

Speciation of Nitrogen in Wastewater by Flow Injection

The
Analyst

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A rapid method for the sequential determination of nitrite, nitrate and total nitrogen is proposed. Nitrite was determined directly by using the Griess reaction, which was also used to quantify nitrate after reduction to nitrite with hydrazine. For total nitrogen determination, the nitrogen-containing compounds (organic substances and nitrite and ammonium ions) were oxidized photochemically using a UV lamp and converted into nitrate, which was then reduced to nitrite and determined spectrophotometrically. Under the optimized conditions, up to $220 \mu\text{mol l}^{-1} \text{N-NO}_2^-$ and $240 \mu\text{mol l}^{-1} \text{N-NO}_3^-$ can be determined, the detection limits being $2 \mu\text{mol l}^{-1} \text{N-NO}_2^-$ and $8 \mu\text{mol l}^{-1} \text{N-NO}_3^-$. The relative standard deviation for nitrite and nitrate are 1.5 and 2.3%, respectively. The photo-oxidation method for total nitrogen determination has a linear range of 30–1000 $\mu\text{mol l}^{-1} \text{N}$, with a relative standard deviation of 3%. The proposed method was applied to the determination of nitrate, nitrite and total nitrogen in wastewaters.

Keywords: Photo-oxidation; flow injection; total nitrogen; nitrate; nitrite; speciation

Introduction

Many methods have been proposed for the determination of inorganic nitrogen compounds (nitrite, nitrate and ammonium ions) and some of them have been adapted to automated procedures for their application for routine analysis.

Usually, the determination of nitrite is based on the Griess reaction: the diazotization of nitrite ion with sulfanilamide in acidic medium, followed by reaction with *N*-(1-naphthyl)-ethylenediamine, gives an azo dye with a maximum absorption at 540 nm. The dye formation can be easily monitored spectrophotometrically. Nitrate can be determined using the same reaction by prior reduction to nitrite. One of the most frequently employed flow injection (FI) methods for the reduction of nitrate to nitrite is that involving a copper-coated cadmium column.^{1–12} However, the interference of phosphate^{13,14} and the need for frequent recalibration make the method inappropriate for continuous analysis of samples with complex matrices (*e.g.*, wastewaters). Furthermore, the method has to be rejected when using strong oxidants such as persulfate that may destroy the column. Reduction by hydrazine either in a batch^{15,16} or in a continuous^{17–19} mode has been successfully applied as an alternative to the Cd–Cu method with the advantage that less calibration steps are needed.

For the determination of total nitrogen, the organic nitrogen-containing substances are first converted into inorganic compounds (usually nitrate or ammonium ion). Different batch methods for the determination of total nitrogen have been developed to overcome the drawbacks of the traditional

Kjeldahl method (tedious, time-consuming and subject to contamination). In 1969, Koroleff²⁰ developed a method based on the oxidation to nitrate using alkaline persulfate. The high temperature and pressure required were achieved by using an autoclave. The method was applied to the analysis of natural waters and sea-water,²¹ effluents from sewage sludge plants²² and soil extracts.²³ Although this method allowed better recoveries for compounds with N–N and N–O linkages²⁴ than the Kjeldahl digestion, it was still too slow for monitoring purposes. Replacing the autoclave with a microwave furnace^{25,26} substantially shortens the digestion time.

One other alternative involved irradiation of the sample with UV light in the presence of an oxidizing reagent (typically hydrogen peroxide or persulfate ion). This approach, proposed by Armstrong and co-workers^{27,28} for the determination of organic carbon, nitrogen and phosphorus in sea-waters, was later modified and applied by other workers^{29,30} to fresh and natural waters. Segmented^{31,32} and non-segmented^{33–35} flow systems with high sampling frequencies have been described. The nitrogen compounds are photo-oxidized and converted into nitrate on-line. The determination of the resulting nitrate is achieved either by direct detection in the UV region,³⁵ or by reduction with a Cd–Cu column^{31,33,34} or with the Devarda alloy.³²

In this paper an FI system for the sequential determination of nitrite, nitrate and total nitrogen in wastewaters is proposed. The method used for nitrite determination is based on the Griess–Ilosvay reaction and was chosen on the grounds of its high sensitivity and selectivity. The same reaction is used to determine nitrate, following reduction to nitrite ion. The hydrazine method for the reduction of nitrate was chosen because of the drawbacks of the Cd–Cu column reduction method for wastewater analysis, as mentioned above.

For total nitrogen determination the photo-oxidation method was chosen. In the presence of persulfate and UV light, organic nitrogen-containing compounds, ammonium and nitrite are converted into nitrate, which is determined as described. The method was applied to the determination of nitrite, nitrate and total nitrogen in raw and treated urban wastewaters.

Experimental

Apparatus

The FI manifold (Fig. 1) consisted of a Rheodyne (Cotati, CA, USA) 5020 injection valve with a loop of 90 μl , and two Rheodyne 5011 selector valves (SVA and SVB in Fig. 1). By using two peristaltic pumps (Gilson (Worthington, OH, USA) Minipuls Models 2 and 3), the aspiration rate for the sample and oxidizing solution was adjusted separately from that for the other reactants. Once flow rates were optimized, a single pump with appropriate tubing could be used. The UV light source was a Heraeus 15 W mercury lamp, with maximum emission at 254 nm, surrounded by an aluminium reflector and cooled by means of an electric fan. Spectrophotometric measurements were made on a Hewlett-Packard (Avondale, PA, USA) HP 8452 diode-

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array detector equipped with a flow-through cell of 18 μl inner volume and 1 cm pathlength.

Both the reactors and the injection loop were constructed from PTFE tubing of 0.5 mm id. The dimensions of the reaction coils are shown in Fig. 1. The temperature was maintained constant by means of a thermostated bath incorporated into the FI manifold. The de-bubbler was a T-piece made of methacrylate in which the photo-oxidized sample, entering from the left, was aspirated with a flow rate of 0.36 ml min^{-1} through the bottom of a conical inner chamber while bubbles and spare flow left for waste through the upper side (Fig. 1).

For nitrate and nitrite determination, the sample was passed through a column packed with XAD-7 non-ionic resin (Amberlite, $480 \text{ m}^3 \text{ g}^{-1}$, 80 Å, 20–50 mesh) before being injected into the FI manifold. The pre-column ($30 \times 1 \text{ mm id}$) was inserted into the sample aspiration channel in order to avoid potential interferences from organic matter. The resin was chosen on the basis of the results obtained by Freeman *et al.*,³⁶ which showed that the non-ionic resins are the most effective in eliminating interference due to organic matter. The XAD-7, a polar poly(methacrylate) resin, is similar in characteristics to that proposed by these workers.

Other manifold designs were tested in order to overcome the problems arising from the high concentrations of persulfate necessary for the oxidation step. An alternative configuration with an additional line of hydrogensulfite, merging with the photo-oxidized sample as proposed by McKelvie *et al.*,³³ was investigated but it did not improve the performance of the system shown in Fig. 1.

Reagents

All the reagents used were analytical-grade chemicals and included the following.

Alkaline persulfate, R1. This contained 15 g l^{-1} potassium persulfate and 3.5 g l^{-1} sodium tetraborate for pH adjustment. The solution was prepared daily by appropriate dilution of a stock containing 40 g l^{-1} $\text{K}_2\text{S}_2\text{O}_8$ and 35 g l^{-1} $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$.

Working reductant, R2. This contained 3 g l^{-1} hydrazine sulfate, 0.006 g l^{-1} CuSO_4 , 1 g l^{-1} ZnSO_4 and 20 g l^{-1} NaOH. This reagent is unstable, so it must be prepared daily from a stock consisting of 10 g l^{-1} $\text{N}_2\text{H}_6\text{SO}_4$, 1 g l^{-1} CuSO_4 , 80 g l^{-1} NaOH and 10 g l^{-1} ZnSO_4 .

Chromogenic reagent, R3. This consisted of 20 g of sulfanilamide, 0.5 g of *N*-(1-naphthyl)ethylenediamine (NED) and 25 ml of concentrated HCl (37%, $d = 1.19 \text{ g ml}^{-1}$).

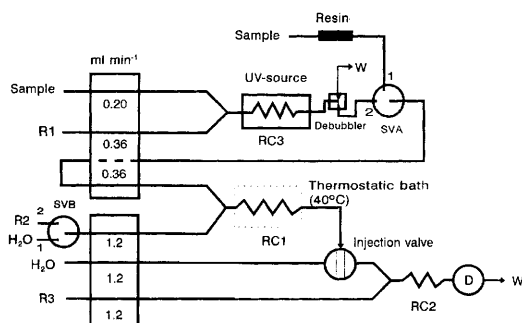


Fig. 1 The FI arrangement for determination of nitrite, nitrate and total nitrogen. R1, persulfate alkaline solution; R2, reducing solution; R3, chromogenic reagent; Resine, Amberlite XAD-7 ($480 \text{ m}^3 \text{ g}^{-1}$; 8 nm, 20–50 mesh); UV-source, ultraviolet lamp (15 W, 254 nm); injection volume, 90 μl ; SVA, SVB, selection valves; RC1, reaction coil ($2 \text{ m} \times 0.5 \text{ mm id}$); RC2, reaction coil ($1 \text{ m} \times 0.5 \text{ mm id}$); RC3, photo-oxidation coil ($3 \text{ m} \times 0.5 \text{ mm id}$); W, waste; D, detector (540–420 nm).

Nitrate and nitrite stock solutions, 0.001 mol l^{-1} . Prepared from their sodium salts and used to prepare working standard solutions by appropriate dilution.

Model nitrogen compounds. In order to evaluate the photo-oxidation efficiency, ammonium chloride, urea, aspartic acid, barbituric acid, nicotinic acid, glutamic acid, EDTA and glycine stock solutions with a nitrogen content of 1 g l^{-1} each were used. All these reagents were >98% pure.

All working standard solutions were prepared by dilution from the stocks.

Procedure

The proposed FI assembly (Fig. 1) allows the sequential determination of nitrite, nitrate and total nitrogen in the same sample by actuating the switching valves (SVA and SVB) as appropriate.

Joint determination of nitrate and nitrite

The sample was aspirated (*via* the pre-column) through port 1 of SVA and mixed with the reductant solution (R2), which was aspirated *via* port 2 of SVB. The resulting stream was passed through reactor RC1 ($2 \text{ m} \times 0.5 \text{ mm id}$), which was heated by immersion in a thermostated bath at 40°C in order to accelerate the reduction. The emerging solution was injected into a distilled water carrier that was then merged with the chromogenic reagent (R3). The absorbance of the azo dye formed was monitored at 540 nm. Spectral oscillations caused by changes in the refractive index were corrected for by subtracting the absorbance at 420 nm, where the absorbance of the reaction product was virtually zero.

Determination of nitrite

The nitrite content in the original sample was determined directly by using the Griess reaction under non-reductive conditions. For this purpose, both switching valves were turned to position 1, so that the hydrazine solution was replaced with distilled water, and the above-described procedure for the joint determination of nitrate and nitrite was repeated.

Determination of total nitrogen

The oxidation of nitrogen-containing compounds and the determination of total nitrogen were addressed by using SVA in position 2. The sample was mixed with alkaline persulfate (R1) and propelled by the peristaltic pump to the photoreactor (RC3, a piece of PTFE tubing of $3 \text{ m} \times 0.5 \text{ mm id}$ coiled around the UV lamp) where ammonium, nitrite and organic nitrogen-containing compounds were converted into nitrate ion. The de-bubbler at the photoreactor outlet facilitated the sweeping of bubbles, formed during the photo-oxidation process, to waste. Only part of the photo-oxidized sample was introduced into the FI system for the determination of nitrogen content by the above-described procedure for nitrate and nitrite, while the remainder left for waste together with the bubbles formed during photo-oxidation.

Also, while SVA was turned to position 1 to determine nitrate and nitrite in the unmineralized sample, the photo-oxidized sample was sent to waste *via* the de-bubbler.

Results and Discussion

Photo-oxidation Conditions

Preliminary experiments were carried out in order to examine the influence of the irradiation time, oxidant concentration and nitrogen content on the mineralization process by using various model nitrogen-containing compounds.

The models were chosen on the grounds of chemical structure. They included substances frequently occurring in wastewaters (ammonia and urea), straight-chain amino acids (glycine, glutamic acid and aspartic acid), cyclic amino acids (nicotinic acid) and other types of compound usually employed in mineralization studies (EDTA and barbituric acid). Initially, experiments were performed by using solutions containing $1 \text{ mg l}^{-1} \text{ N}$ and 4 g l^{-1} persulfate, and an irradiation time of 40 s. Under these conditions, conversion was always below 100% (about 90% for glycine, ammonium chloride and urea, and less than 75% for EDTA and nicotinic, barbituric and aspartic acid). Increasing the irradiation time to 80 s resulted in no significant improvement in the photo-oxidation yield. However, if the persulfate concentration was simultaneously raised, per cent. conversions increased substantially. The effect of the two variables was therefore studied simultaneously. Hence the persulfate concentration was varied between 4 and 20 g l^{-1} at various irradiation times from 40 to 80 s (adjusted by varying the photoreactor feeding flow rate, *viz.*, the summation of those for the sample and persulfate, between 0.4 and 0.9 ml min^{-1}).

A persulfate concentration of 6 g l^{-1} resulted in 80–100% mineralization at all the irradiation times tested. Increasing irradiation time gave rise to increasing photo-oxidation yield for all the compounds studied except for ammonium chloride, which exhibited the opposite trend probably owing to some ammonium being volatilized (as ammonia) during the digestion process.

Irradiation times longer than 50 s resulted in no significant improvement and prolonged the mineralization time unduly. A persulfate concentration of 6 g l^{-1} and an irradiation time of 50 s were therefore used in subsequent experiments.

The effect of the nitrogen content in the samples was also examined. Solutions of test substances with nitrogen concentrations ranging between 1 and $14 \text{ mg l}^{-1} \text{ N}$ were photo-oxidized and analysed. Recoveries were calculated in each instance and plotted against the nitrogen concentration (Fig. 2). Irradiation of solutions containing concentrations below $7 \text{ mg l}^{-1} \text{ N}$ resulted in photo-oxidation yields of 80–100% for all the compounds tested. As the concentration was raised, the mineralization efficiency decreased and was incomplete above 10 mg l^{-1} .

Using the optimized conditions ($[\text{K}_2\text{S}_2\text{O}_8] = 6 \text{ g l}^{-1}$, $t = 50 \text{ s}$), several raw and treated urban wastewaters were analysed; the samples were diluted in order to have a final nitrogen concentration lower than 10 mg l^{-1} . The nitrogen content determined in the unoxidized sample under reductive conditions

was subtracted from that in the photo-oxidized sample and the result compared with the Kjeldahl nitrogen value. The photo-oxidation results were always smaller than the Kjeldahl nitrogen values, as noted by other workers.^{30,37} This may be due to the presence of high levels of organic matter which decreases the amount of oxygen available for oxidizing nitrogen-containing compounds, since part of the oxygen is used to form other compounds, *e.g.*, CO_2 . The problem was solved by raising the concentration of oxidizing reagent up to 15 g l^{-1} . Higher concentrations should be avoided because of the large number of bubbles formed, which interfere with the detection step, while concentrations lower than 12 g l^{-1} are not sufficient for quantitative photo-oxidation of the nitrogen compounds occurring in wastewaters.

The influence of the flow rate ratio of sample (q_s) to oxidant (q_{R1}) was finally examined using urea standards and real samples at $q_{R1} : q_s$ ratios from 0.3 to 2. The optimum flow rates were chosen in order to ensure excess of persulfate even when samples with a high nitrogen content had to be analysed. The final ratio was $q_{R1} : q_s = 1.8$, adjusted as shown in Fig. 1. In this way the irradiation time was 50 s.

Analytical Performance

Calibration graphs were obtained and wastewaters analysed under the conditions given in Fig. 1 using a persulfate concentration of 15 g l^{-1} . The determination of nitrate, nitrite and total nitrogen in the sample entailed constructing four different calibration graphs.

The graph for the determination of nitrite [eqn. (A)] was constructed from sodium nitrite standards of various concentrations under non-reductive conditions. The graph was linear up to $220 \mu\text{mol l}^{-1} \text{ N}$ and the resulting detection limit was $2 \mu\text{mol l}^{-1} \text{ N}$. The calibration equation was:

$$\text{Absorbance (AU)} = 2.00 [\text{mmol l}^{-1} \text{ N}] - 0.0024 \quad (r^2 = 0.9999) \quad (\text{A})$$

The calibration graph for the joint determination of nitrate and nitrite [eqn. (B)] was obtained from sodium nitrate standards that were aspirated through the resin and quantified under reductive conditions. The graph was linear up to $240 \mu\text{mol l}^{-1} \text{ N}$ and the detection limit was $8 \mu\text{mol l}^{-1} \text{ N}$. The graph equation was:

$$\text{Absorbance (AU)} = 1.23 [\text{mmol l}^{-1} \text{ N}] + 0.0018 \quad (r^2 = 0.9998) \quad (\text{B})$$

The graph for the determination of nitrite under reductive conditions [eqn. (C)] was constructed from nitrite standards under reductive conditions and was linear over the range $6\text{--}217 \mu\text{mol l}^{-1} \text{ N}$. The detection limit was $6 \mu\text{mol l}^{-1} \text{ N}$. The calibration equation was:

$$\text{Absorbance (AU)} = 1.20 [\text{mmol l}^{-1} \text{ N}] - 0.002 \quad (r^2 = 0.9998) \quad (\text{C})$$

Finally, the graph for the determination of total nitrogen [eqn. (D)] was obtained by aspirating sodium nitrate solutions of various concentrations, followed by irradiation and analysis. The graph was linear up to $1000 \mu\text{mol l}^{-1} \text{ N}$ and the detection limit was $30 \mu\text{mol l}^{-1} \text{ N}$. The calibration equation was:

$$\text{Absorbance (AU)} = 0.43 [\text{mmol l}^{-1} \text{ N}] + 0.02 \quad (r^2 = 0.9993) \quad (\text{D})$$

From the ratio of the slopes of calibration graphs (A) and (C) it follows that the absorbance of a nitrite standard under reductive conditions was 60% of that under non-reductive conditions. From the ratio of calibration graphs (B) and (C) it follows that the percentage conversion of nitrate into nitrite is nearly 100%.

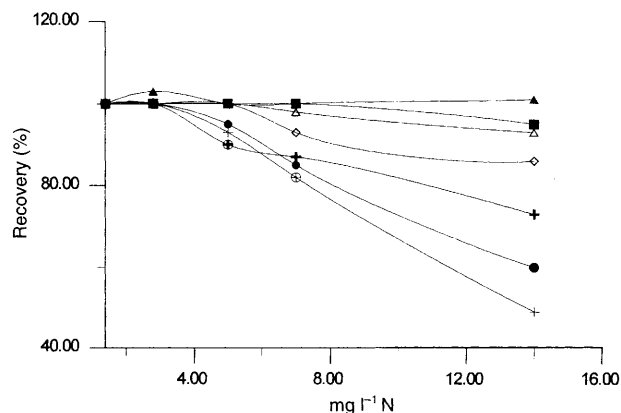


Fig. 2 Influence of the nitrogen content in the photooxidation yields for several nitrogen-containing compounds. ◇, Urea; △, EDTA; +, nicotinic acid; ●, glycine; ■, barbituric acid; ▲, aspartic acid; ○, glutamic acid; and +, ammonium ion.

Speciation

The nitrite content in the samples was determined by direct interpolation on calibration graph (A) of the signal obtained under non-reductive conditions.

The results obtained under reductive conditions allowed the summation of nitrate and nitrite to be performed. If nitrate is to be determined in the original sample, its content can be calculated by subtracting that for nitrite.

The analytical determination of nitrate in the sample following photo-oxidation (by means of calibration graph D), provides the total nitrogen content. This includes nitrate and nitrite in the original sample. In order to obtain total Kjeldahl nitrogen (TKN), the nitrogen content in the photo-oxidized sample is subtracted from that in the unoxidized sample analysed under reductive conditions.

Reproducibility

The reproducibility of the reduction-detection process was determined by using sodium nitrate and nitrite standards. For this purpose, ten successive injections of a $80 \mu\text{mol l}^{-1}$ N-NO_3^- solution were carried out under reductive conditions, and ten injections of $100 \mu\text{mol l}^{-1}$ N-NO_2^- under non-reductive conditions. The relative standard deviations (s_r) thus obtained were 2.3% for nitrate and 1.5% for nitrite. The reproducibility of the photo-oxidation process was studied by aspirating and mineralizing ammonium and urea standards containing $400 \mu\text{mol l}^{-1}$ N. The s_r values obtained from ten injections were 3 and 2.7%, respectively.

Interferences

The interference from foreign ions in the reduction of nitrate to nitrite was examined. No interference due to the following ions and concentrations was observed: Ca^{2+} , 200 mg l^{-1} ; Mg^{2+} , 200 mg l^{-1} ; Fe^{3+} , 100 mg l^{-1} ; Zn^{2+} , 100 mg l^{-1} ; Ni^{2+} , 100 mg l^{-1} ; NH_4^+ , 100 mg l^{-1} ; Cl^- , 500 mg l^{-1} ; SO_4^{2-} , 500 mg l^{-1} ; CO_3^{2-} , 500 mg l^{-1} ; and PO_4^{3-} , 500 mg l^{-1} . Concentrations as low as 6 mg l^{-1} of Cr^{2+} and Cr^{3+} at 10 mg l^{-1} , adversely affected the reduction of nitrate to nitrite. Potential interferences in the Griess reaction are well established and were not re-examined. With respect to the photo-oxidation step, the interference effect on the digestion process from organic matter was also studied. For this purpose different concentrations of carbon in the form of glucose, ranging from 1 to 24 mmol l^{-1} C, were added to solutions of 1 mmol l^{-1} N-urea. For a molar relationship N/C of 1/20 the signal decrease was approximately 10%, but no interferent effect was observed at lower carbon concentrations.

Analysis of Real Samples

Samples were analysed directly, with no pre-treatment. For the determination of nitrate and nitrite in the unoxidized sample, the sample was aspirated through a column packed with XAD-7 resin in order to remove organic matter.

For the determination of total nitrogen (TN), all samples were mixed with persulfate, irradiated and processed. The high nitrogen content in the wastewater samples required a prior dilution in order to ensure a linear working range. The results obtained after the analysis of several samples collected at the inlet and outlet of different wastewater treatment plants are compared with those obtained by the Kjeldahl digestion method (Table 1). The TN values of 26 samples obtained using the UV-FI method were plotted against the $\text{TKN} + \text{N-NO}_2^- + \text{N-NO}_3^-$ values. The regression equation thus obtained was:

$$\text{TN (UV-FI)} = 1.05 \text{ TN (TKN} + \text{N-NO}_2^- + \text{N-NO}_3^-) - 1.00$$

($n = 26$)

Several samples with nitrate and nitrite contents below the detection limits were spiked with various amounts of nitrate and/or nitrite. The results obtained are summarized in Table 2.

An example of the FI signals obtained using the proposed FI configuration is given in Fig. 3.

Conclusions

The proposed FI system allows the speciation of nitrogen-containing compounds in wastewaters. It constitutes a rapid choice for the determination of nitrate, nitrite and total nitrogen in the same sample (all three parameters can be quantified in less than 15 min). The mineralization involved is achieved by irradiation with a UV lamp. The digestion time is fairly short (50 s under the conditions used in this work). The photo-

Table 1 Results of the analysis of raw (in) and treated (out) wastewater samples ($t = 50 \text{ s}$, $[\text{K}_2\text{S}_2\text{O}_8] = 15 \text{ g l}^{-1}$)

Sample	TKN*/ mg l^{-1} N	N-NO ₂ ⁻ / mg l^{-1} N	N-NO ₃ ⁻ / mg l^{-1} N	Total nitrogen Photo- oxidation/ mg l^{-1} N	TKN* + NO ₂ ⁻ + NO ₃ ⁻ / mg l^{-1} N
1 in	43.4	ND†	ND	46.1	43.4
1 out	39.2	ND	ND	43.0	39.2
2 in	50.4	ND	ND	46.4	50.4
2 out	40.6	ND	ND	40.5	40.6
3 in	50.0	ND	ND	47.8	50.0
3 out	42.1	ND	ND	41.2	42.1
4 in	72.6	ND	ND	72.2	72.6
4 out	48.8	ND	3.6	55.9	52.4
5 in	58.6	ND	ND	65.8	58.6
5 out	11.6	2.3	12.8	26.8	26.7
6 in	80.0	ND	ND	98.1	80.0
6 out	4.9	ND	ND	2.5	4.9
7 in	133.0	ND	ND	135.6	133.0
7 out	7.3	ND	18.1	29.1	25.5
8 in	80.9	ND	ND	82.6	80.9
8 out	9.8	50.1	0.3	58.2	60.2
9 in	84.2	ND	ND	90.5	84.2
9 out	11.6	1.0	14.4	29.8	27.0
10 in	76.9	ND	ND	76.3	76.9
10 out	6.7	ND	14.1	19.9	20.8
11 in	89.1	ND	ND	101.6	89.1
11 out	14.4	ND	0.2	14.5	14.6
12 in	76.9	ND	ND	78.4	76.9
12 out	5.1	ND	ND	ND	5.1
13 in	82.4	ND	ND	75.6	82.4
13 out	15.9	0.2	22.1	38.1	38.2

* TKN = Total Kjeldahl nitrogen.

† ND = Not detected.

Table 2 Results obtained for wastewater samples spiked with various amounts of nitrate and nitrite

Sample	NO ₂ ⁻ added/ mg l^{-1}	NO ₂ ⁻ found/ mg l^{-1}	NO ₃ ⁻ added/ mg l^{-1}	NO ₃ ⁻ found/ mg l^{-1}
1	1.84	1.86	2.50	2.64
2	3.68	3.61	5.00	5.84
3	7.36	7.22	10.00	10.82
4	11.04	10.54	14.88	14.23
5	0	0	4.96	4.60
6	1.84	1.80	2.48	2.86
7	3.68	3.71	9.92	9.10
8	5.52	5.61	4.96	5.36
9	3.68	3.74	7.44	7.50

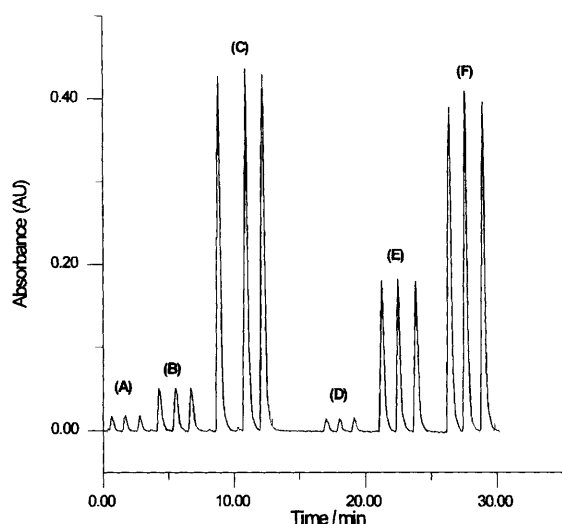


Fig. 3 Analysis of two different wastewater samples. Triplicate injection of: (A) and (D), the unoxidized sample under non-reductive conditions; (B) and (E), the unoxidized sample under reductive conditions; (C) and (F), the photo-oxidized sample under reductive conditions. AU = absorbance units.

oxidation yield ranges from 90 to 100% and is comparable to that provided by the Kjeldahl method used as reference. The proposed method can readily be automated; in addition, it is much faster than the classical Kjeldahl method, hence it is suitable for monitoring total nitrogen in wastewater.

Nitrate in the photo-oxidized and original sample is quantified after reduction to nitrite. Using hydrazine rather than a copper-coated cadmium column for this purpose allows high concentrations of persulfate to be employed with no appreciable adverse effects on the reduction reaction. In this way, the use of a column that degrades with time and must be replaced or continuously renewed is avoided.

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