Desalination and Water Treatment
www.deswater.com

1 (2009) 223–231

1944-3994 / 1944-3986

Nitrogen speciation by microstill flow injection analysis

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Received 22 July 2008; accepted revised 19 November 2008

ABSTRACT

A sequential determination of ammonia, nitrite, and nitrate has been carried out using a flow injection manifold incorporating a Microstill. The nitrogen speciation method has been designed using inorganic acid and base reagents, thus avoiding colorimetric reactions whose associated reagents and products are environmentally unacceptable. The robust manifold requires just three valves to switch measurement conditions for each species. UV irradiation was selected for nitrate reduction and gave acceptable resolution of nitrate and nitrite ions. In solutions containing comparable concentrations of both species, reduction of nitrate by UV irradiation gives a systematic error for nitrate due to nitrite interference at the 95% confidence level, nitrite being partially oxidised to nitrate during sample processing. At 98% confidence the error was not significant. A glass microelectrode provided potentiometric detection in an ammonium chloride post-still collector stream. Ammonium chloride provided adequate baseline recovery when switching from acidic to basic distillation conditions, although resulting in an increase in detection limits over those found for a single analyte by the Microstill technique. The final speciation procedure gave working ranges of 0.03–10 mg/L for ammonia-N, 0.05–5 mg/L for nitrite-N and 0.1–10 mg/L for nitrate-N. The three N species were determined in 12 min for each water sample. The system has had limited trials in river waters containing ammonia and nitrate. Good precision and recoveries were obtained for the two species in the samples tested.

Keywords: Nitrogen speciation; Disinfection; Chloramination; Microstill; Flow injection

1. Introduction

Nitrogen (nitrate, nitrite and ammonia) is a key parameter in drinking, waste and recycled/reuse water management. Using drinking water disinfection as an example, as a public health measure, chloramination is increasingly popular as the disinfection method for microbiologically contaminated waters. Chloramines decay by chemical and biological processes to release ammonia, nitrite and nitrate with the nitrite ion becoming part of the decay cycle through reduction of chloramine to ammonia [1–3]. The three N species are seen as health hazards for different reasons, ammonia causes toxicity problems for fish, nitrite may cause asphyxia in young children, and nitrate in large amounts is toxic and with ammonia takes part in eutrophication [4–7]. Monitoring nitrogen species is thus an important control measure in water quality assessment.

Flow injection methods for ammonia have typically been determined by the modified Berthelot reaction which involves hypochlorite and phenol in the formation of indophenol blue [8]. Nitrate and nitrite are gen-

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erally determined (nitrate after reduction with cadmium) via the Griess process, a diazotization/coupling reaction involving naphthylamines [10–13]. Both processes employ reagents and generate products which may be criticised from an environmental viewpoint. One approach to addressing this question is to reduce reagent requirements, part of the design rationale of flow injection or sequential injection methods [9,14,15]. Some excellent progress has also been made in miniaturization of the apparatus thereby markedly reducing reagent use. The problem of sensitivity must, however, be addressed, and again important steps have been made with detection limits now approaching those needed by the water industry [16].

'Greener' chemical pathways have also been proposed. Thus Miura and Kusakari [17] examined a simple iodine based method for nitrite. The problem remains of retaining selectivity in real samples. Microdistillation enables the analyst to fine tune separation of key species from complex matrices [18]. This in turn means that simple detection methods such as pH or conductance can be employed. Microstill flow injection systems for ammonium and nitrite, have been successful in this regard. The approach has used very simple chemistry with satisfactory detection limits for water samples [19–21]. Low reagent concentrations were also a deliberate strategy in those studies, a feature retained in this work.

The aim of the present study was to implement a microdistillation flow injection (MDFI) method for all three N species while maintaining acceptable throughput. Measuring three species demands a valve-based manifold which has control simplicity, as addressed elsewhere, e.g. in the multicommutation procedure of Rocha and Reis [15], or Naiboo and van Staden's switching procedure [9].

The final stage of the chemistry involved in this paper is a volatilization one. Ammonia is volatile under basic conditions while nitrous acid volatilises under acid conditions and serves as the path for both nitrite and nitrate to the detector. As a nitric acid route is not a useful direction for nitrate determination by distillation, a reduction step for nitrate to nitrite is essential. In keeping with the theme of this study, we wished to avoid a reduction process involving cadmium use. The UV-irradiation method introduced by Takeda and Fujiwara [22] and recommended by Motomizu and Sanada [23] was thus chosen. As Wagner et al. [24] point out, this is a complex process involving some 13 steps, some of which are radical initiated. The key point is that nitrate forms nitrite at a much faster rate than the reverse nitrite oxidation, so a flow method can utilise nitrite for further analysis of nitrate.

Having developed analyses for each of the three nitrogen species using the same sensor unit [19–21,25,26], it seems an obvious step to combine them in an overall inorganic nitrogen speciation procedure. Such a sequential operation should enable the determination of the concentrations of the three species by an automated procedure, using a single flow injection manifold. Such a development requires the resolution of a number of problems not associated with the three single analyte systems. Among these are the necessary switching from basic to acidic distillation conditions, switching of the sample stream through a reduction unit, and the selection of a collector solution which provides adequate sensitivity for all species. The final system should, ideally, be able to determine each species in the range found in treated water samples without carryover effects from species to species, and with peaks for each species emanating from a single stable baseline.

2. Materials and methods

2.1. Apparatus

A schematic diagram of the MDFI manifold is shown in Fig. 1.

The sequential MDFI manifold incorporated the individual elements described for the ammonium [19,26], nitrite [20] and nitrate [21] systems with the addition of two computer-controlled electric solenoid 3-way switching valves (Cole Palmer Instrument Co., Niles, Illinois, USA) to facilitate automated switching between the required flow paths for each determination (V1 and V2 in Fig. 1). The method required an acid/base feed: the acid, 0.05 M sulfuric acid, and the base, 0.03 M sodium hydroxide solution. V1 switches the feed from the basic distillation conditions (V1-1) required for the ammonium determination to the acidic conditions (V1-2) for the nitrite and nitrate measures. Valve V2 controls the flow path of the sample, directing it through the UV irradiation coil for nitrate analysis (V2-2), and bypassing it for ammonium and nitrite determinations (V2-1).

The sampling valve (V3) was provided with a 3.5 mL sample loop. A collector flow rate of 0.25 mL/min and a resample flow rate of 0.20 mL/min ensured no air passed the electrodes. The large sample volume and low post-still collector flow rate also provided a sensitivity gain essential to water quality assessment.

For the sequential MDFI manifold the acid/base flow merged with the sample prior to the sample loop, rather than being fed directly to the Microstill. This change was found to provide a more consistent baseline, as it maintained controlled pH conditions in the Microstill between sample injections.

This dual analysis was performed using the two 2-way switching valves described above in a simple computer-controlled sequence. For the ammonium analysis, both valves were maintained in position 1 so that the sample first bypassed the UV irradiation coil and was then mixed with sodium hydroxide solution. For the nitrate analysis both valves were switched to the 2 posi-

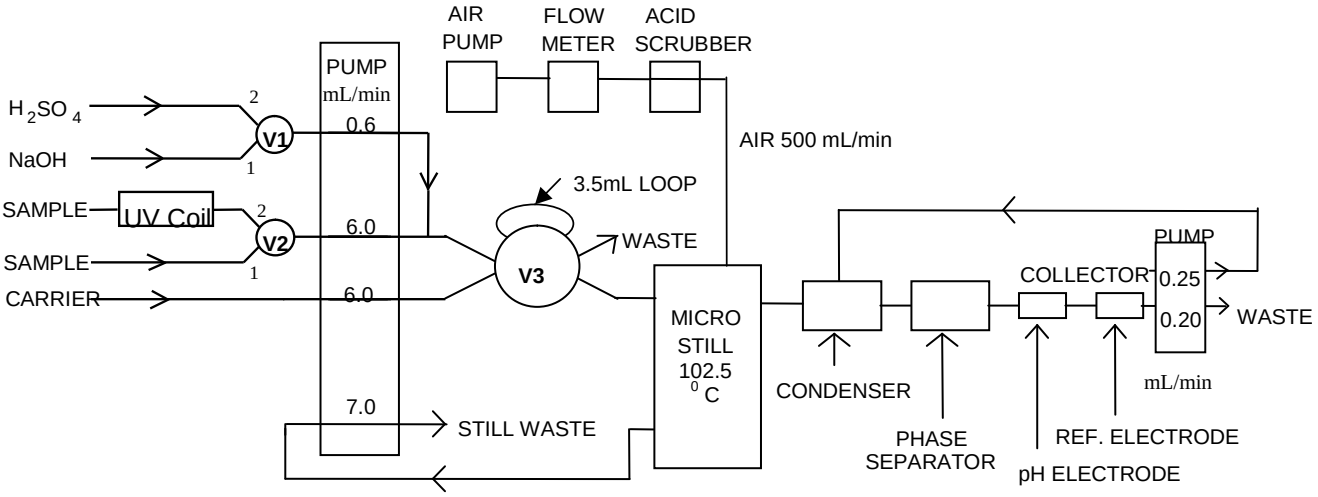

Fig. 1. Diagram of the MDFI system for the sequential analysis of ammonium, nitrite and nitrate. V1 and V2 represent two-way valves. V1 controls NaOH and H_2SO_4 flows, and V2 directs sample past the UV coil for nitrate reduction. V3 is the sample injection valve. Flow rates are shown in mL/min on the diagram.

tion directing the sample through the UV coil and then mixing it with dilute sulphuric acid solution.

2.2. Reagents

All reagents used were analytical grade. The NH_4Cl collector solution was prepared from NH_4Cl (99.5% pure, May & Baker Ltd., Dagenham, England). The 0.01 M sodium hydroxide solution was prepared from 97% pure NaOH pellets. Acidic conditions were maintained in the Microstill by the use of dilute sulphuric acid solutions prepared by dilution of concentrated sulphuric acid (98% minimum purity, Ace Chemical Co., Camden Park, South Australia). As a precaution against precipitation of calcium and magnesium in the Microstill, 0.03M EDTA (disodium salt) was added to the sodium hydroxide solution pumped to the Microstill. Calibration and test sample solutions were made daily by dilution of a 1000 mg/L NH_4^+-N stock solution made from 99.5% pure NH_4Cl which had been dried at 110°C for 12 h. Nitrite standard solutions were prepared by dilution of a 1000 mg/L NO_2^--N stock solution prepared daily from analytical grade sodium nitrite (BDH, Poole, UK). Nitrate standard solutions were prepared by dilution of a 1000 mg/L NO_3^--N stock solution prepared from analytical grade sodium nitrate (Ajax Chemicals, Sydney, Australia). All reagent and calibration solutions were prepared with purified water (Milli Q reagent water system).

3. Results and discussion

3.1. Collector choice

In choosing an appropriate collector solution for the sequential analysis of ammonium, nitrite and nitrate by MDFI it was necessary to identify a collector that provided approximately equal sensitivity to both ammonium and nitrite/nitrate. Calibrations for each of these species, obtained in earlier work [19–21,26] show that simple ammonium chloride collector solutions exhibit a much greater pH response to ammonium samples than to nitrite or nitrate samples of the same concentration (as mg/L-N). The concept of sequentially determining ammonia in a basic still environment followed by nitrate or nitrite with an acidic flow through the Microstill was first tested with ammonium-nitrite samples. In an effort to equalise these responses (sensitivities), a series of experiments was carried out in which the response of 10^{-3} M ammonium chloride collector solution to both ammonium and nitrite samples was determined. Collector solutions were adjusted to different pH levels by the addition of small amounts of sodium hydroxide solution.

The graphs of electrode response versus collector solution baseline pH (Fig. 2) show that at each analyte concentration, low collector pH favoured the ammonium response, and high collector pH favoured the nitrite response. The collector solution baseline pH was defined as the signal from the flow-through pH detector, in pH units, under baseline conditions (i.e. only Milli Q water carrier flowing to the Microstill). An optimum collector baseline pH of 5.8 was identified, at which approximately equal responses to ammonium and nitrite samples of the same concentration (as mg/L-N) were observed. This pH corresponded to the addition of 3.5×10^{-5} M NaOH to the 10^{-3} M NH_4Cl collector solution. Similar experiments were conducted for other collector ammonium chloride concentrations (3×10^{-4} M and 10^{-2} M) and at each concentration an optimum composition was identified. In each case this optimum composition involved the addi-

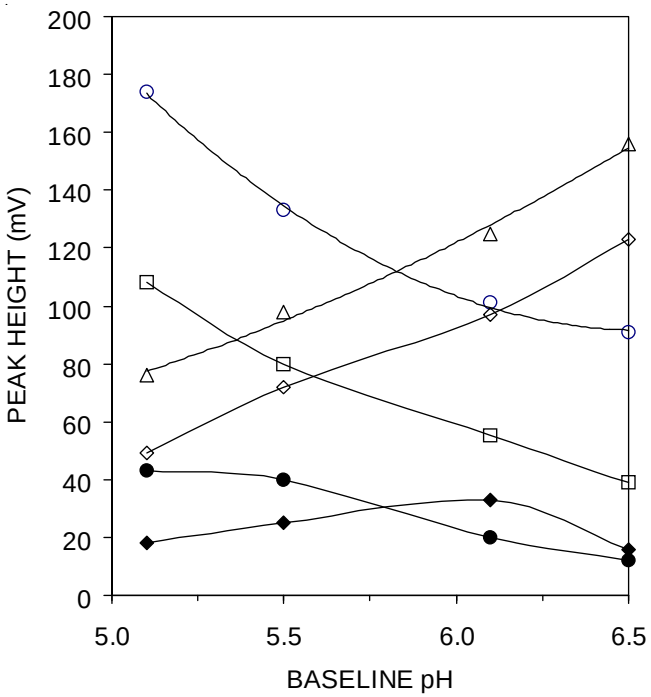

Fig. 2. Peak height vs. collector baseline pH for samples containing ○ 5 mg/L NH_4^+-N, △ 5 mg/L NO_2^--N, □ 0.5 mg/L NH_4^+-N, ◇ 0.5 mg/L NO_2^--N, ● 0.1 mg/L NH_4^+-N and ◆ 0.1 mg/L NO_2^--N. The collector solution was 10^{-3} M NH_4Cl and pH adjustments were made by the addition of NaOH.

tion of sufficient sodium hydroxide to adjust the baseline pH value of the collector to approximately 5.8 when measured with a sample blank.

3.2. Ammonium/nitrite/nitrate sequential analysis

The three individual analyses were combined into a single automated process with the aim of sequentially determining ammonium-nitrogen, nitrite-nitrogen and nitrate-nitrogen from a single sample using one non-specific detector. A series of sample solutions containing between 10 and 0.2 mg/L NH_4^+-N and NO_3^--N and between 2 and 0 mg/L NO_2^--N were prepared. The samples were made alkaline by the addition of 2×10^{-3} M NaOH (to create the correct pH conditions for nitrate reduction) and then analysed using the high concentration experimental settings described in Fig. 1.

The following valve sequence (Table 1) was employed to speciate the three nitrogen forms.

3.3. Calibration data

The raw calibration data (Fig. 3) shows the three peaks for each sample corresponding to ammonium, nitrite, and nitrite plus nitrate. Each of these peaks is well defined, shows good baseline return and stability, and exhibits no signs of carryover from sample to sample. While this method shows good specificity for ammonium and for nitrate in the absence of nitrite, a clear problem arises in resolving the contribution of nitrite to the nitrate peak when nitrate is determined in the presence of significant concentrations of nitrite. This problem is discussed in detail by Takeda and Fujiwara [22].

The calibration plots (Fig. 4) for each species are consistent with those previously observed, the ammonium graph showing good linearity, while the nitrite, and nitrate plus nitrite plots exhibit a typical slight "S" shape.

3.4. Precision

Two separate measurements of the precision of the method with respect to each nitrogen species were made. The first involved calculation of the standard deviations (S.D.) and coefficients of variation (C.V.) of the peak height for sets of three repeats, at two different concentrations for each species, from the calibration data shown above (Fig. 3). These showed good precision at higher concentrations for each species (coefficients of variation of 1.5% or better) with deterioration of the precision at lower concentrations, particularly for the 0.1 mg/L NO_2^--N sample.

Table 1
The operational sequence of the flow injection valve, acid/base switching valve (V1) and sample valve (V2) throughout the 12 min repeating cycle used for the sequential analysis of ammonium, nitrite and nitrate. The sequence restarts after each 12 min cycle.

Time (min)	Flow injection valve position	Acid/base valve (V1) status	Sample valve (V2) status
0	Load (NH_4^+)	V1.1 (OH^- flowing)	V2.1 (bypass UV coil)
3	Inject (NH_4^+)	V1.2 (H^+ flowing)	"
4	Load (NO_2^-)	"	"
7	Inject (NO_2^-)	"	V2.2 (through UV coil)
8	Load (NO_3^-)	"	"
11	Inject (NO_3^-)	V1.1 (OH^- flowing)	V2.1 (bypass UV coil)
12	Load (NH_4^+)	"	"

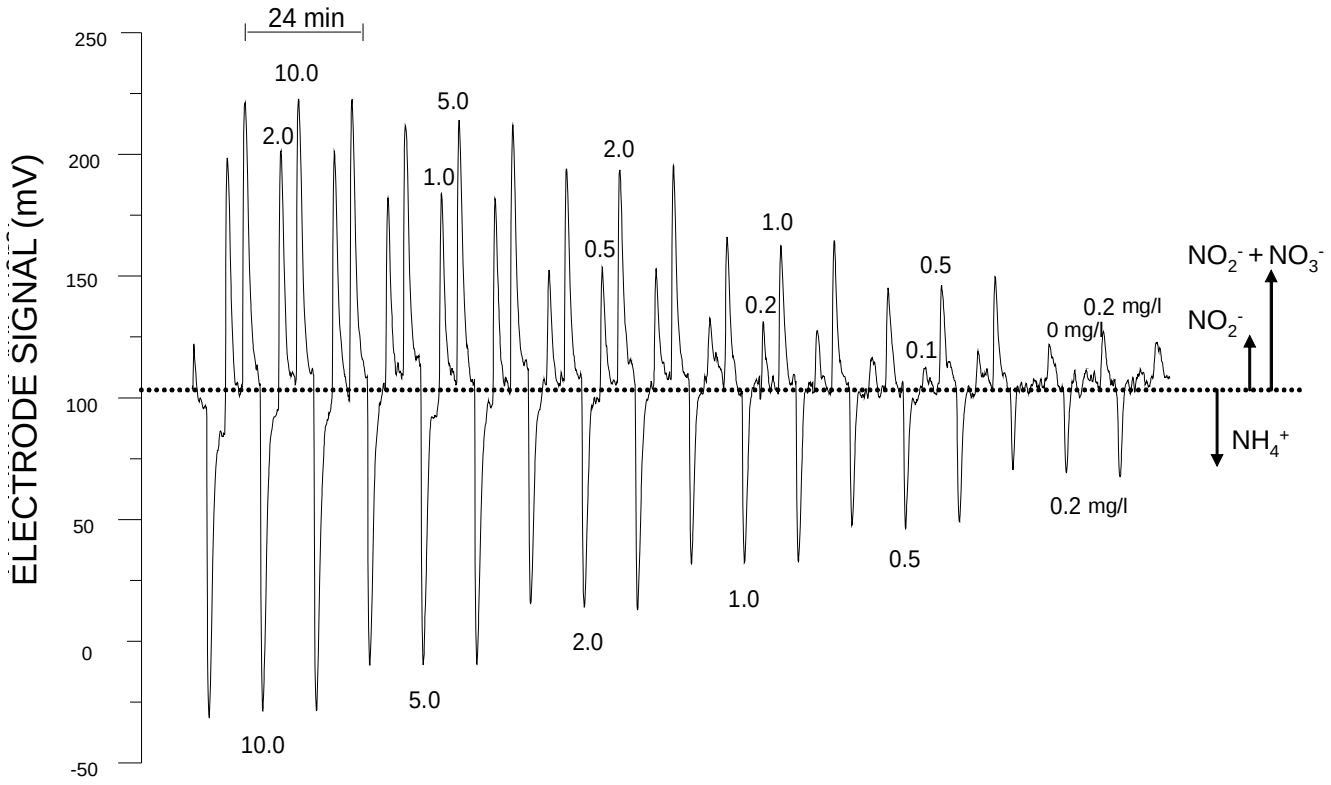

Fig. 3. Calibration data for the sequential analysis of ammonium, nitrite and nitrate. Sample concentrations are shown in mg/L-N above or below each set of three peaks.

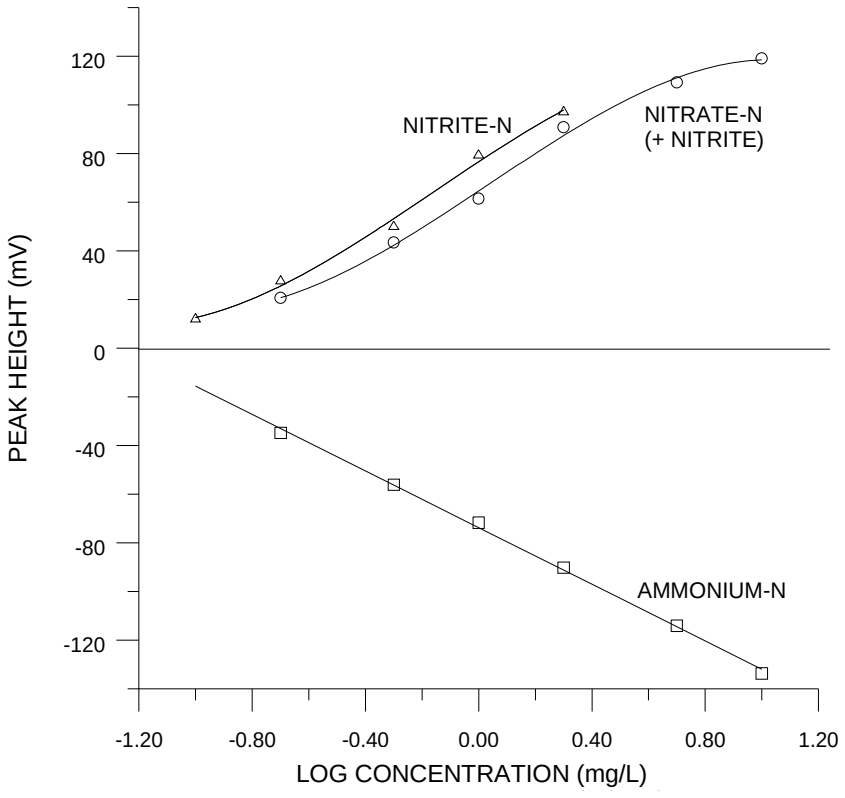

Fig. 4. Peak height vs. log concentration plots (mg/L-N) for ammonium, nitrite and nitrate plus nitrite.

A second measurement of the precision of the peak height, using a larger sample size, was made from repeated measurement of a sample containing 1.0 mg/L NH_4^+-N, 0.2 mg/L NO_2^--N and 1.0 mg/L NO_3^--N. The standard deviations and coefficients of variation are presented in Table 2.

3.5. Carryover

The question of carryover between samples has previously been addressed for each analyte in turn in [19–21]. The sequential MDFI method introduces the possibility of internal carryover effects between the three analytes determined in each sample. This potential problem was investigated by looking at each of the three analytes in turn and examining the signal observed for this species at a given concentration in solutions containing varying concentration of the other two species. In the case of ammonium this was carried out by comparing the signal for samples containing 5 mg/L NH_4^+-N in three different solutions containing different concentrations of nitrite and nitrate. The results of this experiment (Table 3a) show that the signals obtained for the three different samples do not differ significantly at the 95% confidence level. The same can be said for the three different samples containing 0.5 mg/L NO_2^--N as shown in Table 3b.

The results for nitrate determination (Table 3c), however, do show some dependence on the concentration of the other species in the sample. The dependence of the nitrate signal on nitrite concentration is to be expected as the signal for nitrate is the sum of the signal due to nitrate plus that due to nitrite in the original sample. The signals observed for 5.0 mg/L NO_3^--N in sample solutions containing 0.5 and 5.0 mg/L NH_4^+-N (as well as 0.5 mg/L NO_2^--N) do show significant difference at the 95% confidence level although not at the 98% level.

These results show that over the ten-fold changes in concentration conducted in these experiments any internal carryover effects from analyte to analyte are small, and, apart from the expected nitrite/nitrate interaction, are not significant at the 95% confidence level in all but one case. Should this effect prove to be a problem at any point, it could be reduced by extending the loading time in the flow injection cycle to improve both the sample wash-out and baseline return.

An extended run of 20 full analyses over a period of 4 h with a sample containing 1.0 mg/L NH_4^+-N, 0.2 mg/L NO_2^--N and 1.0 mg/L NO_3^--N showed excellent baseline stability. An examination of which indicated a %SD of 1.4% for ammonia, 6% for nitrite, and 3% for nitrite plus nitrate.

3.6. Nitrite/nitrate resolution

The accurate resolution of nitrite and nitrate concentrations in samples containing significant concentrations of both species is difficult. This arises from two aspects of the UV nitrate reduction process. The first of these is the fact that the reduction is not quantitative, with reduction efficiencies typically in the region of 60% at the 1 mg/L NO_3^--N level rising to 90% at the 5 mg/L level. The second factor complicating the analysis is the fact that any nitrite in the sample is partially destroyed in the coil by oxidation to nitrate. Consequently nitrate cannot be determined by a simple difference calculation in

Table 2
Precision data (a) at two different concentrations for ammonium, nitrite and nitrate plus nitrite obtained from the calibration run shown in Fig. 3 and (b) for peak height measurements for ammonium, nitrite, and nitrite plus nitrate. From 10 repeat measurements of a sample containing 1.0 mg/L NH_4^+-N, 0.2 mg/L NO_2^--N and 1.0 mg/L NO_3^--N.

Sample	*n*	Mean (mV)	S.D. (mV)	C.V. (%)
(a)				
5.0 mg/L NH_4^+-N	3	–114.1	0.17	0.2
0.5 mg/L NH_4^+-N	3	–56.1	1.35	2.4
1.0 mg/L NO_2^--N	3	79.3	1.22	1.5
0.1 mg/L NO_2^--N	3	12.0	3.31	28
5.0 mg/L NO_3^--N + 1.0 mg/L NO_2^--N	3	109.3	1.19	1.1
0.5 mg/L NO_3^--N + 0.1 mg/L NO_2^--N	3	43.5	2.40	5.5
(b)				
1.0 mg/L NH_4^+-N	10	64.2	1.20	1.9
0.2 mg/L NO_2^--N	10	28.2	1.51	5.4
1.0 mg/L NO_3^--N + 0.2 mg/L NO_2^--N	10	79.3	2.27	2.9

Table 3
(a) The effect of nitrite and nitrate concentrations on ammonium responses. (b) The effect of nitrate and ammonium concentration on nitrite determination. (c) The effect of ammonium and nitrite concentration on nitrate determination. In each case $n = 3$.

$[NH_4^+]$ mg/L-N	$[NO_2^-]$ mg/L-N	$[NO_3^-]$ mg/L-N	NH_4^+ signal (mV)	S.D. (mV)
(a)				
5.0	0.5	5.0	108.8	0.8
5.0	5.0	5.0	111.4	2.0
5.0	0.5	0.5	110.6	1.1
(b)				
5.0	0.5	5.0	62.4	2.0
0.5	0.5	5.0	63.7	0.8
5.0	0.5	0.5	62.7	1.6
(c)				
5.0	0.5	5.0	111.4	0.5
0.5	5.0	5.0	123.1	0.5
0.5	0.5	5.0	109.0	0.8

the manner used when nitrate is completely reduced on a copperised cadmium column. The flow injection peak for the nitrate stream is in fact composed of contributions from both the nitrite and nitrate concentrations in the original sample. Peak height is proportional to the term:

$$\log\left(C_1[NO_2^-] + C_2[NO_3^-]\right) \quad (1)$$

where C_1 is the fraction of nitrite not oxidised to nitrate in the UV irradiation coil and C_2 is the fraction of nitrate reduced to nitrite in the coil, and both of these factors are variables.

As Table 3c illustrates at the 5 mg/L level, nitrite is partially oxidised to nitrate during sample processing, thus causing a positive systematic error for nitrate at the 95% confidence level. The error was not significant at 98% confidence.

3.7. Recovery experiment

The reliability and accuracy of the ammonium/nitrate sequential MDFI method when applied to the analysis of real samples was investigated through a series of recovery experiments. A volume of river water was taken from the River Torrens in the Adelaide suburb of Klemzig during a period of high flow immediately after substantial rain. Subsequent analysis of the sample, without filtration, showed it to be very low in ammonium (0.032 mg/L NH_4^+-N) and relatively low in nitrate (0.41 mg/L NO_3^--N). No nitrite was detected. From this original sample, a series of eight samples were prepared by addition of standard ammonium chloride and sodium nitrate solutions. By this means samples were prepared which covered the ranges 0.05–1.0 mg/L NH_4^+-N and 0.5–5.0 mg/L NO_3^--N. The samples were prepared to include some which were low in both ammonium and nitrate, some which were high in both, and some high in one and low in the other. The concentrations of the resulting sample solutions are shown in Table 4.

Prior to analysis all standards and samples were buffered to a pH of 9.18 by the addition of 0.01 M Borax. 10^{-3} M EDTA (di-sodium salt) was also added to prevent chloride suppression of the nitrate reduction. Calibration standards were prepared in Milli Q water and analysed according to the conditions described to construct a calibration curve. The raw river water was then analysed in triplicate to determine the background concentrations of ammonium and nitrate before the seven spiked samples were analysed three times each, the first time in numerical order and then twice in random order. The nitrate concentrations determined for sample 8 were not included in the subsequent analysis of the results. The nitrate concentration determined for this 5.41 mg/L NO_3^--N sample was found to be unreliable, as it lay outside the useful range of the method under the chosen conditions (0.1–5 mg/L).

The relationship between the concentrations determined by the sequential MDFI method and the expected results is presented in Eqs. (2) and (3). The data shows good correlation, particularly at the lower concentration levels. The line of best fit for nitrate data is given by:

$$Y = (1.02 \pm 0.04)X + (0.05 \pm 0.09) \quad R^2 = 0.98 \quad (2)$$

Calculation of the 95% confidence intervals for the slope and intercept values shows that neither differs significantly from their ideal values of 1 and 0 respectively.

Table 4
Sequential MDFI recovery trials for solutions prepared by standard additions of ammonium and nitrate to River Torrens water. The river water initially contained 0.032 mg/L NH_4^+-N and 0.41 mg/L NO_3^--N. The expected concentration is therefore the background concentration plus the standard addition.

Sample	NO_3^- expected (mg/L-N)	NH_4^+ expected (mg/L-N)	NO_3^- found (mg/L-N)	NH_4^+ found (mg/L-N)
1	0.51	0.08	0.52, 0.51, 0.60	0.10, 0.09, 0.09
2	0.91	0.83	1.0, 0.93, 0.98	0.79, 0.83, 0.74
3	1.41	0.23	1.51, 1.62, 1.48	0.26, 0.26, 0.22
4	1.91	0.53	2.0, 2.0, 1.82	0.50, 0.56, 0.49
5	2.41	0.33	2.24, 2.63, 2.63	0.32, 0.30, 0.32
6	3.41	0.13	3.39, 3.63, 3.98	0.15, 0.14, 0.14
7	4.41	0.73	4.17, 4.99, 4.17	0.66, 0.71, 0.64
8	5.41	1.03	outside range	1.0, 1.1, 1.0

In the case of ammonium, however, some bias is suggested in the regression data:

$$Y = (0.95 \pm 0.01)X + (0.014 \pm 0.013) \quad R^2 = 0.99 \qquad (3)$$

with the slope representing 95% recovery in the range 0.05–1.0 mg/L NH_4-N.

The principal difficulty in calculating concentrations of ammonium and nitrate from sequential MDFI data, and the probable source of the bias seen in this experiment, lies in defining the baseline. It can be defined quite arbitrarily, as some point approximately midway between the ammonium and nitrate peaks, without introducing error, provided:

- that the same baseline value is used to calculate peak heights for both calibration standards and samples, and,
- that the real baseline does not drift over time.

If the experimental baseline does drift significantly during the course of a set of measurements, peak heights calculated from an arbitrary fixed baseline will result in a positive bias to one analyte and a negative bias to the other.

In order to overcome this potential source of error, it may be necessary to periodically suspend measurement for a few minutes to allow the true baseline to be re-established. This new baseline potential could then be adopted to compensate for any drift in the previous baseline value. This adjustment would only be necessary if the baseline drift is significant over the period of time between calibrations.

While baseline drift may result from a variety of experimental factors, which can be difficult to control, previous analysis of the MDFI system has shown the system to be quite robust with respect to small changes in experimental variables [20]. Repeated analyses of baseline drift over periods of several hours for the various MDFI systems have consistently shown baseline drift rates of 1 mV/h or less. These findings suggest that regular calibration would be sufficient to keep this problem under control. An alternative approach would be the use of a baseline compensation routine in the controlling software to make the necessary adjustments.

4. Conclusion

A sequential MDFI system for the determination of the three principal forms of fixed inorganic nitrogen has been implemented and its operation demonstrated. The method has been shown to operate well for the determination of ammonia and nitrate with good detection limits, selectivity and precision while some difficulty remains with regard to the resolution of nitrite and nitrate concentrations in the small number of situations where samples containing significant concentrations of both species are encountered. Several possible strategies for overcoming this have been suggested.

The operation of the system under real sample conditions has also been demonstrated by the sequential determination of ammonium and nitrate spikes in water from the River Torrens which contained no significant concentrations of nitrite. Good recoveries were obtained in this experiment although a much broader and more rigorous range of tests must be undertaken on a wide variety of water samples to establish the accuracy and reliability of the method for other water types.

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