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Development and evaluation of field methods for ammonia in air

by Jan Rudling BSc, Bengt-Olov Hallberg BSc, May Hultengren, Annika Hultman BSc¹

RUDLING J, HALLBERG B-O, HULTENGREN M, HULTMAN A. Development and evaluation of field methods for ammonia in air. *Scand J Work Environ Health* 10 (1984) 197–202. Three methods for measuring ammonia in air have been evaluated. Filters impregnated with 10 % (volume/volume) phosphoric acid in methanol were used for two methods. Sampling was done either with a filter cassette connected to a pump or with the filters placed in a passive monitor (Gasbadge). The filters were leached with distilled water after the sampling and analyzed with ion chromatography or colorimetry (Nessler). The third method tested was a colorimetric air-monitoring badge system (ProTek). The tests showed that the accuracy of the filter methods is good and that the results are not affected by humidity. If ion chromatography is used for the analysis, amines do not interfere. The Gasbadge monitors increased their uptake when the air velocity over the sampler was raised from 0.2 to 1.0 m/s. The accuracy of the ProTek method was poor, the method was biased, and blank samples showed high values. In field tests carried out in a foundry and at a fertilizer plant, the agreement between the filter methods was good, whereas the results of the ProTek method deviated drastically from those of the other methods.

Key terms: field tests, ion chromatography, passive monitor, sampling.

Ammonia (NH₃) is used and encountered in various industrial and natural processes. It is used in the manufacture of fertilizers and explosives and as a refrigerant and cleansing agent. Ammonia is a known irritant to respiratory organs, skin, and eyes. In Sweden the standard for occupational exposure to ammonia is 25 ppm (time-weighted average limit) and 50 ppm (ceiling value for a 5-min period).

The most widely used method for sampling ammonia is the use of midjet impingers with dilute sulfuric acid as an absorbing solution followed by analysis with an ion selective electrode or colorimetry (8, 12). The disadvantages of using impingers for sampling are well known, and consequently other procedures have been developed. Vincent et al (14) and the National Institute for Occupational Safety and Health (NIOSH) (9) have used silica gel as the adsorbent. Filters impregnated with oxalic acid (1) or sulfuric acid (3) have also been used. The rapid development of passive monitors based on diffusion have resulted in new methods for sampling ammonia. Mazur et al (7) have developed an ammonia dosimeter in which filters impregnated with phosphoric acid are used as collection media. A passive colorimetric air monitoring badge system, ProTekTM (manufactured by DuPont), has been introduced and documented in a paper (4).

For analysis, the most widely employed methods are colorimetry or the ion selective electrode but in the last several years ion chromatography has been available as a valuable tool to improve sensitivity and selectivity. The method has been used for analyzing the ammonium ion in aerosols (11).

Although one inherent drawback of the method is the high cost of instrumentation, it is possible to use ordinary equipment for high-performance liquid chromatography with minor supplementation for ion chromatographic analysis (5).

The purpose of this work was to perform a comparison study in the laboratory, as well as in the field, for three different methods, a filter method developed at our laboratory, a passive filter method that is a modification of the method proposed by Mazur et al, and the ProTek method. Silica gel tubes were excluded from the study since purchased tubes showed high backgrounds and a prestudy demonstrated that impregnated filters have higher capacity and recovery.

Materials and methods

Sampling and analysis

For the filter method the following procedure is used. Filters (support pads Millipore AP 10, 37 mm) are dipped in 10 % phosphoric acid [10 ml of phosphoric acid is diluted to 100 ml with methanol (analytical purity)], allowed to drip off, and dried at 60°C for 1 h. Treated filters should be stored dry prior to

¹ National Board of Occupational Safety and Health, Stockholm, Sweden.

Reprint requests to: Mr J Rudling, National Board of Occupational Safety and Health, S-171 84 Solna, Sweden.

usage. Sampling is done by loading the filters in an ordinary cassette and connecting the device to a pump with a flow rate of 1.0 l/min, the sampling period being up to 4 h. If a longer storage period is necessary, refrigeration is recommended. After the sampling, the filters are leached with 50 ml of distilled water and shaken gently for 5 min, and after filtration of an aliquot analysis is made by ion chromatography.

Other methods such as colorimetry (Nessler) or the ion selective electrode could also be used for the analysis.

Filters for the passive filter method are prepared in a similar way. Filters (38 × 44 mm) are cut from a disc (Millipore AP 10, 142 mm), and after impregnation they are put in Gasbadge monitors. This type of monitor has been described in several papers (7, 13). After sampling, the analysis is made with the same procedure used for the first filter method presented. If we assume that the sorbent acts as a perfect sink, the sampling rate, f (in cm^3/min), for a passive monitor is given by (6):

$$f = (D \times A \times 60) / L,$$

where D = the diffusion coefficient (cm^2/s), L = diffusive path (cm), and A = cross-section area of the sampler (cm^2).

For practical reasons the sampling rate is usually determined from exposure of the samplers to known

concentrations of ammonia in air. Mazur et al determined the sampling rate to be $96.2 \text{ cm}^3/\text{min}$, and we initially used the same value. This rate is good for 25°C . A temperature correction can be made by:

$$f(t^\circ\text{C}) = f(25^\circ\text{C}) \times \left(\frac{t+273}{298} \right)^{1.5}.$$

For the analysis a Dionex 14 ion chromatograph equipped with an Altex Chromatopac integrator has been used. The ion chromatographic conditions are given in table 1. The limit of detection is below $10 \mu\text{mol/l}$, and the calibration curve is linear up to $200 \mu\text{mol/l}$ with a standard deviation of about $2 \mu\text{mol/l}$. If the coefficient of variation (CV) is to be $\leq 10\%$, the smallest amount to be quantified is $20 \mu\text{mol/l}$. With the outlined procedure and a 5-l air sample, 5 ppm can be analyzed by the filter method. If an 8-h sample is taken for the passive filter method, 0.5 ppm is the limit. These limits could be extended by an increase in the injection volume. The Nessler method has been used for some analyses, and we have used the procedure given by Skare & Stomrud (12), which is equivalent to that given by NIOSH (8).

The ProTek system is also based on diffusion. Gas molecules enter the sampler (see figure 1) through a diffuser and a porous tape into an absorbing solution containing 0.1 mol/l of boric acid and 0.03 mol/l of sodium potassium tartrate solution. The color reagent used for the analysis is a modification of Nessler's reagent for ammonia. The analysis involves pressing the reagent blisters and making the reagents mix with the absorbing solution. The intensity of the color formed is then determined after the sampler, made of a transparent material, is inserted into a specially designed photometer (PT-3). The result is given directly in parts per million times hours. Calibration is accomplished by the use of two calibration cards, span and zero. The range of the method is $50\text{--}500 \text{ ppm} \times \text{h}$. The sensitivity can be improved if the analysis is carried out with the spectrophotometric method supplied by the manufacturer.

Generation of test atmospheres

Ammonia was generated in dynamic systems by the dilution of concentrated gas from a cylinder. For tests of the filter method a certified gas cylinder containing 2,100 ppm of ammonia in nitrogen was used. The flow rate from the cylinder was controlled by a mass flowmeter (Brooks) calibrated against a soap bubble meter. Clean and dry house air, measured via a calibrated rotameter, was used for dilution; it was mixed with the contaminant stream in a 5-l glass bulb and passed forward to a manifold equipped with eight outlet ports for the filters to be tested. For the sampling the filters were connected to a pump via critical orifices.

For a test of the passive filter method and the ProTek procedure a similar generation system was used

Table 1. Ion chromatographic conditions.

Parameter	Material used/setting
Columns	4 × -50-mm Dionex trap column 4 × -50-mm Dionex cation concentrator 4 × -250-mm Dionex cation separator 9 × -100-mm Dionex cation suppressor
Flow	138 ml/h
Eluent	0.005 mol/l of hydrochloric acid
Sample volume	100 μl
Detector	Conductivity
Sensitivity	10 or 30 μmho full scale

Figure 1. ProTek sampler for ammonia.

(see figure 2). The cylinder used contained 32,000 ppm of ammonia in nitrogen and the flow rate of the air was 100 l/min. The monitors to be tested were placed in a glass tube (length = 1,300 mm, diameter = 93 mm) at least 150 mm apart. Under these conditions an air velocity of 0.24 m/s was achieved and used, with some stated exceptions, throughout the tests.

The certified cylinder contents were controlled by the passing of a known amount of gas through a fritted bubbler bottle containing dilute hydrochloric acid with methyl red as the indicator. The time required for the color to change to neutral was registered. The results from the analysis of the two cylinders showed excellent agreement with the certificate supplied by the manufacturer (Alfax).

As an additional control of the test atmosphere a set of seven impinger samples containing 15 ml of 0.0025-mol/l sulfuric acid were taken with each run and analyzed with ion chromatography. The average of these samples was not allowed to deviate more than $\pm 5\%$ from the calculated value. Of a total of 12 runs, one run exceeded the limit and was thus discarded. The average of the remaining 11 runs yielded 99.1 % of the calculated value with a CV of 3.2 %.

For the generation of humidity, the air stream was passed through fritted bubblers with distilled water. The relative humidity (RH) was controlled with a humidity meter (Vaisala humicap). As a standard condition 10–15 % RH and 20°C was used. Sampling time was about 4 h for the filter method and about 8 h for the passive filter method and the ProTek procedure.

Results and discussion

The collection efficiency for the filter method was determined by the following process: an impinger with 0.0025-mol/l sulfuric acid was connected after a filter, 25 ppm of ammonia was sampled for various times, and the proportion collected on the filter (= collection efficiency) was determined. A collection efficiency of $> 99\%$ was achieved. The capacity of the filters was determined from the sampling of 50

ppm of ammonia, for which the time was recorded when a breakthrough of $> 5\%$ occurred. This event took place after 6–8 h, which means that the capacity for the filters is at least $300 \text{ ppm} \times \text{h}$.

In tables 2–4 recovery and precision for the three methods are given. Each method was tested at three different concentrations. For the filter method additional tests were carried out. For evaluation we have used the criteria adopted by NIOSH (2); therefore we should be able with 95 % confidence to state that a single result is within $\pm 25\%$ of the true value. This criteria can be expressed as “overall system accuracy (OSA)” (6) according to:

$$\text{OSA} = |\bar{x} - 100| + 2 \times \overline{\text{CV}} \leq 25 \%,$$

where $\bar{x}$ = average recovery in percent and $\overline{\text{CV}}$ = pooled coefficient of variation in percent.

For the filter method we have assumed that the usage of a portable pump for sampling increases the CV. (In the tests critical orifices were used.) We have estimated the CV for a pump to be 5 %. Therefore, the $\overline{\text{CV}}$ in table 2 should be corrected to:

$$\overline{\text{CV}} = \sqrt{2.3^2 + 5^2} = 5.5 \, \%.$$

If we use this value for the filter method, OSA equals 11 %. We can also see from table 2 that short-time samples could be taken with high accuracy and that an alternative method of analysis (Nessler) yields good results. High humidity does not influence the method. Since the passive filter method uses the same type of sorbent, high humidity should not present any problem for that method.

The passive filter method is also in compliance with the NIOSH criteria, OSA equaling 10 %. Since the recovery is slightly less than 100 %, we have corrected the initial sampling rate, and, in the following discussion, we use 94 cm³/min. For the ProTek method OSA equals 37 %, and it is obvious from table 4 that the method is biased. Another fact to be noticed is that the method shows a high background when blank samples are run. This background in-

Figure 2. Apparatus used for generating the test atmospheres.

creases with storage time prior to usage. We have subtracted the background from the results. This procedure is not recommended in the manufacturer's instructions, and, if the method is used the normal way, an additional bias would be registered.

We repeated the experiments for the ProTek method with another lot of badges that were exposed to 21.0 ppm for 6 h. This time the analysis showed 72 ppm $\times$ h with the readout unit (PT-3) and 76 ppm $\times$ h when analyzed with a spectrophotometer. This finding indicates that the calibration factor supplied by the manufacturer is not correct. This inaccuracy was confirmed through the procedure of injecting known amounts of ammonium ion solution

into the badges. Our conclusion is that the sampling system works well for ProTek, but the analytical reagents cannot be stored for a longer period and/or transported by air to Sweden.

Storage stability for the methods are shown in table 5. Each result is the average of three samples. The loss for the filter method is less than 10 % over a five-week period when samples are stored in a refrigerator. The increase noticed for ProTek is most likely due to an increase in background. The storage time is not representative and is explained by the fact that the readout unit was changed, with a resulting delay.

Common interferences for ammonia are amines. Known amounts of three different amines were generated by the injection of liquid solutions of amines with a motor driven syringe into an air stream containing 25 ppm of ammonia. The samples were collected by the filter method and analyzed with ion chromatography and by the Nessler method. The results are given in table 6. The Nessler method is influenced to a moderate degree (+16 %). Since these amines have longer retention times than the ammonium ion, they do not interfere with the ion chromatographic determination. In many sampling situations amines should not present any problem when analyzed by the Nessler method. This is probably also true for ProTek since the same method (modified Nessler) is used for the analysis.

Passive monitors are, to a certain degree, dependent on the velocity of the air passing over the opening area of the sampler (face velocity). From table 7 we can see that the passive monitors, type Gasbadge, used for the passive filter method, increased their uptake as the velocity increased, whereas for the ProTek system it seems that the opposite is true. Our interpretation is that the ProTek system is unaffected within the range that was tested.

Most evaluations concerning passive monitors have been done with a constant face velocity, often

Table 2. Recovery and precision for the filter method.

Run	Ammonia taken (ppm)	Recovery (%)	Coefficient of variation (%)	N
1 ^a	12.0	96	2.2	6
2 ^a	25.0	102	1.6	6
3 ^a	50.0	100	3.0	6
4 ^b	25.0	99	1.0	6
5 ^c	9.4	97	0.8	6
6 ^d	25.0	98	0.8	5
7 ^{b, d}	25.0	104	1.3	5

^a Average recovery = 100 % (run 1–3); pooled coefficient of variation = 2.3 % (run 1–3).

^b Analyzed with the Nessler method.

^c Short-time samples (5 min).

^d High humidity (RH = 80 %).

Table 3. Recovery and precision for the passive filter method.

Run ^a	Ammonia taken (ppm)	Recovery (%)	Coefficient of variation (%)	N
1	6.1	95	3.3	6
2	23.0	106	4.1	6
3	47.0	92	4.6	6

^a Average recovery = 98 %; pooled coefficient of variation = 4.0 %.

Table 4. Recovery and precision for ProTek.

Run ^a	Ammonia taken (ppm)	Background (ppm $\times$ h)	Recovery ^b (%)	Coefficient of variation (%)	N
1	6.1	36	113	8.1	6 ^c
2	22.6	26	117	11.0	6
3	46.8	60	127	6.9	6 ^c

^a Average recovery = 119 %; pooled coefficient of variation = 8.8 %.

^b Background deducted from the results.

^c One sampler burst during analysis.

Table 5. Storage stability.

Method	Ammonia taken (ppm)	Relative humidity (%)	Recovery (%) after storage			
			0 weeks	2 weeks	5 weeks	8 weeks
Filter method	25	15	100	99	93	..
Filter method	25	80	100	..	91	..
ProTek	25	20	100	..	..	118

Table 6. Effect of interferences of amines.

Method	Ammonia taken (ppm)	Recovered amount (ppm)				N
		Methylamine	Diethylamine	Triethylamine	Ammonia	
Ion chromatography	25	17	20	7	24	3
Nessler	25	.	.	.	29	3

Table 7. Influence of air velocity on passive monitors.

Method	Ammonia taken (ppm)	Air velocity (m/s)	Recovery (%)	Coefficient of variation (%)	N
Passive filter method	26.4	0.09	76	6.5	6
Passive filter method	26.2	1.0	124	5.2	6
ProTek	28.0	0.09	139 ^a	13.1	6
ProTek	24.8	1.0	123 ^a	12.0	6

^a Background 60 ppm × h deducted from the results.

Table 8. Average results from field samples. (S = stationary samples, P = personal samples, CV = coefficient of variation)

Location	N	Filter method		Passive filter method		ProTek	
		Ammonia (ppm)	CV (%)	Ammonia (ppm)	CV (%)	Ammonia ^a (ppm)	CV (%)
Fertilizer plant (S)	10	12.2	7.4	11.9	6.6	26	10.4
Foundry (S)	12	1.24	6.5	1.64	24	< 7	.
Fertilizer plant (P) + foundry (P)	9	3.5	.	3.8	.	13	.

^a Background 53 ppm × h deducted from the results.

Figure 3. Field tests: Passive filter method versus the filter method. **Figure 4.** Field tests: ProTek versus the filter method.

around 0.5 m/s. Tompkins & Goldsmith (13) claim that face velocities above 0.08 m/s do not influence the uptake for Gasbadge, but they present no data to support this argument. Samimi & Falbo (10) have found that for styrene the uptake in a Gasbadge monitor increases 27 % when the face velocity is increased from 0.06 to 0.36 m/s. Obviously more research is needed in this area. In the field, we are likely

to encounter velocities in the range of 0.1 to 1 m/s (Lars Olander, personal communication).

Our study was completed by field tests in two different environments, a fertilizer plant and a foundry. At every plant six stationary and six personal sampling sites were picked out (sampling time 8 h). The stationary samples were taken as duplicates and the sampling devices were mounted on a rack (with a

maximum distance of 40 cm between the samplers) with randomized positions of the samplers. The personal samples were taken with samplers affixed as close as possible to each other. The results are summarized in table 8. Due to pump malfunction some samples were discarded.

The CV for the methods to be tested was calculated for each plant from the stationary samples according to:

$$CV = \frac{100}{\bar{x}} \times \sqrt{\frac{\sum d_i^2}{n}},$$

where $\bar{x}$ = mean value in parts per million, d_i = difference in parts per million between duplicates, and n = number of samples.

With the actual set-up of the field tests it is probably more correct to estimate the CV from a logarithmic transformation of the data since the standard deviation for an air sampling method is usually proportional to the mean (constant CV). However, the difference between such an estimation and the proposed one (which is simpler) is in this case insignificant.

In figures 3 and 4 the individual values for the passive filter method and the ProTek system are plotted against the values obtained by the filter method. Values below 2.5 ppm (= 10 % of the Swedish standard) have been omitted. Agreement was good between the two filter methods although at the foundry the passive filter method showed significantly higher values than the filter method. The ProTek method demonstrated a drastic deviation from the other methods in spite of the fact that a background of 53 ppm $\times$ h was deducted from the results. As can be seen from figure 4, there is a distinct pattern indicating that, if an additional background is deducted and another calibration factor is used, better agreement would be obtained.

Conclusions

Both the laboratory and field tests showed that the two filter methods are in compliance with standards that could be set up for a field method. As has been demonstrated by the laboratory tests, high air velocities could be a problem for passive monitors like the Gasbadge. The ProTek system is, in its present state, not usable as a field method. But it must be stressed that it is our belief that the method is basically sound and that it can be improved if the sampling and analysis are separated and the users prepare their own reagents and calibration curves.

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