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### Automatic System for Simultaneous Determination of Nitrates and Nitrites in Waters

J. Maimó<sup>a</sup>; A. Cladera<sup>a</sup>; F. Mas<sup>a</sup>; R. Forteza<sup>a</sup>; J. M. Estela<sup>a</sup>; V. Cerdá<sup>a</sup>

<sup>a</sup> Department of Chemistry, Univ. Illes Balears, Palma de Mallorca, Spain

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## AUTOMATIC SYSTEM FOR SIMULTANEOUS DETERMINATION OF NITRATES AND NITRITES IN WATERS

J. MAIMÓ, A. CLADERA, F. MAS, R. FORTEZA, J. M. ESTELA and V. CERDÁ

*Department of Chemistry, Univ. Illes Balears. E-07071, Palma de Mallorca, Spain*

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An automatic FIA system for simultaneous determination of nitrates and nitrites in waters is described.

The method is based on the classical azodye reaction for nitrites. The sample is split into two flows: (a) one is directly treated with the azodye reagent and sent to the sample flow cell of a double beam spectrophotometer, which gives positive absorbance values, allowing direct determination of nitrites in the sample, (b) the other flow goes through a cadmium reduction microcolumn, where nitrates are reduced to nitrites. The sample is then treated with the azodye reagent and the overall mixture is sent to the reference cell of the same double beam spectrophotometer, which gives negative peaks corresponding to the sum of the absorbances of nitrates and nitrites. Thus deducing the nitrate content in the original sample from the difference.

The procedure has been automatized by connecting a digital potentiometer, provided with a RS232C interface, to the register output of the spectrophotometer. The potentiometer is used as a data acquisition interface for an Amstrad 128 microcomputer.

A specific program has been developed, allowing: (a) data storage of the successive experiments, (b) data treatment for calculation of the calibration curves and automatic reports of the samples nitrates and nitrites contents.

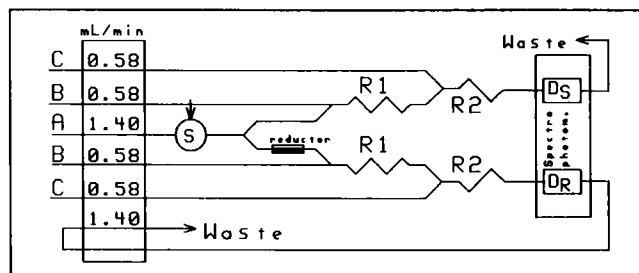
**KEY WORDS:** Nitrates, nitrites, water, FIA, azodye reaction, spectrophotometry, automation.

### INTRODUCTION

Nitrites are dangerous for health, since they may be metabolized to cancerous nitrosamines. Nitrates, on the other hand, are essential for life, but also may be harmful in high concentrations, as they could be transformed into nitrites by the organism.

The wide and uncontrolled use of nitrogenated fertilizers may dramatically increase the nitrate concentration in underground waters. Therefore, nitrite and nitrate concentrations are routine parameters to be determined in potentially polluted waters, flow injection analysis (FIA) thus being a very appropriate technique when a great number of samples are to be considered.

Anderson<sup>1</sup> determined nitrites and nitrates in sea, drinking and waste waters, injecting the sample into a carrier which was split in two flows. The reagents were then added in each channel, one of them having a cadmium microcolumn in order



**Figure 1** Flow diagram for the simultaneous colorimetric determination of nitrites and nitrates. (a) Carrier stream, (b) sulfanilamide solution, (c) N-(1-naphthyl)ethylenediammonium dichloride solution. S: injection valve, R1: 10 cm reaction coils, R2: 30 cm reaction coils.

to reduce nitrates to nitrites. This method presents very favourable determination limits, yet sample throughput is not very high.

Bergamin *et al.*<sup>2</sup> increased the cadence up to 90 samples per hour based on the merging zone method, and using a two position switching injector, one for the sum of nitrates and nitrites, the other for only nitrites. It is a sequential technique using only one detector.

Van Staden<sup>3</sup> introduced a modified method, where the nitrates were reduced in a microcolumn placed in one of the loops of a double injection valve.

Finally, Shu-Un *et al.*<sup>4</sup> substituted the N-(1-naphthyl)ethylenediamine by the  $\alpha$ -naphthylamino-7-sulphonic acid which is a non-cancerous compound.

In a research line directed towards analytical automation, a number of different techniques were developed in our laboratory: potentiometric,<sup>5</sup> conductometric, thermometric<sup>6</sup> and spectrophotometric titrations, fluorometry,<sup>7</sup> kinetic spectrophotometry, and potentiometric stripping analysis. Once having an automated technique, specific applications of interest in routine analysis, mainly in the pollution field, were established.

In this paper, we have worked on automatic routine procedures based on the use of the simple and quick FIA technique. Automatic and simultaneous nitrates and nitrites determination, was selected due to its interest indeed, from the practical point of view.

## EXPERIMENTAL

### *Apparatus and manifold*

Figure 1 represents the schematic diagram of the automatic spectrophotometric FIA system, which was constituted by:

- Gilson Minipuls 2 peristaltic pump, 8 channels.
- Rheodyne 50 injection valve.
- Thermostat.
- ACTA CIII double beam spectrophotometer, provided with two spectrophotometric flow-through cells of 18  $\mu$ L and 1,000 cm.

- Crison Digilab 501 potentiometer, with RS232C interface.
- Amstrad CPC6128, provided with a RS232C interface and floppy disk for data massive storage.

All reactor coils and sample loop tubes were made of PTFE (0.5 mm i.d.).

### Reagents

All reagents were of analytical-reagent grade were prepared as in the original paper.<sup>1</sup> Cadmium granules (0.5 mm) were coated with copper by dipping them into a  $\text{CuSO}_4$  1% solution. The reduction glass tube (60 mm long and 1 mm i.d.) was filled with copperized cadmium, and held in position with glass wool plugs:

- The carrier was a 0.4 M  $\text{NH}_4\text{Cl}$  and 0.3 M  $\text{NaCl}$  solution.
- 2.5 g of sulfanilamide were dissolved in 13 mL of concentrated hydrochloric acid and diluted with the carrier to 250 mL.
- 0.25 g of N-(1-naphthyl)ethylenediamine and 10 g of  $\text{NaCl}$  were dissolved and diluted to a final volume of 250 mL with the carrier.
- 0.001 M standard stock solutions of sodium nitrate and sodium nitrite were prepared in 0.7 M sodium chloride. Working standard solutions were obtained by diluting the stock solutions with 0.7 M sodium chloride.

### Procedure

Samples were injected into the carrier, which was then split into two flows:

a) One was directly treated with the azodye reagent and sent to the *sample* flow cell of the double beam spectrophotometer, giving *positive* peaks. This allowed direct determination of nitrites in the sample.

b) The other flow went through the cadmium reduction microcolumn, where nitrates were reduced to nitrites. The sample was then treated with the same azodye reagent and the overall mixture sent to the *reference* flow cell of the same double beam spectrophotometer, giving *negative* peaks as a result of the sum of the absorbances of nitrates and nitrites. Thus deducing the nitrate content in the original sample from the difference. Due to the longer residence times, these peaks merged after the positive ones.

Aspiration was performed with the peristaltic pump in order to compensate the resistance of the reduction column.

When nitrates were injected, negative peaks were obtained since their absorbance was measured in the reference cell, whereas nitrites gave both positive (sample flow cell) and negative peaks (reference flow cell). Diagrams are represented in Figure 2.

### SOFTWARE

The software was built taking into account the RS232C communication protocols

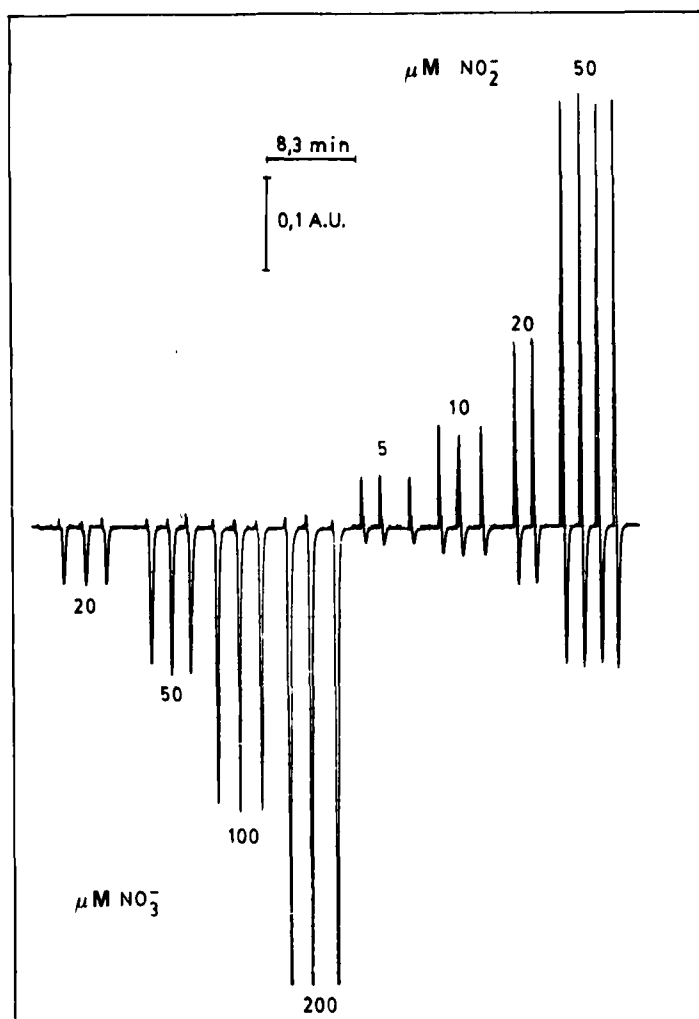


Figure 2 Simultaneous determination of nitrites and nitrates.

of both the CRISON potentiometer and Amstrad 128 computer, which are stored in their corresponding EPROM and ROM.

From the analytical point of view, the obtained data might then be treated in two different ways:

a) Using two calibration curves, one for the positive peaks of nitrites, the other for the negative peaks of nitrates. Nitrite concentrations might be deduced from the first calibration curve, whereas the second would give the sum of nitrites and nitrates, thus deducing the nitrate content from the difference.

b) Using three calibration curves, one for the negative nitrate peaks, the second for the nitrite positive peaks, the third for the nitrite negative peaks. Nitrite

concentration could be directly deduced from the second curve. In order to calculate the nitrate content, the negative signal corresponding to nitrites had to be first deduced from the third calibration curve and subtracted from the overall negative peak signal, thus giving the nitrate from the first calibration curve.

We preferred to use the second option, as different signal response from the two detectors was expected, due to the great difficulties in obtaining equivalent flows through both sample and reference cells.

The developed program is constituted by two different parts: (a) one for the obtention of calibration curves, and (b) the data obtention and treatment of unknown samples.

#### *a) Calibration curves*

When this option is selected, the screen is divided in three windows: (1) in the first (top-left), diagrams are represented, which allows us to monitor the validity of the acquired data, (2) in the second (bottom-left), an optional menu and computer messages are displayed, and (3) in the third the data obtained in each measure is displayed, i.e. maximum and minimum of the peaks.

The analyst may introduce the successive standards in any desired order, with their corresponding concentrations. Once all standards have been introduced, the computer makes the graphics representation of the experimental data and the calibration curves. By menu, the undesired points may be removed, additional standards introduced, or the overall process aborted.

Once all the calibration curves have been confirmed, the computer saves their equations and correlation coefficients on a floppy disk and, optionally, a printed hardcopy of all points and equations may be obtained.

Once the calibration curves have been saved, it is only needed to confirm their validity from time to time by injecting new standards.

#### *b) Sample determination*

The corresponding part of the program performs data acquisition of each sample, computes the maximum and minimum of the curves and, from the calibration curves, the nitrates and nitrites concentrations are automatically deduced.

The computer screen has been organized in a similar way than for the calibration subroutine. The maximum and minimum of each peak are displayed in the window for results, together with the concentrations computed for nitrates and nitrites. The acquired data may be saved on a floppy disk.

Calculations may be performed from the data obtained directly, as well as from those previously saved in magnetic memory.

If the data are saved during the process, any desired number of injections for each sample may be carried out. However, only four measurements for each sample may be simultaneously displayed on the screen.

**Table 1** Linear interval for nitrates and nitrites determination

<i>1: nitrates</i> <i>Linear interval: 10–200 μm</i>			<i>2: nitrites</i> <i>Linear interval: 2.5–50 μm</i>			<i>3: nitrites</i>		
<i>Samp.</i>	<i>Conc.</i>	<i>Peak height</i>	<i>Samp.</i>	<i>Conc.</i>	<i>Peak height</i>	<i>Samp.</i>	<i>Conc.</i>	<i>Peak height</i>
1	0	–0.006	1	0	–0.006	1	0	0.011
2	20	–0.066	2	5	–0.022	2	5	0.065
3	50	–0.165	3	10	–0.033	3	10	0.118
4	100	–0.315	4	20	–0.065	4	20	0.211
5	200	–0.594	5	50	–0.160	5	50	0.472

**Table 2** Analytical performances of the method

<i>Sample conc.</i>	<i>Found</i>			<i>Average</i>	<i>Error %</i>	<i>σ</i>
10 μM NO <sub>2</sub> -	10.94	10.90	10.29	10.7	7	0.36
40 μM NO <sub>3</sub> -	36.08	47.47	37.79	40.4	1	6.14
5 μM NO <sub>2</sub> -	4.13	4.85	4.12	4.4	12	0.42
20 μM NO <sub>3</sub> -	18.5	17.55	20.8	18.9	5.5	1.67
5 μM NO <sub>2</sub> -	4.12	3.92		4.1	18.0	0.14
200 μM NO <sub>3</sub> -	208.9	210.78		209.8	4.9	1.33
20 μM NO <sub>2</sub> -	26.39	20.66	20.69	22.6	13	3.30
20 μM NO <sub>3</sub> -	14.06	17.8	20.7	17.5	12.5	3.32
50 μM NO <sub>2</sub> -	46.58	46.77		46.7	6.6	0.13
100 μM NO <sub>3</sub> -	108.02	105.87		106.9	6.9	1.52
50 μM NO <sub>2</sub> -	50.52	51.78		51.2	2.4	0.89
0 μM NO <sub>3</sub> -	–0.14	–0.86		—	—	—
5 μM NO <sub>2</sub> -	4.97	5.48		5.2	4	0.36
0 μM NO <sub>3</sub> -	–3.73	—		—	—	—
50 μM NO <sub>2</sub> -	48.16	45.68		46.9	1.85	1.75
0 μM NO <sub>3</sub> -	–0.21	–0.55		—	—	—
200 μM NO <sub>2</sub> -	201.6	207.6		204.6	2.3	4.25
0 μM NO <sub>3</sub> -	–0.75	–0.39		—	—	—

Optionally, hardcopy of the results may be printed for each work session. These results are ordered according to the sample number and the order number for each sample.

## RESULTS

In Tables 1 and 2, the application range for nitrates and nitrites are shown, together with the reproducibility of the methods and determination errors. The frequency of the analysis was up to 60 samples per hour.

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