CONTINUOUS MONITORING OF AMMONIA IN THE ATMOSPHERE USING AN AERODISPERSE ENRICHMENT UNIT

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Continuous monitoring of low concentrations of ammonia in the gas phase is described. The rather low limit of detection is achieved by the absorption of ammonia from the atmosphere in the polydispersed aerosol of water and by the selective detection of ammonia in the concentrate by means of the gas-phase ion-selective NH_3-electrode (ISE-NH_3). The worked out monitor is computer-controlled and it was used in the veterinary service for testing the microclima of buildings for agricultural use. The reliability of the method was checked by the reference standard method.

Atmospheric ammonia is the principal alkaline component of the atmosphere that plays a dominant role in the decrease of its acidity (NO_x, SO_2, H_2SO_4). In higher concentrations it has a toxic effect on living organisms, e.g., it decreases the yields of large-scale breeding of domestic animals and poultry. In spite of the indisputable importance of the ammonia monitoring, there is no simple selective method for the measurement of its concentration in the atmosphere, particularly in concentrations of the order of ppm (v/v) and lower.

The indirect methods are based on the conversion of ammonia to nitrogen oxides and on their determination by chemiluminescence[1,2]. The classical wet techniques require the quantitative absorption of ammonia in a suitable absorbent. After dissolution, ammonia is usually determined by photometry[3−5]. Ammonium ions can be determined in the solution also by conductometry[6] or potentiometry, using an ion-selective electrode[7,8]. Detection tubes[9] are used for the estimation of the ammonia concentration in the gas phase. In the Czechoslovak hygienic service[10] ammonia is determined photometrically using the addition of the classical Nessler's reagent to liquid samples transported to control laboratories. All these analytical procedures are discontinuous and time-consuming, and particularly the last-mentioned method of ammonia determination with the Nessler's reagent is subject to many considerable errors.

More modern methods for the measurement of ammonia content in the gas phase make use of the membrane technique and their preparation, or, eventually, they use

techniques based on the production procedures of semiconducting materials[11-15]. Higher concentrations of ammonia can be determined by the absorption of ammonia molecules in the infrared spectral region, cf. ref.[16].

In this paper a compact analytical system is described that renders the possibility to obtain quickly and continuously the reliable data on the low concentrations of ammonia in the atmosphere. This system is based on the transfer of ammonia from the atmosphere into the aqueous solution using the pneumatic dispersing enrichment unit[17]. Ammonia is continuously transferred from a flow of air, of the volumes of about liters per minute, into microliter volumes of water passing through the enrichment unit during the same period of time. After alkalizing the concentrate, ammonia is determined by potentiometry, using the ion-selective electrode, the signal of which is processed by a simple microprocessor.

EXPERIMENTAL

Description of the System

The continuous monitor of ammonia consists of the following parts (Fig. 1): the central processor (microcomputer PMI 80) (1), display (2), detector with the gas-phase ion-selective NH_3 electrode (3), two peristaltic pumps for the solution transport (4a NaOH solution, 4b solution of the standard). Further, the analyzer contains two interruptors of the liquid flow (5), mixer for mixing the NaOH solution either with the concentrate or with the solution of the standard (6), and the enrichment unit (7). The analyzer is equipped with the inlet of the air sample into the enrichment unit (8), with the tubing for standard solutions (9, 10) and NaOH solution (11) and it is joint to a vacuum pump (12).
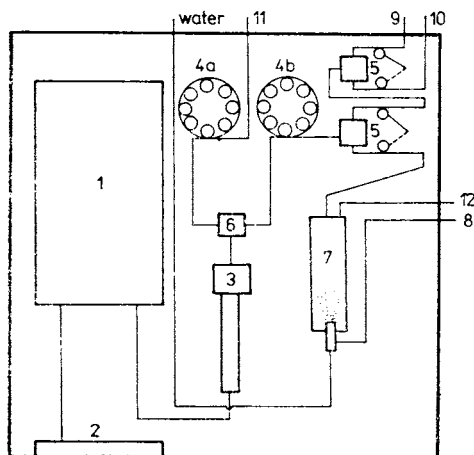

Fig. 1

Scheme of the NH_3 monitor. 1 Central processor, 2 display, 3 gas-phase ion-selective NH_3 electrode, 4a, 4b peristaltic pumps, 5 interruptors of the flow of liquids, 6 mixer of solutions, 7 the enrichment unit, 8—11 inlet of the atmosphere sample, inlets of standard solutions and the NaOH solution, 12 connection to the vacuum pump

RESULTS AND DISCUSSION

The apparatus described above was tested in the laboratory for the analysis of ammonia contents in air, ranging from 0·5 to 50 ppm (v/v), particularly from the point of view of the enrichment unit operation and also with respect to the reliability of ammonia determination and determination of parameters affecting the function of the gas-phase ion-selective electrode, as temperature, quality of the polytetrafluoroethylene membrane, measurement technique, or, eventually, the presence of interfering compounds accompanying ammonia. Air samples with well-defined contents of ammonia were prepared by continuous dilution of a standard calibration mixture (882 ppm (v/v) $\pm$ 5 rel. %) (cf. ref.[18]).

The enrichment efficiency of the aerodispersive unit was measured at the air-flow rate of 3·63 l min^{-1}, containing a known amount of ammonia, and at the aqueous concentrate flow rate of 476 μl min^{-1}. After adjusting pH to 12·5, the ammonia concentration in the concentrate was measured by the gas-phase ISE-NH$_3$ electrode, calibrated by the standard NH$_4$Cl solution. Under these conditions (46 ± 2) % of ammonia is absorbed in water, corresponding thus to the experience with this type of enrichment unit[17]. Changing the concentration of the standard NH$_4$Cl solution by an order of magnitude (i.e., for $c(NH_4^+)$ ranging from 10^{-6} to 10^{-2} mol l^{-1}) we have found that the slope of the dependence of the gas-phase ISE-NH$_3$ electrode response on the logarithm of the NH$_4^+$ concentration, log $c(NH_4^+)$, varies within $54-58$ mV, depending on the permeable membrane used. However, the response is time-independent during, at least, two weeks. It has been also found that in the flow regime it is impossible to eliminate the perturbations caused by the pulsation of the peristaltic pump and the effect of the electrokinetic potential on the gas-phase ISE-NH$_3$ electrode response; in the course of the measurements with the gas-phase ion-selective electrode it is necessary to prevent any flow of the concentrate along the polytetrafluoroethylene membrane. After the step-wise change of the NH$_4^+$ ion concentration from 10^{-5} to 10^{-4} mol l^{-1} a constant response is established within 2 minutes.

In our sample the amines of low molecular weight, the presence of which can be expected in the air from stables or other similar agricultural buildings, have to be considered as the most important interfering substances. The response of the gas-phase ISE-NH$_3$ to the step-wise changes of the methylamine, ethylamine, and diethylamine concentrations from 10^{-5} to 10^{-4} mol l^{-1} was 44, 37, and 48 mV, respectively. However, taking into consideration that the chromatography of air from agricultural buildings confirmed that the content of these interfering contaminants is by two orders of magnitude lower than the content of ammonia, the error of ammonia determination due to their presence, is negligible.

The reliability of results obtained by the NH$_3$ monitor was verified by the standard mixture of nitrogen with 882 ppm (v/v) ($\pm$5 rel. %) of ammonia that was further

diluted to concentrations in the range from 5 to 30 ppm (v/v). For a given concentration the measurements were repeated 10 times and the average obtained from these data was plotted against the actual concentration of ammonia in the gas. The dependence is linear, it passes through the coordinate system origin and the correlation factor is equal to 0·9948. The slope of this dependence is 0·9378. The precision of measurements increases with the increasing content of ammonia in the gas and it has been determined that the error is $\pm 5\cdot3$ rel. % for the ammonia contents of about 5 ppm (v/v) and ± 2 rel. % for 30 ppm (v/v) of ammonia.

The correctness of the method was evaluated by a comparison with the results obtained by the standard photometric method[10]. Four samples with the expected ammonia content of 10 ppm (v/v) were measured using the photometric method. The results were compared with the results obtained by the continuous ammonia monitor for the expected value of 10 ppm (v/v), the total number of determinations was 7. The agreement between the two methods was tested by the Moore test. The value of $U = 0\cdot278$, i.e., the results obtained by the two methods are identical on the significance level $\alpha = 0\cdot05$.

The operation of the NH_3 monitor was tested also in real conditions, measuring the content of ammonia in breeding stables. The described monitor is suitable for the measurements of low contents of NH_3 in the air in situations where monitoring of ammonia contents in the real time is required. The results obtained in modelled conditions have the relative standard deviation of 10%. The correctness of the analysis of the standard mixture shows that the relative error of this method is equal to 2% for ammonia contents of about 30 ppm (v/v) and increases up to about 8% for the ammonia contents of abut 10 ppm (v/v).

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