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Evaluation of ion-exchange chromatography for nitrate determination in wastewaters[☆]

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ABSTRACT

Two methods of nitrate measurement have been compared: colorimetric with salicylate and conductimetric with ion-exchange chromatography. For samples with low nitrate concentrations, the salicylate method is similar to the ion chromatographic method. However, for samples with high nitrate concentrations, such as wastewaters from biological plants, ion-exchange chromatography is preferable: it is more accurate, even after dilution, and is not subject to interferences by organic or inorganic constituents.

INTRODUCTION

Nitrate is the most oxidized form of nitrogen compound produced by the biological decomposition of organic matter. It is frequently found in effluents after biological treatment. Nitrate in river water can arise from sewage effluents, drainage from agricultural land treated with artificial nitrogen fertilizers and from effluents of certain industries (*e.g.* chemicals, explosives and fertilizers) [1]. Under certain circumstances, nitrates can stimulate the growth of algae to such an extent as to cause problems for the aquatic life (eutrophication).

The Italian law relevant to wastewaters is Legge Merli No. 319/76, in which the limit for nitrate nitrogen is either 20 or 30 mg/l (N), depending on their use. More precisely, in this

law two references (Tables A and C) are fixed for wastes in surface water or in public sewers. The same law establishes the limits for chloride and sulphate anions, respectively 1000 mg/l and 1200 mg/l, in both surface water and sewers. In Italy wastewater samples frequently contain chloride concentrations near the maximum allowable limit, whereas sulphate is usually much lower than the allowable limit.

EXPERIMENTAL

Apparatus

For the salicylate method [2], a Beckman DU20 spectrophotometer was used at 420 nm, with matched silica cells of 1 cm light path. Chromatography was performed on a Dionex system 2000i/SP ion chromatograph equipped with a conductivity detector (range 30 μ S) with suppression (Model AMMS). A separator column (HPIC-AS4A) with a guard column (HPIC-AG4A) was used. The volume of the sample loop was 50 μ l. The integrator model was HP 3390A. The eluent used was 1.8 mM sodium carbonate plus 1.7 mM sodium bicarbonate at a

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flow-rate of 2 ml/min. The suppressor was regenerated with 0.0125 M sulphuric acid.

Reagents

Purified water was obtained from a Milli-Q purification system (Millipore). All the solutions were prepared from analytical reagent-grade chemicals: sodium salicylate solution (0.5 g in 100 ml) and Seignette salt solution (sodium and potassium tartrate 60 g in 1 l, basified with sodium hydroxide 400 g in 1 l). The acidifying agent was concentrated sulphuric acid.

Methods

The determination of nitrate is difficult because of the relatively complex procedures required, the high probability that interfering constituents will be present and the limited concentration ranges of the various techniques. The official Italian method for nitrate in wastewater is a colorimetric analysis with sodium salicylate to form a coloured dye [3]. It allows measurement of nitrate at concentrations between 0.5 and 5.0 mg/l as nitrogen. Interlaboratory tests using this method have verified its applicability [4].

A 1-ml volume of sodium salicylate was added to 10 ml of sample in a porcelain dish and the solution evaporated in a water bath. After cooling the residue, 2 ml of concentrated sulphuric acid was added and carefully mixed to completely rinse the dish surface. After 10 min, 15 ml of deionized water and 15 ml of Seignette salt solution were added and mixed. The resultant yellow solution was analysed spectrophotometrically at 420 nm [5].

The main disadvantage of this method is the presence in most samples of interfering substances: coloured compounds, iron, nitrites and chlorides. When the chloride concentration is greater than 400 mg/l, treatment with silver sulphate is suggested to precipitate silver chloride. However, this procedure is not ideal because of the precipitate is difficult to eliminate.

Alternatively, ion-exchange chromatography (IEC) provides a single instrumental technique that may be used for rapid and sequential measurement of common anions [6]. The minimum

detectable concentration of an anion is a function of the sample size and the conductivity scale used. In this work, with a range of 30 $\mu\text{S}/\text{cm}$ and a 50- μl sample loop, the minimum detectable concentration is 0.05 mg/l as nitrogen. The main disadvantages of this method are: any substance that has a retention time coinciding with that of any anion to be determined will interfere; a high concentration of an ion also interferes with the resolution of the others [7]. Therefore, it is necessary to respect the maximum tolerable concentration of interfering anion. For example, the concentration ratios for the nitrates are [8,9]:

$\text{NO}_3^-/\text{Cl}^-$	1:500 mg/l
$\text{NO}_3^-/\text{Br}^-$	1:100 mg/l
$\text{NO}_3^-/\text{SO}_4^{2-}$	1:500 mg/l

RESULTS AND DISCUSSION

The accuracy of the IEC method was verified by analysing a stock standard solution of anhydrous potassium nitrate in deionized water, 2.50, 5.00 or 10.00 mg/l as nitrate. These solutions were successively diluted (1:2.5, 1:5, 1:10) to obtain the same final concentrations. The chromatography calibration was obtained using four concentration levels of nitrate. One of these was at a concentration near, but above, the minimum detectable concentration, and the other concentrations were as near as possible to the expected range of values found in real samples. The working calibration curve was verified daily by the measurement of the 5.00 mg/l nitrate calibration standard.

In Table I the average experimental concentrations for the different dilutions are reported; the relative error (RE) percentage was calculated by five repeated measurements. The results show that the same concentrations obtained by suitable dilutions give a similar relative error percentage. For wastewater and sewage samples analysed in this paper, RE was lower than 10%.

The accuracy and precision of the salicylate and IEC methods were compared. Potassium nitrate standard solutions, at different concentrations, were prepared and five determinations

TABLE I

AVERAGE EXPERIMENTAL CONCENTRATIONS AND RELATIVE ERROR PERCENTAGE FOR THE DIFFERENT DILUTIONS

Theor. conc.	2.50 mg/l		5.00 mg/l		10.00 mg/l	
Dilutions	Average expt. conc. (mg/l)	RE (%)	Average expt. conc. (mg/l)	RE (%)	Average expt. conc. (mg/l)	RE (%)
Just like	2.54	1.6	5.08	1.6	10.36	3.6
1:2.5	1.02	2.0	2.04	2.0	4.05	1.2
1:5	0.54	8.0	1.04	4.0	2.04	2.0
1:10	0.29	16.0	0.53	6.0	1.03	3.0

TABLE II

COMPARISON OF ACCURACY AND PRECISION FOR NITRATE STANDARDS

Nitrate (mg/l)	Nitrogen (mg/l)	Salicylate method mg/l N		IEC method mg/l N	
		$x \pm S.D.$	RE (%)	$x \pm S.D.$	RE (%)
0.20	0.05	0.09 \pm 0.0034	+80	0.051 \pm 0.0026	+2
1.00	0.22	0.26 \pm 0.0022	+18	0.230 \pm 0.0020	+5
2.00	0.45	0.51 \pm 0.0046	+13	0.463 \pm 0.0029	+3
2.50	0.56	0.61 \pm 0.0029	+9	0.576 \pm 0.0011	+3
5.00	1.13	1.22 \pm 0.0050	+8	1.145 \pm 0.0022	+1
8.86	2.00	2.21 \pm 0.0036	+10	2.054 \pm 0.0025	+3
10.00	2.26	2.46 \pm 0.0015	-9	2.323 \pm 0.0026	+3

for each method were made. The standard deviations of the average values and the RE values are indicated in Table II.

A comparison of the linearity range and of the minimum detectable concentration between the different methods is shown in Table III.

The effects of chloride concentration on the nitrate determination were studied because chloride is present in all real samples. The salicylate and IEC methods were compared in three different chloride concentration ranges (Fig. 1A): $Cl^- > 1000$ mg/l; $Cl^- 100$ – 1000 mg/l; $Cl^- < 100$ mg/l. It was verified that the IEC is applicable in the following conditions:

(a) $Cl^- > 1000$ mg/l, when the concentration

of nitrate is greater than 2.0 mg/l, with dilution 1:10.

(b) $Cl^- 100$ – 1000 mg/l, when nitrates are between 1.0 and 20.0 mg/l, with dilution 1:5, and

TABLE III

COMPARISON OF LINEARITY RANGE AND MINIMUM DETECTABLE CONCENTRATION

Method	Linearity range (mg/l as N)	Minimum detectable conc. (mg/l as N)
Salicylate	0.5–5.0	0.5
IEC	0.05–4.00	0.05

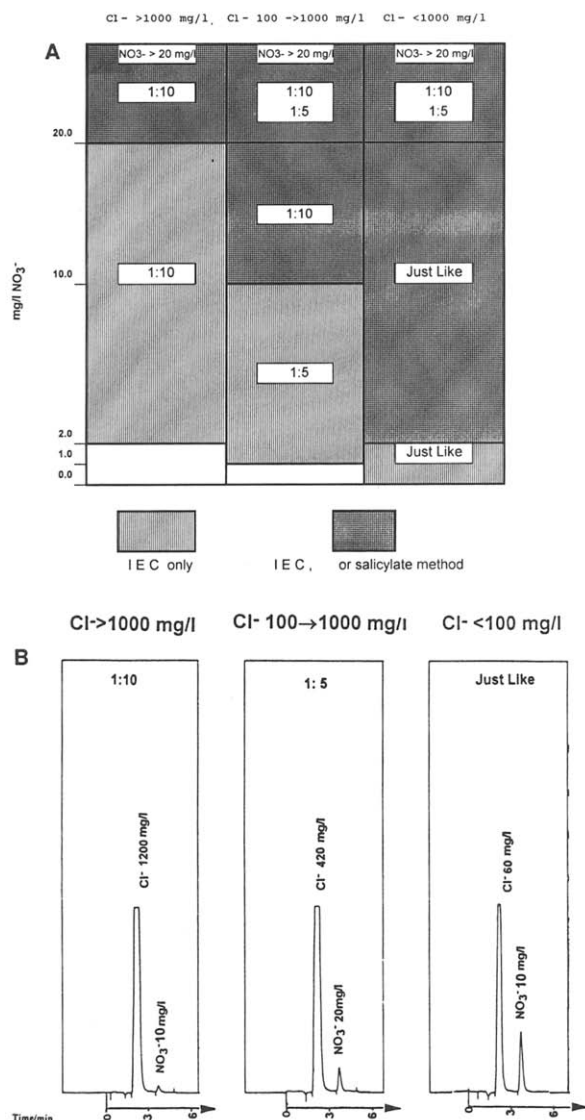


Fig. 1. (A) Chloride interferences in the nitrate determination. (B) Chromatograms of variable chloride–nitrate ratio.

when nitrates are higher than 20.0 mg/l, with dilution 1:5 or 1:10.

(c) Cl⁻ < 100 mg/l, when nitrates are higher than 0.2 mg/l, without dilution, and when nitrates are higher than 20.0 mg/l, with dilution 1:5, or 1:10.

The most suitable dilutions for the simultaneous determination of nitrate and chloride are shown in Fig. 1B.

This study also verified that, in complex matrices analysis, excellent results can be obtained by IEC. The advantages include:

(1) Simultaneous reduction in interferences, either organic or inorganic. Also, when the chemical oxygen demand (COD) value was higher than 100 mg/l as oxygen, it was possible to determine nitrates without organic anion interferences. Coloured compounds that may influence the UV or visible measurements did not cause any problems.

(2) Rapid and sequential analysis that allows different anions to be determined simultaneously.

(3) Elimination of hazardous reagent use.

(4) Small samples volumes are required.

(5) The greater sensitivity of the IEC method allows the analysis of samples with a low concentration of nitrate, but high concentration of chloride, for which the dilution is necessary.

For all these reasons, it is to be hoped that in future the ion-exchange chromatography method becomes an approved national procedure.

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