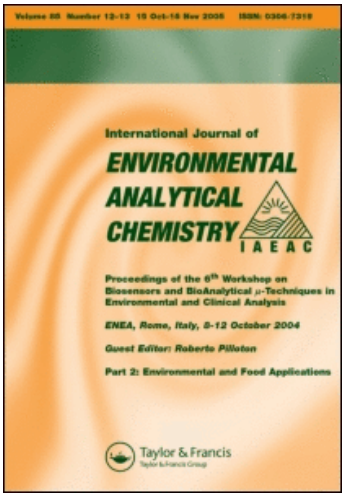


**International Journal of Environmental Analytical Chemistry**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

# A multisyringe flow injection system coupled with a gas diffusion cell for ammonium determination

Jana Klimundová; Rafael Forteza; Víctor Cerdà

Online publication date: 24 June 2010

**To cite this Article** Klimundová, Jana , Forteza, Rafael and Cerdà, Víctor(2003) 'A multisyringe flow injection system coupled with a gas diffusion cell for ammonium determination', International Journal of Environmental Analytical Chemistry, 83: 3, 233 — 246
**To link to this Article: DOI:** 10.1080/1030673102100004858 2
**URL:** http://dx.doi.org/10.1080/10306731021000048582

*Intern. J. Environ. Anal. Chem.*, Vol. 83, No. 3, pp. 233–246



# A MULTISYRINGE FLOW INJECTION SYSTEM COUPLED WITH A GAS DIFFUSION CELL FOR AMMONIUM DETERMINATION

JANA KLIMUNDOVÁ[a], RAFAEL FORTEZA[b] and VÍCTOR CERDÀ[b,*]

[a]*Faculty of Pharmacy in Hradec Králové, Charles University, Prague, Czech Rep.;*
[b]*Department of Chemistry, University of the Balearic Islands, Carretera de Valldemossa, km. 7.5, E-07071 Palma de Mallorca, Spain*

*(Received 6 May 2002; In final form 16 August 2002)*



A multisyringe flow injection system for ammonium determination based on the coupling of a gas-diffusion separation cell has been developed. By using a multisyringe burette equipped with additional three-way solenoid valves, the system allows the use of different reagents or samples with further propelling into a gas-diffusion unit. Two possibilities were tested to increase the sensitivity and repetitivity: flow delay during the diffusion of the ammonia formed and use of successive flow reversals.

The proposed MSFIA system is compared with the FIA and SIA techniques based on the same principle and has been validated applying the method to the determination of ammonium in environmental samples.

*Keywords:* Multisyringe flow injection analysis (MSFIA); Ammonium; Gas diffusion

## INTRODUCTION

Multisyringe flow injection analysis (MSFIA) has been recently developed with the aim to include in the same methodology the advantages of the previous FIA and SIA techniques [1]. The basic element of the former methodology is a multisyringe burette constructed by adaptation of an automated syringe pump analogue to that employed in SIA manifolds in order to simultaneously move 4 syringes, which are connected in block to the same step by step motor. Each syringe presents at the head a 3-way solenoid commutation valve, analogue to those employed in multicommutation methods, which allows its connection with the system (ON) or with the reagent reservoir (OFF), independently from the piston displacement. At the same time, external 3-way valves can be connected, thus, simplifying in this way the MSFIA technique and increasing the number of modalities for dispensing the sample plug into the flow system.

*Corresponding author. E-mail: vcerda@p01.uib.es

ISSN 0306-7319 print: ISSN 1029-0397 online © 2003 Taylor & Francis Ltd
DOI: 10.1080/1030673102100048582

These solenoid valves can either work as injection valves or be used in multicommuted injections.

The main differential characteristics of MSFIA with regard to precedent flow techniques can be summarized in the following points:

A robustness analogue to that of SIA assemblies with syringe pumps is achieved. This methodology allows the use of aggressive reagents as well as organic solvents and, therefore, the constrains derived from the wear out flexible tubes of peristaltic pumps in FIA are avoided.

Saving of reagents with regard to FIA, since they are only injected at the precise moment of carrying out the analytical determination.

The sampling rate values are increased in relation to SIA due to the fact that sequential stacking of both reagent and sample plugs into a holding coil becomes unnecessary. There are different configurations and alternatives for the injection of precise sample volumes.

As reagent and sample segments are simultaneously propelled through T or Y type connectors, the radial mass transfer between zones is feasible. This leads, for the same coil length, to a higher reaction yield than that of SIA assemblies, in which the axial mass transfer prevails on the segment interfaces.

Flow injection methods using gas diffusion separation have been described for the determination of volatile analytes and analytes which can be transformed into volatile species after a chemical reactions [2–5]. Ammonium is an example of the latter [6–15]. It can be effectively determined by transforming it, at alkaline pH, into ammonia, which permeates across the membrane. This process adds the advantage of making the extraction of the analyte and other interfering species from the matrix feasible, with the possibility of preconcentration. Spectrophotometric detection is carried out using an acid–base indicator as an acceptor solution [7–9].

In this article we discuss the improvements and differences between the multisyringe system and other usual flow techniques such as FIA and SIA. Finally, the proposed methodology is applied to the determination of ammonium in compost and fertilizer samples.



## EXPERIMENTAL

### Reagents

All solutions were prepared in distilled water. Standard solutions of ammonium in the range 0.5–220 mg/L were prepared by suitable dilution of a stock solution of 1000 mg/L of $NH_4^+$ in chloride form.

A sodium hydroxide solution within the range 0.001–0.05 M was prepared by appropriate dilution of a stock solution of 0.1 M.

The acid-base indicator was bromothymol blue (BTB), in sodium salt form due to its higher solubility. A concentration of 0.08 mM was prepared by diluted of a stock solution of 0.16 mM, adjusted by adding sodium hydroxide to obtain a pH from 6.0 to 8.0. The optimum pH happened to be 6.8. BTB was also used at a pH higher than 10.0 (basic form) as a dye, in order to optimize the washing and filling steps in the procedure.

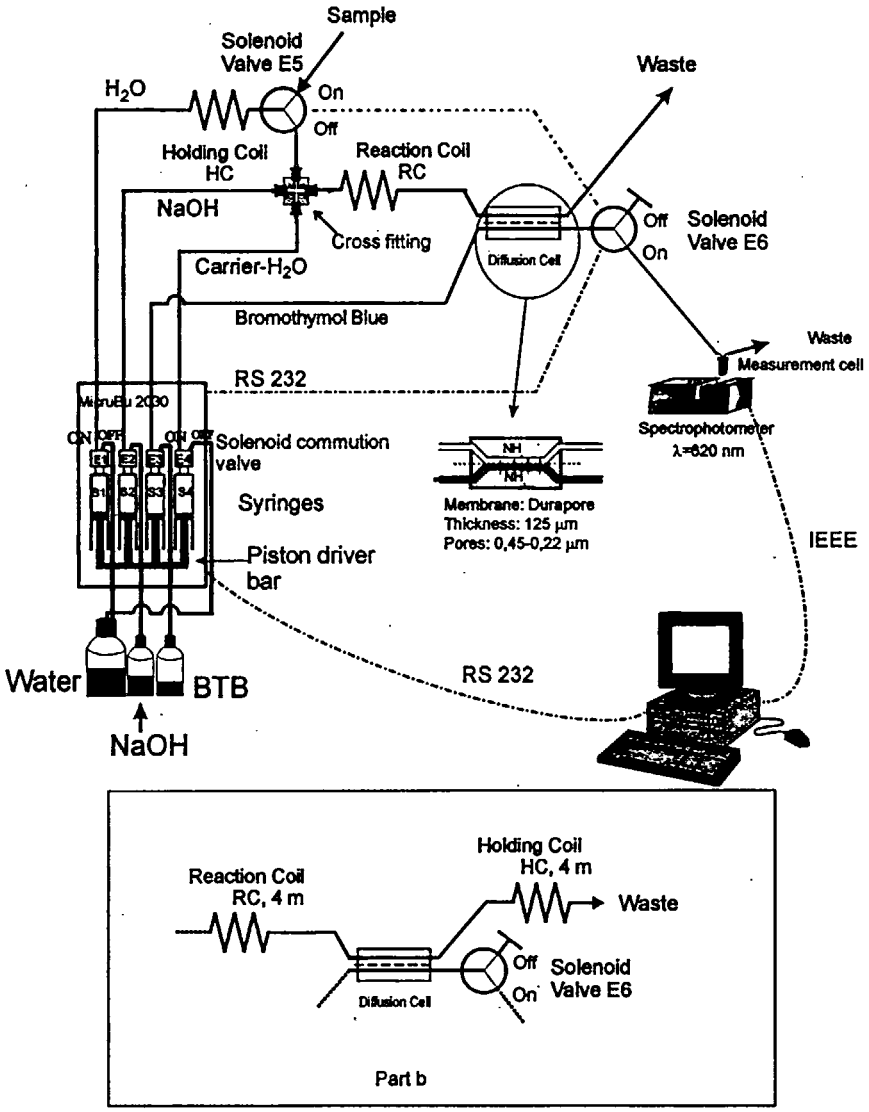


FIGURE 1 Manifold of the MSFIA for ammonium determination coupled with a gas diffusion cell.

## Apparatus

The configuration used is shown in Fig. 1. All instruments were controlled by personal computer, using the software Autoanalysis, developed by the authors' group[1], written in Delphi (Version 4) and Visual C++ (Version 5). This program also permits acquisition and treatment of the spectrophotometric data [16].

The multisyringe burette (MicroBU 2030, Crison Instruments, Alella, Spain) allows to pick up or dispense precise volumes of reagents or samples. It comprises four

[1]These programs may be requested at aest@p01.uib.es

syringes (in Fig. 1, S1–S4) of different capacities (5, 5, 10, 10 mL) whose pistons are displaced simultaneously, being connected in block to the same stepping motor (5000 steps). Each syringe has a three-way isolation solenoid valve on each head (in Fig. 1, E1–E4). With position OFF, E1 is connected to the bottle with water, E2 – to the bottle with NaOH, E3 – to the bottle with BTB and E4 – to the bottle with water. The multisyringe burette has also two additional independent three-way isolation solenoid valves (E5, E6) (N-Research, Cladwell, NJ, USA). E5 allows the connection of the holding coil with the sample reservoir or with the reaction coil through a cross connector. E6 is used to close the acceptor channel of the diffusion cell when the procedure with the acceptor channel stopped and the donor channel flowing is required.

Absorbance measurements were performed by using a Hewlett Packard 8453 diode-array spectrophotometer at a wavelength of 620 nm and a correction wavelength of 750 nm (to correct inexact results due to refractive index variation). It was equipped with a glass flow-through cell of 18 µL inner volume and 1 cm optical path. Data provided by the spectrophotometer are acquired via a HP-IB interface at a frequency of 2 Hz.

The diffusion cell was made of two symmetric methacrylate blocks, with two independent channels 2 mm wide and 0.3 mm deep, of circular shape with a radius of 13 and 16 mm, respectively (67 or 83 mm long). The cross section of the inner channel is rectangular. The channel 67 mm long, with a volume of approximately 40 µL was used. The hydrophobic gas permeable membrane, Durapore® (Millipore, USA) of 0.45–0.22 µm pore size, was placed between the acceptor and the donor channels.

The holding coil was of PTFE tubing 2.5 m long, 1.5 mm i.d (4.4 mL of capacity).

The reaction coil was of PTFE tubing 1 m long, 0.8 mm i.d (0.5 mL of capacity).

The tubing from syringes to the bottles was of 1.5 mm i.d, and the remaining tubes of 0.8 mm i.d.



## Preparation of Fertilizer and Compost Samples

The commercial NPK fertilizers with a nominal concentration of N in ammonia form of 7 and 17% were weighted (0.6 g) and dissolved in hot water. Finally, they were made up to 1 L with distilled water. These solutions (three replicates) were analyzed by the Kjeldahl method without including the mineralization step and with the multisyringe system proposed in this article.

The compost sample was firstly homogenized and, then, 4 g were weighted and extracted with 200 mL of KCl 2 M, stirring during 30 min. Finally, the solution was centrifuged at 4000 rpm and filtered through a 0.45 µm filter.

## Procedure

One of the most outstanding features of the MSFIA technique is its versatility and, therefore, its capability to implement several manifolds, thus, allowing different possible uses of the diffusion cell employed. In this way, both the isolation and concentration of ammonia are feasible, with few changes in the manifold. Bearing in mind the above-mentioned three procedures have been investigated: (a) donor and acceptor channels flowing, (b) acceptor channel stopped and donor channel flowing and (c) acceptor channel stopped and donor channel with reversal flows.

The multisyringe and the additional independent three-way isolation solenoid valves (E5, E6) are connected to the computer via RS 232, which allows to program all steps in order to carry out the determinations. These steps are shown in Table I and are described next.

### *(a) Procedure with Donor and Acceptor Channels Flowing*

*Steps 1–3 in procedure*: Led to the acquisition of the blank spectrum corresponding to the bromothymol blue indicator, BTB, at an initial pH = 6.8 (without changes due to the diffusion of ammonia).
*Step 4*: Begins with a cycle to obtain several peaks corresponding to the same sample.
*Steps 5 and 6*: Are used for filling the sample aspiration tube and cleaning the holding coil (HC) with water from syringe S1.
*Steps 7–10*: 4.0 mL of new sample are aspirated by the same syringe (S1) towards HC with valve E5 in position ON. In order to achieve a good repetitivity aspiration of the sample at a low flow rate is required. After that, position of valve E5 is changed to position OFF and 0.2 mL of the sample is propelled to the system to fill the tubing before the cross fitting. The sample excess after the cross fitting is washed out with water dispensed by syringe S4.
*Steps 11–13*: BTB in the acceptor channel of the diffusion cell is cleaned using syringe S3 in order to avoid measuring the ammonium passed through the diffusion cell during previous steps.
*Steps 14–22*: Measuring of spectrophotometer is started at an analytical wavelength of 620 nm (maximum absorbance for BTB) and with the correction wavelength at 750 nm (to avoid inexact results due to refractive index variation, Schlieren effect). At the same time a loop, which enables the obtaining of several peaks corresponding to the same sample, is started. The first step in this loop is to clean BTB in the system before each sample is dispensed (0.16 mL of BTB) to attain the same conditions for each peak. Then, a sample volume of 0.250 mL is dispensed by syringe S1 from the holding coil, with valve E5 in position OFF, together with the same volume of sodium hydroxide propelled by syringe S2 (with the presumption that the tube between this syringe and the cross fitting is loaded with NaOH due to a previous measuring). Both are mixed after the cross fitting. The mixture is propelled with 3.0 mL of water from syringe S4 at a flow rate of 1.0 mL/min to pass through the diffusion cell. Ammonium reacts with NaOH to give ammonia, which passes through the gas-permeable membrane to the acid–base indicator BTB, which is flowing on the other side of the membrane simultaneously with the sample (3.0 mL volume and a flow rate of 1.0 mL/min). After passing the diffusion cell the sample reaches the waste and BTB is propelled towards the detector to measure color changes caused by ammonia.

In order to minimize the effect of the existence of overpressures within the system, which are responsible for the liquid not remaining still but continuing to move when finishing a certain step, with the corresponding lost of repetitivity, it is advisable to include a delay of two seconds as in steps 8, 12 and 19, to achieve pressure equilibration.

### *(b) Procedure with Acceptor Channel Stopped and Donor Channel Flowing*

This method was performed by using the same manifold as depicted in Fig. 1.

TABLE I Method operations of the procedure with donor and acceptor carriers flowing

| *Step* | *Vol.*[1] (mL) | *Flow rate* (mL/min) | *Operation* | *Position of solenoid valves* | | | | | | *Description* |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | *E1* | *E2* | *E3* | *E4* | *E5* | *E6* | |
| 1 | 1.25 | 4.1 | Multisyringe. dispense | off | off | on | off | off | on | BTB washing |
| 2 | | | HP 8453. measure blank | | | | | | | Measuring the blank with BTB |
| 3 | 1.25 | 15 | Multisyringe. pickup | off | off | off | off | off | off | Putting syringes at initial position |
| 4 | | | Loop 'new sample' | | | | | | | |
| 5 | 0.3 | 4.1 | Multisyringe. pickup | on | off | off | on | off | off | Filling sample aspiration tube |
| 6 | 4.1 | 4.4 | Multisyringe. dispense | on | off | off | on | off | off | Washing diffusion cell and holding coil |
| 7 | 4 | 2 | Multisyringe. pickup | on | off | off | off | on | off | Filling HC with a new sample |
| 8 | | | Multisyringe. wait 2 s | | | | | | | |
| 9 | 0.2 | 2 | Multisyringe. dispense | on | off | off | off | off | off | Filling the tube before the cross fitting with sample |
| 10 | 1 | 1.5 | Multisyringe. dispense | off | off | off | on | off | off | Cleaning RC |
| 11 | 0.8 | 6.8 | Multisyringe. dispense | off | off | on | off | off | on | Refreshing BTB |
| 12 | | | Multisyringe. wait 2 s | | | | | | | |
| 13 | 2.1 | 15 | Multisyringe. pickup | off | off | off | off | off | off | Filling syringes (equilibrate volumes) |
| 14 | | | HP 8453. measuring the absorbance | | | | | | | |
| 15 | | | Loop 'injections' | | | | | | | |
| 16 | 0.08 | 2.5 | Multisyringe. dispense | off | off | on | off | off | on | Beginning of the peak |
| 17 | 0.25 | 1 | Dispense | on | on | off | off | off | off | Sample and NaOH injection |
| 18 | 1.5 | 1 | Multisyringe. dispense | off | off | on | on | off | on | Dispensing BTB to the measurement cell |
| 19 | | | Multisyringe. wait 2 s | | | | | | | |
| 20 | 1.83 | 15 | Multisyringe. pickup | off | off | off | off | off | off | |
| 21 | | | Repeat 5 times from step 15 | | | | | | | |
| 22 | | | Repeat *n* times from step 4 | | | | | | | |

[1]All volumes are referred to syringe 1. The volumes of the four syringes are 5, 5, 10 and 10 mL, respectively.

TABLE II New steps of the method with acceptor carrier stopped and donor carrier flowing

| *Step* | *Vol.*[1] (mL) | *Flow rate* (mL/min) | *Operation* | *Position of solenoid valves* | | | | | | *Description* |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | *E1* | *E2* | *E3* | *E4* | *E5* | *E6* | |
| 16 | 0.75 | 1 | Multisyringe. dispense | on | on | off | off | off | off | Sample injection |
| 17 | 0.3 | 1 | Multisyringe. dispense | off | off | off | on | off | off | Sample dispensing |
| 18 | 1 | 1 | Multisyringe. dispense | off | off | on | on | off | on | BTB dispensing |
| 19 | 2.05 | 15 | Multisyringe. pick up | off | off | off | off | off | off | Filling syringes |
| 20 | | | Repeat 5 times from step 15 | | | | | | | |
| 21 | | | Repeat n times from step 4 | | | | | | | |

[1]All volumes are referred to syringe 1. The volumes of the four syringes are 5, 5, 10 and 10 mL, respectively.

The cleaning steps in this procedure were the same as those in procedure with donor and acceptor carriers flowing. Only the steps after 15 were substituted by those described in Table II.

*Steps 16–17*: 0.75 mL of sample were dispensed through the diffusion cell (with the same volume of NaOH) and then 0.6 mL of water from syringe S4 were dispensed to propel the mixture. The solenoid valve E3 of the syringe with BTB (S3) was in position OFF (which means that BTB is returned to its reservoir). Also, E6 was in position OFF to avoid BTB being thrown out of the acceptor channel by pressing of the permeable membrane. In this way, BTB remains stopped in its channel. Initially, the experiments were carried out by propelling the sample with 2.0 mL of water from syringe S4, instead of 0.6 mL, the peaks obtained, thus, being very small, with a base-line drift and negative peaks occurred at the beginning of each peak. These inconveniences were due to the fact that the amount of water was too large and, therefore, the ammonia striped back from the acceptor channel to the donor channel.

*Steps 18–19*: Finally, in the acceptor channel, 2.0 mL BTB were propelled to the detector in order to carry out the corresponding measurement.

### *(c) Procedure with Acceptor Channel Stopped and Donor Channel Reversal Flow*

This method was performed by slightly modifying the manifold: introducing two holding coils capable of containing 2 mL of mixture of sample and sodium hydroxide, one coil being placed before the diffusion cell and the other after. The resulting solution, mixture of sample and sodium hydroxide will flow several times through the donor channel of the diffusion cell in order to achieve a larger amount of ammonia passing through the permeable membrane. The reaction coil of 1 m long, 0.8 mm i.d. (0.5 mL of capacity) was changed by another of 4 m long, 0.8 mm i.d. (2 mL of capacity) and another coil of 4 m long, 0.8 mm i.d. was added after the output of the diffusion cell (see Part b in Fig. 1).

The cleaning steps in the method were those as in the procedure with donor and acceptor carriers flowing. Only the steps after 13 were substituted by new ones described in Table III.

*Step* 15: 0.75 mL of sample were dispensed through the diffusion cell (with the same volume of NaOH).

TABLE III New steps of the method with acceptor carrier stopped and donor carrier with reversal flows

| *Step* | *Vol.*[1] (mL) | *Flow rate* (mL/min) | *Operation* | *Position of solenoid valves* | | | | | | *Description* |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | *E1* | *E2* | *E3* | *E4* | *E5* | *E6* | |
| 14 | | | Loop 'injections' | | | | | | | |
| 15 | 0.75 | 1 | Multisyringe. dispense | on | on | off | off | off | off | Sample injection |
| 16 | | | Loop 'reversals' | | | | | | | |
| 17 | 1 | 1 | Multisyringe. dispense | off | off | off | on | off | off | Sample dispensing |
| 18 | 1 | 1 | Multisyringe. pickup | off | off | off | on | off | off | Sample reaspirated |
| 19 | | | Repeat 5 times from step 16 | | | | | | | |
| 20 | 0.7 | 1 | Multisyringe. dispense HP 8453. measuring the absorbance | off | off | off | on | off | on | Sample eliminating |
| 21 | 1 | 1 | Multisyringe. dispense | off | off | on | on | off | on | BTB dispensing and measuring |
| 22 | | | HP 8453. stop measure | | | | | | | |
| 23 | 2.45 | 15 | Multisyringe. pick up | off | off | off | off | off | off | Filling syringes |
| 24 | | | Repeat 5 times from step 14 | | | | | | | |
| 25 | | | Repeat *n* times from step 4 | | | | | | | |

[1]All volumes are referred to syringe 1. The volumes of the four syringes are 5, 5, 10 and 10 mL, respectively.

*Steps 17–20*: 2 mL of water from syringe S4 were dispensed to propel the mixture, and the solenoid valve E3 of syringe with BTB (S3) was in position OFF. Also, E6 was in position OFF. Next, the same volume was flow reversed. These instructions can be repeated the number of times required.

## RESULTS AND DISCUSSION

### Optimization of Experimental Conditions

In preliminary studies, the system was investigated by using only one dye (BTB of pH higher than 10) with the aim to obtain good repetitivity between injections of the same sample or when the sample was changed. It is a question, therefore, of avoiding dilution of the aspired sample in the holding coil and achieving a satisfactory degree of cleaning after each sample is dispensed. For the first condition, it is only necessary to have enough amount of sample in the holding coil in order to avoid using the end of the sample segment aspirated, which would lead to the achievement of smaller final peaks owing to the dilution of the end of the sample segment by water. The holding coil should be large enough to avoid the aspirated sample reaching the syringe, since the latter would be difficult to clean whenever the sample should be changed. If a sufficient amount of sample was not available dispersion could be avoided by aspirating a small air bubble between the sample and the water from the syringe.

On the other hand, the system does not allow the use of high flow rates since they may produce high overpressures and, therefore, flow rates lower than 2 mL/min for filling the holding coil should be employed. Waiting steps were also added between each movement of the syringes (about 2 s each), the repetitivity being, thus, enhanced. The length of the reaction coil after the cross fitting where the mixture between the sample and the sodium hydroxide is produced is of great importance. Several

experiments have been carried out without coil (tube of 0.2 m) and with coils of 1, 2 and 3 m. When changing from 0.2 to 1 m repetitivity is considerably enhanced, however, this is not so when using a length of 2 to 3 m. On the other hand, the peak height decreases when a larger tube is employed (between 10 and 15% less per added meter).

The coil of 1 m length will be used since it enhances repetitivity between series and avoids appearance of shoulders at the end of peaks. When implementing this reaction coil a better mixture between the sample and sodium hydroxide is then achieved, bearing in mind these two solutions present very different ionic strengths.

Another important parameter to be taken into account is the length of the channels in the gas-diffusion unit and their shape. All tested channels were of a rectangular section of 2 mm wide and 0.3 mm deep. The tested lengths of the cells with straight channels were the following: 3, 6 and 12 cm long. Besides, two diffusion cells with circular channels and a radius of 1.3 and 1.6, respectively, were assessed (length 6.66 cm and 8.25 cm). We have observed a better gas transfer efficiency with circular cells which might be owed to the higher turbulence in the inside of both donor and acceptor channels, which helps the transport phenomena. The best results were obtained with the circular cell of 1.3 cm radius.

Finally, a volume of 3.0 mL BTB was chosen since smaller amounts prevented from the obtaining of whole peaks.

Next, several of the most relevant studies performed to optimize the obtained signal are presented:



### Procedure with Donor and Acceptor Channels Flowing

#### *Influence of Sample Volume and Flow Rate*

The volumes 0.05, 0.1, 0.15, 0.20, 0.25, 0.40 and 0.50 mL of the sample were investigated. Results are represented in Fig. 2.

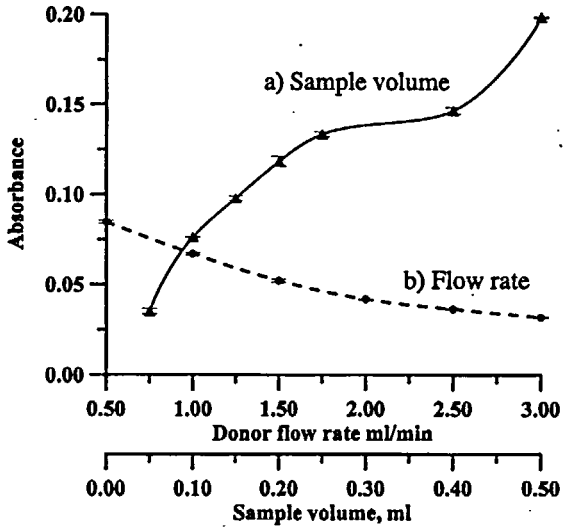


FIGURE 2 Effect of the flow rate and the sample volume in the procedure with donor and acceptor carriers flowing.

The arising tendency at the end of the curve is caused by the fact that when the volume of sample is greater than 0.25 mL, this volume, plus the same volume of sodium hydroxide is larger than the reaction coil (0.5 mL) and the beginning of the mixture passes through the diffusion cell, however, BTB in the acceptor channel remains still. Another variable which is likely to have a great influence is the flow rate at which the mixture of the sample and the sodium hydroxide by the donor channel, on the one hand, and BTB by the acceptor channel, on the other hand are simultaneously being flowed (Step 18 in procedure (a)). Results are shown in curve (b), Fig. 2. As expected, the higher the flow rate through the diffusion cell, the smaller the peak obtained as a consequence of the kinetic restrain of the transfer of ammonia through the permeable membrane. A volume of 0.25 mL and a rate of 1.0 mL/min were chosen owing to both the peak height and the low standard deviation achieved.

### Influence of Bromthymol Blue, pH and Sodium hydroxide Concentration

The pK of BTB is 7.1 and this is the reason why it is more sensitive near this pH. pH 6.8 was chosen for the solutions of this reagent in the acceptor channel. The shape of the peaks was not acceptable at pH 7.0 (small 'negative peak' occurred at the beginning of each peak). In the donor carrier when the pH is sufficiently high to achieve full transformation of the ammonium to ammonia, not more signals will, therefore, be obtained. This fact occurs when the concentration of NaOH is higher than 0.005 M. We have chosen 0.01 M.

### Procedure with Acceptor Channel Stopped and Donor Channel Flowing

#### *Sample Volume Investigation*

In a previous article we have established that one possibility to increase the gas transfer efficiency was by accumulation of the analyte having the acceptor carrier static while the sample is flowing along the donor side, and the accumulation depends on the sample volume. Multisyringe methods can improve this possibility in relation to the SIA configuration. In sequential injection operations, increasing the sample volume is not an effective way to enhance sensitivity because the overlapping of the sample and the alkaline solution is not complete due to the use of stacked zones which are not completely mixed during their transport to the diffusion unit and, consequently, the production of ammonia is not increased. Volumes 0.25; 0.5; 0.75 and 1.0 mL of sample were measured and the results can be seen in Fig. 3, overlapped with the corresponding values of the procedure with acceptor and donor carriers flowing. It can be observed that the improvement is fair up to 0.75 mL of sample but larger volumes do not increase the signal because the transfer efficiency of ammonia through the Durapore® membrane is only about 15% [7] and after a short time, the equilibrium between the liquid layers next to the membrane is established and, therefore, there is no significant diffusion of ammonia across the membrane. One way of increasing the diffusion is by generating turbulence in the donor channel and refreshing the layer liquid near the membrane and, therefore, the molecules for away from the membrane are transported close enough to diffuse through it. This can be reached with the use of low reversal.

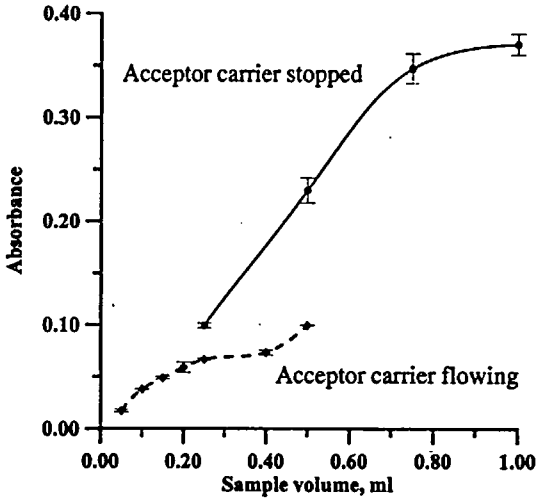


FIGURE 3 Effect of the sample volume in the procedure with acceptor carrier stopped and donor carrier flowing. Comparison with donor and acceptor carriers flowing.

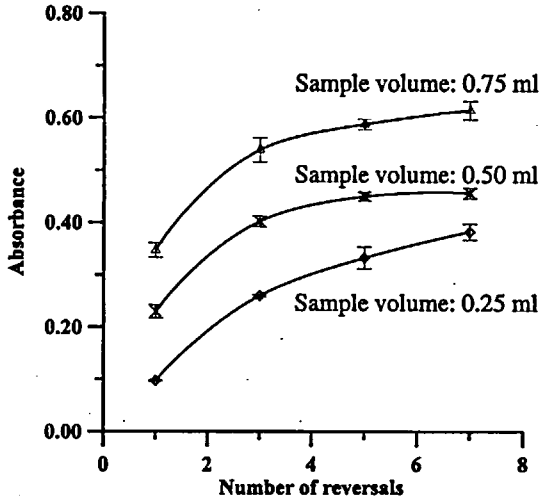


FIGURE 4 Effect of number of reversal flows for three sample volumes, 0.25, 0.5 and 0.75 mL, in the procedure with acceptor carrier stopped and donor carrier reversal flowing.

### Procedure with Acceptor Channel Stopped and Donor Channel Reversal Flows

1, 3, 5 and 7 reversal flows through diffusion cell with sample volumes of 0.25, 0.5 and 0.75 mL were tested.

Results shown in Fig. 4 prove that the behavior is the same for the three volumes of sample used. Passing the mixture of sample and NaOH till 3 times enhanced considerably the sensitivity, whereas when a larger number of reversal flows were used the increase was negligible.

## Calibration Graphs

A set of experimental measurements were carried out with the aim to check the capabilities of these approaches to improve the sensitivity of the method. Calibration graphs are obtained for the three procedures above mentioned described and the results are in Fig. 5. The main analytical characteristics are summarized in Table IV.

In terms of sensitivity when comparing the different slopes, the procedure with the acceptor carrier stopped and the donor carrier with five reversal flow exhibits a slope 3.3 times greater than that regarding the donor and acceptor carriers flowing, and 1.5 times larger than that with the acceptor carrier stopped and the donor carrier flowing. The latter with a slope 2 times greater than that corresponding to the donor and acceptor carriers flowing.

The detection limit using 0.75 mL of sample and 5 reversal flows was 0.07 mg/L. It was calculated from $3Se/b$, where $Se$ is the blank standard deviation and $b$ is the sensitivity of the method calculated as the slope of the calibration graph. The value of LOD is higher in the case of the procedure with the donor channel with flow reversals than those in the cases in which flow reversals are not carried out. The calibration curve slope is in fact larger in the procedure where flow reversals occur, however, less satisfactory results are attained from the repetitivity point of view and, consequently, for the detection limit values.



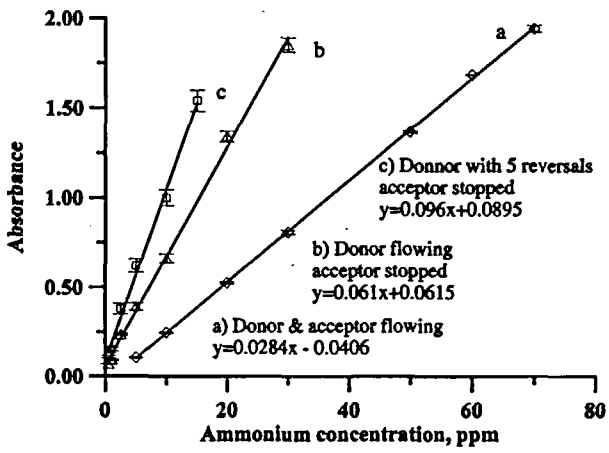


FIGURE 5 Calibration graphs for the three procedures: donor and acceptor carriers flowing, acceptor carrier stopped and donor carrier flowing and acceptor carrier stopped and donor carrier reversal flowing.

TABLE IV Analytical characteristics of GD-MSFIA methods for ammonium determination

| | *MSFIA* | *MSFIA stopped* | *MSFIA reversal flow* |
|---|---|---|---|
| Sample volume | 0.25 mL | 0.75 mL | 0.75 mL |
| Calibration graphs ($[NH_4^+]$ in mg $L^{-1}$) | Abs = 0.028 $[NH_4^+]$ + 0.041 | Abs = 0.061 $[NH_4^+]$ + 0.062 | Abs = 0.096 $[NH_4^+]$ + 0.089 |
| Linear range | 5–70 mg $L^{-1}$ | 0.5–30 mg $L^{-1}$ | 0.5–15 mg $L^{-1}$ |
| RSD (5 mg $L^{-1}$, $n = 10$) | 1.3% | 2.8% | 3.2% |
| LOD ($3\sigma$) | 0.03 mg $L^{-1}$ | 0.03 mg $L^{-1}$ | 0.07 mg $L^{-1}$ |
| *Injection throughput per hour* | 20 | 15 | 10 |
| Sample throughput per hour | 4 | 3 | 2 |

TABLE V Determination of ammonium by MSFIA in fertilizer samples

| *Product* | *Determination of ammonium by MSFIA* % N | *Determination of ammonium using reference method* % N |
|---|---|---|
| Fertilizer (NPK)[1] | 7.0±0.3% ($n=3$) | 6.9±0.2% ($n=3$)[3] |
| Fertilizer (2)[2] | 17.0±0.3% ($n=3$) | 17.3±0.3% ($n=3$)[4] |

[1,2]Nominal concentration of N in ammonia form of 7 and 17%, respectively; [3]By Kjeldahl method. Significance level of hypothesis test for the comparison of two means (two tailed test): 0.54; [4]By Kjeldahl method. Significance level of hypothesis test for the comparison of two means (two tailed test): 0.16.

TABLE VI Determination of ammonium by MSFIA in compost samples

| *Method* | | | | | | | | *Average*±*SD* |
|---|---|---|---|---|---|---|---|---|
| Berthelot, % of N | 0.113 | 0.125 | 0.112 | | | | | 0.120±0.006 ($n=3$)[1] |
| MSFIA, % of N | 0.115 | 0.118 | 0.116 | 0.115 | 0.118 | 0.120 | 0.119 | 0.117±0.002 ($n=7$)[1] |
| FIA, % of N | 0.119 | 0.106 | 0.106 | | | | | 0.110±0.007 ($n=3$)[1] |

[1]Significance level of hypothesis test by ANOVA: 0.08.

Interference studies reported in a previous article [7] demonstrated the good selectivity of the GD methods. In the former studies it was proved that the most frequent ions do not interfere, however, serious variations of the signals are suffered in the presence of other volatile amines, e.g., methylamine, ethylamine, etc.

### Application in Analysis of Real Samples

The new MSFIA approach described in this article was applied to the determination of ammonium in fertilizer and compost samples as described in 'Preparation of Fertilizer and Compost Samples'.

The results of the determination of fertilizer samples were compared by statistical *t*-test with those obtained by Kjeldahl method, without the mineralization step to avoid the determination of other *N*-species.

The results of compost samples were compared by ANOVA test with those obtained by the Berthelot [17] and FIA methods [7].

The results are summarized in Table V and VI. In all cases the conclusions of the statistical inference tests were of no significance differences ($\alpha=0.05$).

## CONCLUSIONS

To establish the advantages and drawbacks of MSFIA against other usual flow techniques we have checked the main features of these methodologies in the same set of conditions, i.e., using the same laboratory, reagents, apparatus and analyst. The results are summarized in Table VII.

As observed the most important features are similar for all methodologies, moreover, some interesting aspects should be outlined: MSFIA is very robust, enables the use of solvents and aggressive reagents without additional measures, although involving a philosophy analogue to that of FIA since it allows the simultaneous flow of the solutions and, consequently, the obtaining of a better mixture. At the same time, a larger volume of sample is feasible when preconcentration is required. In sequential

TABLE VII Main features of the flow techniques studied

| *Parameter* | *FIA* | *SIA* | *MSFIA* | *MSFIA with acceptor carrier stopped* | *MSFIA with reversal flow* |
|---|---|---|---|---|---|
| Detection limit ($mg\,L^{-1}$) | 0.08 | 0.04 | 0.03 | 0.03 | 0.07 |
| Linear range ($mg\,L^{-1}$) | 5–220 | 0–30 | 5–70 | 0.5–30 | 0.5–15 |
| %RSD | 1.8 | 2.5 | 1.3 | 2.8 | 3.2 |
| Injection throughput (s/h) | 30 | 15 | 20 | 15 | 10 |
| Sample throughput (s/h) | 6 | 3 | 4 | 3 | 2 |
| BTB consumption (mL) | 2.2 | 3.6 | 3.8 | 3.8 | 3.8 |
| NaOH consumption (mL) | 1.4 | 0.5 | 0.25 | 0.75 | 0.75 |
| Sample volume (mL/inj.) | 0.1 | 0.25 | 0.25 | 0.75 | 0.75 |
| Sample volume needed for analysis of one sample (mL/inj.) | 1.3 | 0.25 | 0.5 | 1.0 | 1.0 |

injection operations, increasing the sample volume is not an effective way to enhance sensitivity because the overlapping of the sample and reagent solution is not complete, since the stacked zones are mixed only during their transport. MSFIA, as in SIA systems, presents the advantages of being very versatile, very well adapted to stopped techniques and a lower consumption of reagents and sample is required.

Among the drawbacks it can be mentioned that MSFIA, like SIA, needs to be controlled by a computer using an appropriate software and it has lower sample throughput in comparison with FIA systems. This fact can be solved by using an autosampler, taking advantage of the robustness and versatile features.



## *Acknowledgments*

The authors acknowledge the financial support of the CICyT (Spanish Ministry of Science and Education) through project PPQ 2001-0347 and PPQ 2001-0474. J. Klimundová acknowledges the grant provided by the AEST (Association of Environmental Sciences and Techniques).

## *References*

[1] V. Cerdá, J.M. Estela, R. Forteza, A. Cladera, E. Becerra, P. Altimira and P. Sitjar, *Talanta*, **50**, 695–705 (1999).
[2] W.E. Van der Linden, *Anal. Chim. Acta*, **151**, 359–369 (1983).
[3] M. Valcarcel and M.D. Luque de Castro, *Trends Anal. Chem.*, **10**, 114–121 (1991).
[4] G.D. Clark, D.A. Whitman, G.D. Christian and J. Ruzicka, *Crit. Rev. Anal. Chem.*, **21**, 357–375 (1990).
[5] M. Valcarcel and M.D. Luque de Castro, *Non-Chromatographic Continuous Separation Techniques*. The Royal Society of Chemistry, Cambridge (1991).
[6] M.T. Oms, A. Cerdà and V. Cerdà, *Electroanal.*, **8**, 387–390 (1996).
[7] M.T. Oms, A. Cerdà, A. Cladera, V. Cerdà and R. Forteza, *Anal. Chim. Acta*, **318**, 251–260 (1996).
[8] M. Van Son, R.C. Schothorst and G. den Boef, *Anal. Chim. Acta*, **153**, 271–275 (1983).
[9] I.D. Eremina, L.K. Shpigun and A.Y. Zolotov, *Zh. Anal. Khim.*, **48**, 35–42 (1993).
[10] W. Frenzel and Ch.Y. Liu, *Fresenius J. Anal. Chem.*, **342**, 276–280 (1992).
[11] G. Schulze, Ch.Y. Liu, M. Brodowsky, O. Elsholz, W. Frenzel and J. Möller, *Anal. Chim. Acta*, **214**, 121–136 (1988).
[12] R. Liu and B. Sun, *Anal. Lett.*, **30**, 1255–1265 (1997).
[13] D. Lee, V. Nguyen and S. Littlefield, *Commun. Soil Sci. Plant Anal.*, **27**, 783–793 (1996).
[14] R. Liu, B. Sun and I. Johns, *Analyst*, **120**, 2845–2848 (1995).
[15] H.S. Yim, G.S. Cha and M.E. Meyerhoff, *Anal. Chim. Acta*, **237**, 115–125 (1990).
[16] E. Becerra, A. Cladera and V. Cerdà, *Lab. Rob. Autom.*, **11**, 131–140 (1999).
[17] J. Kempers and A. Zweers, *Commun. Soil Sci. Plant Anal.*, **17**, 715–723 (1986).