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Simultaneous determination of total nitrogen, phosphorus and sulphur by means of microwave digestion and ion chromatography

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Abstract

A method for the oxidation of nitrogen, phosphorus and sulphur to nitrate, phosphate and sulphate ions using 22% (v/v) hydrogen peroxide and closed-vessel microwave assisted digestion in two stages is described. Solutions of a variety of nitrogen-, phosphorus- and sulphur-containing compounds with formic acid added to prevent hydrolysis were used to test the efficiency of the procedure. The products of oxidation were determined by ion chromatography. Good recoveries of nitrogen, phosphorus and sulphur were obtained. The results for the NIST reference materials, oyster tissue and Buffalo River sediments agree well with the certified values. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The nitrogen, phosphorus and sulphur cycles are of particular significance to a number of biological and non-biological processes in the environment [1]. Natural and anthropogenic effects can cause localised inter-related changes to the cycles. In order to assess the impact and extent of the changes, it is essential to develop analytical methods which allow the simultaneous determination of two or all of the three constituents in a wide variety of environmental samples.

In one of the first attempts at simultaneous determination, Ebina et al. [2] developed a method of oxidizing nitrogen and phosphorus to nitrate and phosphate, respectively using alkaline potassium peroxodisulphate. The composition of the oxidizing solution was carefully chosen so that its pH changed from basic to acidic during the oxidation step. The change in pH was necessary because oxidation with potassium peroxodisulphate of nitrogen and phosphorus occurs under basic and acidic conditions, respectively. The nitrate and phosphate ions were then determined colorimetrically.

In a different approach, Nygaard and Sotera [3] used inductively coupled plasma atomic emission spectrometry (ICP-AES) to determine water-soluble nitrogen and phosphorus in fertilisers. More recently, Matilainen and Tummavuori [4] investigated the application of ICP-AES to the determination of water soluble sulphur in fertilisers and reported on spectral and interelement effects.

To be able to analyse both bound and water soluble fractions, samples have to be digested. However, existing digestion methods are not easily adapted to simultaneous determinations because the use of oxidants such as nitric and sulphuric acids and potassium peroxodisulphate precludes the determination of one or more of the analytes.

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The use of hydrogen peroxide avoids this problem. In addition, water is the main product when the oxidizing strength of hydrogen peroxide is spent, and as a result the digest is amenable to analysis by techniques such ion chromatography (IC) and ion selective potentiometry. UV-induced photoxidation using hydrogen peroxide has been applied successfully to the oxidation of nitrogen, phosphorus and carbon in sea water [5].

In this study, we report results from an investigation of the use of hydrogen peroxide at low pH in combination with closed-vessel microwave assisted digestion for the oxidation of various nitrogen-, phopshorus- and sulphur-containing compounds. The nitrate, phosphate and sulphate ions formed were determined by IC.

2. Experimental

2.1. Apparatus

A Dionex QIC analyser ion chromatograph equipped with a Dionex AG4A guard column, a Dionex AS4A anion separation column, and a Dionex AMMS-II suppressor and conductivity detector was used. The sample was injected into the chromatograph via a 100-μl sample loop, and eluted with a solution of 1.8 m*M* sodium carbonate–1.7 m*M* sodium hydrogencarbonate at a flow-rate of a flow-rate of 1 ml min^{-1}. A chart speed of 0.5 cm s^{-1}, conductivity range setting of 30 μS, and conductivity suppressor solution of 12.5 m*M* H_2SO_4 were used throughout.

A Milestone Model MLS-1200 Mega microwave system (24010 Sorisole, Italy) was used for the digestion of the samples. The digestion programme was as follows:

Step	Power (W)	Time (min)
1	250	5
2	0	15
3	600	10
4	Ventilation	10

2.2. Reagents

The column eluent was prepared from reagent grade sodium carbonate and bicarbonate, and distilled deionized water (18 MΩ cm, nanopure, Millipore, MA, USA) The suppressor solution was prepared from 1.4 ml AristaR grade sulphuric acid (Merck, Poole, UK) and made up to 2 l with distilled deionised water. The following analytical grade compounds were subjected to the digestion treatment: sodium nitrite, urea, L-cysteine and ammonium nitrate (all supplied by Merck), L-lysine and sodium pyrophosphate (both supplied by Aldrich, Gillingham, UK), sodium sulphite (East Anglia Chemicals, UK).

A 22% (v/v) solution was prepared from AristaR grade 30% (v/v) hydrogen peroxide.

2.3. Sample preparation

To test the efficiency of the oxidation procedure, solutions containing 50 μl of formic acid and 40–100 mg l^{-1} in nitrogen, phosphorus or sulphur were prepared.

Standard reference materials oyster tissue (NIST, SRM 1566a) and Buffalo River sediment (NIST SRM 2704) were used to validate the digestion procedure.

2.4. Stock standard solutions

Individual 1000 mg l^{-1} stock standard solutions of nitrate (N), phosphate (P), sulphate (S) and nitrite (N) were prepared from Aristar grade reagents (supplied by Merck) by dissolving 6.0679 g $NaNO_3$, 4.3937 g KH_2PO_4, 1.8141 g K_2SO_4 and 0.2020 g of $NaNO_2$, respectively, in distilled deionised water.

Mixed anion standard solutions of 1.0, 2.5, 5.0 and 10.0 mg l^{-1}, respectively, were used to calibrate the ion chromatograph.

2.5. Sample digestion

Ten ml of hydrogen peroxide solution were added to 5 ml of sample or 0.2 g of a reference material and 50 μl of formic acid in the microwave sample vessel. The mixture was capped and the microwave programme initiated. At the end of the first run, the

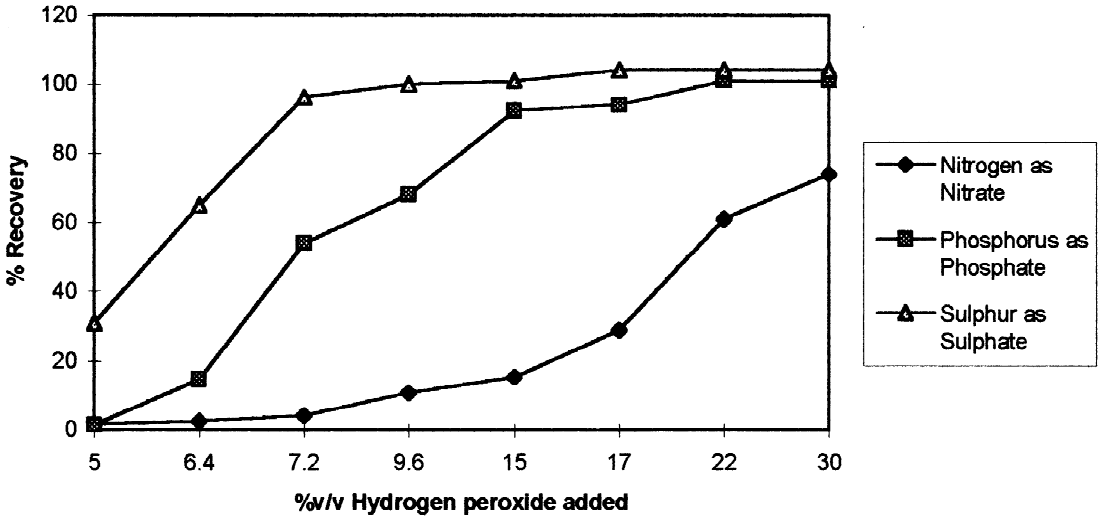

Fig. 1. Effect of varying hydrogen peroxide concentration on the recovery of nitrogen, phosphorus and sulphur from urea, sodium pyrophosphate, and L-cysteine, respectively after the first digestion.

sample was allowed to cool to room temperature, a further 10 ml of the same strength hydrogen peroxide solution was added and then the same programme was repeated. After oxidation, the digest was cooled to room temperature, made up to 100 ml with distilled deionised water, and analysed on the ion chromatograph. Each compound was digested and analysed at least five times.

3. Results and discussion

3.1. Concentration of the oxidizing solution

Fig. 1 represents the effect in percent recovery by varying hydrogen peroxide concentrations on the conversion of urea, sodium pyrophosphate and L-cysteine in the presence of formic acid to nitrate,

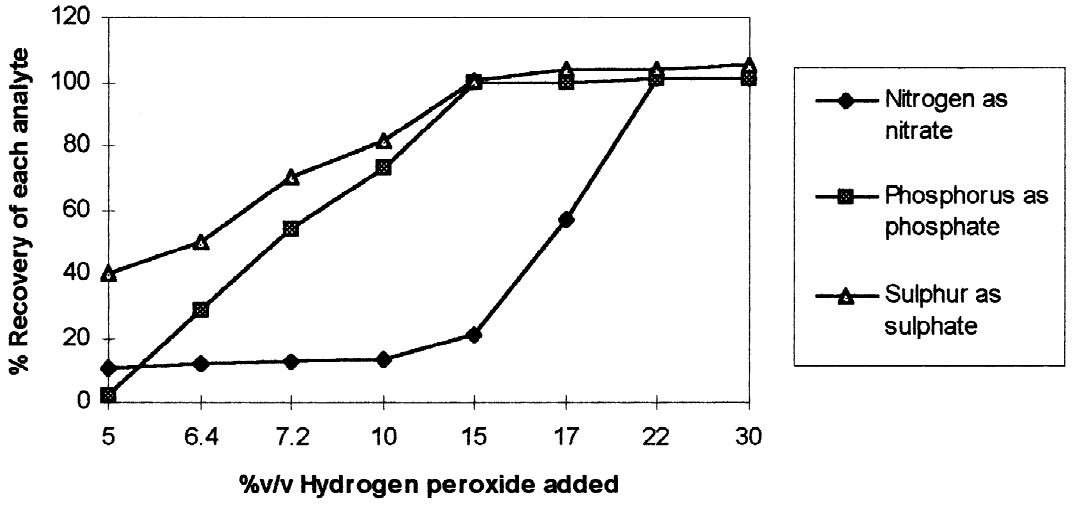

Fig. 2. Effect of varying hydrogen peroxide concentration on the recovery of nitrogen, phosphorus and sulphur from urea, sodium pyrophosphate and L-cysteine, respectively after the second digestion.

Table 1
Recoveries of N, P and S as nitrate, phosphate and sulphate ions from different concentrations (mg l^{-1}) of pure compounds after digestion with 22% (v/v) hydrogen peroxide ($n=5$)

Compound	N-NO_3^{-1} expected	N-NO_3^{-1} found	P-PO_4^{-3} expected	P-PO_4^{-3} found	S-SO_4^{-2} expected	S-SO_4^{-2} found
Urea	9.93	9.96±0.62				
L-Lysine	4.00	4.01±0.04				
Ammonium nitrate	6.49	6.68±0.06				
Sodium nitrite	10.0	10.02±0.08				
L-Cysteine	2.26	2.12±0.01			5.17	6.10 ± 0.01
Sodium pyrophosphate			9.78	9.80±0.13		
Sodium sulphite					5.38	5.35±0.04
Mix L-cysteine and sodium pyrophosphate	2.26	2.12±0.01	9.78	9.65±0.26	5.17	6.11±0.02

phosphate and sulphate, respectively. Formic acid was added to the samples in order to prevent the hydrolysis of the compounds. However, it has been suggested that the oxidizing power of hydrogen peroxide is enhanced when it is activated by either acid, metal ions or is exposed to UV light [6]. This aspect was not investigated.

The extent of conversion of urea to nitrate was much improved (Fig. 2) when a second 10-ml aliquot of the same concentration hydrogen peroxide solution was added and the sample subjected to the microwave programme for a second time. In subsequent experiments, 22% (v/v) hydrogen peroxide and the two-stage digestion procedure were used to test the efficiency of the oxidation process on a variety of compounds. Tables 1 and 2 summarise the extent of oxidation expressed as recoveries of total nitrogen, phosphorus and sulphur. Varying the amounts of urea, L-cysteine and sodium pyrophosphate did not affect the extent of oxidation (see Table 2). The very good recovery values indicate that the oxidation process is efficient at converting N, P and S in the form they occur in the compounds. The efficiency of the procedure in oxidizing compounds containing nitrogen–nitrogen bonds or amide groups, and condensed polyphosphates is currently being assessed. A comparison of the expected and found values for N, P, S (Table 1) using a paired-*t* test was found not to be statistically significant at the 95% confidence limits except for the L-cysteine for which

Table 2
Recoveries of nitrogen, phosphorus and sulphur using different concentrations of analyte and 22% (v/v) hydrogen peroxide

Compounds	Concentration expected (mg l^{-1})	Concentration found (mg l^{-1})	Recovery (%)
Urea (N-NO_3^{-1})	5.00	4.85	97.0
	9.93	10.40	104.7
	6.00	5.42	90.3
	6.24	5.50	88.1
	8.00	7.45	93.1
L-Cysteine (S-SO_4^{-2})	23.10	22.59	97.7
	11.48	12.11	105.4
	15.11	14.44	95.5
	10.00	10.50	105.0
	5.17	6.10	117.0
Sodium pyrophosphate	10.00	9.56	95.6
(P-PO_4^{-})	20.50	22.19	108.2
	6.49	6.72	103.5
	31.8	30.13	94.7
	9.78	9.70	99.2

high recoveries were obtained. The difference in the results could be due to the poorer sensitivity for the determination of sulphate ions at low concentrations.

3.2. Analytical performance

A chromatogram of a mixture of L-cysteine and sodium pyrophosphate after oxidation is shown in Fig. 3. The mean±SD retention times for nitrate, phosphate and sulphate ions were: 4.11±0.14, 6.60±0.05 and 8.65±0.24 min, respectively. The three peaks are very well resolved and as a result samples containing widely different proportions of the analytes can be analysed without interferences.

Calibration graphs obtained from mixed anion standards gave the following highly linear best-fit equations: nitrate: $y=1.18\cdot10^{7}x-7.18\cdot10^{6}$ ($r^2=$ 0.9970); phosphate: $y=4.71\cdot10^{7}x-3.78\cdot10^{6}$ ($r^2=$

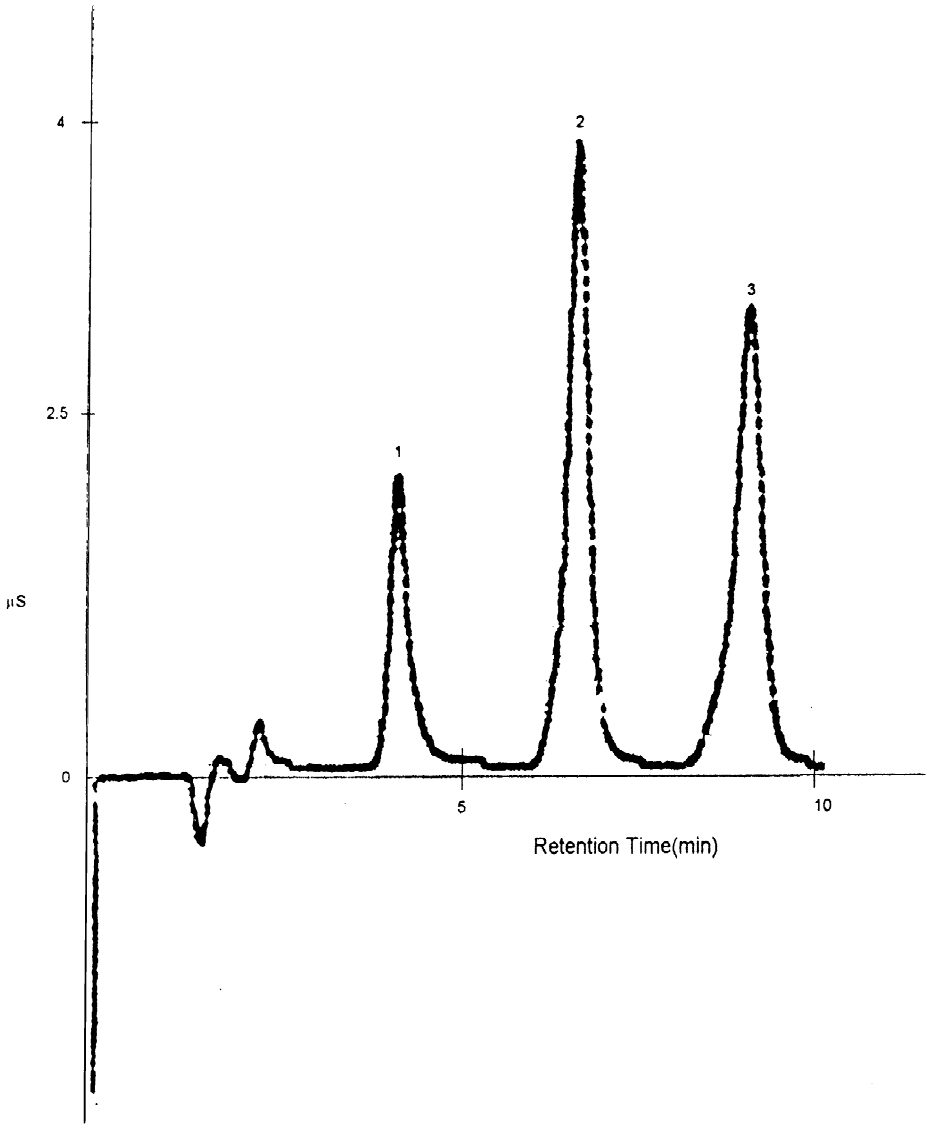

Fig. 3. Chromatogram of a sample containing L-cysteine and sodium pyrophosphate after oxidation to nitrate (1), phosphate (2) and sulphate (3).

Table 3
Comparison of the quantities of N, P and S found using the proposed method and the reported values for the standard reference materials ($n=3$)

Element		Oyster tissue (%, w/w± 95% confidence limit)	Buffalo River (%, w/w± 95% confidence limit)
N	Found	6.62±0.28	
	Reference value	6.81	
P	Found	0.619±0.020	0.0888±0.0125
	Certified	0.623±0.020	0.0998±0.0003
S	Found	0.872±0.011	0.432±0.045
	Certified	0.862±0.021	0.397±0.0005

0.9886); sulphate: $y=4.37\cdot10^{6}x-3.76\cdot10^{6}$ ($r^2=$ 0.9865) where $y=$peak area (arbitrary units) and $x=$anion concentration (mg l^{-1}).

Detection limits were calculated from the calibration graphs using the method of Miller and Miller [7]. The results were 0.123 mg/l nitrate, 0.251 mg/l phosphate and 0.850 mg/l sulphate. The detection limits based on 0.2 g of sediment were 0.006% (w/w) N, 0.012% (w/w) P and 0.042% (w/w) S.

3.3. Method validation

The N, P and S contents for NIST SRM 1566a oyster tissue and NIST SRM 2704 Buffalo River sediment samples digested with 22% (v/v) hydrogen peroxide are given in Table 3. Satisfactory agreement with the certified values was obtained. The presence of a sample matrix did not have an adverse effect on the recoveries.

4. Conclusions

The proposed method for the oxidation of N, P and S followed by the determination of the nitrate, phosphate and sulphate ion by IC gave satisfactory results for the compounds tested. The effectiveness of this procedure is demonstrated by the good recoveries obtained for the two SRMs, oyster tissue and Buffalo River sediment. Current work is focused on the application of the method to more recalcitrant compounds where the N, P and S atoms are in ring systems.

Acknowledgements

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