# CONDUCTIMETRIC GAS SEPARATION–FLOW INJECTION DETERMINATION OF AMMONIA IN GASEOUS PROCESS STREAMS

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Ammonia (up to 0.3 vol.%) can be determined (RSDs < 2%) after separation from a process gas stream containing (vol.%): carbon dioxide (0.3–20), hydrogen sulfide (< 0.4), hydrogen cyanide ($< 1.5 \cdot 10^{-4}$), sulfur dioxide (1), carbon monoxide (< 3) in 50–90 vol.% nitrogen and hydrocarbons. The ammonia content in sample is determined through changes in the conductivity of an acceptor stream (3 mM boric acid) caused by absorption of the analyte passed through a Nafion capillary membrane.

**Key words:** Flow injection analysis; Ammonia; Conductimetry; Process analysis; Gas analysis.

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Ammonia is produced from nitrogen-containing organic compounds (proteins, urea, amino acids, *etc.*) by reductive chemical and, in anaerobic conditions, microbial processes. Ammonia is present in areas with livestock industry, municipal waste water and sewage treatment plants and in farmyards. Ammonia and ammonium ions are also increasingly found in waters as a result of excessive use of nitrogen fertilizers in agriculture. Considerable quantities are also produced by technological processes such as desulfurization of oil and coal, coke-oven, *etc.*, and by combustion of fossil fuels.

FIA methods for the determination of ammonia and/or the ammonium ion as well as total nitrogen are based on selective gas permeation or distillation followed by measurement of changes in the acidity of a suitable acceptor solution. The analytical finish is either photometric[1–15], employing acid/base indicators (bromothymol blue, phenolphthalein, cresol red, bromothymol violet or their mixtures) in deionized water or in highly dilute sodium hydroxide or in a suitable buffer solution (phthalate, ammoniacal buffer, TRIS) at pH 6–8, or potentiometric[16–27]. The methods give precise and accurate results, with LOD ranging from hundreds of ppb to ppm, but their sensitivity and range of applicability depend strongly on the buffer capacity and on the type and concentration of the acid/base indicator[1–27]. Acid gases also easily penetrate through the membrane and, owing to their buffering ability (carbon dioxide, hydrogen sulfide *etc.*), bring about signal and sensitivity lowering.

Spectrophotometric FIA methods are based on Nessler's reagent[28–32] or phenolate (Berthelot's, Indophenol Blue) reaction[6,8,33–49]. The two methods are selective and sensitive but the former uses a toxic mercury compound and the product is unsufficiently defined, whereas the latter is rather slow and requires a long incubation time even at elevated temperatures. Methods based on the absorption of UV radiation[50,51] and on the reaction with *o*-phthaldialdehyde (OPA) and 2-mercaptoethanol[52] or sulfite[53] have also been used for the determination of ammonia and/or ammonium ions. Fluorometric methods with OPA and sulfite or 2-mercaptoethanol[54–62], chemiluminescence[63,64], optosensors[65,66], the indirect atomic absorption method[67], and other methods[68] play an important role as well.

Conductimetric detection has been used for a sensitive determination of ammonium ions and/or total nitrogen in Kjehldahl digests, water and air[6,8,34,40,69–74]. This approach is based on the absorption of ammonia (after distillation or gas diffusion) from a gaseous or alkaline aqueous sample stream in deionized water or dilute boric, sulfuric or hydrochloric acid followed by measurement of the conductivity change. Deionized water brings about a higher sensitivity but the calibration curves are non-linear due to the low degree of ionization of the ammonium species ($NH_3 . H_2O$) and presence of acid gases (mainly carbon dioxide).

In recent studies it was demonstrated that pH discrimination of mass transport of molecular species through microporous PVDF and nonporous tubular silicone rubber membranes can be used as a tool for the separation and preconcentration of analytes from aqueous and gaseous samples[75–80]. In the present work, the membrane separation technique is employed for a selective determination of ammonia in gaseous samples.

## EXPERIMENTAL

### Chemicals and Equipment

Distilled and deionized water, benzoic, barbituric, and boric acids (0.01–50 mmol/l) and hydrochloric, sulfuric and nitric acids (5–100 μmol/l) were tested as the acceptor streams for the determination of ammonia. A mixed single-bed ion-exchange column (5 mm i.d., 10 cm length, Amberlite MB-1, an equimolar mixture of Amberlite IRA-400 in the OH-form and Amberlite IR-120 in the H-form 16–50 mesh, Sigma) was used for additional water purification in the former two cases.

The test gases contained, respectively: 1.00 vol.% ammonia (gas $A_1$), 1.00 vol.% carbon dioxide (gas $A_2$), 0.30 vol.% ammonia, 0.40 vol.% hydrogen sulfide or 16.97 vol.% carbon dioxide, 3.00 vol.% carbon monoxide, 0.49 vol.% ethane, 2.69 vol.% methane and 0.18 vol.% propane (gas B), each in nitrogen (all certified cylinder gases, Scott Specialty Gases Inc., Houston, TX, U.S.A.). The test gases, pure and dry house air and/or pure carbon dioxide were metered by using mass flow meters (model 820, Sierra Instruments, Monterey, CA, U.S.A.) or mass flow controllers (model FC 280, Tylan General, Torrance, CA, U.S.A.) to dilute the test gases A, B by means of a 100 cm mixing coil.

Nafion 815 super-acidic cation exchanger (with perfluorosulfonate functional groups, Sigma–Aldrich, active length 2 or 10 cm), poly(vinylidene difluoride) microporous membranes (PVDF, 0.56 μm pore size, 1.2/1.8 mm i.d./o.d., Enka, Wuppertal, Germany, active length 2 or 10 cm), and tubular silicone rubber membranes (0.4/0.6 mm i.d./o.d., Patter Products, Beaverton, MI, U.S.A., active length 2 or 20 cm) were tested as the barrier media for the separation of ammonia. The membrane modules, tube-in-shell devices were made from capillary membrane tubing with Teflon tubing (from 30 ga to 1.4 mm o.d.) inserted at the termini for connections and barbed polypropylene T-joints (Ark-Plas Inc., Flippin, AR, U.S.A.). The flow injection apparatus (see Fig. 1 for manifolds) was set up using the same parts as in the previous studies[75–80]. The tightly coiled mixing capillary 30 cm long was placed between the membrane device and the detector to ensure the lowest dispersion possible.

The gas and purified air were sampled by an electronically controlled six-port PTFE valve into the outer part of the membrane device with acceptor streams flowing inside the tubular membrane in the continuous flow mode (Fig. 1b). The ammonium ions collected in the acidic acceptor stream were fed directly into the conductivity detector. The gas also flowed continuously on the outer part of the membrane device while the acceptor stream was stopped for a preselected period (Fig. 1a). Ammonia which had penetrated through the membrane was collected in the acceptor liquid enclosed inside the tubular membrane connected to the sample loop ports of the valve and fed directly into the conductivity detector.

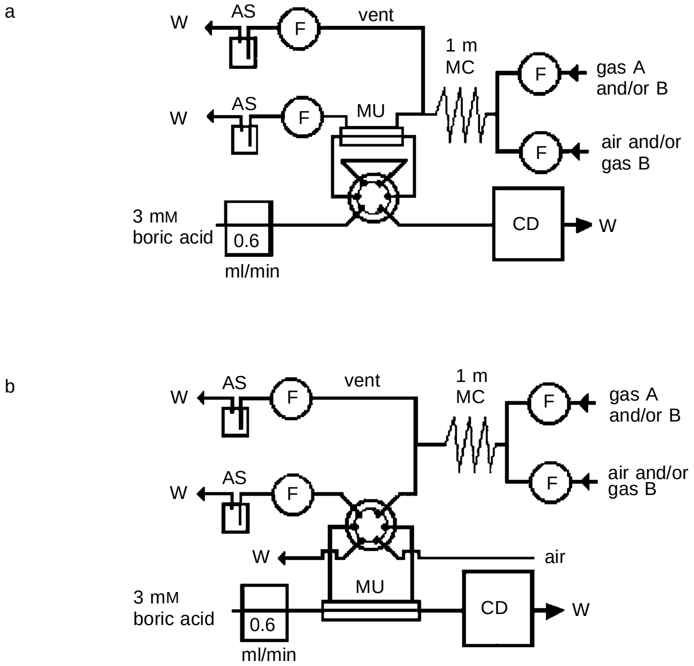

FIG. 1

FIA manifolds for conductimetric determination of ammonia in the "on-loop" membrane device stop-flow mode (a) and in the continuous flow mode with gas sample injection (b). AS absorbing solution, F flow meter, MC mixing coil, MU membrane unit, CD conductivity detector, W waste, BA 3 mM boric acid as the acceptor solution, P peristaltic pump

## RESULTS AND DISCUSSION

### *Selection of the Membrane*

The PVDF membrane exhibited the largest efficiency of the transmembrane transition and the sensitivity was too high to handle the process gas stream. This membrane also gave the fastest response to the increase or decrease of the ammonia concentration when switching between the sample gas and pure air (Fig. 1b). These excellent properties, however, were offset by a low selectivity of the membrane with respect to the transport of acid gases (see Table I). The response to hydrogen sulfide, carbon dioxide and sulfur dioxide was intolerably high when the compounds were present in the process stream at the highest expected concentrations (0.4, 16.7 and 0.3 vol.%, respectively). The membrane was also unusable if gaseous samples were to be handled because its microporous structure was very sensitive to fouling by particulate matter and to overpressure on the donor side. In the latter case the gases penetrated through the membrane material and induced “bubble” spikes on the record. Membranes possessing the lowest possible porosity are preferable in such case.

The silicone rubber membrane, on the other hand, displayed the lowest transmembrane efficiency for ammonia of all the membranes tested. The washing time was also much longer than for the other membranes (see Fig. 2). In the continuous flow mode, the sensitivity was so low that a 20 cm membrane had to be used to obtain a measurable signal. The membrane was only suitable in the stopped flow arrangement with relatively long preconcentration/washing times. The selectivity of the transmembrane transition was insufficient for sulfur dioxide or carbon dioxide, so that the two gases

TABLE I

Analytical signals (in µS/cm) of intereferents for Nafion, PVDF, and silicone rubber membranes[a]

| Interferent | Content[b] | Membrane | | | | | |
|---|---|---|---|---|---|---|---|
| | | Nafion | | silicone | | PVDF | |
| | | boric acid | water | boric acid | water | boric acid | water |
| $H_2S$ | 0.4 | 0 | 0 | 0.02 | 0.04 | 0.12 | 1 |
| $SO_2$ | 1.0 | 0.1 | 0.2 | 15 | 18 | 550 | 565 |
| $CO_2$ | 16.7 | 0.01 | 0.01 | 2.2 | 2 | 4 | 4 |
| $CO_2$ | 100 | 0.15 | 0.15 | 5 | – | 9 | – |

[a] Signals 16 or 12 µS/cm for 0.3 vol.% $NH_3$, 1 min injection, 10 min washing, 100 ml/min flow rates, RSDs < 1.9% for $n = 7$; [b] highest expected content.

interfered seriously (see Table I). Its selectivity was acceptable for hydrogen sulfide in the above quantities.

Because of the insufficient selectivity of the transmembrane transport of the membranes and also for the detection principle, the Nafion ion-exchange membrane was tested. Its transmembrane transport efficiency was roughly 20-fold higher than that of the silicone rubber membrane but about 10-fold lower than that of the PVDF membrane. The membrane responded relatively fast when switching between sample and pure air out, the washing time was over 10 min for water as the acceptor. The washing time was significantly reduced, down to 2–5 min, when dilute solutions of HCl or $HNO_3$ were used as the receptor streams, and to 5–10 min, when boric acid was used. Nafion membranes were the sole membranes to possess a sufficiently high transmembrane selectivity for the acid gases, giving signals below the 3 S/N level for all gases (see Table I).

No interference was found for any of the above-mentioned concentrations of the gases. Thus ammonia can be determined with a satisfactory sensitivity and selectivity owing to the unique domain structure of the Nafion membrane and unusual solubility of ammonia in salt solutions (mobility is *ca* $10^3$ times higher than for hydrogen, nitrogen, or other gases). The Nafion ionomer membrane consists of two phases (domains) – an ionic cluster (region with high concentrations of ions) and a perfluorinated matrix (hydrophobic backbone structure similar to that in PVDF). They are formed by molecular aggregation of the hydrophilic and lipophilic parts of the polymer. The cluster domains (chambers 5–10 nm i.d.) contain most of the sulfonated groups and adsorbed water. The domains are connected to each other by interfacial structure narrow channels containing a small amount of water, a few sulfo groups, and pendant side chains. The structure is crucial for the transport properties since it provides the pathway for the

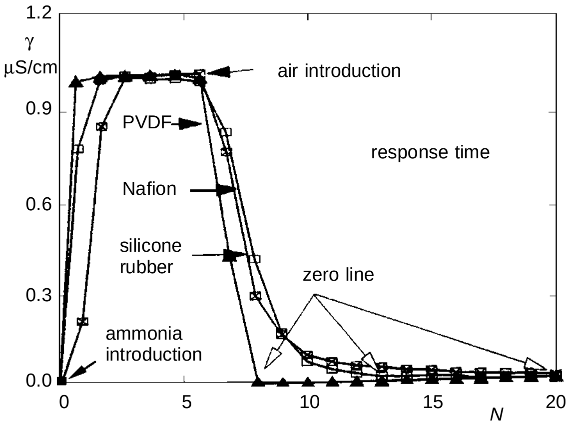

FIG. 2
Response times (in number of injections *N*, 4 min per injection) for PVDF (2 cm, ▲), silicone rubber (20 cm, ❍) and Nafion (2 cm, ❐) membranes when switching between sample gas (1 vol.% ammonia in nitrogen, 6 injections) and pure air (after 7th injection). Zero line after 1, 12 and 6 injections, respectively. Flow rate 100 ml/min for both, 2 min preconcentration/injection time, 0.3 mmol/l boric acid

transport of ions and molecules. Simple diffusion–solubility, diffusion–reaction and mobile carrier mechanisms of transmembrane transport can be expected.

### *Selection of Acceptor Liquid*

Ammonia, as well as the acidic gases, can be easily absorbed in distilled or deionized water. The initial conductivity of water continuously changes due to absorption of carbon dioxide from the laboratory air, and the analytical signal of ammonia varies with time. Thus, additional purification with a mixed monobed ion-exchange column (Amberlite MB-1) is necessary to obtain reproducible results.

Ammonium as a weak base (p$K$ 9.25) is not fully dissociated in water, therefore the calibration graphs are always non-linear. The repeatability of the measurement is also relatively poor (2%). These are the most important disadvantages of ammonium with respect to the practical application in process analysis. Benzoic, barbituric, and boric acids at 0.01–50 mmol/l concentrations and nonbuffered solutions of strong mineral acids (5–100 μmol/l, initial conductivities have been established with HCl, $H_2SO_4$ or $HNO_3$ over the range of 1 000–1 μS/cm) were tested as potential modifiers of acceptor streams for conductimetric measurements.

The analytical signal is positive for deionized water and boric acid and increases with decreasing concentrations of boric acid, the optimum being 2–8 mmol/l. The signal is approximately twice higher for 3 mmol/l boric acid than for pure water at higher ammonia contents ($w$ > 0.5 vol.%) and nearly the same at the lower concentrations. The corresponding decrease in the background conductivity of the solution from 9 to 1 μS/cm at the above concentrations of boric acid reduces the baseline noise. The very low background conductivity, its better stability and, in particular, resistance to absorption of carbon dioxide make boric acid superior to deionized water as the acceptor liquid. Deionized water gives a sufficient sensitivity but the calibration curves are non-linear due to the low ionization of the ammonium ion ($NH_3 . H_2O$) and presence of acid gases (mainly carbon dioxide).

A decrease in the initial conductivity of all the other streams (negative analytical signals) is observed due to the decrease in the concentration of hydronium ions. The analytical signal is comparable for barbituric and benzoic acids and decreases with decreasing concentration of the two acids but it is still lower than for boric acid and water. The background signal (100–20 μS/cm) is reduced with the appropriate decrease in higher concentration and ionization in both cases. The baseline noise is high due to the high levels of background conductivity. Thus, the application of the weak acids offers no advantage over water or boric acid.

The analytical signal is several times higher for all solutions of strong mineral acids and is influenced substantially by the acid concentration (or initial conductivity of the acceptor stream) and concentration of ammonia in the donor stream. The dependence of the analytical signal *vs* background conductivity (or concentration of acids) of the acceptor stream has three distinguished segments (Fig. 3) with two points of intersection which express quantitative consumption of the modifier (acid) in the acceptor stream by permeated ammonia. The conductivity and the concentration of hydronium ion are reduced by the same value in the horizontal segment where it is present in a very high excess over the ammonia transported and the analytical signal is constant at the constant concentration of ammonia. In the second segment, the amount of hydronium ions in the acceptor stream is insufficient and is consumed completely by the reaction with ammonia forming the ammonium ion, the excess ammonia reacts with water, and conductivity decreases or increases after reaching the background conductivity of $NH_4^+$, $Cl^-$ and water by the combination of decrease of $H^+$ ions and increase of $OH^-$ ions.

The mass transfer of ammonia both in the membrane and in the solution bulk is complicated by ionization, as the $NH_3/NH_4^+$ equilibrium obviously exists in both media. Ammonia must first react with the membrane matrix to form free ions, which diffuse through the membrane and pass through the solution/membrane interface into the acceptor fluid where the acid/base reaction takes place. The acid/base reaction is a fast chemical step whose kinetics rarely affects the rate of transport. The diffusion of the modifier (acids) in the acceptor solution near the solution/membrane interface, however, is not always fast, and so the local absence may inhibit the transport of ammonia from the membrane into the solution bulk. The modifier can also be locally depleted completely, giving rise to a double, sinusoidal or totally deformed shape of the peaks or even negative signals.

The position of the point of intersection depends on the concentration of ammonia passed through the membrane and of course on its concentration in sample (Fig. 3). This point can be used to determine the absolute concentration of the transported species when a constant concentration of the penetrated analyte can be expected and so to study the transportation process. The point also determines the limits of concentration of the strong acid or initial conductivity of the acceptor solution over which the

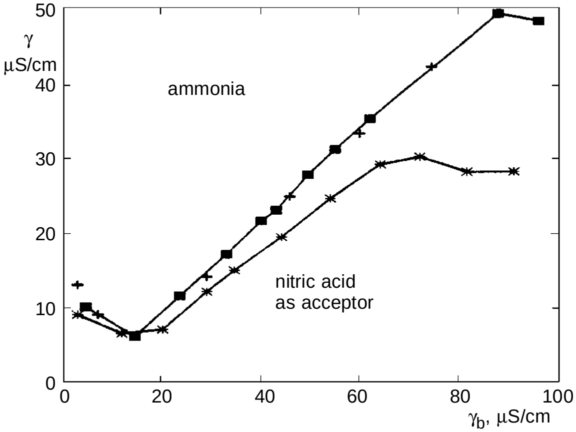

FIG. 3
Dependence of the analytical signal (γ, μS/cm) on the initial conductivity of the acceptor streams ($\gamma_b$, μS/cm) containing nitric acid, for 1.0 (✚, ■) and 0.6 vol.% (✶) ammonia. Nafion membrane, 2 cm active length, 1 min preconcentration period, 100 ml/min

calibration graph is linear, and so the linear range and the sensitivity of determination can be varied through the acceptor stream parameters (>100, >50 and >20 μS/cm are the limits giving the best sensitivity for concentrations of ammonia down to 1, 0.5 and 0.1 mmol/l, respectively).

### *Optimization of FIA Manifold Parameters*

The Nafion membrane and 3 mmol/l boric acid were selected as the best combination of membrane and acceptor stream for practical purposes. From among the manifolds tested (Fig. 1), the manifold (Fig. 1b) with a continuous flow of the acceptor stream and a time controlled introduction of the tested gas mixture and pure air (and/or standard gas mixture) is preferable, giving a lower baseline noise and a more favourable baseline shape owing to the elimination of pressure pulses caused by the switching of the injec-

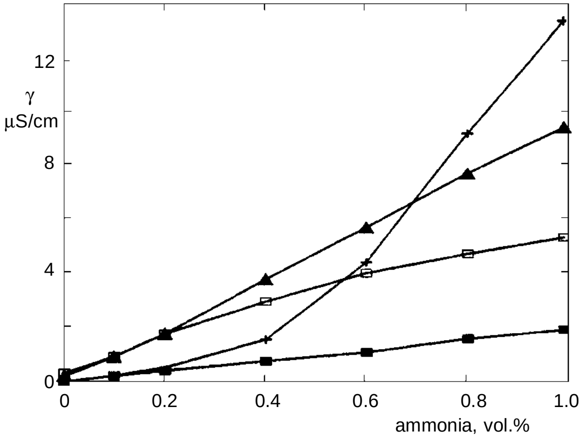

FIG. 4

Calibration graphs of ammonia for nitric acid (✚), boric acid (▲), barbituric acid (■) and water (❐) as the acceptor streams; 1 min preconcentration, remaining parameters as in Fig. 2

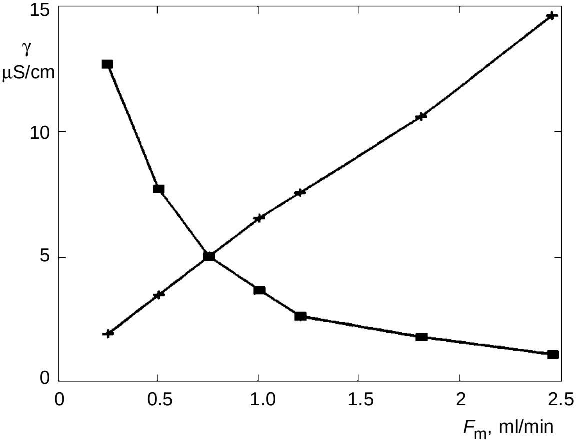

FIG. 5

Dependence of the conductivity γ in μS/cm (■) and the washing time *t* in min (✚) on the flow rate $F_m$ of the acceptor stream (3 mM boric acid, other parameters as in Fig. 2) tion valve. Manifold (Fig. 1b) also allows simpler variation among the introduction of the sample, standard and washing gas, respectively, and also a larger variability in the amount of ammonia transported through the membrane by changing the injection period.

The calibration graphs are non-linear for water, strong acids, and barbituric acid over the concentration range of 0–1 vol.% ammonia in nitrogen and also for water over the range of 0–0.3 vol.% ammonia (Fig. 4). Linear segments exist for higher concentrations of strong acids (>0.3 vol.% $NH_3$), with an appropriate increase in sensitivity. The calibration graphs are linear for 3 mmol/l boric acid and both concentration ranges with a very good long-term repeatability (<2% for a 5-h interval) and a sufficient sensitivity.

In addition, the sensitivity can be easily controlled through the flow rate of the acceptor stream, because the analytical signal decreases with increasing flow rate. The washing time also increases in this order (Fig. 5). Therefore, the value of $Q$ = 0.6 ml/min was chosen as a compromise between sensitivity and sample throughput. Water can be used as the acceptor for the determination of very low concentrations of ammonia in such complex matrices. The sensitivity is slightly higher for the lowest concentrations as compared to boric acid but the washing time is higher, too.

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