

## GAS/DIFFUSION FLOW INJECTION DETERMINATION OF AMMONIUM IONS IN RIVER AND WASTE WATERS BY CONDUCTOMETRY

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An FIA conductometric method for monitoring of ammonium ions in river and waste waters is proposed. A very good detection limit ( $x_D$  5.6  $\mu\text{mol l}^{-1}$ ) was obtained at 100/20 s preconcentration/rinsing times and 2 ml sample consumption per analysis at the flow rate 0.8  $\text{ml min}^{-1}$ . The detection limit  $x_D$  can be further improved at longer preconcentration/rinsing times. Precipitation of polyvalent metal ions (mainly Fe(III)) was eliminated by addition of 0.5  $\text{mmol l}^{-1}$  EDTA prior to injection. The results are comparable with those obtained by spectrophotometry (Nessler's reagent).

**Key words:** Ammonium; Flow injection analysis; Gas diffusion; River water; Waste water; Conductometry; Electrochemistry.

Increasing amounts of ammonium ions are found in surface and ground waters because of excessive use of nitrogen fertilizers in agriculture. Considerable quantities are also produced from organic nitrogen-containing compounds (proteins, urea, amino acids, *etc.*) by reductive chemical and, under anaerobic conditions, microbial processes in livestock industry, municipal waste water and sewage treatment plants and in technological processes like desulfurization of oil and coal.

Methods for FIA determination of ammonium ion<sup>1-4</sup> are based on selective gas permeation or diffusion techniques with subsequent quantification of changes in acidity of a suitable acceptor solution either by spectrophotometry or by potentiometry. Conductometric detection has been used for sensitive determination of the ammonium ion and/or total nitrogen in Kjeldahl digests, water and air<sup>5-14</sup>. Conductometric detection is based on the absorption of ammonia transported through a semipermeable membrane from alkaline aqueous sample stream into deionized water or dilute boric, sulfuric or hydrochloric acid and subsequent quantification of the changes in conductivity. Deionized water gives higher sensitivity but cali-

bration curves are nonlinear due to the low ionization of ammonia ( $\text{NH}_4\text{OH}$ ) and the presence of acid gases (mainly carbon dioxide).

In recent studies, the pH discrimination of the mass transport of molecular species through tubular membranes made of microporous poly(vinylidene difluoride) (PVDF) and nonporous silicone rubber was described as a tool for separation and preconcentration of analytes from aqueous and gaseous samples<sup>15-18</sup>. In the present work, the membrane separation technique is used for selective determination of ammonium in river and waste waters.

## EXPERIMENTAL

### Chemicals

A standard  $1 \text{ mol l}^{-1}$  solution was prepared by dissolution of  $\text{NH}_4\text{NO}_3$  of analytical grade purity (Lachema Brno, Czech Republic) and standardized by titrimetry after Convey microdistillation. Working solutions were diluted with acidified water to the required concentration. Other chemicals (NaOH, EDTA, boric and sulfuric acids, *etc.*) were commercial samples of analytical grade purity (Lachema Brno, Czech Republic). Bidistilled water from a quartz apparatus Bi-18 Destamat (Heraeus Quarzschmelze, Hanau, Germany) was used.

### Apparatus

FIA manifolds were constructed from a basic FIAAnal 01 unit (MikroLaAp, Košice, Slovak Republic) equipped with an electronic part, a UV-VIS spectrophotometric detector, a six-way loop injector (Model 5020, Rheodyne, Cotati, U.S.A.) and a four-channel constant speed peristaltic pump (40 rpm, Ismatec, Switzerland). A reaction system was mounted from Teflon capillaries (0.5 mm i.d.) and polypropylene T-pieces (Ark-Plas. Inc., Flippin, U.S.A.). A conductometric CD 01 detector (Ecom, Prague, Czech Republic) was connected to a TZ 4620 line recorder (Laboratory Instruments, Prague, Czech Republic). The FIA apparatus was controlled by a PC *via* A/D-converter JNP 01 using a computer program FIANALPC (MikroLaAp, Košice, Slovak Republic).

Acidity of solutions was measured by a pH meter OP 208/1 equipped with an OP 0808P combined electrode (Radelkis, Budapest, Hungary). The instrument was regularly checked with a set of standard buffer solutions S 1306, S 1326 and S 1336 of pH 2.18, 7.00 and 9.18, respectively, at 25 °C (Radiometer, Copenhagen, Denmark).

### FIA Manifolds

Basic schemes of FIA manifolds are depicted in Fig. 1. A four-channel peristaltic pump delivered water as an acceptor, a sample solution and a modifier (NaOH solution). The flow rate of the streams was regulated by i.d. of tygon tubing and by the pressure of segments. The reaction coil (30, 60 and 90 cm, 0.5 mm i.d.) was connected to the pump using the T-pieces.

Membrane units were home-made devices. The coaxial membrane unit<sup>4</sup> was made of an outer Teflon tube (1.7 mm i.d., 2.5 mm o.d.), polypropylene T-pieces and an inner microporous PVDF capillary membrane (0.8 mm i.d., 1.0 mm o.d., 4.5  $\mu\text{m}$ , Enka, Wuppertal,

Germany). The donor stream passed in the annular space between the two tubes rather than through the inner part of the membrane capillary. The acceptor stream was oriented through the inner part of the microporous membrane. A classic sandwich membrane unit<sup>4</sup> was made of two pieces of Teflon blocks with the mirror-oriented grooves separated by a planar microporous Teflon membrane (Sartorius, Heidelberg, Germany). The blocks were fastened with screws. The donor and the acceptor streams were co-current on both sides of the membrane.

A six-way loop injector was interconnected to allow to stop the acceptor solution inside the membrane unit for a preselected period of time corresponding to the preconcentration period in one position and to wash out the sample zone into the reaction coil in the second position (see Fig. 1a for details). Both periods were controlled by time-switch from a PC. The manifold is preferable for determination of trace concentrations of analyte. The sample and the modifier (NaOH or KOH) are pumped into the reaction coil, where ionic forms of the analyte are converted to gaseous species ( $\text{NH}_4^+$  to  $\text{NH}_3$ ). The reaction mixture passes continuously the separation unit from the outer side of the membrane and the gaseous species diffuse through the microporous membrane.

An acceptor solution is transported with a separate peristaltic pump through the injector into the inner part of the membrane separation unit. A defined volume of the acceptor solution is closed inside the membrane unit in one position (preconcentration phase) and gases penetrate the membrane. The penetrated ammonia is absorbed in the stagnant acceptor solution for a preselected period of time and forms ionic species (ammonium ions) with appropriate changes in conductivity of the acceptor solution. A pure acceptor solution is

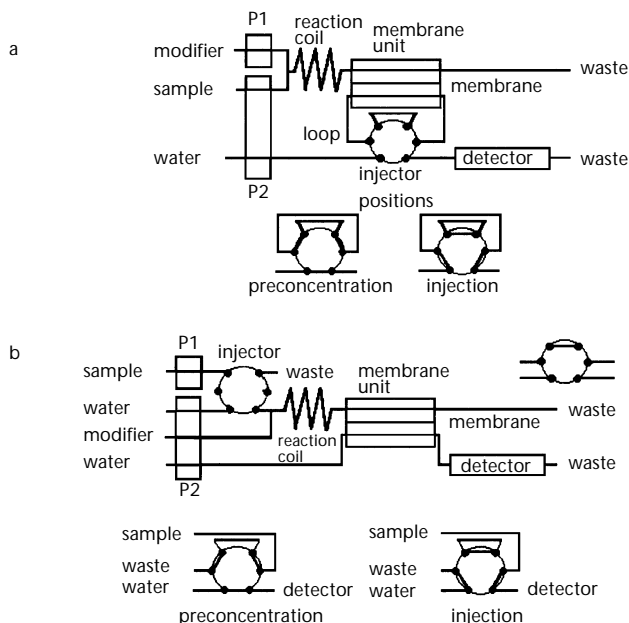


FIG. 1

FIA manifolds (a) and injector positions (b)

transported aside of the membrane unit and passes the flow cell of the conductivity detector during the preconcentration phase and the baseline signal is recorded. The sample plug with the preconcentrated analyte is washed out with a carrier stream from the membrane unit into the flow cell and an analytical signal is recorded as peaks. The peak heights and/or peak areas are proportional to the analyte concentration in original sample.

The second manifold is preferable for samples with a higher content of the analyte when no preconcentration is needed or when dilution is preferred. The six-way injector introduces the defined volume of the sample into a reaction coil. The sample plug merges with a modifier (NaOH solution) and conversion reactions take place inside the reaction coil. The reaction mixture and an acceptor solution pass in a co-current way the membrane separation unit from the opposite sides of the membrane. The liberated gases penetrate into the acceptor solution and form a sample plug. Peaks are registered when the conductive plugs of analytes pass a conductometric detector. Concentration is governed by the transport efficiency, by the flow rate ratio of both streams and by the concentration of analytes in the sample if the conversion and absorption reactions are quantitative.

## RESULTS AND DISCUSSION

### *Optimization of FIA Conditions*

FIA manifolds were optimized for determination of ammonium ions in river water using a preconcentration step (Fig. 1a) and waste waters if the content of ammonium ions was too high for the former method to be applicable (Fig. 1b). The peak height is controlled by the concentration of ammonium ions in sample, by the preconcentration (stopping period) and the rinsing times, the concentration (pH) of modifier (NaOH) in the donor stream, by the composition of the acceptor stream, the lengths of reaction and dispersion capillaries and the flow rate(s) of both streams. The peak shape, on the other hand, depends on the ratio of the preconcentration and the rinsing times.

The peak height increases with  $c(\text{NH}_3)$  over the range 0.005–1.0 mmol l<sup>-1</sup>; the calibration curve is nonlinear and can be transformed to the fifth-order polynomial with the coefficients  $x_0 = -6.8$ ,  $x_1 = 4\ 047.2$ ,  $x_2 = -9\ 439.5$ ,  $x_3 = 15\ 095.2$ ,  $x_4 = -12\ 395.8$  and  $x_5 = 3\ 936.7$  and the correlation coefficient  $r = 0.9995$ . The curved dependence is impractical but for most cases, the narrower concentration interval is acceptable. The curve is with good approximation linear ( $x_0 = -4.2$ ,  $x_1 = 387\ 788.5$  and  $r = 0.99993$ ) over the range 25–300 μmol l<sup>-1</sup>, which corresponds to the usual concentration of ammonium ion in river water.

The peak height increases with the preconcentration time up to 230 s. A curvature appears over the range because of the depletion of absorption capacity of the acceptor solution and the limited dissociation of ammonium

ions. A longer period of injection also increases the peak height in the same way when using scheme in Fig. 1b. Scheme in Fig. 1a was used as an optimum for further experiments at the preconcentration period of 100 s (the value lies in the linear part of the calibration curve). Any prolongation does not improve the sensitivity, only a non-significant increase in the peak height being observed. At least a 5 s period was used for injection. The longer period prolongs the rinsing time and decreases the throughput of samples. The peak height is practically independent of the rinsing time. The ordinary peak shape is deformed and a negative signal appears before the peak only when the rinsing time is longer than the preconcentration period. A decrease in the peak height at shorter rinsing times is due to an incomplete rinsing of the sample plug and to dispersion of sample zones in the acceptor part during their transport through the FIA system. Thus a 20 s period was used which was sufficient for total rinsing of the zones from the separation unit and also from the flow cell. The whole measuring cycle thus takes 120 s.

The NaOH concentration in the donor stream is an important factor influencing the completeness of the conversion of ammonium ions to ammonia. An insufficient quantity of NaOH gives rise to lower peak heights. The signal reaches the limiting value given by the reaction yield. A part of ammonium ions is not converted to ammonia and the amount is totally inactive in transport through the membrane. A small excess of NaOH has to be present in the donor stream to convert all ammonium ions to ammonia. An 0.1 M NaOH was sufficient for most cases when units and tenths of milligrams of ammonium ions per liter were present.

The length of the reaction coil (30, 60 and 90 cm) insignificantly influenced the analytical signal. The signal was constant for 30 and 60 cm lengths and decreased by 5% at 90 cm length. The conversion was fast enough and the mixing efficiency of the shortest coil was sufficient, hence the 30 cm coil was used in Fig. 1a. The reason was to reduce memory effects and to optimize the manifold arrangement.

The peak height depends on the quantity of the analyte absorbed while the peak shape depends on the operational scheme (the ratio of the preconcentration and rinsing times). When the preconcentration period  $t_2$  is much shorter than the rinsing time  $t_2$ , the baseline signal of the acceptor solution at the concentration of ammonium ions given by the concentration of ammonia penetrating the membrane during the rinsing time, the plateau appears at the end of the peak. The pure solution passes the membrane unit in the second position of the injector and thus zero-conductivity

signal appears. A negative part can be registered before the peak or the baseline can be registered at the zero conductivity value.

The pure water signal is registered as the baseline in the case when the preconcentration time is longer than the rinsing time (no negative part appears). The latter case, when only positive values appear, is more practical for determination of the peak height. Also, an easy check of leakage of the donor solution into the acceptor stream due to the rupture of membrane, to incorrect installation of the membrane and to other factors is possible. Any change in the baseline position indicates troubles.

A precipitate appeared in several real water samples after alkalization because of higher contents of heavy metals (mainly Fe(III)). The precipitate was adsorbed on the surface of the membrane and blocked the microporous membrane. The precipitate also influenced the precision and accuracy of the FIA method since the function of membrane was diminished. In an extreme case, the donor channel of the membrane unit was blocked by the precipitate. The blockage caused an enormous overpressure on the membrane and eventual rupture of the membrane with the subsequent leakage of the donor solution into the acceptor stream. Application of a higher flow rate of the donor stream to prevent the blockage was not successful. A small amount of EDTA ( $0.5 \text{ mmol l}^{-1}$ ) was then added to the modifier to prevent precipitation and to eliminate the necessity of filtration of turbid samples before injection.

Deionized water was satisfactorily used as an acceptor for lower concentrations because of a lower background conductivity and a more stable baseline. Boric acid was recommended as the most suitable acceptor medium for higher concentrations<sup>4,14</sup>. Solutions of different concentrations of boric acid have been tested as an acceptor because of their higher absorption capacity than deionized water. The increased absorption capacity improves the difference in partial pressure of ammonia on both sides of the membrane due to the formation of ammonium ions in the acceptor. The peak height could be higher when using boric acid than that in water under the same conditions. A comparison of the results for pure water and different concentrations of boric acid shows that the signal increases with increasing concentration of boric acid in the acceptor stream (up to  $10 \text{ mmol l}^{-1}$ ) over the  $\text{NH}_4^+$  concentration interval of  $1\text{--}100 \text{ }\mu\text{mol l}^{-1}$ . Excessive concentration of boric acid in the acceptor solution insignificantly increases the peak height. The detection limit is also improved when using boric acid, especially for higher concentrations of  $\text{NH}_4^+$ , even though water is preferable for lower concentrations. The boric acid concentration has to be carefully checked because of the background conductivity of the solution.

*FIA Analysis of Real Samples*

The proposed method was applied to the determination of ammonium ions in river waters (Fig. 1a) and the results were compared with those obtained by a classic spectrophotometric method with Nessler's reagent (see Table I). The most common concentrations lie in the range from 56 to 277  $\mu\text{mol l}^{-1}$ . The calibration curve is strictly linear over the range with the detection limit  $x_D = 5.6 \mu\text{mol l}^{-1}$  when using water as an acceptor. Lower concentrations need a longer preconcentration time or a different acceptor. Preconcentration longer than 2 min needs larger volumes of samples and the throughput of the method is seriously reduced. Because of the limited amount of the sample, the 100 s preconcentration time was used.

System in Fig. 1a was also tested using waste waters. Flow rates of the acceptor and donor solutions were twice higher than that of the sample; thus, in-line dilution of the sample was achieved and concentration of ammonium ions in the sample was acceptable. Some samples were additionally diluted to reduce the ammonium concentration (see Table I) or manifold (Fig. 1b) was used. EDTA (5  $\text{mmol l}^{-1}$ ) was added into the modifier solution since precipitation was observed for waste water samples. The calibration curve was linear from 112 to 940  $\mu\text{mol l}^{-1}$  ( $x_0 = 6$ ,  $x_1 = -1$ ,  $x_D = 56 \mu\text{mol l}^{-1}$ ,  $r = 0.9989$ ) for the FIA method. The results were compared with those

TABLE I

Results obtained by the FIA and the Nessler spectrophotometric methods in  $\mu\text{mol l}^{-1}$  for river and waste water samples<sup>a</sup>

Sample no.	River water			Sample no.	Waste water		
	FIA <sup>b</sup>	Nessler <sup>c</sup>	Difference		FIA <sup>d</sup>	Nessler <sup>e</sup>	Difference
1	83	61	22	1	356	350	6
2	128	116	12	2	378	355	23
3	100	94	6	3	822	800	22
4	216	200	16	4	1 027	1 150	-123
5	266	244	22	5	822	967	-145

<sup>a</sup>  $c(\text{NaOH}) = 0.1 \text{ mol l}^{-1}$ ,  $Q(\text{NaOH}) = Q(\text{H}_2\text{O}) = 1.4 \text{ ml min}^{-1}$ ,  $Q(\text{sample}) = 0.8 \text{ ml min}^{-1}$ ,  $c(\text{EDTA}) = 0.5 \text{ mmol l}^{-1}$ , preconcentration time 100 s, rinsing time 20 s; <sup>b</sup> relative standard deviations  $s_r$  0.3–2.7% ( $n = 5$ ); <sup>c</sup>  $s_r$  1.1–3.0% ( $n = 3$ ); <sup>d</sup>  $s_r$  0.9–5.3% ( $n = 5$ ); <sup>e</sup>  $s_r$  1.8–7.1% ( $n = 3$ ); <sup>f</sup> turbid samples with high total nitrogen contents.

obtained by the spectrophotometric Nessler method; consistent results were obtained.

### CONCLUSIONS

The FIA method proposed in the paper is very suitable for determination of ammonium ions in different types of water. A satisfactory agreement of the results was obtained. Mostly positive deviations appear at lower concentrations ( $60\text{--}400\ \mu\text{mol l}^{-1}$ ) while negative values appear for waste water samples with higher concentrations of ammonium ions. The preconcentration period of 100 s and rinsing time of 20 s can be prolonged to improve the detection limits. Total time per analysis is ca 120 s. Four or five cycles are usually necessary for determination of ammonium ions in a single sample to be sure the results are correct. Approximately 10 min is needed for one determination. A relatively small amount of sample (10 ml) is needed at the flow rate of  $0.8\ \text{ml min}^{-1}$ . No harmful operations and no special or toxic substances are used. The cost of analysis is significantly reduced because of conductometric detection.

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