Ammonia

Method number	1
Application	Air analysis
Analytical principle	Photometry
Completed in	April 1991

Summary [1–7]

The ammonia is absorbed from the sample air in diluted sulfuric acid and converted into ammonium sulfate. The ammonium ions form a yellow indophenol pigment with phenol and sodium hypochlorite. The reaction is catalyzed by sodium pentacyanonitrosylferrate (III) (sodium nitroferricyanide). The extinction of the sample solution is determined photometrically at a wavelength of about 620 nm. This is a measure for the ammonia concentration in the sample air. Ammonium ions which are absorbed in the absorption solution during the sampling procedure lead to a corresponding increase of the analytical result.
The quantitative evaluation is carried out by comparing the measured extinctions of the air samples with those of calibration solutions.

Sensitivity:	Reciprocal calibration factor k' 4 · 10^{-2} mg in a concentration range up to about 0.03 mg ammonia under the experimental conditions as mentioned	
Precision:	Standard deviation (rel.)	s_w = 3.5% (4 %)
	Mean variation	u = 7.5% (8 %)
	at concentrations of 35 and 19.7 mg ammonia per m^3 air and n = 10 determinations; the values refer to the complete method applying a critical nozzle for the sampling	
Detection limit:	3 µg ammonia (absolute), corresponding with 0,8 mg/m^3 (1.1 mL/m^3) referring to a sample volume of 4 L	
Recovery rate:	0.98 (98 %)	
Sampling recommendation:		Sampling time 5 min Sample volume 4 L

Ammonia

NH_3

is a colourless, pungent by smelling gas (molecular weight 17.03 g/mole, f. p. –78 °C, b. p. –33 °C, critical temperature 132.4 °C, critical pressure 113 bar, critical density 0.235 g/cm^3). It is a basic product in the chemical industry and serves as an initial material for a great number of synthesis and among others for the production of synthetic fibres, fertilizers and synthetic resins.
Ammonia is an irritant gas showing strong local effects. Systemic toxic effects are not of great importance. The toxicity of ammonia in contact with mucous membranes is due to the formation of ammonium hydroxide which leads to deep necrosis by a high penetration. After inhalation, the strongest effect of ammonia is observed in the upper respiratory tract [8].
The actually valid MAK value (1989) is 50 mL/m^3 or 35 mg/m^3. Ammonia is classified into the Peak Limitation Category I, i. e. at a short-term duration of 5 min the peak concentrations may reach the double of the MAK for a maximum of 8 times per shift at the most [9].

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Contents

1 General principles

The ammonia is absorbed from the sample air in diluted sulfuric acid and converted into ammonium sulfate. The ammonium ions form a yellow indophenol pigment with phenol

and sodium hypochlorite. The reaction is catalyzed by sodium pentacyanonitrosylferrate (III) (sodium nitroferricyanide). The extinction of the sample solution is determined photometrically at a wavelength of about 620 nm. This is a measure for the ammonia concentration in the sample air. Ammonium ions which are absorbed in the absorption solution during the sampling procedure lead to a corresponding increase of the analytical result.
The quantitative evaluation is carried out by comparing the measured extinctions of the air samples with those of calibration solutions.

2 Equipment, chemicals and solutions

2.1 Equipment

Single-beam or double-beam spectrophotometer or filter photometer with a measuring option at 620 nm
Cuvettes of optical glass, path length 10 mm
Thermostate, working temperature of about 50 °C
50, 100 and 1000 mL Volumetric flasks
2, 8 and 20 mL Bulb pipettes
Brown glass bottle Sampling devices (cf. Fig. 1)
Three-way cock equipped with stopcock of PTFE for reversing the airflow
Glass vessel for the uptake of the activated carbon
Wash bottle equipped with frit D 2, volume of 100 mL for the uptake of the absorption solution
Wash bottle as a drop collector to protect pump, gas meter and volume flowmeter
Volume flowmeter suitable for flow rates of about 40 L/h
Thermometer to measure the ambient temperature (t_a)
Barometer to determine the ambient pressure during the sampling (p_a)
Stop watch to measure the sampling time in case of applying the critical nozzle and a watch to determine the beginning of the sampling
In addition, for the sampling with the critical nozzle (compare Fig. 1 a; [10]):
Critical nozzle equipped with a preconnected injection frit D 2, suitable to adjust a flow rate of about 40 L/h
Thermometer to measure the temperature at the critical nozzle (t)
Two pressure gauges to determine the pressure difference before (p_v) and after (p_n) the critical nozzle
Pump to convey the sample air and to generate the necessary pressure gradient at the critical nozzle (> 0.5 mbar)
In addition, for the sampling with a gas meter (cf. Fig. 1 b): Gas meter, wet type, suitable to measure flow rates of about 30–50 L/h
Thermometer to measure the temperature at the gas meter (t)
Throttle valve to adjust the flow rate of about 40 L/h under sampling conditions

2.2 Chemicals

The purity of all chemicals used has to be of analysis grade
Sulfuric acid 96%, analysis grade
Phenol, analysis grade
Calciumhypochlorite, analysis grade (e. g. of Roth Co., Karlsruhe)
Sodium carbonate, anhydrous, analysis grade
Sodium hydroxide, analysis grade
Sodium pentacyanonitrosylferrate (III), sodium ferricyanide, analysis grade (e.g. of Merck Co.)
Ammonium chloride, analysis grade
Water of high purity (according to the ASTM Type 1) or double distilled water

2.3 Solutions

Absorption solution (0.005 M sulfuric acid):
A volume of 400 mL water of high purity is transferred into a 1000 mL volumetric flask, 0.28 mL sulfuric acid (96 %) are added to it and diluted up to the mark with water of high purity.

Phenol solution:
62.4 g of phenol are weighed into a 1000 mL volumetric flask and dissolved in water of high purity. The flask is diluted up to the mark with water of high purity. This solution is stable for at least one week in a brown glass bottle at ambient temperature.

Sodium carbonate solution (3 %):
30 g of sodium carbonate are transferred into a 1000 mL volumetric flask and dissolved in water of high purity. The flask is diluted up to the mark with water of high purity.

3 M Sodium hydroxide:
120 g of sodium hydroxide are transferred into a 1000 mL volumetric flask and dissolved in water of high purity. The flask is diluted up to the mark with water of high purity.

Sodium hypochlorite solution:
8.33 g of calcium hypochlorite (chlorine content about 70%) are suspended in 500 mL sodium carbonate solution (3 %). After stirring and sedimentation the insoluble part of the suspension is filtered off. The filtrate is mixed with 3 m sodium hydroxide solution in a volume ratio of 1:1.
At dark places the sodium hypochlorite solution is stable for several weeks.
The concentration of active chlorine in the hypochlorite solution is about 0.5 % and the free alcaline content is about 6%. Especially if calcium hypochlorite of other producers than of Roth Co. is used these concentrations have to be determined. If necessary, the instructions for preparing the sodium hypochlorite solutions have to be modified. The chlorine concentration of the solution is determined iodometrically. The determination of the free alcaline content is carried out by transferring an aliquot part of the solution into hydrogen peroxide (3 %), boiling away the hydrogen peroxide excess and titrating with hydrogen chloride using methyl red as an indicator.

0.003 M Sodium nitroferricyanide dihydrate solution:
89.4 mg of sodium nitroferricyanide are transferred into a 100 mL volumetric flask and dissolved in water of high purity. The flask is diluted up to the mark with water of high purity. Each day this solution has to be prepared freshly.
Commercially available reagents can also be used for preparing the phenol solution, the sodiumhypochlorite solution and the sodium nitroferricyanide solution (e. g. Merckotest-urea of Merck Co.), but the concentrations of the reactants have to be adapted to the corresponding volumes as mentioned in the described method.

Preparation of the solutions by use of Merckotest-urea (Article number 3334):

Phenol solution containing sodium nitroferricyanide:
Contrary to the manufacturer's instructions the solution is diluted to 100 mL and not to 500 mL if the phenol agent is used.

Sodiumhypochlorite solution:
Contrary to the manufacturer's instructions the hypochlorite agent is diluted to 100 mL and not to 500 mL

2.4 Calibration standards

Initial solution:
2.073 g of ammonium chloride are transferred into a 1000 mL volumetric flask and dissolved in water of high purity. The flask is diluted up to the mark with water of high purity.

Stock solution:
A volume of 10 mL of the initial solution is transferred into a 1000 mL volumetric flask. The flask is diluted up to the mark with water of high purity. 1 mL of this stock solution contains 20.73 µg ammonium chloride corresponding with 6.6 µg of ammonia.

The calibration standards are prepared in 50 mL volumetric flasks. The volumes of the stock solution given in Table 1 are pipetted each in 5 mL volumetric flasks. Two mL of sodium nitroferrcyanide, 8 mL of the phenol solution and 2 mL of the sodiumhypochlorite solution are added and then diluted up to the mark with water of high purity. In case of the application of Merckotest-urea only 5 mL of the phenol solution (instead of 8 mL) and 5 mL of sodium hypochloride (instead of 2 mL) are used.

3 Sample collection and preparation

3.1 Sample collection

The sample collection is carried out by means of a critical nozzle or alternatively by use of a gas meter.
70 mL of the absorption solution are transferred into a wash bottle equipped with frit D 2 and connected with the sampling device. The tightness of the applied sampling arrangement has to be checked.

Table 1. Pipetting scheme for the preparation of the calibration standards.

Volume of the stock solution	Volume of the sodium nitro-ferricyanide solution	Volume of the phenol solution	Volume of the sodium-hypochlorite solution	Final volume of the calibration standards (after dilution with water of high purity)	Concentration of the calibration standards
mL	mL	mL	mL	mL	µg/50 mL
1	2	8	2	50	6.6
2	2	8	2	50	13.2
3	2	8	2	50	19.8
4	2	8	2	50	26.4
5	2	8	2	50	33.0

a) Operation with a critical nozzle (cf. Fig. 1 a) [10]:
The three-way cock (2) is turned into the flow direction over the activated carbon filter (3). The pump (10) is switched on. The adjustment of the pressure relationship between p_n (after) and p_v (before) <0.5 bar necessary for the effectiveness of the critical nozzle has to be awaited. The three-way cock (2) is reversed to draw the sample air through the air inlet (1). At the same time the stop watch is turned on and the sampling time is noted. During the sampling the temperature of the ambient air (t_a) and the sample air at the critical nozzle (t), the pressure before (p_v) and after (p_n) the critical nozzle as well as the barometer (p_a) are read. After 5 min the three-way cock is turned into the initial position and the pump is switched off. During the sampling procedure the pressure relationship between p_n and p_v has to be < 0.5.

b) Operation with a gas meter (Fig. 1 b):
The three-way cock (2) is turned into the flow direction of the activated carbon filter (3). The pump (10) is switched on and the flow rate at the flow meter (6) is adjusted to about 40 L/h by means of the throttle valve (11). The reading of the gas meter (12) is noted and the three-way cock is turned simultaneously into the direction of the air inlet to draw the sample air through the inlet. The flow rate at the flow meter is controlled and readjusted, if necessary. During the sampling the barometer reading (p_a), the ambient temperature (t_a) and the temperature (t) in the gas meter are read off. The pump is switched off after 5 min and the reading at the gas meter is noted.

3.2 Sample preparation

A volume of 20 mL of the absorption solution is taken from the wash bottle and transferred into a 50 ml volumetric flask and 2 mL of nitroferricyanide, 8 mL of phenol and 2 mL of sodium hypochlorite solution are added. The pH value of the solution must be between 11.8 and 12.4 (cf. Sect. 8). After the addition of each solution the flask has to be shaked for better mixing. The volumetric flask is diluted up to the mark with water of high purity and closed. It is kept in a thermostate at a temperature of 50 °C and analyzed.

If commercially available solutions of Merck Co. are used (cf. Sect. 2.3) 5 mL of the phenol solution (instead of 8 mL) and 5 mL of the sodium hypochlorite solution (instead of 2 mL) are added to the absorption solution (20 mL) and prepared as described before. A reagent blank has to be determined in each analysis series. It is prepared and analyzed in the same way as described in Sect. 4 but without drawing the sample air through the absorption solution.

4 Analytical determination

After keeping the sample solution for 60 min at 50 °C the extinction to water of high purity is determined in a 10 mm cuvette at a wavelength of 620 nm. The extinction of the warmed solution does not change significantly within 4 h.
A reagent blank is determined from at least three single measurements in each analysis series. The average of the single extinction values of the reagent blank is substracted each from the individual sample extinctions.

5 Calibration

The calibration standards are prepared as described in Sect. 4 and analyzed in the same way as the samples. The extinctions of the calibration standards are diminished by the reagent blanks and plotted versus the used concentrations.
The calibration function is linear up to a concentration of about 30 µg ammonia per 50 mL analysis solution (10 mm path length). The reciprocal calibration factor k' is about $4 \cdot 10^{-2}$ mg.
An example of a calibration curve is shown in Fig. 2.

6 Calculation of the analytical results

The extinction of the warmed analysis solution is determined and diminished by the average of the single extinction values of the reagent blanks. The ammonia concentration in µg/50 mL analysis solution is taken from the calibration curve. The corresponding concentration ρ_{ammonia} (ammonia in mg/m^3) is calculated according to the following equation:

$$\rho_{\text{ammonia}} = \frac{X}{V_z \cdot \eta} \cdot \frac{273 + t}{273 + t_a} \tag{1}$$

$$\text{and } X = k'(E - E_0) \cdot 3.5 \tag{2}$$

The fact that the aliquot of 20 mL is taken from a total volume of 70 mL is considered by the factor 3.5.

Applying the critical nozzle calculate:

$$V_z = V_k \cdot \frac{p_v}{p_n} \cdot \frac{273 + t_a}{273 \cdot \frac{(273 + t)^{1/2}}{273}} \cdot \frac{\tau}{60} \qquad (3)$$

At 20 °C and 1013 hPa:

$$\rho_{0,\text{ammonia}} = \rho_{\text{ammonia}} \cdot \frac{273 + t_a}{293} \cdot \frac{1013\ \text{hPa}}{p_a}$$

The corresponding concentration σ – independent of the state parameters pressure and temperature – is:

$$\sigma = \rho_{0,\text{ammonia}} \cdot \frac{24.1\ \text{L} \cdot \text{mole}^{-1}}{\text{molecular weight g} \cdot \text{mole}^{-1}}$$

$$= \rho_{\text{ammonia}} \cdot \frac{273 + t_a}{p_a} \cdot \frac{1013\ \text{hPa}}{293} \cdot \frac{24.1\ \text{L}}{17.03\ \text{g}}$$

$$= \rho_{\text{ammonia}} \cdot \frac{273 + t_a}{p_a} \cdot 4.89 \frac{\text{hPa} \cdot \text{mL}}{\text{mg}}$$

At $t_a = 20$ °C and $p_a = 1013$ hPa:

$$\sigma = \rho \cdot 1.42 \frac{\text{mL}}{\text{mg}}$$

Legend:

X	Concentration of ammonia in the analysis solution in mg
V_Z	Read value of the sample volume in m^3; in case of sampling with the critical nozzle V_Z is calculated from the sampling time and the data of the critical nozzle according to equation (3); V_z is read at the gas meter in case of sampling by use of a gas meter
η	Recovery rate
ρ_{ammonia}	Concentration of ammonia in the ambient air in mg/m^3, referring to t_a and p_a
$\rho_{0,\text{ammonia}}$	Concentration of ammonia in the ambient air in mg/m^3, referring to 20 °C and 1013 hPa
σ	Concentration of ammonia in the ambient air in mL/m^3
V_k	Flow rate through the critical nozzle in m^3/h referring to t = 0 °C, p_a = 1013 hPa and $p_n/p_v < 0.5$

t	Temperature in the gas meter or at the critical nozzle in °C
t_a	Temperature of the ambient air in °C
p_a	Pressure of the ambient air in hPa
p_v	Pressure of the sample air before the critical nozzle in hPa
p_n	Pressure of the sample air after the critical nozzle in hPa
k'	Reciprocal calibration factor in mg
E	Extinction of the analysis solution
E_0	Extinction of the reagent blank value (determined from at least three single values)
τ	Sampling time in min

7 Reliability of the method

7.1 Precision

The precision of the complete method is significantly influenced by the sampling method.
The relative standard deviation from 10 single determinations was 4% (3.5%) corresponding with a mean variation of 8 % (7.5 %) in case of the sampling by use of a critical nozzle and by applying an ammonia nitrogen mixture of 19.7 mg ammonia per m^3 air (35 mg ammonia per m^3 air).

7.2 Detection limit

The detection limit of the method is 3 µg of ammonia (absolute) corresponding with 0.8 mg/m^3 air referring to a sample volume of 4 L.

7.3 Recovery rate

The recovery rate was determined by use of an ammonia-nitrogen mixture of a concentration of 35 mg ammonia per m^3. For the described method the mean recovery rate of 98% was calculated from 15 single measurements.

7.4 Sources of error

The substances sulfur dioxide, nitrogen dioxide, hydrogen sulfide, formaldehyde and pyridine do not interfere with the determination of ammonia in the concentration range of their MAK-values. Formaldehyde does not influence the determination of ammonia up to the twofold of its MAK-value. During the development of this method the interferences of piperidine, diethylamine, cyclohexylamine, primary aliphatic amines as well as aniline and its derivatives have not been investigated. As described in the literature nega-

tive deviations were observed for piperidine, diethylamine and cyclohexylamine. Positive deviations occur in the presence of primary aliphatic monoamines [3] (methylamine, ethylamine) and aniline and its derivatives.

8 Discussion

The method is founded on the Berthelot reaction [2]. It was developed on the basis of the VDI-guidelines as given in reference [1]. The sensitivity of the reaction permits the application of a relatively small sample volume corresponding with a short sampling time. Therefore the short-term value can be monitored by means of this measuring technique.

The pH-value of the solution is important during the reaction of ammonium ions with the reactants. The pH-value should range between 11.8. and 12.4. Deviations from this range deteriorate the reproducibility of the measured values.

Apparatus: Photometer Elko II of Carl Zeiss equipped with Filter J 61.8

9 References

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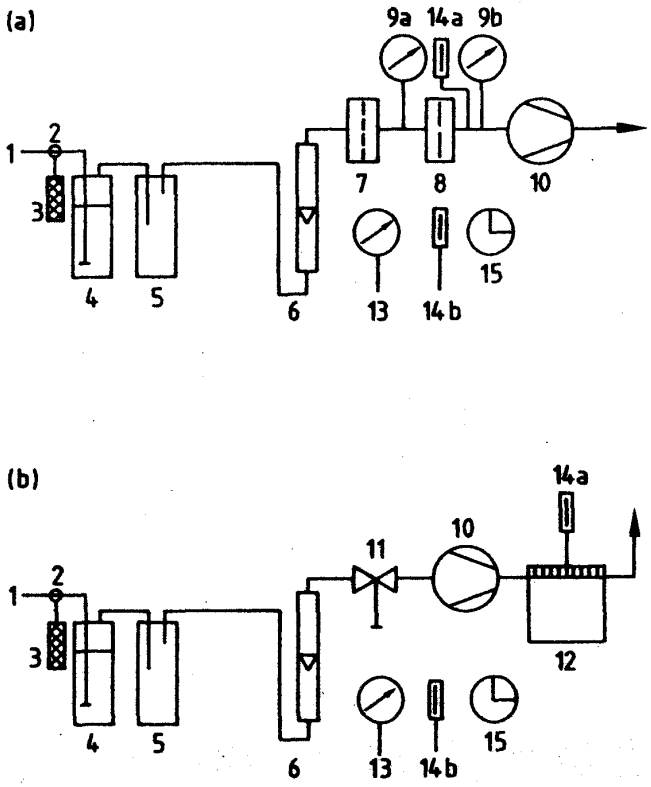

Fig. 1. Experimental arrangement of the sampling device.

a) Arrangement if a critical nozzle is used.

b) Arrangement if a gas meter is used.

1 Sample air inlet; 2 Three-way cock; 3 Activated carbon filter; 4 Wash bottle equipped with frit D 2; 5 Safety bottle; 6 Volume flow meter; 7 Filter to protect the critical nozzle (Frit D 2); 8 Critical nozzle; 9 Pressure gauge: a) before the nozzle (p_v), b) behind the nozzle (p_n); 10 Pump; 11 Throttle valve; 12 Gas meter equipped with thermometer (t); 13 Barometer (p_a); 14 Thermometer: a) to measure the temperature at the critical nozzle (t) or at the gas meter, b) to measure the temperature of the ambient air (t_a); 15 Stop watch.

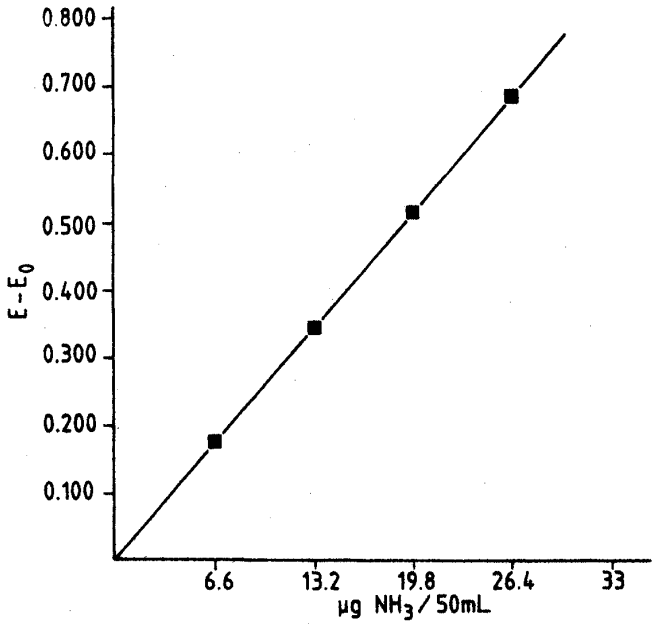

Fig. 2. Example of a calibration curve.
Photometer: Elko II (Zeiss)
Filter: I 61.8 (618 nm)
Path length: 10 mm
Control medium: water
Calibration factor k': $3.9 \cdot 10^{-2}$ mg
Volume of the analysis solution: 50 mL;
E Extinction of the sample; E_0 Extinction of the blank value.