Potentiometric and conductometric determination of ammonium by gas-diffusion flow injection analysis

Wolfgang Frenzel 1 and Cheng-Yu Liu 2

1 Institut für Technischen Umweltschutz, Fachgebiet Luftreinhaltung, Technische Universität Berlin, Strasse des 17. Juni 135, W-1000 Berlin 12, Federal Republic of Germany

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Summary. Considerable enhancement of selectivity in the potentiometric and conductometric determination of ammonium is provided by gas-diffusion separation in flow injection analysis. Ammonium and potassium selective liquid membrane electrodes can be used for determinations in the concentration range 10⁻⁷ - 10⁻² mol/l with high precision and fast sample throughput. No interferences are encountered in the presence of ionic species and molecules that likely adsorb when the sensors are in direct contact with the sample. The selectivity over volatile amines is enhanced due to kinetic discrimination. Conductometric detection is shown to be as sensitive as the potentiometric detection. A major advantage, however, is the linear rather than logarithmic relationship between concentration and conductivity.

Introduction

Gas-diffusion separation in flow injection analysis (GD-FIA) [1 - 5] has proven useful in determining volatile species in complex matrices. The inherent selectivity of the membrane separation process considerably simplifies photometric detection if coloured or turbid samples have to be processed. Moreover, ionic species are effectively excluded from passing through the membrane so that in many instances no interferences are encountered in the acceptor line where detection takes place. This fortunate situation has led us to evaluate the possibility of employing less or even non-selective sensors as detectors in GD-FIA [6].

Ammonium is among the species which can be advantageously determined by GD-FIA. Most commonly the colour change of an acid-base indicator is spectrophotometrically detected [e.g. 7, 8]. Other detection modes, however, have also been used [9 - 11]. In the present paper we report about the conductometric and potentiometric detection of ammonium following gas-diffusion separation in a flow injection system. Emphasis is laid on evaluation of the specifications of the two detection methods with respect to sensitivity, working range, susceptibility to interferences and practicability in routine operation.

Experimental

Apparatus

The flow injection set-up was composed of a multichannel peristaltic pump (Type IPS-8, Ismatec, Switzerland), a homemade teflon rotary valve and a gas-diffusion unit described in detail in previous work [6]. Polypropylene membranes (0.45 μm pore size, 80 μm thick, porosity 75%, Enka, Wuppertal) were used to separate the donor and acceptor channel of the gas-diffusion unit. Flow lines were PTFE-tubing of 0.7 mm i.d. Potentiometric detectors used were the commercially available wall-jet cell (FIAStar 5025, Tecator, Höganas) equipped with potassium selective electrode (Tecator, No. 5000-2417) and purpose-made tubular flow-through cells. The tubular ammonium and potassium selective electrodes were prepared according to Meyerhoff et al. [12, 13] with nonactin/monactin and valinomycin as ionophores, respectively. A saturated Ag/AgCl electrode served as reference in all measurements. The arrangement of the detector cells and the flow system used for potentiometric detection throughout this work are depicted in Fig. 1-3. Potential readings were made with a digital ion-meter (Model 901, Orion, Cambridge) interfaced to a strip-chart. Signal evaluation was done manually by peak-height measurements.

Conductometric measurements were performed with the Wescan ammonium analyzer (model N-360, GAT, Bremerhaven). This instrument is originally designed for ammonia determination in continuous flow mode [14]. The built-in gas diffusion cell, conductometric detector cell and most of the connecting tubes are housed in a thermostated compartment. To provide FIA measurements the sample stream was replaced by the carrier stream and an injection valve was inserted into the carrier line between pump and merging point of carrier and alkaline reagent stream. Temperature control was set to 35°C in all measurements. Flow rates of carrier and reagent steams were adjusted by appropriate choice of the internal diameter of the pump.
Fig. 1. Schematic representation of the Tecator 5025 wall-jet cell. a Ion selective electrode; b Ag/AgCl reference electrode; c sensing membrane; d earthing electrode; e inlet for KCl solution; f sample inlet; g outlet

Fig. 2. Arrangement of the tubular flow through ion-selective electrodes. a Silver rod; b PVC-beaker; c ion sensitive 'window'; d PVC tubing; e teflon tubing; f Ag/AgCl reference electrode

tubing and checked volumetrically (see Results and discussion).

Chemicals and solutions

All reagents were of analytical-grade quality. Solutions were made up with demineralized and doubly-distilled water. For low-level determination of ammonium few drops of sulphuric acid were added to the quartz still to prevent the transfer of ammonia.

By this measure the contamination level could be reduced to approx. $10^{-8}$ mol/l NH$_4^+$. Ammonium standards were prepared daily by serial dilution of a 1 g/l stock solution (Merck Titrisol).

The carrier and alkaline reagent stream were water and 0.1 mol/l NaOH, respectively. Interference studies of metal ions that form hydroxide precipitates were made using alkaline reagent streams to which EDTA was added. The composition of the acceptor stream used in the potentiometric method was 0.02 mol/l Tris/HCl [tris (hydroxymethyl) aminomethan] buffer adjusted to pH 8.0 [12].

In conductometric measurements the acceptor solution was diluted boric acid to which ammonium hydroxide was added. Details are given in Results and discussion.

Solutions used as carrier and reagent streams were carefully degassed by passing through membrane filters (0.45 μm) with the aid of vacuum from a water suction pump. This procedure was particularly necessary in the conductometric method since evolution of microbubbles caused severe detector noise and baseline drift.

Results and discussion

Potentiometric detection

Liquid membrane based ammonium selective electrodes have been developed years ago [15] and are also commercially available (e.g. Philips). The ionophore commonly used in this kind of sensor is a mixture of nonactin/monactin which permits high sensitivity measurements with almost Nernstian slope [16]. The selectivity of this electrode, however, cannot compete with the ammonia gas-sensing probe [17], which for that reason is preferentially used when samples with complex matrix have to be analysed. Particularly, monovalent ions interfere and the sample pH must be rigorously controlled [12, 15, 16].

Renewed interest in the application of the liquid membrane ammonium electrode can be observed since Meyerhoffs group has demonstrated its advantageous features in combination with gas-diffusion separation in flowing streams [12, 18-20]. Low level determination of ammonium [21] and the application to clinical [20] and water samples [22] has been reported.

These works impressively document the benefits of the gas diffusion approach. High sensitivity, excellent precision and fast sample throughput can be achieved. Interferences from ionic species are virtually absent since they do not pass the membrane. This also holds for high molecular weight species which are likely adsorbed at the sensor surface if the electrode is directly immersed into the sample.

Some interferences, however, are still observed. They can be classified into two categories, i.e. those which cause changes in the rate of gas transfer and interferences due to response of the sensing electrode.

An example of the first category is the increased volatility of ammonia in samples with high salt content (salting-out effect) [5]. To avoid this interference standard solutions must be made up with similar salt content or the sample can be matched on-line by addition of salt into the carrier and/or alkaline reagent stream [23]. Another example is the presence...