

A SEQUENTIAL INJECTION ANALYSIS SYSTEM FOR MONITORING OF NITRITE, NITRATE AND SULFATE IN DRINKING WATER AND WASTEWATER

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ABSTRACT: An automated monitoring system for nitrite, nitrate and sulfate based on sequential injection analysis (SIA) was developed. For nitrite determination the Griess-Ilosvay method was used, whereas nitrate was previously reduced to nitrite using a cadmium column followed by the same method. The turbidimetric method was carried out in order to determine sulfate. The results shown that the proposed SIA monitoring system constitutes an effective approach for nitrite, nitrate and sulfate determination since it is able to determine levels required by international agencies that regulate these parameters in water. Detection limits of $0.0207 \text{ mg N l}^{-1}$, $0.0022 \text{ mg N l}^{-1}$ and $3 \text{ mg SO}_4^{2-} \text{ l}^{-1}$ were obtained. The developed technique offers also typical characteristics of the multicommutated systems, as portability, low reagents consumption and a higher sample frequency. The proposed system was satisfactorily applied to drinking water and wastewater samples.

1. INTRODUCTION

The determination of nitrate, nitrite and sulfate is of general relevance due to they are important indicators of water pollution. These species at high levels can cause adverse effects in aquatic environments as acidification indicated by the presence of sulfate or eutrophication caused by nitrogenous compounds including nitrite and nitrate of water bodies as result of their role in the biogeochemistry of those processes [Fung (2008), Pons (2008)]. Although, the presence of sulfate in drinking water does not pose immediate threat to human health, its different for nitrite and nitrate, nitrate can be reduce to nitrite which can react with secondary or tertiary amines present in the body resulting in the formation of nitrosamine some of which are known to be carcinogenic or at high concentrations in blood with Iron (III) of the hemoglobin, forming methemoglobin which has no oxygen carrying ability producing methemoglobinemia [Fung (2008), Monser (2002)], they are important parameters for monitoring the drinking water quality because at high concentrations can lead to a potential risk to human health [Burakham (2004)].

The common methods for determination of nitrite, nitrate and sulfate in water are the colorimetric method, cadmium reduction method, turbidimetric method, gravimetric, ionic chromatography, selective UV spectrometry and ion-selective electrode [Eaton (1998)]. Flow analysis represent a good alternative over the traditional methods of determination used in the environmental field due to its characteristics, like the volumes of sample and reagents used, the frequency of samples injection, and mainly the possibility to develop automated monitoring systems adapting different techniques and instruments. The sequential injection analysis (SIA) allows the integration of different techniques with only one manifold to determinate multiple parameters. Many techniques have been adapted to flow analysis, the most used method for nitrite and nitrate determination has been a colorimetric method in combination with an on-line reduction of nitrate to nitrite, to determine each one or both anions simultaneously [Pons (2008), Burakham (2004), Baeza (2005), Baeda (2001), Cerdà (1998), Ensafi (2004), Gabriel (1998), Kazemzadeh (2001), Legnerova (2002), Mesquita (2009), Somnam (2008), Tsoulfanidis (2008), Zhao (2002)], meanwhile for sulfate determination the turbidimetric method has been employed [Fortes (2008), Melchert (2008), Santelli (1995), van Staden (1996), Vieira (2001)]. Also, other methods have been

developed to determine nitrite and nitrate like detection by sensors [Baeza (2005), Hassan (2007), Miró (2001)], catalytic methods [Yue (2004)], techniques based on the oxidation capacity of different compounds [Monser (2002)], chemiluminiscent methods [Kanda (2003), Mikuska (2003)], liquid chromatography [Butt (2001), Connolly (2001), Zuo (2006)], atomic absorption spectrometry [Noroozifar (2007)] and gas phase molecular absorption [Haghighi (2004)]. Also for sulfate, different arrangements have been proposed like the use of a sensor [Fung (2008)], a reactor column [Burakham (2004)], atomic fluorescence spectrometry [Tyson (2009)] and ion chromatography [Morales (2000)]. However, the well known limitations of the common methods and the drawbacks of some flow analysis systems, have been limited its application to determine nitrite, nitrate and sulfate in drinking water and wastewater with the same system.

Thus, the main objective of this work is the development of a monitoring system based on sequential injection analysis (SIA) for nitrite, nitrate and nitrate determination in drinking water and wastewater. Direct nitrite determination using the Griess-Ilosvay reaction, on-line cadmium reduction column for nitrate following by nitrite determination, in combination with turbidimetric method for sulfate determination, were used in the proposed system.

2. EXPERIMENTAL

2.1 Chemicals and reagents

All the reagents used were analytical grade and deionized water was used throughout. Stock standard solutions of 1000 mg $\text{NO}_2^- \text{N l}^{-1}$, 1000 mg $\text{NO}_3^- \text{N l}^{-1}$ and 1000 mg $\text{SO}_4^{2-} \text{l}^{-1}$ were prepared by dissolving sodium nitrite, sodium nitrate and sodium sulfate in water, respectively. Working standard solutions were obtained by dilution. Chromogenic reagent: 39.6 g of sulphanilamide, 0.99 g of N-(1-naphthyl) ethylene diamine and 99 ml of concentrated HCl (37%, $d=1.19 \text{ g ml}^{-1}$) per litre. Buffer solution A: 80 g l^{-1} NH_4Cl , 15 g l^{-1} $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{ H}_2\text{O}$ and 0.5 g l^{-1} EDTA (disodium salt). Regeneration solution: 38 g l^{-1} EDTA and 12.5 g l^{-1} CuSO_4 , adjusted to pH 7 by adding NaOH. Buffer solution B: 30 g l^{-1} $\text{MgCl}_2 \cdot 6 \text{ H}_2\text{O}$, 5 g l^{-1} $\text{CH}_3\text{COONa} \cdot 3 \text{ H}_2\text{O}$, 1 g l^{-1} KNO_3 , 20 ml CH_3COOH (99%, $d=1.049 \text{ g ml}^{-1}$) and 5% (m/v) arabic gum per litre. Cleaning solution: 0.3% (m/v) EDTA in 0.20 mol l^{-1} NaOH. Precipitating agent: 4.0% (m/v) BaCl_2 solution.

2.2. Apparatus and software

A schematic diagram of the SIA system used in this work is shown in Fig. 1. The manifold included a piston pump type, a selection valve and a spectrophotometer. Besides, a compatible personal computer was used for instrumentation control and for data acquisition and processing. The piston pump type consisted on an autoburette equipped with a 10 ml syringe and connected to a personal computer and controlled through the software Autoanalysis Ver. 5.0 (Sciware). The syringe is used for loading and dispensing the solutions. Spectrophotometric measurements were made using an Ocean Optics USB2000 UV-VIS detector equipped with a flow-through cell (18 ml inner volume, 1 cm optical path) and connected to the computer. Absorbance was measured at 540 nm. An eight-port selection valve was used as a liquid distributor (Crison, Mod. VA 1+1). All flow lines were PTFE tubing of 1.5 mm i.d. except for the reaction coil and the column path length, where tubes of 0.8 mm i.d., were employed. The reduction column was inserted in the detector line between the eight-port selection valve and reaction coil, using a three-way connector.

2.3. Preparation of the reduction column

The column was prepared using cadmium granules as described by Cerdà et al. (1998), these granules were first washed with 0.1 M HCl and subsequently coated with copper by dipping them into a 1% CuSO_4 solution for ca. 1 min. The copperised cadmium granules were washed with distilled water, and packed into a methacrylate tube (55.0 mm length and 4 mm i.d.) and plugged with glass wool.

2.4. Procedure

To carry out the proposed SIA system, one syringe with its corresponding solenoid commutation valve was employed. The position "off" (solenoid disabled) of the valve connects syringe to the right channel and "on" (solenoid enabled) to the left

one. The position “on” of the valve connects to the system through the central port of the selection valve and the position “off” to the carrier bottle.

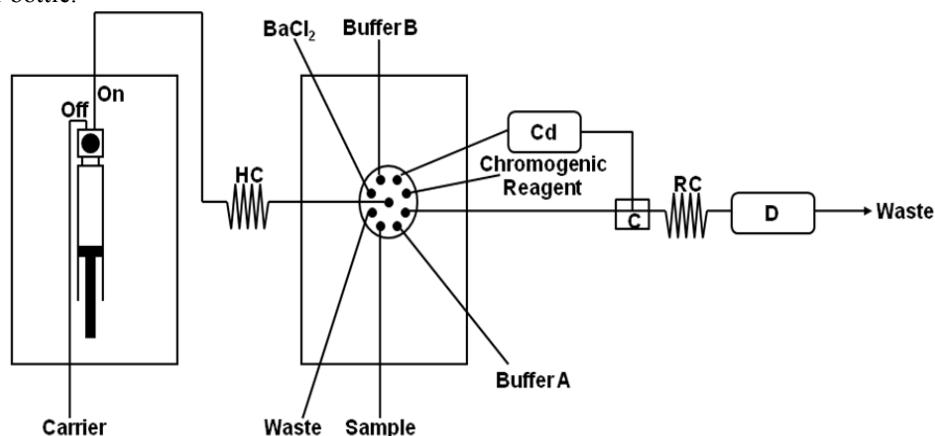


Fig. 1. SIA monitoring system proposed for NO_2^- , NO_3^- and SO_4^{2-} . HC: Holding coil; RC: Reaction coil; C: Three-way connector; Cd: Cadmium column; D: UV-VIS Detector; Buffer A: Ammonium Chloride-EDTA solution; Buffer B: Magnesium Chloride-Acetic Acid- Arabic Gum solution.

The autoburette connected to the eight-port selection valve is used for loading and dispensing the sample and reagents. The management of the sample and reagents through the selection valve were as is following: the sample to the port 2, the chromogenic solution to the port 4, the buffer solution A to the port 5, the buffer solution B to the port 7 and the BaCl_2 solution to the port 8. The port 1 was employed as a waste and to load cleaning solution. The reduction column was connected to the port 6.

Table 1. Optimal operation conditions

Variable	Optimal value
Loading coil	200 cm (i.d. 1.5 mm)
Reaction coil	400 cm (i.d. 0.8 mm)
Carrier	H_2O
For NO_2^- and NO_3^-	
Sample volume	2 ml
Buffer A volume	0.08 ml
Chromogenic reagent volume	0.5 ml
Chromogenic reagent concentration	0.23 mol l^{-1}
Flow rate of sample and reagents	15 ml min^{-1}
For SO_4^{2-}	
Sample volume	1 ml
BaCl_2 volume	0.5 ml
Buffer B volume	0.2 ml
BaCl_2 concentration	4 % (w/v)
Flow rate of sample and reagents	10 ml min^{-1}

The initial step was the filling of the reagents tubes with the corresponding solutions. Then, the instrumental blank was set and the measuring method was started. For NO_2^- determination, 2 ml of sample and 0.5 ml of chromogenic solution were loaded through its respective ports, after that sent to the reaction coil and then to the detector by the port 3. For NO_3^- , 2 ml of sample, 0.5 ml of chromogenic reagent plus 0.08 ml of buffer solution A were loaded from its containers and then impelled through the reduction column located in the port 6, after the reduction of NO_3^- to NO_2^- , the mixture was completed

in the reaction coil and the determination was carried out by the detector. For SO_4^{2-} , 1 ml of sample, 0.5 ml of BaCl_2 solution and 0.2 ml of buffer solution B were loaded through its respective ports and then sent to the reaction coil and after that to the detector. After each SO_4^{2-} determination, a washing process was performed to remove the precipitate added to the tubing, loading 2 ml of the cleaning solution through port 1 and impelling it by the port 3 to the reaction coil and the detector, leaving the system for further analysis. During the measuring cycle a sandwich technique [Cerdà (1998)] was used to improve the mixture of the reagents and sample, which consisted in put sections of reagent and buffer between small sample volumes. In a turbidimetric determination, it is necessary to maintain the suspension of the precipitate as homogeneous as possible, in order to improve the precision of the measurements. The arabic gum included in the buffer solution B was employed to stabilize the suspension.

3. RESULTS AND DISCUSSION

3.1. System dimensioning

At the beginning, the sandwich arrangement was chosen; with the sample placed between two reagent zones until accomplish the total volume, led to the highest readout per sample injected. The optimal values shown in Table 1 were determined for each one by performing a Box-Behnken response surface experimental design with the model 2^k , performed with Minitab 15 (Minitab Inc.) software giving a total of 53 experimental runs. The reduction column dimensions of 55 mm per 4 mm, length and internal diameter respectively, were chosen to allow a better packed of the cadmium granules, reducing the possibility of bubbles formation which reduce the area for the conversion of nitrate to nitrite. Under optimized conditions the analytical figures of merit were established and the method was applied to the determination of nitrate, nitrite and sulfate in drinking water and wastewater.

3.2 Analytical figures of merit

The analytical performance of the system was evaluated in terms of detection limit, quantification limit, sensibility, correlation coefficient (R^2), linear range, repeatability and reproducibility, and injection frequency. Table 2 summarizes the figures of merit presented by each parameter approaches studied in the present work. Detection limits and quantification limits were calculated from the standard deviation of the blank ($n=10$, 3σ and 10σ , respectively). The detection limits and lineal ranges of this work contained in Table 2, were below the parametric values established by the European Union (EU) of 50 mg l^{-1} for nitrate, 0.5 mg l^{-1} for nitrite and 250 mg l^{-1} for sulfate [EU (2009)]; the maximum contaminant levels regulated by United States Environmental Protection Agency (US EPA) of 10 mg l^{-1} for nitrate, 1 mg l^{-1} for nitrite, 250 mg l^{-1} for sulfate [US EPA (2009)]; and the recommended values given by the World Health Organization (WHO) of 50 mg l^{-1} for nitrate, 3 mg l^{-1} for nitrite and 500 mg l^{-1} for sulfate [WHO (2008)]. The detection limits of 0.18 mg N l^{-1} , 0.1 mg N l^{-1} and $1 \text{ mg SO}_4^{2-} \text{ l}^{-1}$, established in the standard methods [Eaton (1998)] were almost completely surpassed by the ones achieved in this work, with the exception of the sulfate detection limit that was slightly above, due to the instability of the precipitate formed through the path to the detector.

Three calibration runs were carried out in order to establish the working ranges, one using a set of nitrite standards with concentrations in the range $0.014\text{-}0.42 \text{ mg N l}^{-1}$, a second with nitrate solutions of concentrations ranging from 0.14 to 1.82 mg N l^{-1} and a third using a set of sulfate standards with concentrations in the range $75\text{-}300 \text{ mg SO}_4^{2-} \text{ l}^{-1}$ and good R^2 of 0.9951, 0.9952 and 0.9994 have been obtained with these three calibration runs. The values of relative standard deviation (RSD) obtained for repeatability of 0.46%, 1.34% and 1.96% and 2.13%, 3.39% and 4.76% for reproducibility shown in Table 2 have demonstrated that the results obtained with the proposed system have a good level of accuracy being below the 5%, these values of RSD were obtained by processing a $1.4 \text{ mg l}^{-1} \text{ N}$, $0.28 \text{ mg l}^{-1} \text{ N}$ and $200 \text{ mg l}^{-1} \text{ SO}_4^{2-}$ reference solutions for nitrate, nitrite and sulfate, respectively. The injection frequencies were also calculated for the proposed system. Values of 12 and 15 injections per hour were obtained for the system as a consequence of the two-step procedure (sampling into a holding coil and delivering towards the reaction coil) and the washing steps necessities in this flow methodology.

3.3 Efficiency of the reduction column

The effectiveness of the reduction column was tested running three calibration graphs (Fig. 2), one for nitrate under reductive conditions and two for nitrite, one under non-reductive and the other under reductive conditions.

When the reduction activity of the column falls below 85%, a regeneration of the column was required. With this purpose the on-line method proposed by Cerda et al. (1998) was modified, consisting on the aspiration of 2 ml of the regeneration solution through port 1 of the selector valve and subsequent dispensed through port 6. The regeneration solution passing through the column provided new copper to regenerate the external coating of the cadmium granules and EDTA to avoid the precipitation of $\text{Cd}(\text{OH})_2$ or other hydroxides on the reductor. The column was finally flushed with water, leaving the system ready for further analysis. The repetitive running of the regeneration solution not only decreased the sampling rate but also shortened the lifetime of the column due to the breakdown of the cadmium granules into smaller particles.

Table 2. Figures of merit for SIA system

	Nitrate	Nitrite	Sulfate
Detection limit	0.0207 ^b	0.0022 ^b	3 ^a
Quantification limit	0.0692 ^b	0.0073 ^b	10 ^a
Sensibility	0.5531 ^d	2.0887 ^d	0.0024 ^c
R ²	0.9951 (n=7)	0.9994 (n=8)	0.9952 (n=7)
Lineal range	0.14-1.82 ^b	0.014-0.42 ^b	75-300 ^a
Repeatability ^e	1.96 (n=10)	0.46 (n=10)	1.34 (n=10)
Reproducibility ^e	4.76 (n=5)	3.39 (n=5)	2.13 (n=5)
Injection frequency ^f	12	15	12

^a mg $\text{SO}_4^{2-} \text{ l}^{-1}$, ^b mg N l^{-1} , ^c l $\text{mg}^{-1} \text{SO}_4^{2-}$, ^d l $\text{mg}^{-1} \text{N}$, ^e %, ^f h^{-1}

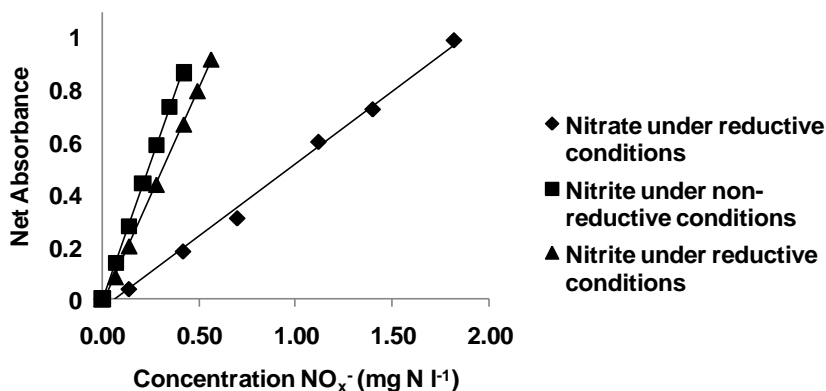


Fig. 2. Calibration graphs for nitrate under reductive conditions and nitrite under reductive and non-reductive conditions

3.4 Interferences.

For this study, at a time, foreign ion of a known concentration was added to a solution containing fixed concentrations of 1.12 mg N l^{-1} for nitrate and $200 \text{ mg SO}_4^{2-} \text{ l}^{-1}$ for sulfate, respectively. A given ion was considered to interfere with the determination if it resulted in a signal variation greater than 10%.

For nitrate, was examined the effect of the PO_4^{3-} in the reduction column, which was found as the mayor interference by Cerdà et al. (1998), in this work, the presence of PO_4^{3-} was not interference due to the flow rate used causing a short contact time between the ion and the column, despite that the ion was present in high concentration. A concentration range from 2 up to $300 \text{ mg PO}_4^{3-} \text{ l}^{-1}$ was studied without variations greater than 10%. For sulfate, were studied the interfering effect of these three cations: Ca^{+2} , Mg^{+2} and K^{+} , commonly found in water samples [Fung (2008)], a concentration of $500 \text{ mg l}^{-1} \text{ Ca}^{+2}$ and $40 \text{ mg l}^{-1} \text{ K}^{+}$ had an interfering effect in the precipitation of Ba_2SO_4 , meanwhile, up to $800 \text{ mg l}^{-1} \text{ Mg}^{+2}$ did

not interfere. The reduction of the effect of cations was avoided with the addition of EDTA to keep a constant low value of pH during the precipitation of Ba_2SO_4 .

Table 3. Analytical results and recovery tests obtained for nitrite with SIA and standard methodology

Sample	Nitrite*			Sulfate		
	Addition (mg N l^{-1})	Concentration (mg N l^{-1})	Recovery (%)	Addition ($\text{mg SO}_4^{2-} \text{l}^{-1}$)	Concentration ($\text{mg SO}_4^{2-} \text{l}^{-1}$)	Recovery (%)
Ground water	0	0.0018 ± 0.0027	95.1	0	80.7835 ± 9.4377	97.4
	0.2	0.1920 ± 0.0027		80	158.7134 ± 9.4377	
Tap water	0	0.0035 ± 0.0039	93.4	0	1.5149 ± 4.2865	105.2
	0.2	0.1903 ± 0.0039		80	85.6530 ± 4.2865	
Wastewater inlet	0	0.0040 ± 0.0044	97.1	0	100.6710 ± 16.1416	94.6
	0.2	0.1983 ± 0.0044		80	176.3435 ± 16.1416	
Wastewater outlet	0	0.0066 ± 0.0203	87.8	0	189.4765 ± 16.5037	92.9
	0.2	0.1823 ± 0.0203		80	263.7910 ± 16.5037	

The results are expressed as three replicates average \pm standard deviation.

* Samples were diluted with water 1:1 before the analysis.

3.5 Application to samples

In order to investigate the applicability of the proposed method to the analysis of drinking water such as tap water and ground water, and wastewater, from inlet and outlet of a treatment plant were analyzed for nitrite and sulfate. Before injecting the samples into the system, the wastewater samples were filtered. Table 3 show the analytical results and recovery tests obtained with the proposed method. Furthermore, the t-test at 95% was applied to compare the results obtained, no significant differences were found.

4. CONCLUSIONS

The proposed SIA system allows the automated monitoring of nitrate, nitrite and sulfate with a low consumption of reagents, a good reproducibility and repeatability, and more over is its high speed of analysis compared with the standard methods. The method shows a good accuracy in its working range for the monitoring of the three ions which is suitable for drinking waters and wastewater samples. Although some warns with the reduction column and the manifold can be necessary to keep the reduction efficiency of nitrate to nitrite and to avoid that the Ba_2SO_4 formed can adhere to the walls of the tubes, with the regeneration of the reduction column when the reduction efficiency decrease and washing steps after the sulfate determination this troubles do not affect the system performance. Due to the quite simplicity and rapid response of the proposed method, it could be used to monitor nitrate, nitrite and sulfate in certain fields where the continuous assessment of these ions is necessary (e.g. wastewater treatment plants or industrial processes).

5. ACKNOWLEDGEMENTS

This work was funded by FOMIX CHIH-2008-C02-92172. A. Ayala acknowledge to CONACYT for the scholarship given to support this work.

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