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Determination of nitrate by suppressed ion chromatography after copperised-cadmium column reduction[☆]

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Abstract

The nitrate-selective copperised-cadmium (Cu-Cd) reduction reaction coupled directly to the highly sensitive nitrite ion chromatographic detection, produced a more precise method for determination of nitrate than any one of the two conventional methods. A borate buffer solution used in the reduction reaction, in place of the conventional ammonium–EDTA buffer solution, eliminated interferences from co-eluting ions in the subsequent ion chromatographic detection of nitrite. Optimised experimental conditions included using a packed-bed Cu-Cd reductor column length of 12.5 cm, a solution flow rate of 3.0 ml/min, and using 10.0 ml of borate buffer solution for each 20.0 ml of nitrate-containing solution. Precision was high for results obtained within a greatly extended linear dynamic range of 0.006–1.20 mg/l NO_3^-, with a much lower limit of detection of 0.40 μg/l NO_3^-. Cu-Cd reductor column efficiency was 98.20 $\pm$ 6.03%. Validation of the method was undertaken using certified reference materials. The method was successfully applied to analysis of dam water, river water and storm water samples, producing more precise results than either the conventional colorimetric method or the conventional ion chromatographic method.
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1. Introduction

Concentrations of nitrates in most natural waters are, in general, extremely low. Higher concentrations in natural water are usually a result of inputs from agricultural [1,2], domestic and industrial wastewaters, and to a small extent, atmospheric processes [3]. Adverse health effects, due to the high nitrate concentrations in the food chain, have been reported [1]. High nitrate concentrations have also caused environmental concerns, especially the nitrate-stimulated excessive aquatic plant production which negatively impacts freshwater and estuarine environments [2,4,5]. As a matter of public concern, nitrate concentrations in natural waters must, therefore, be monitored to facilitate adaptive changes in water quality management.

Most current methods for determining the low concentrations in water are based on reduction of nitrate to nitrite,

with subsequent colorimetric determination of the nitrite produced. The most widely used conventional method involves the use of columns containing copperized cadmium to reduce nitrate to nitrite [6–10]; commercially available cadmium granules or filings that have been pretreated with dilute copper sulphate solution are packed in a glass column. A buffered nitrate-containing sample solution is then passed through the column. Nitrate is reduced quantitatively to nitrite in the presence of cadmium. Nitrite produced is commonly determined after diazotizing with sulfanilamide and the product coupled with *N*-(1-naphthyl) ethylenediamine dihydrochloride to form a highly colored azo dye measured colorimetrically at 543 nm. This method is very selective for nitrate analysis. Nitrite, if present in the sample, is determined without the use of the reductor column. The procedures are operator and reagent intensive, and the reaction products are unstable causing imprecision in the colorimetric results. A major limitation of this method is that colorimetric detection is not sensitive enough for trace nitrate determination. When performed manually, the applicable working range is 0.01–1.0 mg/l NO_3^- for natural waters. Poorer detection limits of about 0.5 mg/l NO_3^-

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have been reported for automated versions of the procedure [11] and these require frequent recalibration.

Non-suppressed ion chromatography with indirect fluorescence detection has recently been used to determine nitrate [12]. The limitation of this approach is the interference from ions which can quench the fluorescence of tryptophan, from natural samples. Also the use of fluorescing medias limits this method to a small group of reagents that can be used. Ion chromatography with suppressed conductivity detection has also been widely used for the determination of nitrates in natural water [13–20]. This is a result of the speed and simplicity associated with the method. Also, the method is well suited to analysis of lake, stream and rainwater samples, which are often simple, pure matrices containing only low concentrations of additional organic and inorganic constituents. The most widely used approach is as follows; a nitrate-containing water sample is injected into a stream of carbonate–hydrogen bicarbonate eluent and pumped through a separator ion exchange column. The nitrate ions (NO_3^-) are separated and selectively eluted off the separator column onto a strongly acidic cation-exchange column (suppressor column) where they are converted to their highly conductive form, HNO_3, detected in conductance cell. Chromatograms are displayed and quantitation is by peak area or peak height measurement. Calibration using nitrate standard solutions is necessary for quantitation. With this approach, large sample volumes are usually required due to the low concentrations of nitrate ions in natural water. However, use of large sample loops is known to cause "water deep" problems in the subsequent chromatograms [21]. In addition, this method suffers from interferences due to other ions with similar retention times. On the other hand, the method is of high precision and sensitivity. Low concentrations of nitrate ions can be detected [10]. By use of a concentrator column [22] the resultant pre-column enrichment enhances the sensitivity of the method to less than μg/l levels.

There is a definite need for a relatively simple, reliable and sensitive method, free from matrix interferences for a long-term environmental monitoring of nitrates in natural waters.

The objectives of the work outlined in this paper were to investigate the possibility of coupling the nitrate-selective Cu-Cd column reduction method to the more sensitive suppressed ion chromatographic detection, for routine determination of nitrate in water samples. Also, to optimize experimental conditions for use of the method and to demonstrate its application to natural water sample analysis.

2. Experimental

2.1. Instrumentation and apparatus

For ion chromatographic (IC) sample analysis, a Dionex DX-100 (Sunnyvale, CA, USA) ion chromatograph was used. The instrument was equipped with an Anion Self-Regenerating Suppressor column, ASRS-Ultra 4 mm,

and a flow-through, temperature-compensated conductivity detector. Analyte chromatograms were plotted, and data handled using a Dionex-4000 integrator, which was also programmed to run the whole ion chromatographic system. Dionex automated sampler, ASM-3, was used for automatic sample loading. IonPac AS14 (250 mm × 4.0 mm) analytical column, IonPac AG14 (50 mm × 4.0 mm) guard column and IonPac TAC-2 (35 mm × 3.0 mm) anion concentrator column, were used for this work.

pH measurements were undertaken using a digital pH meter (Phillip Harris, Lichfield, UK). Spectronic 20 (Milton Roy, NJ, USA) spectrometer was used for colorimetric determination of nitrite. Cu-Cd reductor columns were prepared using 50 ml AR-Glas burette tubes. Milli-Q A-10 water purification system, (Millipore, Bedford, MA, USA) was used for provision of ultra pure water.

2.2. Chemicals, reagents and materials

Freshly prepared ultra high purity water was used throughout. Analytical-grade reagents were used. 5–20 mesh size cadmium granules (Aldrich, Dorset, UK), copper sulfate crystals (NT Laboratory Supplies, Johannesburg, RSA) and concentrated hydrochloric acid (BDH, Poole, UK) were used in preparation of Cu-Cd reductor columns. Disodium tetraborate (BDH), boric acid, ammonium chloride, disodium ethylenediamine tetraacetic acid, EDTA, (all from Saarchem, Johannesburg, South Africa) were used in preparation of buffer solutions. Phosphoric acid, sulfanilamide (both from BDH, Poole, UK) and *N*-(1-naphthyl)ethylenediamine dihydrochloride, NED, (Saarchem) were used in preparation of coloring reagent for the colorimetric determination of nitrate. Eluent stock solutions for ion chromatography were prepared using sodium carbonate and sodium hydrogen bicarbonate (both from Saarchem). Nitrate and nitrite stock standard solutions were prepared using sodium nitrate and sodium nitrite (Saarchem), respectively.

Certified reference material GBW08606 was obtained from the Laboratory of the Government Chemist, Teddington, UK. Certified reference material CRM 0479 was obtained from the European Commission, Institute for Reference Materials and Measurements, Brussels, Belgium. Surface water samples were obtained from Gaborone dam and Notwane river, both in Gaborone city, Botswana. Wastewater samples were collected from storm water drains in Gaborone city, Botswana.

2.3. Procedures

2.3.1. Preparation of reagents

Borate buffer solution was prepared by dissolving disodium tetraborate (8.80 g) and boric acid (4.65 g) in ultra pure water and diluting to 1000 ml. The pH of this solution was 8.92. Ammonium chloride–ethylenediaminetetraacetic acid (NH_4Cl–EDTA) buffer solution was prepared by

dissolving ammonium chloride (13.00 g) and disodium ethylenediaminetetraacetate (1.70 g) in ultra pure water, adjusting the solution pH to 8.5 with ammonia solution, and diluting the solution to 1000 ml. A coloring reagent for colorimetric determination of nitrate was prepared by adding phosphoric acid (100 ml), sulfanilamide (10.0 g) and NED (1.0 g) to ultra pure water, stirring to complete dissolution, and diluting the solution to 1000 ml. Nitrate and nitrite stock standard solutions (1000 mg/l) were each prepared in 1000 ml volumetric flasks by dissolving sodium nitrate (0.1371 g) and sodium nitrite (0.1500 g) in ultra pure water. All above solutions were stored, in glass bottles, in a cold room at 4 °C.

Eluent stock solution for ion chromatography was prepared first by dissolving separately sodium carbonate (26.49 g) and sodium hydrogen carbonate (21.00 g) in ultra pure water and diluting each solution to 500 ml. The eluent solution (a mixture of 3.5 mM Na_2CO_3 and 1.0 mM $NaHCO_3$) was prepared from the stock solutions by pipetting 35.0 ml of sodium carbonate and 10.0 ml sodium hydrogen carbonate solutions in a 5000 ml volumetric flask and making to volume with ultra pure water.

2.3.2. Preparation of copperized-cadmium (Cu-Cd) reductor column

To prepare copperised-cadmium (Cu-Cd) granules, 20.0 g of cadmium granules (5–20 mesh size) were gently swirled in 6.0 M HCl in a beaker. The acid was decanted and the granules rinsed by swirling in 100 ml portions of ultra pure water, at least twice. The washed granules were then swirled in 100 ml of 2% (w/v) copper sulfate solution until the partial fading of the blue color of copper sulfate solution. The washing was repeated, each time decanting the solution, until a brownish precipitate of copper began to form. The copperised granules were gently flushed with water several times, each time decanting the washings to remove the precipitated copper, but with care not to remove the copper layer coating on the cadmium granules. Cu-Cd granules were packed in a water filled burette tube (50 ml burette) to a known packed-bed length. A buffer solution was passed through the packed column, and during storage when not in use, the column was filled with the buffer solution to a level above the granules.

2.3.3. Ion chromatographic analysis

For IC determination of nitrate and nitrite in the various solutions, the Dionex DX-100 IC system was set up as follows: The pump was always primed for about 60 s before use, maximum pressure cut-off was set to 2700 psi and the pumping rate set to allow for an eluent flow of 1.00 ml/min. The Dionex-4400 integrator was programmed to control the IC system's operations of sample loading and injection, recording of chromatograms and integration of data.

Using nitrate standard solutions and certified reference materials, experiments were undertaken to establish the working range, accuracy, precision and detection limits of the method. Application to real samples was ascertained by analysis of natural surface water and wastewater samples.

3. Results and discussion

3.1. Optimisation of experimental conditions

Previous workers have demonstrated that nitrate is quantitatively reduced to nitrite on a Cu-Cd reductor column [10,23]. For this study, this was ascertained by calculation of recoveries of nitrate using standard solutions of nitrate and solutions of standard reference materials, GBW 08606 and CRM 479, passed through a Cu-Cd reductor column.

Experiments were also undertaken to optimize the length of the Cu-Cd packed-bed column, and eluent flow rate to ascertain the nitrate reduction efficiency of the Cu-Cd column. Generally, due to interferences from co-eluting ion peaks in chromatograms, the first 10 ml of eluent solution from the Cu-Cd reductor column was always discarded, and subsequent portions transferred to the Dionex autosampler for IC analysis.

3.1.1. Selection of buffer solution

Conventionally, NH_4Cl–EDTA buffer solution is added to a nitrate-containing sample solution to sustain a high reduction activity on the Cu-Cd reductor column [24]. Using this buffer solution does not lead to any adverse effects in the subsequent colorimetric determination of reduced nitrite, in the column eluent. However, for ion chromatographic detection of the reduced nitrite, the high concentrations of Cl^- and $EDTA^-$ ions derived from the use of the NH_4Cl–EDTA buffer solution adversely interfere; a large buffer-derived Cl^- ion peak overlaps and masks the expected low sample-derived NO_2^- peak in the ion chromatograms. NH_4Cl–EDTA buffer solution could not, therefore, be used in the quantitative determination of NO_2^- in the column eluent by ion chromatography. Using nitrate standard solutions, experiments were therefore undertaken to choose a suitable buffer solution and to optimize its volume in use.

A specific hydrogen ion concentration is required for quantitative reduction of nitrate to nitrite on a Cu-Cd reductor column [11]. A pH range of 8.0–10.0 has been reported to be most suitable; too high a hydrogen ion concentration can cause further reduction of nitrite to such species as NH_3OH^+ or NH_4^+, while a pH below 8.0 leads to poor precision in the quantitative reduction of nitrate [11]. It has also been reported that the higher the pH the broader the required optimum range of solution flow rate in the Cu-Cd reductor column.

Based on above considerations and after experimentation with several buffer solutions, borate buffer solution was selected for use in this study. Prepared borate buffer solutions had a pH in the range 8.65–9.00, well within the reported suitable pH range for quantitative reduction of nitrate to nitrite.

3.1.2. Volume of borate buffer solution

Addition of 5.0–75.0 ml borate buffer solution to a 20.0 ml nitrate standard solution and passing the resultant mixtures through the Cu-Cd reductor column, resulted in different nitrate percentage recoveries, ranging from 70.0–98.0%. This was attributed mainly to the expected variation in ionic strength of the resultant solution mixture, and hence, varying nitrate reduction efficiency on the Cu-Cd reductor column. Large content of buffer solution also caused baseline instability in the ion chromatograms. Borate buffer solution (10.0 ml) added to 20.0 ml of nitrate-containing solution was found optimum for this work, giving nitrate recoveries exceeding 95%, and with a stable baseline in the ion chromatograms. Selection of the eluent fraction analyzed was also important for the determination of nitrite by ion chromatography; the first 10.0 ml of eluent from the Cu-Cd reductor column was always discarded as this contained co-eluate ions with peaks overlapping the analyte NO_2^- peak in the ion chromatograms.

3.1.3. Cu-Cd reductor column length and solution flow rate

Optimum time of contact between copperised-cadmium metal and the nitrate-containing sample is required for maximum nitrate reduction efficiency. Factors known to affect the time of contact include surface area of the metal granules per unit solution volume, metal bed volume in the reductor column, the solution flow rate through the column, properties of the nitrate-containing solution, etc. [10]. For a given experimental set-up of a specified Cu-Cd preparation and sample solution, the optimal time of contact would be determined by the flow rate only. Cu-Cd column lengths between 10.0 and 30.0 cm and solution flow rates in the range 2.50–10.00 ml/min. were studied. Results are presented in Fig. 1a and b. Although factors such as mesh size of the Cu-Cd granules and reductor column dimensions are expected to vary for the various experimental set-ups, the results obtained demonstrate the importance of optimizing column length and flow rate before analysis of calibration standard and sample solutions. To provide a reasonable sample throughput, a packed bed column length of 12.5 cm and flow rate of 3.00 ml/min gave the best nitrate recoveries, for the Cu-Cd granules (5–20 mesh size) and the glass burette tubes used in this study.

3.2. Performance evaluation

Nitrite (NO_2^-) standard solutions of varying concentrations, treated in the same way as the nitrate-containing solutions, were passed through the Cu-Cd reductor column. The column, together with the use of borate as the buffer solution, had no adverse effect on nitrite; nitrite passed unaffected through the reductor column. All nitrite added to the column was quantitatively recovered; a graphical plot gave a 1:1 relationship with a correlation coefficient for a linear least-square fit, r, of 0.9999 between the nitrite added to, and the nitrite recovered from, the Cu-Cd reductor column.
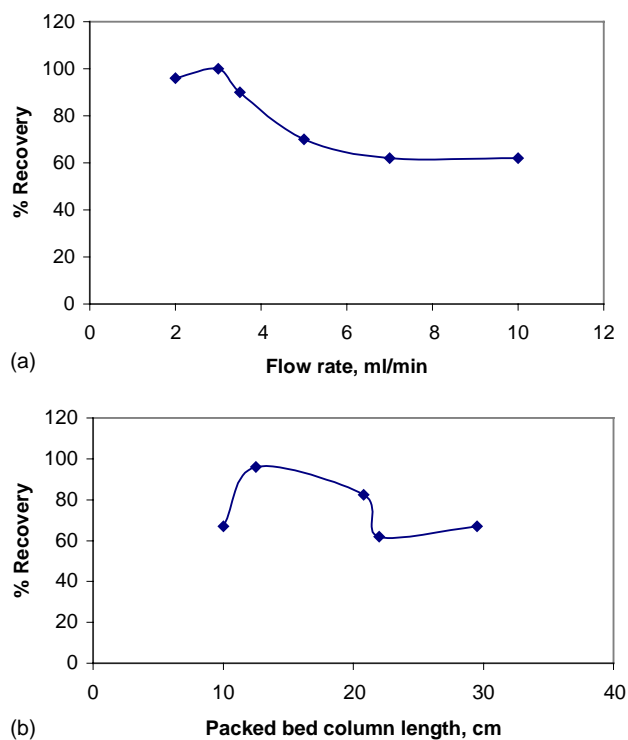

Fig. 1. Optimization of (a) solution flow rate in the Cu-Cd reductor column and (b) Cu-Cd packed bed column length.

Fig. 2 shows a chromatogram obtained after passing 0.50 mg/l nitrate standard solution through the Cu-Cd column. The quality of the chromatogram indicates that chromatographic peaks due to borate and sulfate ions are not expected to interfere with the quantitative determination of nitrite because of the differences in retention times.

3.2.1. Linearity of the method

Using nitrate standard solutions, experiments were conducted over a nitrate concentration range of 0.006–15.0 mg/l. The results of our experiments demonstrate the direct
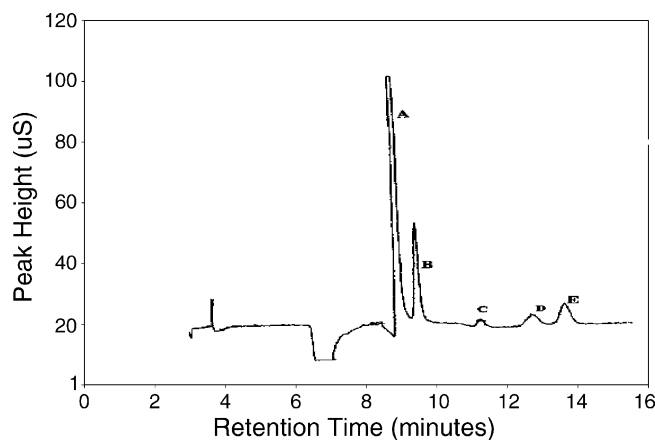

Fig. 2. IC chromatogram of 0.50 mg/l of nitrate standard solution, after Cu-Cd column reduction (peak identification: A, Cl^-; B, NO_2^-; C, NO_3^-; D, $B_2O_6^{2-}$; E, SO_4^{2-}).

correlation between the nitrate amounts added to the Cu-Cd reductor column and the resultant nitrite amounts detected in the column eluents by ion chromatography. In the range 0.10–0.90 mg/l NO_3^-, a linear calibration $y = 0.733x + 0.0155$ with $r = 0.9873$ was obtained for a graphical plot of nitrate amounts added to, and the nitrite amounts recovered from, the Cu-Cd reductor column. Similarly, in the range 0.02–0.1 mg/l NO_3^- a linear calibration $y = 0.87x + 0.0038$ with $r = 0.9871$ was obtained. Sensitivity of the method is high as indicated by the slopes of the graphical plots, 0.733 and 0.87, respectively. The correlation coefficients for a linear least-square fit, r, of 0.9873 and 0.9871, show good linear response. Linear dynamic range was 0.006–1.20 mg/l NO_3^-. This is a significant improvement compared to the conventional methods that are linear over very narrow concentration ranges. Method dynamic range was up to 11.00 mg/l NO_3^-, beyond which the response to nitrate was very low, as indicated also by the low correlation coefficients, r, obtained for graphical plots in ranges beyond this nitrate concentration. For nitrate concentrations above 11.00 mg/l, the reduction efficiency of the Cu-Cd reductor column dropped drastically. However, a working range of up to 11.00 mg/l NO_3^- covers the concentration range of nitrate found in most natural water systems [25], and this is a much higher dynamic range than is possible with current conventional methods [6–10] for determination of nitrate.

3.2.2. Precision, detection limit and accuracy of the method

Good precision in results was obtained within the linear dynamic range of 0.006–1.20 mg/l NO_3^-. For 10 repeat analyses of a 0.50 mg/l NO_3^- standard solution, a coefficient of variation of 0.54% was obtained. Using results obtained for analysis of 0.006 mg/l NO_3^- standard solution, the limit of detection (3σ) was calculated [24] as 0.40 μg/l NO_3^-.

Analysis time for each solution did not exceed 16 min, allowing for detection of the last eluting IC peak due to sulfate ions. However, if based on samples per hour passed through the Cu-Cd reductor column, sample throughput could be up to 12 samples. For this study, the Cu-Cd column efficiency, in reducing NO_3^- to NO_2^-, was determined as 98.20 ± 6.03%. Regeneration of the column, due to loss of efficiency, was normally required after 11 repeat analyses of a 0.1 mg/l nitrate standard solution. Regeneration of the column involved passing copper sulphate solution through the column and rinsing with borate buffer solution. With high nitrate concentrations, especially outside the linear dynamic range, regeneration was after fewer repeat analyses. Activity of the Cu-Cd reductor column diminished slowly with prolonged exposure to nitrate. It has previously been reported [11] that the copper precipitate washed off the Cu-Cd granules increases in amount with each repeat usage of the reductor column and this affects the rate of reduction of nitrate to nitrite. Lower nitrate recoveries were obtained each time the column was regenerated, and as a result a column could be regenerated up to five times only.

Table 1
Percentage recoveries of nitrate in certified reference materials and nitrate

Nitrate-containing solution	P recovery (%) (mean ± S.D. for $n = 5$)
Reference material GBW08606	92.6 ± 0.19
Reference material CRM 479	108 ± 0.44
0.10 mg/l NO_3^- standard solution	96.60 ± 3.29
0.90 mg/l NO_3^- standard solution	94.67 ± 5.90
2.00 mg/l NO_3^- standard solution	97.7 ± 3.70
8.00 mg/l NO_3^- standard solution	95.5 ± 0.11

Standard solutions analyzed by ion chromatography after Cu-Cd column reduction.

Method validation was undertaken using a series of laboratory prepared nitrate standard solutions and certified reference materials GBW08606 and CRM479. Table 1 shows the results obtained. Accuracy of the method was good, as indicated by the percentage nitrate recoveries exceeding 90%. Good precision in results was obtained with values less than 3%, indicating small errors associated with the analysis.

The results from analysis of nitrate standard solutions indicate that this is an efficient method for determination of nitrate with low limits of detection, an extensive linear range and high sensitivity. Such features are attractive for nitrate determination in water samples.

3.3. Application to analysis of real samples

Real water samples were analyzed together with standard reference materials using the optimized experimental conditions. For comparative evaluation of the method samples were analyzed using two other methods; the conventional ion chromatographic method [26] and the conventional colorimetric detection after the Cu-Cd column reduction [8,9].

Using the developed method, most of the nitrate, NO_3^-, in the water sample solutions was reduced to nitrite, NO_2^-, on passage through the Cu-Cd reductor column. This, together with the nitrite naturally present in the sample constituted the total concentration of nitrite detected by the method. Fig. 3a and b show the ion chromatograms from a water sample obtained by conventional IC method [26] and by IC after the Cu-Cd column reduction, respectively. However, for some natural water samples, both nitrate and nitrite were detected in the Cu-Cd reductor column eluents, especially when the reductor column efficiency was low.

In light of the above observations, the results obtained are best discussed and compared to those obtained by the conventional methods after calculation of total oxidized nitrogen (TON); the sum of concentrations of nitrite and nitrate detected by IC in the Cu-Cd reductor column eluents.

For the analyzed Gaborone dam water, Notwane river water and Gaborone storm water samples, TON content determined was in the range 0.40–94.50 mg/l TON. Table 2 shows the results obtained. Generally, for each respective sample, TON values obtained using the proposed IC to Cu-Cd reductor column coupled method were higher than those obtained

Table 2
Results from analysis of natural water samples by conventional ion chromatography and by ion chromatographic detection after Cu-Cd column reduction

Laboratory Sample Code	Conventional IC (mg/l) of TON ($n = 3$)	IC after Cu-Cd reduction (mg/l) of TON ($n = 3$)	Calculated t-value ($P = 0.05$, d.f.: 2)
MCF/C3[a]	0.935 ± 0.003	0.942 ± 0.004	2.47
MCF/C4[a]	0.441 ± 0.072	0.553 ± 0.064	2.70
MCF/C6[a]	0.498 ± 0.063	0.632 ± 0.055	3.63
MCF/C7[a]	0.871 ± 0.014	0.892 ± 0.012	1.98
MCF/C9[a]	1.703 ± 0.030	1.627 ± 0.027	4.53
BNPC[b]	53.0 ± 3.40	60.4 ± 2.90	3.72
Kgale CJSS[b]	4.40 ± 0.51	5.22 ± 0.53	2.73
Sewer-9[b]	82.3 ± 4.1	94.4 ± 3.6	4.99
NR-2[c]	9.37 ± 0.34	10.2 ± 0.24	4.23
NR-5[c]	5.03 ± 0.12	5.40 ± 0.09	2.59

[a] Gaborone dam water samples.
[b] Storm water samples around Gaborone.
[c] Notwane river water samples.

using any one of the two conventional methods; possibly due to reduced interference effects and increased sensitivity in analysis.

Using the paired t-test (at $P = 0.05$) evaluation [27], results obtained using IC detection after Cu-Cd column reduction were not significantly different from those obtained by either the conventional colorimetric method or the conventional ion chromatographic method. Generally, by comparing squared standard deviation, the F-tests [27] show that neither of the two conventional methods had similar precision to the proposed method. The results obtained using the proposed method generally had lower values of standard deviations, indicating therefore better precision using this method. This is a great advantage over the many methods developed to determine nitrate in natural water samples.

Miniaturized Cu-Cd reductor columns can be fabricated and the whole experimental procedure automated with the column eluent fractions for analysis transferred directly to the IC system auto sampler vials.

4. Conclusions

Suppressed ion chromatographic detection can be coupled to the conventional Cu-Cd reductor column method for a more precise and sensitive method of analysis of nitrate in water samples. Use of borate buffer solution in the Cu-Cd column reduction step improves the quality of the ion chromatograms obtained by IC analysis of the column eluents.

For analysis of natural water samples, the coupled-method gives more precise results, though not significantly different from those obtained using either the conventional colorimetric method or the conventional ion chromatographic method. For samples with more complex matrices, such as wastewater, the method combines the nitrate-selective capabilities of the Cu-Cd reductor column reaction with the high sensitivity of ion chromatographic detection.
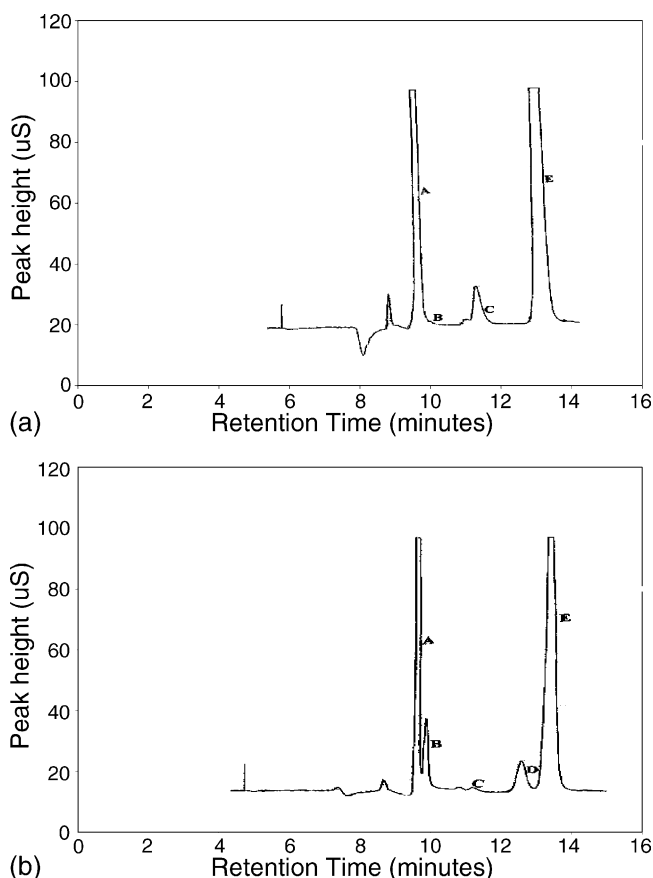

Fig. 3. (a) Chromatogram of natural water sample C6 by conventional IC detection (peak identification: A, Cl^-; B, NO_2^-; C, NO_3^-; E, SO_4^{2-}). (b) Chromatogram of natural water sample C6 by IC detection after Cu-Cd column reduction (peak identification: A, Cl^-; B, NO_2^-; C, NO_3^-; D, $B_2O_6^{2-}$; E, SO_4^{2-}).

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