

A Method for Personal Sampling and Analysis of Nanogram Amounts of Formaldehyde in Air

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An air sampling and analytical system for formaldehyde measurements based on a solid sampler is described. The samplers were tested on a standard atmosphere in the range of 0.2 to 0.8 mg/m³ dry air. A single 340 mg sorbent section had without drying sections a capacity of 16 µg formaldehyde in dry air and 3 µg at 70% RH, 23°C. The precision of fluorimetric analysis was better than 6% for samples of 300, 600 and 1200 ng formaldehyde, and the accuracy was better than 10%. The precision of a colorimetric analysis was 12% for a 300 ng sample and 2% for 600 and 1200 ng samples. The accuracy of this method was better than 7%. Both the fluorimetric and the colorimetric analyses are found to be accurate and sensitive analytical methods for the determination of low formaldehyde concentrations. However, if measurements of more than 15 minutes duration are taken and a desiccant is used, the accuracy still remains to be verified. Positive interference from acrolein (5-7% interference when equimolar amounts are present) was found, but there was no interference from other aldehydes.



Introduction

The background for this study was a suggested reduction of the Danish TLV for formaldehyde in industrial indoor environments from 1.2 mg/m³ to 0.4 mg/m³ and a recommended maximum concentration for non-industrial indoor environments of 0.15 mg/m³. Several methods for personal sampling of formaldehyde in air using solid sorbent sampling tubes have been described in the literature.⁽¹⁻⁴⁾ However, due to low sensitivity, none of these methods are suitable for short sampling periods, (15 minutes) or for measurements of concentrations well below 0.15 mg/m³.

The Institute of Technology, Århus, Denmark (JTI) has, however, developed a method for monitoring exposure to formaldehyde at nanogram levels, which is described and tested here. It forms the basis of a commercial Formaldehyde Sampling Tube recently released from SKC.⁽⁵⁾ It involves collection of formaldehyde by chemisorption on a coated solid sorbent, desorption with concentrated sulphuric acid, and colorimetric or fluorimetric determination of the reaction product.

This investigation was a result of a cooperation between The Institute of Hygiene, University of Århus (HI) and the Danish National Institute of Occupational Health (AMI).⁽⁶⁾

Principles of the Method

The standard sampling tube consists of three sections. The first section contains a drying agent, which removes water vapor from the air sample. The second section contains a solid sorbent material, which during exposure to formaldehyde forms a fluorescent compound.

This compound can be measured colorimetrically or fluorimetrically in strong acid solution, where the compound is protonated and turns yellow, $\lambda_{ex} = 470$ nm, $\lambda_{em} = 520$ nm. In neutral or basic solution the compound's absorbance can

be measured at 622 nm (blue color). The third section of the tube is a back-up section containing the same sorbent material as the second section.

Equipment

Analytical Apparatus

At HI a Beckman spectrophotometer (DU model G 2400) was used for the colorimetric measurements. For the fluorimetric measurements a filter fluorimeter (Aminco J4-7439) equipped with 470 and 520 nm interference filters was used. At AMI only fluorimetric measurements were performed, using a Perkin-Elmer 204 fluorescence spectrophotometer.

Sampling Tubes

The sampling tubes used for testing the method were prepared in the laboratory at HI from a coated solid sorbent supplied by JTI. The formaldehyde sorbent material was Chromosorb W coated with 0.6% 7-amino-5-hydroxy-2-naphthalenesulfonic acid (J-acid) in concentrated sulphuric acid. The load was 35% solution to 65% solid substrate. The sulfonic acid (7-amino-5-hydroxy-2-naphthalenesulfonic acid, Fluka 08800 Tech 90% pure) was cleaned before use. The heavy soluble Zn-salt of the acid was washed in water, boiled in acetone, washed in dimethylformamide, boiled in acetone and finally washed several times with water before removing the zinc by EDTA-extraction.

The tubes were prepared as follows: 1 cm³ (0.34 g) of coated solid sorbent material was packed into 6 mm i.d. glass tubing, 8 cm in length. The sorbent was fixed by plugs of glass-wool and the tubes were capped off with Teflon® caps. As the method is very sensitive to formaldehyde, the cleaning of the glass tubing, the glass-wool and the Teflon caps was performed by ultrasonic cleaning, first in water and then in methanol. Finally, the glass parts of the tube were heated to about 200 °C (the Teflon parts to about 100 °C).

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Normally, a first drying section of the tube containing manganese sulphate on Chromosorb P, should be applied. As most of our tests were performed in dry air, normally no drying sections were used. When drying sections were used it will be mentioned.

The drying sections were packed into separate tubes identical to the sorbent tubes and used in series with these.

Solvents and Standards

For the desorption of the reaction product between formaldehyde and the coating material, concentrated sulphuric acid must be used. Standard formaldehyde solutions were prepared by dissolving 4.4703 g of sodium formaldehyde bisulphite (Eastman Kodak Cat. No. P6450)⁽²⁾ in water, followed by dilution to 1000 mL. This solution (standard "A") contains 1.00 mg formaldehyde/mL. This solution is stable for at least three months when stored cool. Formaldehyde solutions "B₁" (50 µg/mL) and "B₂" (10 µg/mL) were prepared by dilution of solution "A" (20 and 100 times respectively). Any dilutions of standard "A" must be made daily.

Analytical Method

The absorber sections of the samples were desorbed in 10.0 mL of sulphuric acid (p.a.) for at least one hour. Two unexposed tubes were handled like the exposed samples.

After centrifugation (3000 RPM for 10 min) the absorbance at 470 nm was measured, using a 1 cm cell, with conc. sulphuric acid (p.a.) as reference. A calibration curve was determined over the range 0-10 µg formaldehyde in 10 mL of conc. sulphuric acid. For determination of small amounts of formaldehyde (500 ng) fluorimetric determination was used. The excitation wavelength is 470 nm and the emission wavelength 520 nm. The measurements were performed with conc. sulphuric acid as reference. The standard curve was determined over the range 0-1.5 µg formaldehyde in 10 mL of conc. sulphuric acid.

The standard solutions for the colorimetric or fluorimetric determination of formaldehyde were prepared by addition of known amounts of formaldehyde to sorbent sections. The procedure was:

1. Transfer the sorbent sections to the testtube
2. Add 2.0 mL of conc. sulphuric acid to release the adsorbed reagent.
- 3a. Colorimetric analysis: Add 0, 10, 20, 50, 100 and 200 µL of standard solution B₁ (see section on Solvents and Standards) corresponding to 0; 0.5, 1.0, 2.5, 5.0 and 10.0 µg of formaldehyde.
- 3b. Fluorimetric analysis: Add 0, 10, 25, 50, 100 and 150 µL of standard solution B₂ (see section on Solvents and Standards) corresponding to 0, 0.1, 0.25, 0.5, 1.0 and 1.5 µg of formaldehyde.
4. After at least one hour, 8.0 mL of conc. sulphuric acid is added to the test tube, which is centrifuged before measurement.

Formaldehyde Standard Atmosphere

Formaldehyde is a very reactive gas, hence a dynamic generation method of a formaldehyde standard was required. For

this reason the permeation principle was used. Permeation tubes consisted of Teflon tubing (8 mm o.d., 7 mm i.d. and length 10 cm) filled with α -polyoxymethylene⁽⁷⁾ produced by heating paraformaldehyde to 100 °C for two hours in a dry nitrogen atmosphere. Also commercial permeation tubes were used (AID, Avondale, Pennsylvania). The permeation rate of formaldehyde depends on the temperature and the permeation tube material.

In the formaldehyde standard atmosphere (Figure 1) clean, dry compressed air was passed through the flow control system consisting of an air supply line for the thermostated permeation chamber and a dilution air line. The flow through the chamber was constant (0.7 L/min) and the formaldehyde concentration in the exhaust air was controlled by the dilution air flow (0-13 L/min). Mass flow controllers ensured a constant downstream airflow independent of fluctuations in the back pressure of the air supply. The temperature in the permeation chamber was regulated to within ± 0.1 °C. The temperature in the chamber was chosen typically in the temperature range 80-100 °C. The permeation rate was found to vary about 10% per degree celsius, and was determined gravimetrically. The airflow through the system was measured by calibrated mass flowmeters.

The air humidity was regulated by pumping distilled water (0-10 mL/h) into a primary mixing chamber, placed after the permeation chamber and kept at 60 °C. A sampling manifold for six samples was placed after a second mixing chamber kept at room temperature. Simultaneous sampling was performed using a sampling pump, equipped with six calibrated mass flowmeters (0-350 mL/min) and a vacuum regulator.

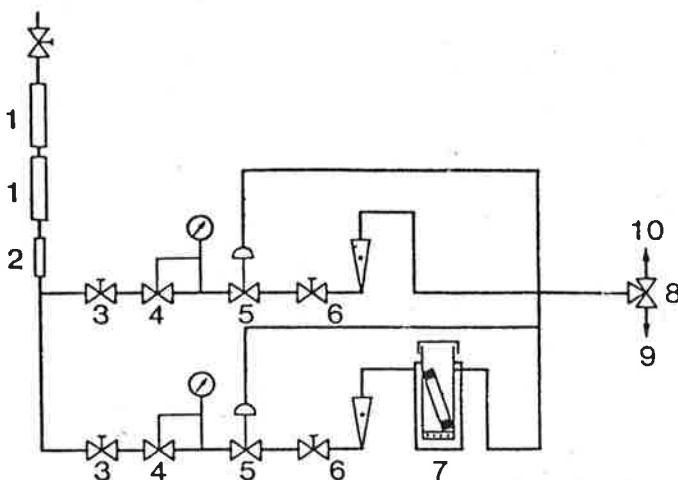


Figure 1 — Flow control system of the standard atmosphere (flow sheet).

- 1: Filter container (charcoal, purafil)
- 2: Dust filter
- 3: ON/OFF valve
- 4: Reduction valve
- 5: Flow controller
- 6: Flow meter with needle valve
- 7: Permeation chamber
- 8: Three turn valve
- 9, 10: Exit to ventilation and sampling chamber respectively.

Method

The sampling tubes were exposed to formaldehyde concentrations in the range 0.2-0.8 mg/m³.

Some few experiments demonstrated that the intended drying material (manganese sulphate on Chromosorb P), supplied by JTI, interfered with the sampling process for formaldehyde. Therefore most tests for the evaluation of the sampling and analytical principle were performed in dry air and without drying sections, leaving that problem to be solved later.

During 15-minute measurements of formaldehyde, a drying section may be unnecessary, as the sulphuric acid in the reagent zone of the tube acts as a desiccant. Some few measurements were therefore performed to investigate the effect of water vapor on the sampling and analytical process.

Capacity Studies

Four sampling tubes were exposed to 0.80 mg/m³ formaldehyde in dry air at a sampling rate of 0.5 L/min. The sample size was 13 L corresponding to 10.4 µg of formaldehyde. Because of the sharp boundary between the reacted and nonreacted part of the sorbent section, the capacity of the sorbent could be estimated by simple linear measurements. A similar experiment was performed at 70% RH. Here the sample size was 2.2 L corresponding to 1.76 µg of formaldehyde.

Interference

The interference from other aldehydes was determined by addition of equimolar amounts of formaldehyde, acetaldehyde, propionaldehyde and acrolein (10, 15, 19 and 18 µg respectively) to reagent solutions prepared by addition of 10.0 mL conc. sulphuric acid to a sorbent section. The absorbance/fluorescence of the solutions were measured relative to a reagent blank.

Sampling and Analytical Performance

The performance of the analytical method was evaluated over the range 0.2-0.8 mg/m³ of formaldehyde in dry air by collecting 1.5 L air samples at a flow of 0.2 L/min.

The stability of the formaldehyde samples was investigated in nine experiments at different concentration levels. In each experiment some samples were analyzed immediately while the rest were analyzed from two up to nine days after exposure. For each experiment the observed daily change (relative to the first measurement) was calculated.

The overall sampling and analytical precision and accuracy were measured according to NIOSH^(8,9) at 0.2, 0.4 and 0.8 mg/m³ corresponding to 1/2 x, 1 x and 2 x the Danish TLV for indoor industrial environment. At each concentration 14 samples of 1.5 liter (0.2 L/min) were exposed from HI's standard atmosphere. Two days after exposure 18 samples (six for each concentration) were analyzed at AMI using the fluorimetric method. At the same time the remaining 24 samples (eight for each concentration) were analyzed both fluorimetrically and colorimetrically at HI.

Results and Discussion

The capacity studies in dry air showed that a single sorbent section had a minimum formaldehyde capacity of 16 µg for the degree of coating used here (0.6%). In humid air (70% RH, 23 °C) the capacity was reduced to a minimum capacity of about 3 µg of formaldehyde. The same capacity was found when a drying zone was applied. Thus the drying zone supplied by JTI reduced the capacity. This effect was not due to a reduced absorption efficiency, e.g. not caused by overloading, as a sharp absorption limit was seen in the tube. An adequate drying zone remains to be developed for measurements of more than 15 minutes duration. Under the conditions used here the principle worked well without a drying

TABLE I
Intercalibration Between 2 Laboratories Performed at AMI and HI.
The results of the formaldehyde concentrations are expressed as the mean and SD of n measurements. Relative standard deviations (RSD) and Recovery (R) are also given.

| | Concentrations of formaldehyde (standard atmosphere, mg/m ³) | Analytical results (mg/m ³) | | |
|--------------------------|--|--|--------------------------------|-------------|
| | | AMI | HI | HI |
| | | fluorescence λ _{ex} = 470 nm λ _{em} = 520 nm | colorimetrically λ = 470 nm | |
| n | | 6 | 8 | 8 |
| [CH ₂ O] ± SD | 0.79 | 0.70 ± 0.02 | 0.74 ± 0.02 | 0.74 ± 0.02 |
| RSD (%) | | 2.4 | 4.7 | 2.1 |
| R (%) | | 89 | 93 | 93 |
| n | | 6 | 8 | 8 |
| [CH ₂ O] ± SD | 0.41 | 0.42 ± 0.02 | 0.43 ± 0.01 | 0.42 ± 0.06 |
| RSD (%) | | 5.7 | 2.4 | 1.4 |
| R (%) | | 102 | 104 | 102 |
| n | | 6 | 8 | 8 |
| [CH ₂ O] ± SD | 0.22 | 0.26 ± 0.01 | 0.22 ± 0.01 | 0.23 ± 0.03 |
| RSD (%) | | 3.7 | 4.2 | 12.3 |
| R (%) | | 119 | 101 | 105 |

TABLE II
Results of Intercalibration.
Ratios between results, obtained at two laboratories (fluorimetric method, $\lambda_{ex} = 470$ nm, $\lambda_{em} = 520$ nm). Ratio between results, obtained at HI, using colorimetric and fluorimetric methods respectively. Average recovery for AMI and HI are given, using both analytical methods.

| Concentrations of formaldehyde (standard atmosphere, mg/m ³) | Fluorimetric analysis [CH ₂ O] AMI [CH ₂ O] HI ± SD (%) | Ratio between results obtained, using colorimetric and fluorimetric methods (HI, ± SD%) | Average recovery ± SD (%) for AMI and HI (using both analytical methods) |
|--|---|---|--|
| 0.792 | 95.5 ± 3.5 | 100.1 ± 3.4 | 91.7 ± 2.5 |
| 0.413 | 98.4 ± 6.1 | 98.1 ± 2.7 | 102.7 ± 1.1 |
| 0.217 | 117.1 ± 6.6 | 103.6 ± 13.5 | 108.6 ± 9.5 |

zone. In the commercial tubes a more effective drying section consisting of manganese sulphate on Chromosorb W is used. However, this drying material was not available for this project.

For the colorimetric determination in acid solution the calibration curve was found to be linear over the range 0-10 µg formaldehyde/10 mL. The calibration curve used for fluorimetric determination in acid solution was linear over the range 0-1.5 µg formaldehyde/10 mL. In both cases the linear correlation coefficients obtained in a least square fit varied from 0.9990 to 0.9998. The detection limit for the fluorimetric method was 60 ng formaldehyde/10 mL. At this concentration the fluorescence intensity relative to sulphuric acid was about twice the intensity of the solution blank.

For the colorimetric method the interference from equimolar amounts of acetaldehyde and propionaldehyde was about 1%, while no interference from these compounds was observed in the fluorimetric method. Equimolar amounts of acrolein interfered about 5-7% for both analytical methods. The stability of the formaldehyde samples was good. The average daily change in nine stability experiments was (1.7 ± 3.5)%. Hence it seems possible to store the samples at room temperature for at least 10 days.

The results of the intercalibration of the method between AMI and HI are shown in Table I, together with the gravimetrically determined formaldehyde concentrations of the standard atmosphere. The results are given as average values and standard deviations for 6-8 samples. Also, the ratios of the analytical results and the standard atmospheric concentrations are given (recoveries). The precision^(8,9) of the overall sampling and fluorimetric method is better than 6% for all three formaldehyde concentrations. For the colorimetric method the precision (RSD) is about 12% at 0.2 mg/m³ (300 ng formaldehyde in the sample) while the precision at the other concentration levels is about 2%. By sampling 3 liters of air the colorimetric method would be applicable for formaldehyde concentrations at a level of 0.1 mg/m³.

Table II shows the ratios of the results of fluorimetric analysis performed at AMI and HI (at three concentration levels). Also the ratios between the fluorimetric and colorimetric results at HI are shown. Finally, the average recoveries for the results obtained at both AMI and HI are shown.

The results for the fluorimetric method (470/520 nm) show an agreement between the two laboratories better than 5% for formaldehyde concentration of 0.4 and 0.8 mg/m³. For 0.2 mg formaldehyde/m³ there is agreement within 18%.

It can also be seen that the agreement between the fluorimetric and colorimetric method at a single laboratory is better than 5%. The accuracy of the method calculated as the ratio between the analytical results obtained and the primary calibrated formaldehyde concentration of the standard atmosphere varies between 89 and 119%. The average recovery (all nine analytical results) was found to be 101 ± 8% (95% confidence limits).

Conclusions

A procedure for personal sampling by chemisorption and fluorimetric and colorimetric analysis of formaldehyde in air is described and evaluated in the laboratory.

Conclusions

Both a fluorimetric and colorimetric determination in acid solution were adequate for measurements of small amounts of formaldehyde in air.

The precision of the fluorimetric method (RSD, two laboratories) was better than 6% for samples of 300, 600 and 1200 ng formaldehyde (1.5 liter air samples at 0.2, 0.4 and 0.8 mg/m³) and the accuracy (average recovery, two laboratories) was better than 10%. The precision of the colorimetric method (RSD, one laboratory) was 12% for a 300 ng sample and 2% for 600 and 1200 ng samples. The accuracy of this method, measured as the recovery at one laboratory, was better than 7%.

Both the fluorimetric and the colorimetric analyses (for 3 liter air sample) are accurate and sensitive analytical methods for determining low formaldehyde concentrations. However, if measurements of more than 15 minutes duration are taken the adequacy of a desiccant still remains to be verified. When equimolar amounts are present, positive interference from acrolein (5-7%) was found but there was no interference from other aldehydes.

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