

AIC 1140  
1762

QUANTITATIVE DETERMINATION OF FORMALDEHYDE IN AIR  
USING THE ACETYLACETONE METHOD.

KEY WORDS: Formaldehyde, Acetylaceton method, Absorber sampling



Paul Bisgaard<sup>+</sup>, Lars Mølhave<sup>+</sup>, Bernd Rietz<sup>++</sup> and Peter Wilhardt<sup>++</sup>

- + ) Institute of Hygiene, University of Aarhus, Universitetsparken 180, DK-8000 Aarhus, Denmark.
- ++ ) Danish National Institute of Occupational Health, Baunegaardsvej 73, DK-2900 Hellerup, Denmark.

ABSTRACT

The quantitative determination of formaldehyde in air using the fluorimetric acetylaceton method is described. Known concentrations of formaldehyde were generated and collected in water using absorbers. The sampling rate was 0.5 l/min, and the sampling volumes varied from 2 to 20 l, depending on the concentration level. Under these conditions the entire sampling and the analytical method were evaluated over a range of 0.2 - 1.7 mg formaldehyde per m<sup>3</sup> of air.

The precision of the method expressed as a mean value of the relative standard deviation of 7 independent measurements (6 single determinations each) was (3.4 ± 1.6) % (SD). The accuracy was (101 ± 5) % (SD).

1457

The detection limit of the method was estimated to be 0.040 mg formaldehyde per  $\text{m}^3$  of air (5 liter air sample).

#### INTRODUCTION

Numerous methods are available for the determination of formaldehyde. Some methods have been used in many years. The method, described by Lin et. al.<sup>1</sup>, uses 3-methyl-2-benzothiazolinone hydrazone as reagent. Unfortunately, this method lacks specificity: other aldehydes interfere.

The use of the pararosaniline<sup>1,2</sup> or phenylhydrazine<sup>3</sup> methods for the analysis for formaldehyde is limited for the same reason.

The chromotropic acid procedure<sup>4</sup> is useful for the determination of formaldehyde, but requires that the aldehyde is collected over a time period of several hours at the workplaces. Consequently, the procedure is not sensitive enough for 15 minutes measurements (collections) of formaldehyde in the air of polluted areas as required by the Danish TLV (0.3 ppm  $\text{CH}_2\text{O}/\text{m}^3$  of air).

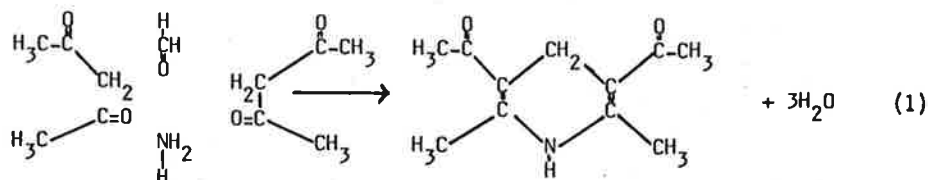
In this paper the application of the fluorimetric acetylacetone method developed by Belman<sup>5</sup> is described. The method is useful for the determination of small concentrations of formaldehyde in air. The sampling medium is water, and the method is therefore most suitable for stationary sampling.

The method was evaluated in the laboratory by sampling at known formaldehyde concentrations from a standard generator based on the permeation principle.

#### PRINCIPLES OF THE METHOD

The determination of formaldehyde in aqueous solution by the acetylacetone method has been described in detail by Nash (colorimetric determination<sup>6</sup>) and by Belman (fluorimetric determination<sup>5</sup>).

The method is based on the Hantzsch reaction: formaldehyde, ammonia and acetylacetone form 3,5-diacetyl-1,4-dihydrolutidine (DDL), which is fluorescent. The reaction scheme is



The fluorescence of DDL is measured in aqueous solution at  $\lambda_{\text{em}} = 510$  nm. The molecular extinction has its maximum at  $\lambda_{\text{ex}} = 410$  nm. The reaction is complete in the pH-range 5.5 to 6.5. The reaction time is, however, strongly dependent on temperature<sup>6</sup>

### Experimental

#### Analytical Apparatus

A filter fluorimeter (Aminco J4 - 7439) equipped with a 405 nm bandpass filter and a 465 sharp cut-off filter was used for the fluorimetric measurements at the Institute of Hygiene, Aarhus.

Measurements at the Danish National Institute of Occupational Health were performed using a Perkin Elmer 204 fluorescence spectrophotometer (grating instrument).

#### Sampling Equipment

The sampling equipment consists of two absorbers connected in series. Different types of filters (silica, active charcoal and dust filter) were used to protect the pumps. The sampling medium was distilled water.

#### Solvents and Standards

The Hantzsch reagent consists of the following:

- 0.2 ml acetylacetone (Merck art. 9600),
- 0.3 ml acetic acid (Merck art. 63) and
- 15.4 g ammonium acetate (Merck art. 1116).

The components are dissolved in distilled water and diluted to 100 ml. The reagent was prepared daily.

Standard formaldehyde solutions were prepared by dissolving 4.4703 g of sodium formaldehydebisulphite (Eastman Kodak Cat. No. P.6450) in 1000 ml of distilled water. This solution (standard "A") contains 1.00 mg formaldehyde/ml.

Formaldehyde standard solution "B" (2  $\mu$ g formaldehyde/ml) and other standards were prepared daily by dilution of solution "A".

#### 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 consisting of Teflon tubing (8 mm o.d., 7 mm i.d. and length 10 cm) filled with  $\alpha$ -polyoxymethylene<sup>7</sup> produced by heating paraformaldehyde to 100°C for two hours in a dry nitrogen atmosphere. Also commercial permeation tubes were used (AID, Avondale, Pa.). The permeation rate of formaldehyde depends on the temperature and the permeation tube material.

In the formaldehyde standard atmosphere (Fig. 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  $\pm 0.1^\circ\text{C}$ . The temperature in the chamber was typically chosen in the temperature range 80-100°C. The permeation rate was determined gravimetrically and found to vary about 10% per degree celsius. The airflow through the system was measured by calibrated mass flowmeters.

The air humidity was controlled by pumping distilled water (0-10 mL/h) into 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.

#### Method of Analysis

The air samples from the standard atmosphere were collected at a flowrate of 0.5 l/min in two absorbers connected in series, each containing 15 ml distilled water.

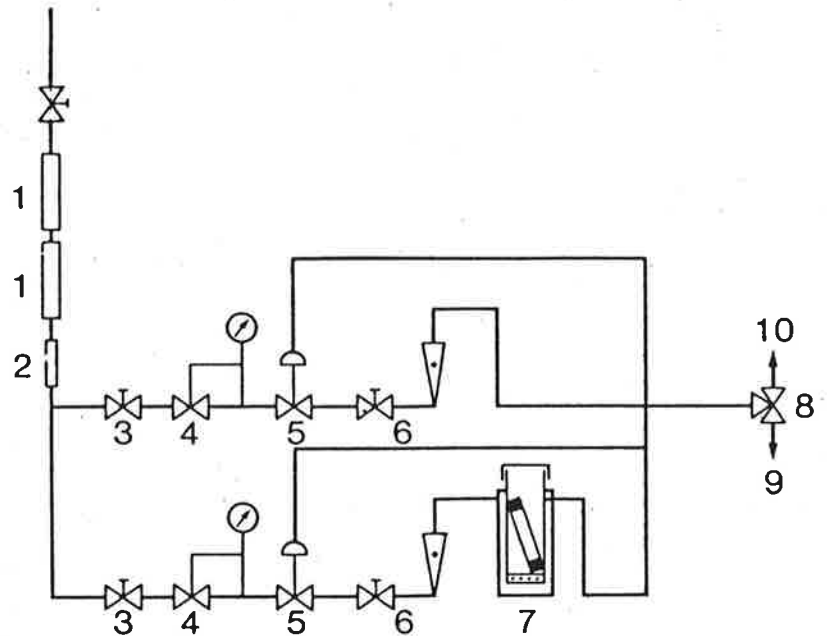


Fig. 1

Flow control system of the standard atmosphere. (Flow sheet).

- 1: filter holder (charcoal, purafil)
- 2: dust filter
- 3: tipping valve
- 4: reduction valve
- 5: flow controller
- 6: flow meter with needle valve
- 7: permeation chamber
- 8: three way valve
- 9, 10: exit to ventilation and sampling chamber respectively.

63 sets of measurements were performed covering 9 different concentration levels in the range 0.2 - 1.7 mg/m<sup>3</sup> (see table 1). Each set of measurements consisted of 2 to 6 single measurements of the actual formaldehyde concentration. For 22 sets consisting of at least 3 single measurements the relative standard deviation (RSD) was determined, and the mean value of these was used to indicate the precision of the overall sampling and analytical method. For all 63 sets of measurements the accuracy of the method was calculated as the ratio between the mean values of the experimentally measured formaldehyde concentration  $[\text{CH}_2\text{O}]_{\text{exp}}$  and the formaldehyde concentration of the standard atmosphere  $[\text{CH}_2\text{O}]_{\text{std}}$ .

The stability of the samples at room temperature was examined for three concentrations in the range 0.05 - 0.2 µg/ml. The stability by storing in a refrigerator was examined at 0.1 µg/ml.

Finally, the collection efficiency (60 single measurements) was measured for one single absorber by collecting in 15 ml water at a flowrate of 0.5 l/min. The collection efficiency is given by the ratio between the amount of formaldehyde in the first absorber and the total amount of formaldehyde in the two absorbers.

#### Sampling Procedure

Each of the two absorbers with glass frits contained approx. 15 ml distilled water.

The setup for stationary sampling is shown in Fig. 2. Teflon or polyethylene tubes may be used for connections between individual parts of the setup.

With a flowrate of 0.5 l/min the collection efficiency for one absorber is larger than 95%, and with two absorbers connected in series the total collection efficiency was found to be 99%. The formaldehyde content of each absorber was analysed separately.

The target value of the flowrate was 0.50 l/min, and the air volume could be measured with an accuracy better than  $\pm 5\%$  (gas meter). The air volume should be large enough to ensure that the concentration in the colour changed solution is fairly above the detection limit of 0.005 µg/ml.

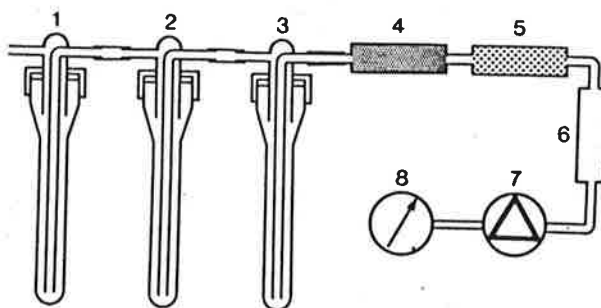


Fig. 2.

Apparatus for stationary air sampling.

- 1, 2: absorbers, each containing approx. 15 ml dest. water
- 3 : empty absorber for collection of possible overflow
- 4 : silicagel-filter
- 5 : charcoal-filter
- 6 : dust-filter
- 7. : pump and flowmeter
- 8 : gasmeter

Prior to analysis the sample was transferred quantitatively to a 20 ml volumetric flask and filled up to the mark with distilled water. 10 ml of the aliquot was transferred to another bottle containing 10 ml Hantzsch reagent. The bottle was closed tightly (screw cap with a teflon washer), marked, and then sent for analysing.

Two blank samples consisting of 10 ml distilled water and 10 ml Hantzsch reagent followed the other samples in the analysis.

The samples are stable during 8 days after sampling when stored in a refrigerator.

The samples were placed in a water bath at 60°C for 15 min. After cooling the fluorescence of the solutions was measured relatively to the blank samples.

Solutions from the two absorbers belonging to an air sample were marked "1" and "2". The amount of formaldehyde in the collected air sample is calculated as the sum of the amount of formaldehyde in the two absorbers.

Standards were prepared in distilled water from the stock solution ("A").

The following dilutions were used:

Stock solution 1000 µg/ml ("A")

"A" is diluted 500 times to 2 µg/ml ("B")

0.2, 0.5, 1.0, 2.0 and 3.0 ml of solution "B" were diluted to 20 ml giving concentrations of 0.02, 0.05, 0.10, 0.20 and 0.30 µg/ml.

4 ml from each standard solution were pipetted off, and colour development and measurement performed as described above.

The standard curve was determined by linear regression using the equation

$$I = \alpha \times [\text{CH}_2\text{O}] + \beta$$

where I is the fluorescence intensity, and  $[\text{CH}_2\text{O}]$  the concentration of formaldehyde in the standard solutions.

The correlation coefficient should be larger than 0.9998 corresponding to 2% uncertainty on the slope  $\alpha$  (95% confidence limit).

#### RESULTS AND DISCUSSION

The mean of the RSD of 22 (out of 63) sets of measurements, each consisting of at least 3 single measurements was  $2.5 \pm 0.6\%$ .

This value covers the total measuring method in the concentration range 0.2 - 1.7 mg/m<sup>3</sup>. For the remaining 41 sets the RSD was not calculated, because each set consisted of 2 measurements only.

No concentration dependence of the RSD of the method was observed, which is due to the fact that different air volumes (2- 20 l) were collected at different concentration levels to ensure that the formaldehyde con-



centration in the samples was suitably above the detection limit of 0.01  $\mu\text{g}$  formaldehyde/ml.

Table 1 shows the mean values of observed accuracies  $[\text{CH}_2\text{O}]_{\text{exp}}/[\text{CH}_2\text{O}]_{\text{std}}$  for 9 different concentration ranges. No concentration dependence was observed here either. Mean value and standard deviation of the accuracies of all 63 sets of measurements was  $99 \pm 6\%$  (SD). The proportions observed were in the range from 87 to 112%.

Table 2 shows analytical results for the sets of measurements in which 6 single measurements were performed. The mean accuracy observed here was

Table 1.

The accuracy of the acetylacetone method for formaldehyde in air, calculated as the ratio of the mean values of the measured formaldehyde concentrations  $[\text{CH}_2\text{O}]_{\text{exp}}$  and the concentrations of formaldehyde in the standard atmosphere  $[\text{CH}_2\text{O}]_{\text{std}}$ .

Each set of measurements consists of 2 - 6 single measurements.

Concentration range ( $\text{mg}/\text{m}^3$ )	Number of measurement sets	Accuracy $\frac{[\text{CH}_2\text{O}]_{\text{exp}}}{[\text{CH}_2\text{O}]_{\text{std}}}$
0.20 - 0.23	9	$99.2 \pm 3.6$
0.29 - 0.30	8	$99.6 \pm 5.4$
0.37 - 0.44	8	$98.9 \pm 7.5$
0.55 - 0.65	11	$97.0 \pm 7.2$
0.77	1	96.2
0.90 - 0.97	3	$102.2 \pm 1.7$
1.08 - 1.25	7	$101.9 \pm 7.8$
1.33 - 1.42	14	$98.2 \pm 6.9$
1.67 - 1.73	2	$100.3 \pm 4.5$

Table 2.

Absorber collection and subsequent analysis with the acetylacetone method: Observed accuracies and relative standard deviations at 7 different formaldehyde concentration levels.

6 measurements performed at each level.

The accuracy is calculated as ratio of mean values obtained at each level.

$[\text{CH}_2\text{O}]_{\text{std}}$ ( $\text{mg}/\text{m}^3$ )	Observed average $[\text{CH}_2\text{O}]_{\text{exp}}$ ( $\text{mg}/\text{m}^3$ )	Relative standard deviation %	Accuracy $\frac{[\text{CH}_2\text{O}]_{\text{exp}}}{[\text{CH}_2\text{O}]_{\text{std}}}$
1.36	1.34	2.5	98.8
1.15	1.20	5.0	104.3
0.90	0.91	6.3	101.1
0.56	0.53	2.1	93.8
0.55	0.57	2.4	104.4
0.20	0.20	2.5	99.0
0.20	0.21	2.8	107.0
Mean value $\pm$ SD		3.4 $\pm$ 1.6	101.0 $\pm$ 4.5

(101  $\pm$  4.5) % (SD), whereas the mean value of the RSD was (3.4  $\pm$  1.6) % (SD).

The loss of formaldehyde from samples with concentrations in the range 0.05 - 0.2  $\mu\text{g}/\text{ml}$  was less than 10% after 24 hours at room temperature. After 48 hours losses between 10 and 50% were observed. Aqueous formaldehyde samples should therefore be analysed not later than the day following the sampling. If possible, the samples should be stored in a refrigerator. This increases the stability essentially, as no measurable

loss of formaldehyde was observed from a 0.1 µg/ml solution after 8 days storing in a refrigerator.

The absorption efficiency for one single absorber was, on the basis of 60 single measurements, measured to be  $(97 \pm 2) \%$  (SD). The use of two absorbers is thus not necessary for obtaining the accuracy wanted. It should, however, be pointed out that the collection efficiency depends on the flowrate at which the air samples are collected.

#### CONCLUSIONS

The acetylacetone method was tested in combination with air sampling in aqueous solutions. The detection limit was found to be 0.04 mg/m<sup>3</sup>, when 5 liters of air were sampled in 20 ml water corresponding to 0.005 µg/ml of the solution, used for analysis. The reproducibility was in average  $\pm 2.5\%$  depending on the formaldehyde concentration in the liquid sample. The accuracy of the method was calculated as the ratio between the mean values of the experimentally determined formaldehyde concentrations and the formaldehyde concentrations, obtained by using the standard atmosphere. This accuracy was found to be  $99\% \pm 6\%$  (SD). The concentration of formaldehyde in aqueous samples at room temperature decreased less than 10% per 24 hours. No losses were detected in samples stored 8 days at 5°C. Absorption efficiency of one absorber was 97%. Losses less than 4% per day were found, if acetylacetone solution was added to the samples before storage.

In conclusion the method based on sampling in distilled water combined with acetylacetone analysis was found to fulfil the requirements to a recommended method for routine measurements.

#### ACKNOWLEDGEMENT

This study was partly financed by the Danish Occupational Health Foundation (Grant No. 1980-04).

#### REFERENCES

1. Chin-I, Lin., R. N. Anaderio, D. W. Anthon, L. Z. Fanning and C. D. Hollowell, Lawrence Berkely Laboratory, University of California, Energy & Environment Division (1979).

2. G. Lyles, F. B. Dowling and V. J. Blanchard, J. of Air Poll., Contr. Associates. 15, 106-108 (1965).
3. W. E. Ruch, "Quantitative Analysis for Gaseous Pollutants", Ann Arbor Science, Michigan, pp. 108-114 (1970).
4. A. P. Altshuller, Int. J. Air Water Poll., 6, 381 (1962).
5. S. Belman, Anal. Chem. Acta. 29, 120-126 (1963).
6. T. Nash, Biochem. 559, 416-421 (1953).
7. J. F. Walker, Formaldehyde, 2nd. ed., Reinhold, New York (1967).

Received September 27, 1983  
Accepted October 4, 1983

# Analytical Letters

---

EXECUTIVE EDITOR:

G. G. GUILBAULT  
*Department of Chemistry  
University of New Orleans  
New Orleans, Louisiana 70122*

## Part A— CHEMICAL ANALYSIS

---

**Associate Editor for Chemical Analysis**

RONALD F. EVILIA  
*Department of Chemistry, University of New Orleans, Louisiana*

**Assistant Editor for Chemometrics**

BRUCE KOWALSKI  
*Department of Chemistry, University of Washington, Seattle*

## Part B— CLINICAL AND BIOCHEMICAL ANALYSIS

---

**Assistant Editor for Clinical Analysis**

MORTON K. SCHWARTZ  
*Sloan Kettering Memorial Institute, New York*

**Assistant Editor for Pharmaceutical Analysis**

JAMES W. MUNSON  
*The Upjohn Company, Kalamazoo, Michigan*