

IVL

SWEDISH WATER AND AIR POLLUTION RESEARCH INSTITUTE

INSTITUTET FÖR VATTEN- OCH LUFTVÅRDSFORSKNING

HÅLSINGEGATAN 43
STEN STUREGATAN 42

BOX 21060
BOX 5207

S-100 31 STOCKHOLM
S-402 24 GOTHENBURG

SWEDEN
SWEDEN

TEL. 08-24 96 80
TEL. 031-81 02 80

METHOD FOR DETERMINATION OF ATMOSPHERIC AMMONIA

Martin Ferm

B 494

Gothenburg

April

1979

1 Utförande institution/Rapportutgivare

Institutet för Vatten- och Luft-
vårdsforskning, Box 5207, 40224 GbgPROJEKTBESKRIVNING
 TITELBLAD-RAPPORTER
3 Datum

2 Accessionsnr

4 Ärendebeteckning (Diariernr)

PR

1979.04.23

Läs anvisningarna innan blanketten fylls in!
Denna sida får kopieras!

5		6		7 MI projektnr	
8 Projekt					
<input type="checkbox"/> 1 Uppläggning		<input type="checkbox"/> 2 Komplettering		<input checked="" type="checkbox"/> 3 Avslutat	
10		11 Kontraktnr		12 Startår 1978	
				13 Slutår 1979	
14 MI projektnr (i förekl fall)					
15 Finansierande organ Statens naturvårdsverk, Solna. IVL, Stockholm					
16 Projektbeskrivning/Rapportens titel och undertitel Method for determination of atmospheric ammonia.					
17 Projektledare/Författare Martin Ferm, fil.mag.					
18 Sammandrag (ange gärna målsättning, metod, teknik, resultat m m) Determination of ammonia in air is complicated by interference from particle-borne ammonium ions. This problem can however be solved by utilizing the well-known fact that when ambient air passes through a tube, gas molecules diffuse much more quickly than particles to the tube wall. The here presented method is based on both theoretical considerations and practical tests.					
					19 Sammandraget skrivet av Förf.
20 Förslag till nyckelord Atmospheric ammonia					
21 Klassifikationssystem och klass Y					
22 Indexterm (ange källa)					
23 Övriga bibliografiska uppgifter				24 ISSN	
				25 ISBN	
26 Hemligt <input type="checkbox"/> Nej <input type="checkbox"/> Ja jämlikt		27 Språk Eng.		28 Antal sidor 32	
29 Pris					
30 Projektbeskrivning/Rapporten beställs hos Institutet för Vatten- och Luftvårdsforskning, Box 21060, 10031 Stockholm					

Försöksversion MDN 5 1975-02 15 000

Blanketten beställs hos

MILJÖDATANÄMNDEN

Postadress
Jordbruksdepartementet
Fack
103 20 STOCKHOLM

Telefon

08 - 763 10 00

Abstract

Determination of ammonia in air is complicated by interference from particle-borne ammonium ions. This problem can however be solved by utilizing the well-known fact that when ambient air passes through a tube, gas molecules diffuse much more quickly than particles to the tube wall. The here presented method is based on both theoretical considerations and practical tests.

INTRODUCTION

The ambient air continuously receives ammonia primarily through the decomposition of organic material. Ammonia may then react reversibly with acid airborne particles which as a result will contain more or less acid ammonium salts. The latter have been the subject of numerous investigations. Ammonia in gaseous phase, on the other hand, has been studied only very sparsely. The reason is probably the difficulty in developing measurement methods giving a sufficiently low detection limit at the same time as preventing the results from being affected by the presence of ammonium-containing particles.

So far no method has been described which fully meets the above-mentioned requirements. Two procedures have, however, been used.

One procedure is based on separating the particle phase through filtration and absorbing the NH_3 -gas passing through the filter in an acid medium (Shendikar and Lodge, 1975). As will be shown below, this procedure can give incorrect results.

The other procedure is based on the ability of fine particles to pass through a solution without being washed out (Hryniewicz, pers. comm.). As ammonium salts principally form part of fine particles, their content of ammonium will thus be retained only to a very small part in the acid solution absorbing the gaseous ammonia. However, as a rule there is a minor content of ammonium salts also in coarse particles. Most of these remain in the washing solution which thereby receives a contribution of ammonium ions not originating from the gaseous phase.

However, there is yet another means of separating gaseous and particulate phases. It is based on the fact that gas diffuses much more quickly than particles. Using a sampling

procedure based on this principle, a method for determination of gaseous ammonia ($\text{NH}_3(\text{g})$) has been developed in our laboratory.

A detailed description of the method itself will be given below. It is followed by a discussion of the theoretical prerequisites including test results primarily concerning optimization of the sorption efficiency of $\text{NH}_3(\text{g})$ with simultaneous minimization of particle deposition on the sorbent. Finally, a number of tests will be reported which were initially intended to determine the reproducibility of the measurements in field conditions, but which also gave some unexpected results.

DESCRIPTION OF METHOD

Sorption part of the sampling equipment

The sorption part of the sampling equipment is made up of a glass (pyrex) tube coated on the inside with a layer which sorbs NH_3 .

The glass tube is 50 cm long and has an internal diameter of approximately 3 mm. The sorbent is oxalic acid, previously used in this context by Shendrikar and Lodge (l.c.).

The coating is applied by sucking up a 1.5% oxalic acid solution in methanol until it is 35 cm high in the tube and then emptying it. Immediately following this, dry, particle- and ammonia-free air is pumped through the tube, which will be dry after 2-3 s at an air flow of 10 l/min. After the drying procedure, the tube is sealed at both ends as fast as possible with parafilm. In this shape, the tube can be preserved in room atmosphere without taking up any measurable amount of NH_3 .

Even if ester formation between oxalic acid and methanol occurs very slowly, it is recommended that a new solution is prepared on each coating occasion.

The most simple way of removing NH_3 from the air used for drying the coating is filtration through a filter impregnated with oxalic acid.

Sampling

The sampling tube is mounted vertically and connected on its uncoated end to a funnel and on its coated end to a tubing leading to the gas meter and pump, as outlined in fig. 1. Air is sucked through the tube at a flow of 3 l/min. Sampling is discontinued after 24 h, the tube is closed at both ends with parafilm and transported to the laboratory for analysis.

Analysis

The analytical procedure is based on dissolving the oxalic acid layer with its content of ammonium ions and determining the NH_4^+ amount in this solution using an ion specific electrode. (Interference from amines, when present, can be avoided by using ion chromatography instead of the electrode).

Dissolution of the sorption layer is obtained through sucking up 2 ml of a 0.1 M NaOH solution. Leaching will take only a few seconds. After emptying the leaching solution in a 10 ml beaker with a diameter slightly larger than the electrodes, it is sucked up in the tube anew, and emptied back into the beaker. In this way, the liquid film remaining in the tube will have the same concentration as the solution in the beaker. A magnetic stirrer and an Orion electrode 95-10 are now introduced into the beaker. The system is slanted about 30° in order to prevent the attachment of air bubbles on the membrane of the electrode. The electrode

will give a more stable signal if parafilm is wound around the empty space between the beaker and the electrode. The magnetic stirrer is started, and as a rule, the emf can be read after 3 min. At very low concentrations, however, the emf will stabilize after a somewhat longer period. The time of response can be shortened by placing the electrode briefly in a buffer solution with pH = 4.

Tests have ascertained that the oxalic acid does not affect the results.

The chemical part of the method described above gives a detection limit of 2 nmole per tube, which corresponds to a concentration of 0.5 nmole/m^3 at the flow mentioned and 24 h sampling.

THEORETICAL AND PRACTICAL EXAMINATION OF THE METHOD

General

In designing the sampling procedure, the aims were to optimize the sorption process and minimize interference from ammonium-containing particles. In principle, this meant solving the following problems:

1. Choice of sorbent
2. Choice of the sorbent's surface concentration
3. Choice of tube dimensions
4. Choice of tube material
5. Choice of air flow

Examining sorption efficiency

When air is sucked through a tube the gas molecules will collide with each other and with present particles, in the same way as in the air outside the tube. They will also collide with the tube wall. If this wall is coated with a substance able to act as a sorbent of ammonia, a fraction of this will be retained on the sorbent. The magnitude of this fraction is dependent on several parameters, among others the nature and surface concentration of the sorbent as well as the dimension of the tube and the air flow. The choice of these parameters was made by means of the considerations and tests reported below.

Two substances have formerly been used as sorbents of NH_3 , namely oxalic acid, $\text{H}_2\text{C}_2\text{O}_4$, and phosphorous acid, H_3PO_3 . Both are very effective. However, it has been found that the low point of deliquescence of phosphorous acid is a disadvantage, at least in sampling of longer duration.

The sorption efficiency of such coated tubes was the subject of a closer examination. The theoretical point of departure

was an expression given by Davies (1966) for a perfect sorbent. In our case, such a sorbent will reduce the partial pressure of ammonia at the tube wall to zero. The expression is as follows.

$$\frac{\bar{c}}{c_0} = 0.819 \exp(-14,6272\Delta) + 0.0976 \exp(89.22\Delta) + 0.01896 \exp(-212\Delta) \dots (1)$$

where

$$\Delta = \frac{D \cdot L}{\gamma \cdot Re \cdot d} \dots (2)$$

In these equations.

\bar{c} = mean concentration in gas emanating from the tube

c_0 = concentration in incoming gas

D = diffusion coefficient

L = length of tube (here 35 cm)

d = internal diameter of the tube

γ = kinematic viscosity of the gas

Re = Reynolds number

Furthermore, it is known that

$$Re = \frac{\bar{v} \cdot d \cdot \rho}{\eta} \dots (3)$$

and

$$\gamma = \frac{\eta}{\rho} \dots (4)$$

where

\bar{v} = the mean velocity of the gas

ρ = the density of the gas

η = the dynamic viscosity of the gas

If, finally, instead of \bar{v} , the flow F is introduced where

$$F = \bar{v} \cdot \pi \cdot \left(\frac{d}{2}\right)^2 \dots\dots (5)$$

a more simple expression for the function Δ will be obtained

$$\Delta = \frac{\pi \cdot D \cdot L}{4F} \dots\dots (6)$$

Determination of $\frac{\bar{c}}{c_0}$ was carried out in the following manner:

Ammonia containing air was first sucked through a sampling tube and then through a filter holder loaded with an oxalic acid impregnated Whatman 40 filter. Ammonia was obtained from a permeation tube. The ammonia concentration and the r.h. of the air were regulated with a dilution system. Sampling time was 2 h and temperature 22°C. The filter was found to have 100% sorption efficiency at all flows used independent of the r.h. of the air. In spite of great caution, the filters usually contained a background amount of about 25 nmole of ammonium. For this reason, it was found to be better to use a second sampling tube instead of a filter when only small amounts left the tube. The results of these measurements are summarized in Table 1.

When an impregnated filter was used, the sorption efficiency e was calculated from

$$e = \frac{a}{a + b} \dots\dots (7)$$

where a is the amount of NH₃ sorbed in the first sampler (tube) and b is the amount sorbed in the second sampler (filter).

When two tubes were used in series, e was calculated as follows:

Assume that c nmoles of NH_3 have entered the first tube, of which a nmoles have been sorbed. Thus, in the second tube, $c-a$ nmoles are introduced. Of this, b nmoles are sorbed. Consequently, the sorption efficiency e can be expressed

$$e = \frac{a}{c} = \frac{b}{c-a}$$

which gives

$$e = \frac{a-b}{a} \quad \dots\dots\dots (8)$$

The determination of the sorption efficiency was carried out in two series. The first comprised determinations of sorption efficiency at varying flow and ammonia concentration but with the same kind of sorbent layer. This was achieved by means of 1.5% oxalic acid solution in methanol in a procedure previously described. Methanol has been found to be the solvent which, through its rapid evaporation at room temperature, has given the most even coating.

In the second series, the flow was kept about constant. The ammonia concentration was varied and for the coating of the tube, more concentrated oxalic acid solutions as well as an H_3PO_3 solution were used.

It was then examined whether the data obtained satisfied equation 6 and if, consequently, the sorbents concerned were perfect or imperfect.

Δ was calculated from equation 1 and $\frac{c}{c_0}$ from 1-e.

The results of these measurements are summarized in Table 1.

A diagram showing Δ as a function of $\frac{1-c}{F}$ is given in Fig. 2.

The equation of the corresponding regression line is

$$\Delta = 6.80 \cdot 10^{-6} \cdot \frac{1}{F} - 0.0018 \quad (r = 0.989, n = 10)$$

The slope of the line gives

$$D = 2.47 \cdot 10^{-5} \text{ m}^2/\text{s}$$

The value $2.36 \cdot 10^{-5} \text{ m}^2/\text{s}$ has been given as diffusion coefficient of ammonia in air at 1 atm. and 25°C (Coulson and Richardson, 1954).

The agreement obtained shows that in all tests at laminar flow reported in table 1, perfect sorption was likely.

From table 1 it can first and foremost be seen that the sorption efficiency drops initially with increasing Reynold's number, reaches a minimum at $Re \approx 2300$, then rises again. As the gas flow can be considered to be laminar for $Re < 2000$ and turbulent for $Re > 3000$, the sorption minimum seems to occur in the transition from laminar to turbulent flow.

As will be shown in the next section, only laminar flow is of interest in this context. Both detection limit, particle deposition and sorption efficiency decrease when the flow in the laminar interval increases. However, the sampling is desired to give a detection limit and a particle deposition as low as possible at a reproducible and acceptably low sorption efficiency. The lowest acceptable sorption efficiency was chosen to be 90%. According to table 1 it corresponds to a flow of about 3 l/min.

As can be seen from table 1, the measurements of the sorption efficiency described above were carried out for relatively high ammonia concentrations (500-3000 nmole/m³). However,

the corresponding measurements were also made under completely realistic conditions using ambient air. The concentration range in this case was 2-18 nmole/m³ and the sampling time was 24 h. Two identically prepared sorption tubes coupled in series were used.

The ambient temperature in this test was about 0°C. The tubes were placed in a box with a few degrees higher temperature. The sorption efficiencies were calculated from equation 8.

The results of the eight tests are shown in table 2.

The values in table 2 give a mean value of the sorption efficiency of 90.5 ± 3.7%, i.e. in good agreement with that previously obtained (90.6% at 2.94 l/min., table 1).

In parallel with the above measurements, the sorption efficiency was investigated at a turbulent flow (10 l/min.). The particle phase was filtered off with a 25 mm membrane filter (Fluoropore FALP) prior to sampling of the gas phase. In this test, a sorption efficiency of 93.3 ± 1.5% was obtained (table 2). This is in good agreement with the laboratory test (95.6% at 10.8 l/min., table 1).

Investigation of particle interference

Interference from particles may occur in two different ways.

- 1) The particles may release NH₃ since, when passing through the tube, they will be in an atmosphere with lower partial pressure of NH₃ than that of the ambient air. This may result in measurements giving too high values.
- 2) The particles themselves may be deposited on the tube wall. This too may lead to values that are too high.

As will be shown below, these interferences can be limited to values of the same order of magnitude as those caused by analytical-chemical factors.

Regarding the first type of interference it is to be expected that a contribution, if any, from particles via the gas phase must be very small, as the residence time of the particles in the tube at a flow of 3 l/min. is only 0.05 s. The interference in question can also be determined directly using equation (8). If the sorption efficiency is measured in the presence and absence of particles by means of tubes coupled in series, we will get

Without particles:

$$e_g = \frac{a_g - b_g}{a_g} \dots\dots\dots (9)$$

With particles:

$$e_{g+p} = \frac{a_g + a_p - (b_g + b_p)}{a_g + a_p} = \frac{a_g - b_g}{a_g + a_p} + \frac{a_p - b_p}{a_g + a_p} \dots\dots\dots (10)$$

g indicates here sorbed ammonia deriving from the gas phase and p indicates ammonia originating from the particle phase.

The NH_4^+ content of the particles is mostly sufficiently large not to be completely consumed due to release of NH_3 during passage through the tubes. As the partial pressure of ammonia is lower in the second than in the first tube, the amount of ammonia released from the particles and sorbed in the first tube (a_p) must not exceed that sorbed in the second (b_p). This implies

$$e_{g+p} < e_g \dots\dots\dots (11)$$

An example may be appropriate. Assume that the sorption efficiency in one case for particle-free gas is 90%.

$$\therefore 0.9 = \frac{a_g - b_g}{a_g}$$

Assume further that in the presence of particles, 10% of the ammonia in the first tube derives from these, i.e.

$$a_p = 0.1 (a_g + a_p)$$

$$a_g = 0.9 (a_g + a_p)$$

Assume finally that

$$a_p = b_p$$

which is a permitted approximation. In that case,

$$e_{g+p} = \frac{0.9(a_g + a_p) - 0.1 \cdot 0.9(a_p + a_g)}{(a_p + a_g)} = 0.81.$$

The sorption efficiency in the presence of particles is thus 81% whereas in the absence of particles it is 90%.

It has previously been shown in a field test (table 2) that ambient air gave a sorption efficiency close to that obtained for particle-free air (table 1). These experiments show that the interference from particulate NH_3 -release during sampling is small and likely to be negligible here.

The second type of interference occurs when the particles themselves are deposited on the tube wall. This occurs for a number of reasons, primarily

1. Electrostatic attraction
2. Turbulent flow

These two effects can be minimized by using suitable tube material and ensuring that the flow is laminar. But also at laminar flow, particle deposition may occur as a result of

- 3. Diffusion
- 4. Gravitation

Deposition of particles in tubes of different materials has been investigated by Steen and Andréasson (1973). They found that the particle deposition in the size range 0.3-13 μm was least for glass. On the basis of these findings, glass was used as tube material in all tests reported here.

Laminar flow is obtained when

$$\left. \begin{array}{l} L > 0.05 \cdot d \cdot Re \\ Re < 2000 \end{array} \right\} \dots\dots\dots (12)$$

where

L = the distance necessary for the gas to be transported to create a laminar flow. L is thus the part of the tube which is not coated with a sorbent, as described above.

It is further necessary that the flow is constant (constancy is obtained through placing a gas meter between the pump and the glass tube).

However, deposition of particles occurs on the tube wall at laminar flow through diffusion as a consequence of the Brownian molecular motion.

According to Fuchs (1964) this can be expressed

$$\frac{n}{n_0} = 2.56 \mu^{2/3} - 1.2 \mu - 0.177 \mu^{4/3} \dots\dots\dots (13)$$

$$\mu = \frac{\pi \cdot D \cdot L}{F} \quad (= 4\Delta \text{ according to equation 6})$$

where

D = diffusion coefficient of the particles

n_0 = original number of particles per unit volume of air

n = number of particles per unit volume of air deposited on the tube wall.

Thus the deposition by diffusion is reduced when the flow through the tube increases.

The particles may deposit on the tube wall through the force of gravitation as well. By using Stoke's formula it is easily shown that the portion of the particles deposited in a horizontal tube is

$$\frac{n}{n_0} = \frac{g \cdot \tau \cdot L \cdot d}{F} \dots\dots\dots (14)$$

where g is the gravitation constant and τ is the relaxation time. The relaxation time is the time needed for a particle to adapt itself to an applied force. It is derived from

$$V_s = g \frac{2r^2 \rho}{9 \eta} = g\tau \dots\dots\dots (15)$$

where

V_s is the terminal velocity of a particle of the radius r falling in a gas due to gravity.

Particle deposition as a result of gravitation thus declines with increasing flow and reduced tube diameter.

The particle deposition ($\frac{n}{n_0}$) as a function of the particle diameter was calculated both for the diffusion case (equation

13). and the gravitation case (equation 14). Required values for D and \mathcal{T} were taken from Fuchs (l.c). The result is shown in fig. 3.

Numerous field measurements have shown that the mass of particle-borne ammonium ions is normally associated to an extent of 80-90% to particles $< 4 \mu\text{m}$. It is small for particles $< \approx 0.1 \mu\text{m}$ as the total mass of these fine particles is small. In the light of this, it is of interest to examine the curves in fig. 3 for the particle size range $0.1 - 4 \mu\text{m}$. As can be seen optimum conditions (lowest $\frac{n}{n_0}$ value) prevail at $\approx 0.5 \mu\text{m}$. At horizontal placement of the sorption tube, deposition increases rapidly with increasing particle size. This source of error may however be almost fully eliminated by placing the tube vertically.

Deposition as a result of diffusion increases with decreasing particle diameter in order for the ammonia molecule ($r = 1.54 \text{ \AA}$) to reach a value for $\frac{n}{n_0}$ of near 0.90. Thus, it is of interest in this context to determine the order of magnitude of the error which may be caused by diffusion.

In the particle size range $0.1-4 \mu\text{m}$, NH_4^+ concentrations observed in Sweden are normally $10-400 \text{ nmole/m}^3$. For an average concentration of 400 nmole/m^3 , $\frac{n}{n_0}$ must consequently lie at $\frac{0.5}{400} = 1.25 \cdot 10^{-3}$ in order for the deposition to be as large as the previously mentioned analytical detection limit (0.5 nmole/m^3).

The value $1.25 \cdot 10^{-3}$ has been introduced as a line in fig. 3. As can be seen, this line intersects the deposition curve in question at a particle diameter of $\approx 0.1 \mu\text{m}$.

The above information may thus be summarized as follows. At the conditions given above and with the sorption tube in vertical position, together with maximum observed particle-borne ammonium concentrations the tube wall may be expected

to receive a maximum NH_4^+ addition of the same order of magnitude as the analytical detection limit.

Tests were made for the purpose of experimentally verifying the above theoretical conclusion concerning the deposition of the particle phase during NH_3 -determination.

Three samplers were mounted as shown in fig. 4 in which the air passes a funnel, an uncoated tube and a filter. Then the ammonium deposition was determined in the funnels, in the lower 15 cm and in the upper part of the tubes as well as on the filters.

As only a small part of the particle phase could be expected to be deposited in the tubes, the test was run for about two weeks, and 1 m long tubes were used. The results are given in table 3.

The mean value of the NH_4^+ deposition in the critical part of the tube (35 cm) obtained with probes 1 and 2 is 0.095 nmole/m^3 at a particulate NH_4^+ concentration of approx. 77 nmole/m^3 .

If the particulate NH_4^+ concentration at the same particle size distribution had been 400 nmole/m^3 (extreme value) the corresponding deposition would have been

$$\frac{400 \cdot 0.095}{77} = 0.5 \text{ nmole/m}^3$$

This result validates the theoretically deduced conclusion that interference from the particle phase will be of the same order of magnitude as the analytical detection limit (0.5 nmole/m^3) only at extremely high particulate NH_4^+ concentrations ($\sim 400 \text{ nmole/m}^3$)

As regards the upper concentration limit of the method it can be calculated from table 1 that it is above 500 nmole/m^3 .

Reproducibility of the method. Filter effect

The method developed has been subject to several field tests. Interesting results were obtained from these, particularly in the measurements carried out in October - November, 1977 at a clean-air station about 40 km south of Gothenburg.

On this occasion, the sampling equipment used was made up of a box containing 4 sorption tubes in horizontal position together with pumps and gas meters. The glass tubes were connected to uncoated glass probes equipped with downward funnels as protection against rain (and coarse particles) see fig. 5.

The temperature in the box was a few degrees higher than the ambient air.

For two of the tubes, sampling was carried out exactly as described above. The other two tubes were each equipped with a filter holder containing a membrane filter (Fluoropore FALP) in front of the sorption tube.

As the particles in the latter case had been removed before the air entered the sorption tube, the flow could be increased to 10 l/min. corresponding to 95% sorption efficiency (table 1). The intention of this arrangement was to study the reproducibility of the method as well as to determine in what way a filter in front of the sorption tube could affect the result.

The analysis of sorbed NH_3 was carried out as described earlier. The filters were leached in $5 \cdot 10^{-5}$ M HClO_4 and the NH_4^+ concentration was determined with the same method. In addition, strong acid was determined (according to Brosset and Ferm, 1978). The results of these tests are shown in table 4. These data were used to calculate the standard deviation.

of the method with the assumption that the deviation was log-normally distributed. For $\text{NH}_3(\text{g})$ the standard deviation obtained was 15% (n=12).

Of great interest is the observed increase in NH_3 -concentration obtained when the air stream has passed a filter before the sorption tube. As theoretically shown by Brosset (1979) release of ammonia from the particle phase will occur if fine particles, which are often acid and contain NH_4^+ , get into contact with coarse particles which are mostly alkaline. Filtration before sorption of NH_3 may thus give completely incorrect results. This was proved in the above tests.

SUMMARY

The method for determination of gaseous ammonia in ambient air can be described as follows:

Air is sucked through a vertical glass tube. The tube is inside coated with oxalic acid. After finished sampling the coating is dissolved and the NH_4^+ amount is determined. The detection limit of the method is 0.5 nmole/m^3 of air (0.01 ppb) for a sampling period of 24 h. Interference from particulate NH_4^+ is at extremely high concentrations ($\sim 400 \text{ nmole/m}^3$) of the same order of magnitude as the detection limit. Measurements made so far have shown a standard deviation of 15%.

In practical tests it has been shown that removal of the particle phase, by filtration prior to sorption of ammonia, may give completely incorrect results.

REFERENCES

- Brosset, C. (1979). Possible changes in aerosol composition due to departure from equilibrium conditions during sampling. Paper presented at the Division of Environmental Chemistry of the American Chemical Society (ACS) meeting, Hawaii, April 1-6, 1979.
- Brosset, C. and Ferm, M. (1978). Man-made airborne acidity and its determination. *Atm. Environ.* 12, 909-916.
- Coulson, J.M. and Richardson, J.F. Chemical Engineering, 1, Pergamon Press, London 1954, p. 239.
- Davies, C.N. Aerosol Science, Academic Press, London 1966, p. 410.
- Fuchs, N.A. The Mechanics of Aerosols, Pergamon Press, London 1964, p. 205.
- Hryniewicz, R. National Institute of Hydrology and Meteorology, Warsaw. Personal communication.
- Shendrikar, A.D. and Lodge, J.P. (1975). Micro determination of ammonia by the ring oven technique and its application to air pollution studies. *Atm. Environ.* 9, 431-435.
- Steen, B. and Andréasson, K. (1973). Deposition of ambient air particles in tubes of 4.5-6.5 mm diameter at flow rates of 1.4 and 3 l/min. IVL publication B 129, Swedish Water and Air Pollution Research Laboratory, Gothenburg, Sweden.

ACKNOWLEDGEMENT

I wish to thank professor Cyrill Brosset for his assistance and valuable advice in the work presented here.

Table 1

Determination of the sorption efficiency (e) in tubes coated with acid in methanol. a and b represent amount sorbed in the tube and on the filter, respectively. Time of exposure: 2 h. Temperature: 22°C

Acid and its conc.	Flow F l/min	Reynolds number Re	a mmole	b mmole	100·e %	$\frac{10^{-4}}{F}$ s/m ³	Δ
1.5% (COOH) ₂	0.975	437	2133	4.6 ^{x/}	99.8	6.15	0.406
"	1.50	672	2813	36.4 ^{x/}	98.7	4.00	0.284
"	1.85	829	2433	53.6 ^{x/}	97.8	3.24	0.247
"	2.23	999	2676	225	92.2	2.69	0.161
"	2.94	1317	1840	192	90.6	2.04	0.148
"	4.45	1993	2071	558	78.8	1.35	0.092
"	5.22	2338	536	166	76.4		
"	5.67	2540	1826	485	79.0		
"	8.42	3772	651	79	89.2		
"	10.8	4838	1342	58.7 ^{x/}	95.6		
3% (COOH) ₂	3.26	1460	1343	217	86.0	1.84	0.121
5% (COOH) ₂	3.13	1402	1275	199	86.5	1.92	0.123
1.5% H ₃ PO ₃	2.60	1165	1219	140	89.7	2.31	0.142
"	2.71	1214	505	54	90.3	2.21	0.146

^{x/} sorption tube instead of filter

Table 2.

Determination of the sorption efficiency^(e) using two sorption tubes. a and b represent measured amount sorbed in the first and second tube, respectively.

Date	a	b	100.e	Flow	Conc.
1977	nmole	nmole	%	l/min	nmole/m ³
	NH ₃	NH ₃			NH ₃ in air
15-16/12	16.0	1.4	91.3	3	4.26
	17.6	1.3	92.6	3	4.61
	66.5	3.3	95.0	10	4.78
16-17/12	10.3	0.5	95.1	3	2.77
	8.0	0	100	3	2.11
	173	14.5	91.6	10	12.7
	260	12.8	95.0	10	18.4
17-18/12	13.1	1.9	85.5	3	3.46
	18.5	2.6	85.9	3	4.89
	245	11.8	95.2	10	17.5
	174	10.2	94.1	10	12.4
24-25/12	18.8	2.5	86.7	3	5.01
	20.3	2.7	86.7	3	5.42
	221	18.8	91.5	10	16.0
	165	15.9	90.4	10	11.7

At 3 l/min the mean value obtained for $e = 90.5 \pm 3.7\%$

At 10 l/min the mean value obtained for $e = 93.3 \pm 1.5\%$

Table 3.

Test of particle interference

Sampling time: 28 August 1978, 09.35 - 11 September 1978, 16.16 h.

Location: Centre of Gothenburg

Flow: 2.9 l/min

Amount of air having passed each of the vertically placed tubes: 59.19 m³.

The amounts of NH₄⁺ deposited in the different parts of the samplers are expressed in nmole/m³.

Probe no.	1	2	3
Funnel	0.92	0.67	0.75
Tube lower 15 cm	0.071	0.061	0.091
upper 85 cm recalculated per 35 cm	0.105	0.084	0.113
Filter	77	77	(64) ^{x)}

x) leakage in filter holder

Table 4

Investigation of NH_3 in gas phase and NH_4^+ , H^+ and SO_4^{2-} in particle phase.
 All concentrations are expressed in nmole/m^3 . Sampler number refers to fig. 5.

Date	Time	GAS PHASE			PARTICLE PHASE						
		sampler		no.	sampler		no.				
		2	4	1	3	1	3				
		NH_3 without filter		NH_3 with filter	Ammonium		Strong acid		Sulphate		
26-27/10	15-15	21.7	20.7	46.5	42.4	133.5	131.0	8.0	11.3	87.2	74.9
28-29/10	15-15	36.1	30.8	48.4	49.7	28.7	29.9	-0.9	0.6	24.8	24.1
1-2/11	15-15	16.5	13.4	19.3	23.7	47.9	41.9	1.4	1.8	24.7	23.9
2-3/11	15-15	6.7	5.6	27.6	31.6	65.3	64.2	1.0	1.6	33.2	31.8
4-5/11	15-15	23.3	19.7	28.5	28.5	6.2	6.4	-1.3	-1.7	6.0	6.4
7-8/11	15-15	17.4	12.4	82.4	80.3	46.0	45.2	-1.0	-0.7	33.0	30.8
10-11/11	11-11	19.5	16.9	36.7	26.8	62.9	60.4	1.3	1.3	37.7	36.8
11-12/11	15-15	16.9	15.8	49.1	46.4	18.5	18.3	-0.7	-0.7	19.4	18.8
15-16/11	14-16	4.26	4.61	4.81	4.78	49.2	47.8	12.2	11.3	28.8	28.1
16-17/11	17-13	2.77	2.11	12.7	18.4	50.7	52.2	0.3	0.3	24.6	23.7
17-18/11	14-14	3.46	4.89	17.5	12.4	42.4	42.8	0.7	-0.7	9.7	18.5
24-25/11	10-10	5.01	5.42	16.0	11.7	19.5	18.2	0.7	2.0	10.5	10.0
Mean value		13.6		31.9		47.0		2.0		27.8	

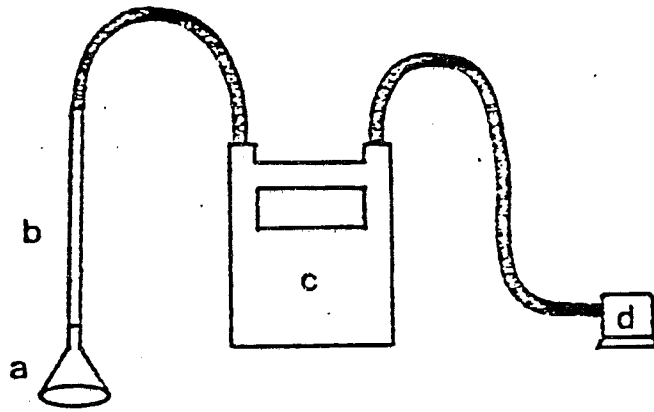
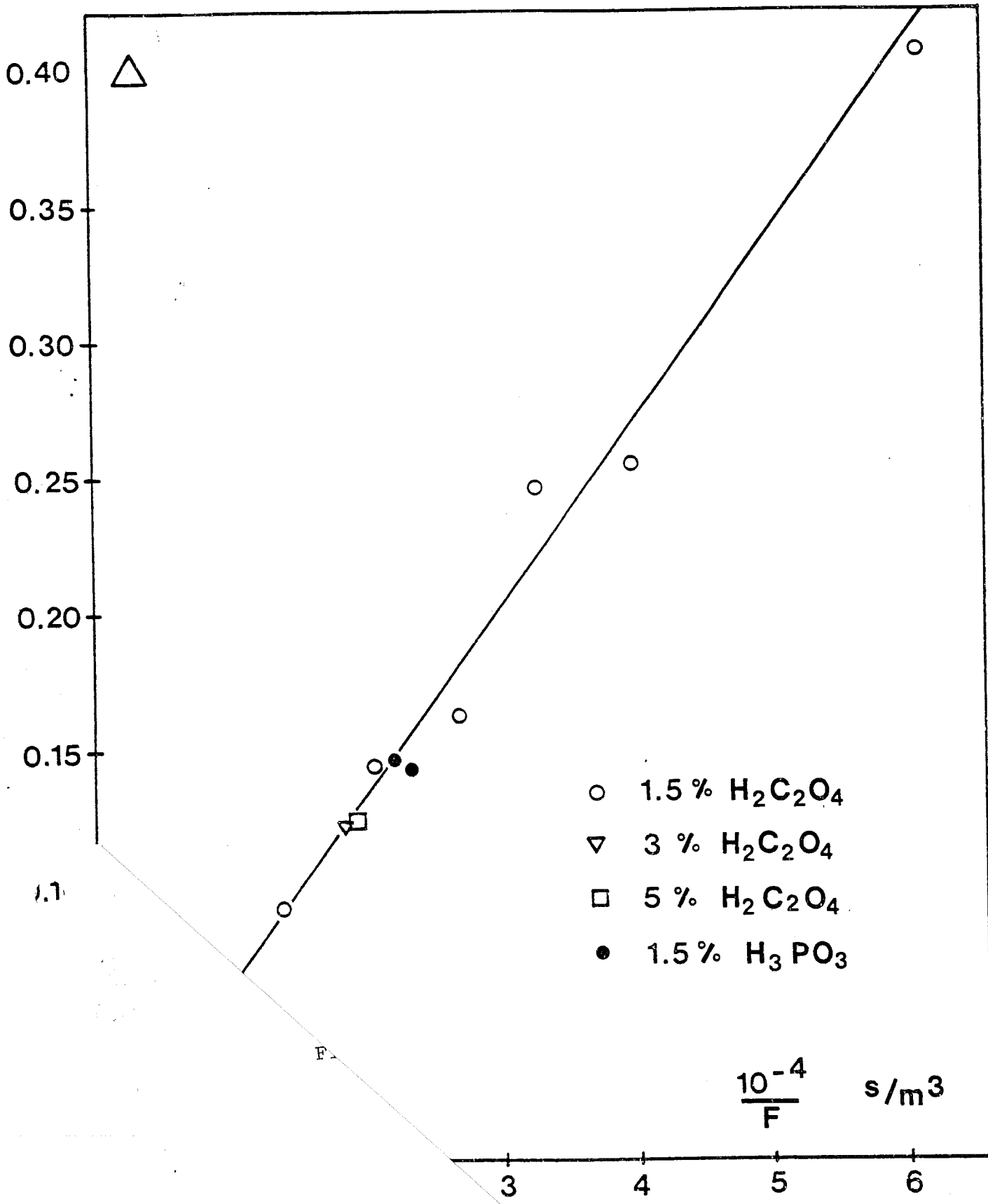


Fig. 1 Sampling equipment for ammonia analysis.
a funnel, b sampling tube, c gas meter and
d pump.



between \triangle and $\frac{10^{-4}}{F}$

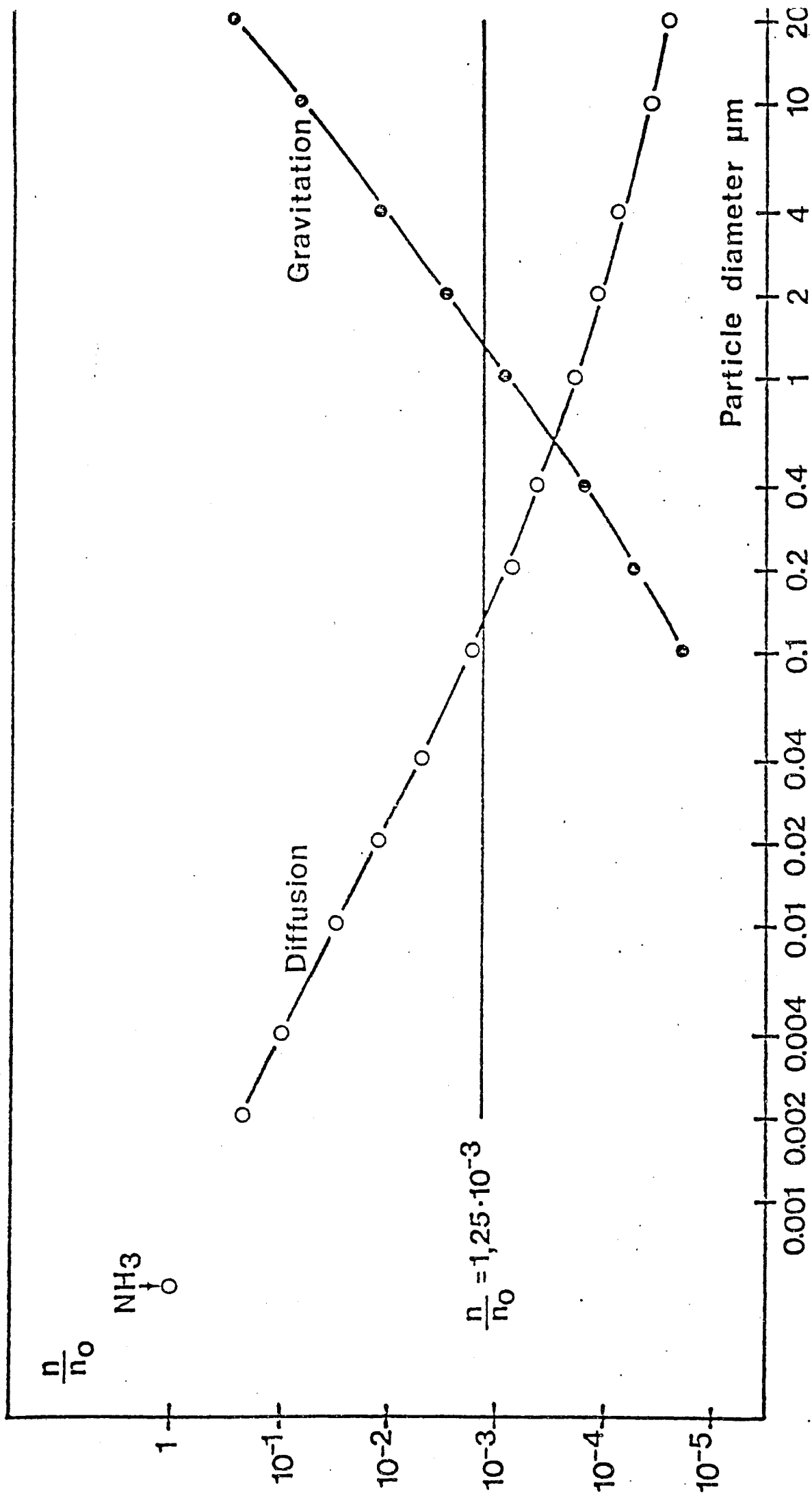


Fig. 3 Particle deposition ($\frac{n}{n_0}$) due to diffusion and gravitation as a function of particle diameter

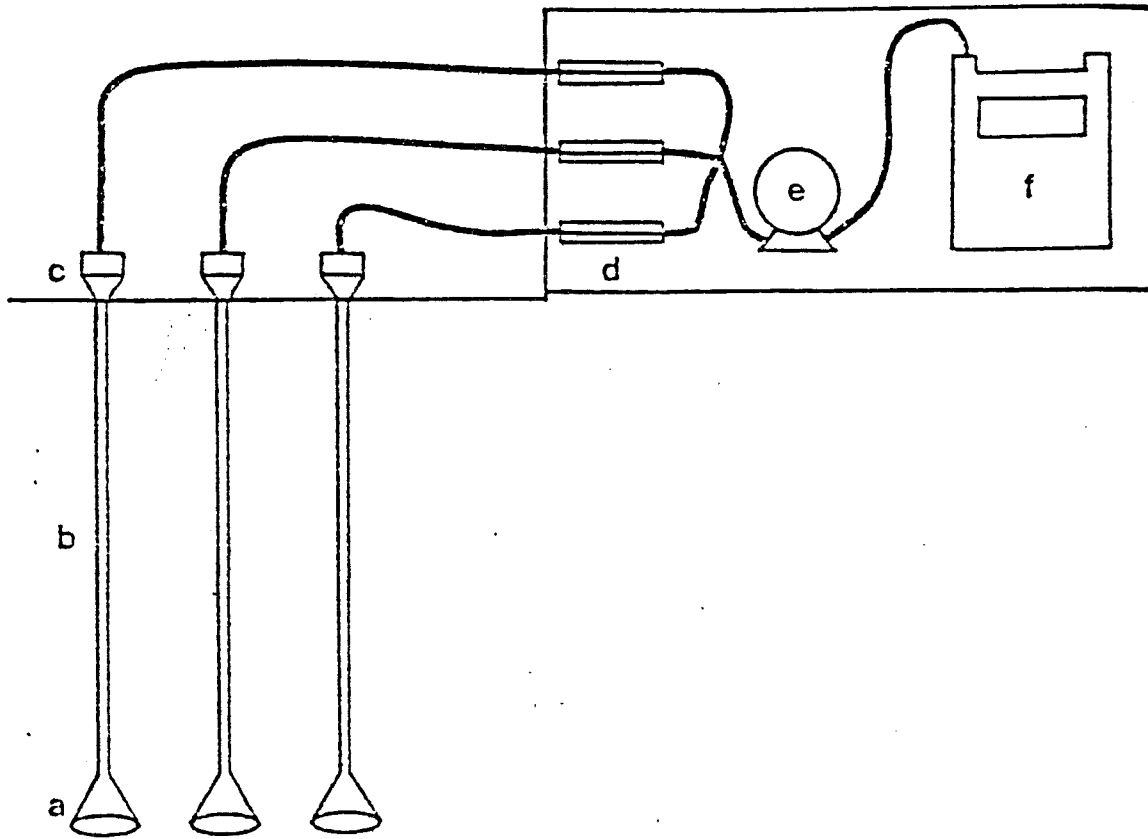


Fig. 4 Equipment used for test of particle deposition.
 a funnels, b non-impregnated glass tubes,
 c filter holders, d critical orifices, e pump,
 f gas meter.

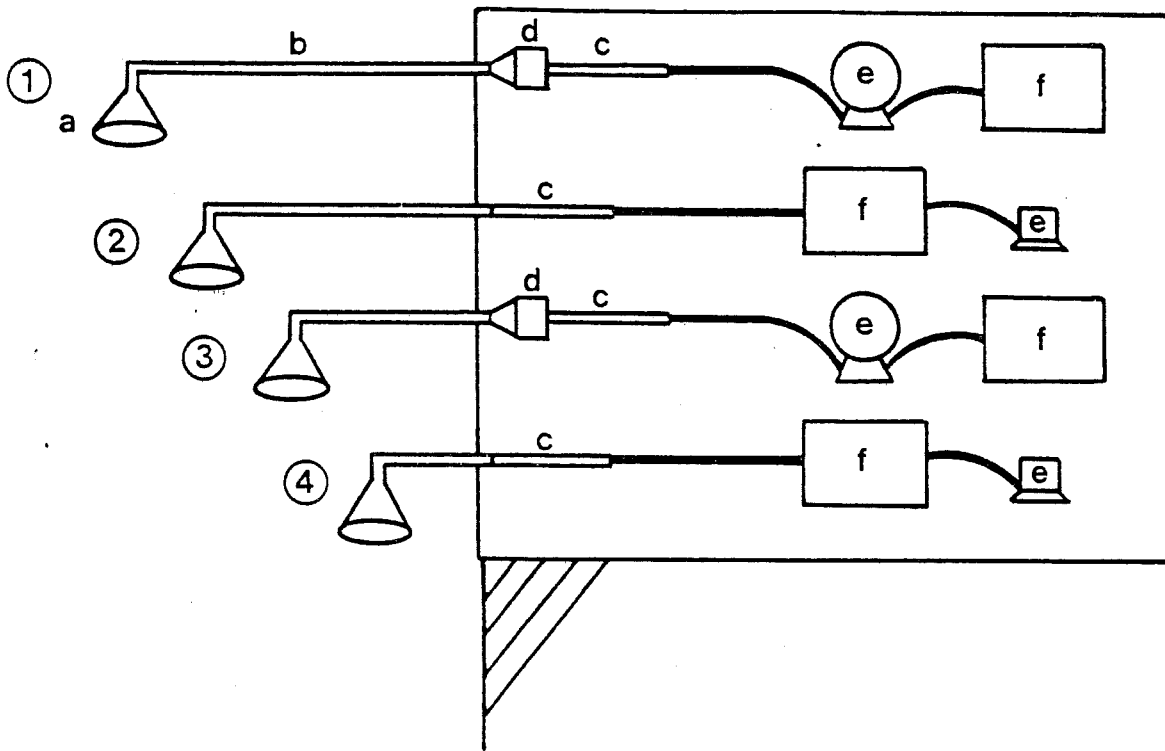


Fig. 5. Equipment used in field tests during October - November, 1977.
 a funnels, b uncoated glass tubes, c coated sampling tubes, d filter holders, e pumps, and g gas meters.