride and phos-

phate) remained constant during the neutralization. The recoveries of other ions (fluoride, nitrite and bromide) were also tested and the results obtained were very close to published values [12].

In the experiment in which electrolysed 18 M Ω /cm water was used as the donor of H₃O⁺ ions, the conductivity of the dialysed sample remained fairly constant after the minimum value has been reached (curve B). This experiment confirms the superiority of in-dialysis cell generation of H₃O⁺ ions by electrolysis of 18 M Ω /cm water for the electro dialysis sample neutralization, because no sample contamination was observed and therefore a constant dialysis time was not needed.

3.2. Validation of Na₂O₂ fusion decomposition in combination with IC analysis

To evaluate the analytical procedure for Cl, S and P determination in organic materials, the proposed method was verified by an independent analytical method and/or by the analysis of standard reference materials with certified Cl, S and P contents.

The accuracy of the IC determination of chlorine after sodium peroxide fusion decomposition and electro dialysis neutralization was verified titrimetrically with 0.1 M AgNO₃ with potentiometric indication of the equivalence point. The results of the comparison of chlorine content determinations in different used lubricating oils by titrimetric and electro dialysis–IC determination after sodium peroxide fusion decomposition are summarized in Table 1. It is evident that IC determination of chlorine after electro dialysis neutralization gives results comparable to those obtained titrimetrically, with the exception of sample 802, for which the result obtained titrimetrically is 32% higher than that obtained by IC. In that sample, the concentration of chloride was only slightly higher than the detection limit for the applied titrimetric method, which resulted in an inaccurate chloride determination.

The accuracy and precision of the determination of chlorine, sulphur and phosphorus in an

Table 1

Comparison of the chlorine content (%) in used lubricating oils obtained titrimetrically and by IC analysis after Na₂O₂ decomposition

Sample No.	Potentiometric titration with Ag ⁺	HPIC determination after dialysis neutralization
798	7.63	7.46
799	1.16	1.19
801	8.85	8.93
802	0.53	0.40
803	6.61	6.64

organic material were tested by determining these elements in a used lubricating oil and in SRM 1557b Bovine Liver. When used lubricating oil was analysed, the precision of the proposed method for the determination of chlorine and sulphur content was tested. The used lubricating oil contained 0.40% of chlorine and 0.16% of sulphur. The calculated R.S.D. for chlorine and sulphur was found to be 7.1% and 9.0% ($n = 6$), respectively. Using SRM 1557b Bovine Liver, the accuracy and precision of the proposed procedure were tested. The certified values for chlorine, phosphorus and sulphur in the SRM were 0.278% (R.S.D. 2.2%), 1.10% (R.S.D. 2.7%) and 0.785% (R.S.D. 0.8%), respectively. The same three elements were determined using the proposed analytical procedure and in five parallel determinations the results obtained were 0.23% (R.S.D. 9.4%), 1.19% (R.S.D. 3.5%) and 0.78% (R.S.D. 5.5%), respectively (Table 2). It is evident that the accuracy of the simultaneous determination of chlorine, sulphur and phosphorus using the proposed procedure is within required limits.

The accuracy and precision of chlorine, sulphur and phosphorus determinations using the proposed procedure were additionally verified by analysing different SRMs. The results, summarized in Table 2, show good agreement in the accuracy of the simultaneous determination of chlorine, sulphur and phosphorus with the certified values even in organic materials with significant differences in matrix composition.

Table 2

Results of the determination of chlorine, sulphur and phosphorus in different standard reference materials

Sample	Determined concentration (%) (±R.S.D., %)			Certified concentration (%) (R.S.D., %)		
	Cl	P	S	Cl	P	S
SRM 1084 Wear-Metals in Lubricating Oil	–	–	0.19 (±5.0)	–	–	0.220 ^a
SRM 1085 Wear-Metals in Lubricating Oil	–	–	0.42 (±5.1)	–	–	0.480 ^a
SRM 1548 Total Diet	0.88 (±3.1)	–	0.24 (±5.0)	0.872 (±4.6)	–	0.258 (±10.1)
SRM 1577b Bovine Liver	0.23 (±9.4)	1.19 (±3.5)	0.78 (±5.5)	0.278 (±2.2)	1.102 (±2.7)	0.785 (±0.8)

^a R.S.D. not stated.

4. Conclusions

The efficiency and compatibility of sodium peroxide fusion decomposition of organic samples as a sample preparation step for the IC determination of the anions of interest have been demonstrated and validated. The decomposition process results in a strongly alkaline solution, and this can be successfully neutralized by electro dialysis. To prevent sample contamination by hydronium co-anion in classical Donnan dialysis neutralization, a commercially available electro dialysis cell was used. This cell permits the in-cell generation of H_3O^+ ions in the anode compartment and OH^- ions in the cathode compartment. By electrolysis of 18 MΩ/cm water, further contamination of the sample was avoided. In the validation of the proposed procedure, both the precision and the accuracy of the results were found to be within acceptable limits. In proposed procedure, detection limits of 0.005% for chlorine and 0.008% for sulphur and phosphorus were achieved when 0.1–0.3 g of sample was analysed.

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