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Journal of Chromatography A 822 91998) 162–166

JOURNAL OF CHROMATOGRAPHY A

Short communication

Use of column-switching ion chromatography for the simultaneous determination of total nitrogen and phosphorus after microwave assisted persulphate digestion

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Received 2 February 1998; received in revised form 8 May 1998; accepted 7 July 1998

Abstract

A method for the simultaneous determination of total nitrogen and total phosphorus in environmental and waste waters is proposed. Samples were digested by alkaline persulphate solution in a microwave oven and the resulting solutions were analysed by ion chromatography without any sample pretreatment. The excess of sulphate (4.5 $g\,l^{-1}$), generated from the digested persulphate, was eliminated by a column switching technique applied to a system composed of two serially connected columns. The detection system showed good reproducibility and accuracy in the typical concentration range used for wastewater. The limits of quantification were 9.0 $\mu equiv.\,l^{-1}$ (0.12 mg $N\,l^{-1}$) for total nitrogen and 3.3 $\mu equiv.\,l^{-1}$ (0.10 mg $P\,l^{-1}$) for total phosphorus.

Keywords: Persulphate digestion, microwave-assisted; Water analysis; Nitrogen; Phosphorus

1. Introduction

Phosphorus and nitrogen are released into environmental waters by many different sources, e.g. animal and chemical fertiliser run-off and sewage. Excessive amounts of these nutrients activate eutrophication, the process of rapid growth of phytoplankton, algae and plants. Subsequent decay of these materials causes dissolved oxygen to be removed from a water body and with it the ability to sustain life. A large number of studies have illustrated the dynamic nature of the nitrogen speciation and phosphorus fractionation balances in natural waters, and the significance of the organic nitrogen and particulate phosphorus fractions in contributing to the total nutrient loading in a water body [1,2]. So a rapid method for the simultaneous determination of total nitrogen (TN) and total phosphorus (TP) is needed, both for environmental studies on natural waters and routine control of sewage and wastewater.

Persulphate digestion of water and sediment samples is the only digestion technique for simultaneous TN and TP determination [3–5]. This digestion procedure is accepted in the official methods of TP analysis [6,7]. The determination of nitrate and phosphate, formed in the oxidising procedure, is usually performed by colorimetry [6,7] or ion chromatography [8], but to date no simultaneous method of detection has been published. Simultaneous determination by IC is prevented by the presence of a high amount of sulphate formed by the decomposi-

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0021-9673/98/$19.00
PII: S0021-9673(98)00569-X

tion of the persulphate. The samples can be diluted for nitrate determination [8] but the detection limits of phosphate become too high for environmental application. The excess of sulphate can be eliminated by using a barium loaded anion-exchange cartridge [9], by liquid–liquid extraction [10] or by precipitation with lead perchlorate [11], but total analysis time and costs limit the use of these techniques. A column switching technique was applied to the determination of phosphate in high saline matrix in unsuppressed IC, but nitrate was not analysed [12]. In our work column switching was used for eliminating sulphate after microwave assisted persulphate digestion in order to get a fast simultaneous determination of TN and TP by suppressed ion chromatography without any sample pretreatment. Dynamic range, reproducibility and detection limits of this method were investigated to assess the applicability of this method to routine analysis of wastewater samples.

2. Experimental

2.1. Materials

All solutions were prepared by dissolving salts of analytical grade in ultra pure (18 $M\Omega\,cm^{-1}$ quality) water produced by a Milli-Q system (Millipore, Bedford, MA, USA). Concentrated standard solutions (50 mequiv. l^{-1}) were prepared from sodium dihydrogen phosphate (Fine Chemicals, Milan, Italy) and sodium nitrate (Carlo Erba, Milan, Italy) salts. Working standard solutions were prepared by dilution of these concentrated solutions with previously digested Milli-Q water. The oxidising mixture for digestion was composed of 0.185 *M* potassium persulphate, 0.485 *M* boric acid and 0.35 *M* NaOH (all from Merck, Darmstadt, Germany) [3].

2.2. Microwave digestion of samples

Digestion was carried out in closed advanced composite vessels, equipped with temperature and pressure control, using a CEM MSP 1000 Microwave sample preparation system (Matthews, NC, USA) capable of 1% microwave power adjustments up to a maximum of 1000 W. A 50-ml volume of sample was digested with 7 ml of oxidising mixture for 30 min at 120°C and 95% microwave power. Samples with a COD content higher than 35 mg l^{-1} were appropriately diluted before digestion [4].

2.3. Instruments and chromatographic conditions

The separation system comprised a Dionex (Sunnyvale, CA, USA) ion chromatograph equipped with a 4500i gradient pump (GP), a 2000i analytical pump (AP), an AMMS-II chemical suppressor and a CDM-II conductivity detector. The chromatographic separation was carried out using two low capacity anion-exchange analytical columns: Dionex IonPac AS4A (250×4.6 mm I.D.; d_p: 15 μm) and a Dionex IonPac AS4A-SC (250×4.6 mm I.D.; d_p: 12 μm).

An additional inert double stack four-way slider valve was introduced between the two analytical columns. The gradient pump module controlled the injection valve, equipped with a 50-μl loop, and the four-way slider valve. A Dionex AI-450 chromatographic data system was used for instrument control and data collection and processing.

Analyses were performed using a 2.97 m*M* Na_2CO_3–2.80 m*M* $NaHCO_3$ eluent solution at a flow-rate of 1.6 ml min^{-1}; 12.5 m*M* H_2SO_4 at a flow-rate of 5 ml min^{-1} was used as a regenerating solution. Eluent was prepared daily, filtered and degassed.

2.4. Column switching procedure

In Fig. 1 the scheme of the chromatographic system is shown. At 0.0 min, valves A and B were off. The sample was loaded into the sample loop while the GP was pumping eluent into both columns and the AP was pumping eluent into the waste. At 0.1 min valve A was switched on and valve B kept off. In this configuration the eluent delivered by the GP flushed the sample loop and passed through the analytical columns. At 2.7 min valve B was switched on, so that GP pumped the eluent through the second column to proceed the analysis, and the AP drove the excess of sulphate from the first column to the waste. At 7.0 min valves A and B were switched off to

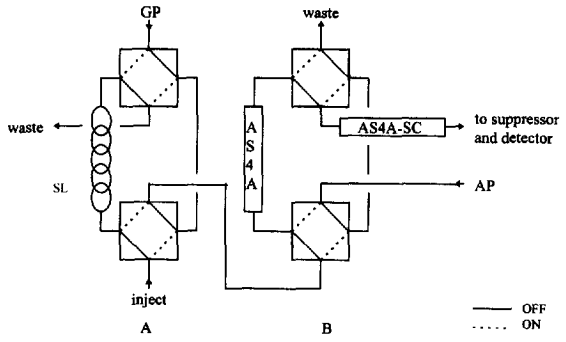

Fig. 1. Scheme of the switching system; GP=gradient pump; AP=analytical pump; SL=sample loop.

recover the starting conditions. The total analysis time was 9 min.

3. Results and discussion

After microwave assisted persulfate digestion, water samples were injected into the ion chromatograph to determine total nitrogen and total phosphorus as nitrate and phosphate. The presence of about 4500 mg l^{-1} of sulphate, derived from the digested persulphate, makes it impossible to analyse phosphate with the usual precolumn and column configuration (Fig. 2a) or by using two serially connected separation columns (Fig. 2b). Furthermore the total amount of sulphate which flows through the system negatively influences the efficiency of both the separation and suppression systems. The application of the column switching technique to the two-column system allowed the simultaneous determination of nitrate and phosphate without any sample treatment after the digestion step (Fig. 2c). The total time of analysis was reduced to 9 min, including the time needed to restore and stabilise the system backpressure after switching the pneumatic driven valve B. The use of a double pump configuration enabled the whole system to be flushed during the entire analysis time (Fig. 1).

The dynamic range has been estimated by injecting nitrate and phosphate standards prepared in digested Milli-Q grade water. Standard concentrations ranged from 3 to 1000 μequiv. l^{-1} in order to span the full range of concentrations of natural

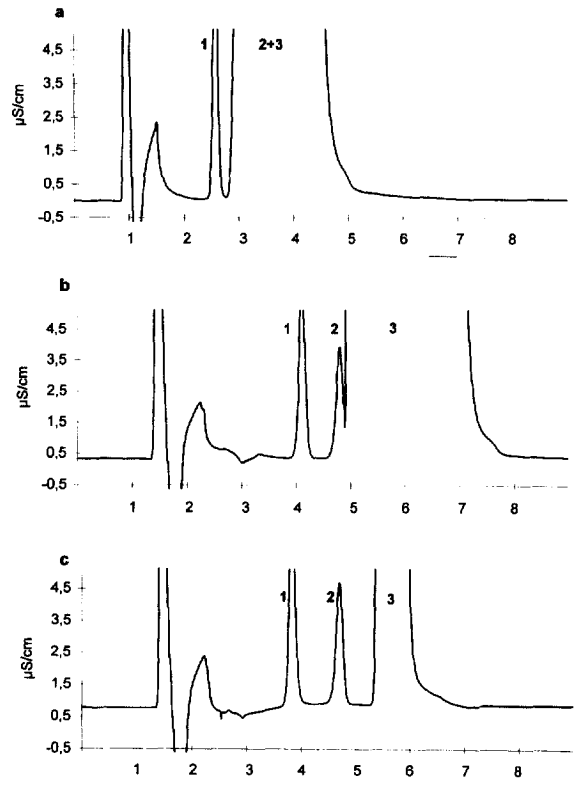

Fig. 2. Chromatograms of a wastewater sample obtained (a) by using a single column with precolumn; (b) two serially connected columns, (c) two serially connected columns with the switching system (see text for chromatographic conditions) (time scale in min). Analytes: 1, nitrate (1.5 mg l^{-1}); 2, phosphate (3 mg l^{-1}); 3, sulphate (4500 mg l^{-1}).

waters and wastewater. The repeatability of the chromatographic procedure was determined by injecting the standard solutions five-fold: the R.S.D. values of the standard peak areas ranged from 5 to 10% at 3–6 μequiv. l^{-1} to <1% at 1000 μequiv. l^{-1}, showing an exponential-like relation of the relative error vs. concentration. Heteroscedastic distribution of the associated errors made it necessary to use a weighted regression to fit the best calibration line. Since the calibration curves showed an evident deviation from linearity, which is typical of the suppressed IC technique [13,14], they were divided into three different weighted linear regression curves (each of an order of magnitude) instead of using a single quadratic curve on all the dynamic range.

The quantification limit (LOQ) of the TN de-

Table 1
Accuracy experiments for total nitrogen (TN) and total phosphorus (TP)

TN (mg $N l^{-1}$)	Expected value	Found
Simulated freshwater A	2.0±0.0	1.97±0.03
Simulated freshwater B	3.3±0.1	3.4±0.1
TP (mg $P l^{-1}$)	Spectrophotometric measurement	Found
Lambro river	0.861±0.005	0.82±0.01
Urban wastewater treatment plant A: inlet (diluted 1:10)	1.860±0.005	1.64±0.03
Urban wastewater treatment plant B: inlet (diluted 1:10)	3.262±0.005	3.16±0.01
Urban wastewater treatment plant C: inlet (diluted 1:10)	0.26±0.02	0.21±0.03
Urban wastewater treatment plant C: outlet (not diluted)	1.110±0.003	0.98±0.01
Industrial wastewater treatment plant: outlet (diluted 1:10)	0.661±0.001	0.47±0.03

termination was limited by the presence of nitrate in the digestion blank, derived from the impurities of the oxidising reagents, particularly potassium persulphate. The LOQs, calculated according to the IUPAC [15] summing blank mean area and ten-fold its standard deviation, were 9.0 μequiv. l^{-1} (0.12 mg $N l^{-1}$) for TN and 3.3 μequiv. l^{-1} (0.10 mg $P l^{-1}$) for TP.

Internal quality control of the method was carried out using a control sample created by mixing different real digested samples. The control sample was injected three times at the start of each analytical session for 2 consecutive weeks. The R.S.D.s of the mean concentrations — 1.64±0.21 mg $N l^{-1}$ (R.S.D., 13%) for TN and 0.98±0.08 mg $P l^{-1}$ (8.5%) for TP (n=18) — gave an estimate of the reproducibility of the chromatographic procedure.

Two samples of simulated freshwater from a recent intercomparison exercise [16] were analysed in order to evaluate the accuracy of the method (Table 1). Expected total phosphorus values (0.060±0.005 and 0.150±0.010 mg $P l^{-1}$) were around the quantification limit of our method, and they could not be used to evaluate the accuracy of TP determination. Measured TN values (1.97±0.03 and 3.4±0.1 mg $N l^{-1}$, respectively) were not statistically different from the expected values of 2.0±0.0 and 3.3±0.1 mg $N l^{-1}$. A comparison of the present method for TP determination with a well established one based on the spectrophotometric determination of the blue phosphomolybdic complex [3] showed that they were in a satisfactory agreement (Table 1).

In order to verify the absence of systematic error derived from the column switching procedure, recovery experiments on real matrices, spiked after the digestion step with pure nitrate and phosphate solutions, were carried out; the method showed a high

Table 2
Recovery experiments for total nitrogen (TN) and total phosphorus (TP)

Sample	TN (mg $N l^{-1}$)				TP (mg $P l^{-1}$)			
	Before addition	Amount added	Found	Recovery (%)	Before addition	Amount added	Found	Recovery (%)
Lambro river	5.96±0.08	0.7	7.04±0.07	105.7	0.82±0.01	1.55	2.5±0.1	105.7
Urban wastewater treatment plant C: inlet (diluted 1:10)	2.74±0.02	0.7	3.45±0.06	100.3	0.21±0.03	1.55	1.76±0.22	100.1
						3.10	3.37±0.22	101.9
						7.74	7.76±0.63	97.6
Urban wastewater treatment plant C: outlet	2.1±0.2	0.7	2.7±0.2	96.4	0.98±0.01	1.55	2.85±0.01	112.5
Industrial wastewater treatment plant: outlet (diluted 1:10)	5.64±0.04	0.7	6.36±0.05	100.2	0.47±0.03	1.55	1.94±0.17	95.8

degree of accuracy (recovery >95%) both for TN and TP in the full range of wastewater samples (Table 2).

This method was found to be independent of matrix composition: no interferences were found by analysing real samples from urban and industrial wastewater.

4. Conclusions

The coupling of microwave assisted digestion, instead of traditional autoclaving, and simultaneous determination by column switching IC makes this method accurate and fast both for TN and TP determination in wastewaters; unfortunately, it is not sufficiently sensitive for the determination of TP in all kinds of freshwaters. The LOQs, were 9.0 μequiv. l^{-1} (0.12 mg Nl^{-1}) for TN and 3.3 μequiv. l^{-1} (0.10 mg Pl^{-1}) for TP, which is too high a limit for oligotrophic lake analysis.

The overall cost of our proposed method can be reduced by avoiding the use of the second pump AP for flushing the first column: experiments performed with this simpler instrumental configuration gave good results, the only drawback being a much longer equilibration time between consecutive analyses.

Acknowledgements

The authors thank Mr. De Luca (CEM, Italia) for providing the instrumentation for the digestion experiments and for invaluable technical support.

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