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Short Communication

Determination of formaldehyde in air by chemisorption on glass filters impregnated with 2,4-dinitrophenylhydrazine using gas chromatography with thermionic specific detection

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ABSTRACT

A capillary gas chromatographic method using thermionic specific detection (GC–TSD) is presented for the determination of formaldehyde in air. Formaldehyde was sampled with the use of standard miniature glass-fibre impregnated with 2,4-dinitrophenylhydrazine (DNPH). The 2,4-dinitrophenylhydrazone derivative formed was desorbed with acetonitrile. When the solution was eluted through a cation-exchange column the excess of reagent was effectively removed. The eluate was then evaporated to dryness and the residue dissolved in toluene containing the internal standard. The detection limit, defined as three times the filter blanks, was estimated to be 300 ng of formaldehyde per filter, corresponding to a detection limit of formaldehyde in air of *ca.* 10 $\mu g/m^3$ or *ca.* 1/60th of the present Swedish threshold limit (TLV) for a 30-min sampling period. The detection limit for the chromatographic system, defined as three times the noise, was 4 pg of formaldehyde. The overall recovery for filters spiked with 600 ng of formaldehyde was 92 ± 5%. The calibration graph for 1–6 μg of formaldehyde per filter was linear with a correlation coefficient of 0.998.

INTRODUCTION

Formaldehyde is an important industrial chemical and is used commercially in resins for adhesives in the production of explosives, pharmaceuticals, plywood, fibreboard and particleboard. It is also a component in hair shampoo, detergents and in wrinkle-free textiles. Formaldehyde is most commonly used as a bactericidal agent. It is also found in car exhaust fumes.

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Formaldehyde in the gas phase is lachrymatory and an irritant in contact with the eyes, nose and throat, and as a liquid it is a skin irritant. It is known to be sensitizing, can cause contact eczema and is suspected to be a mutagen and carcinogen [1].

The use of formaldehyde is regulated in most countries by threshold limit values (TLVs); the Swedish TLV is 0.6 mg/m^3.

Methods for the determination of formaldehyde as formaldehyde dinitrophenylhydrazone using gas or liquid chromatography [2–8] have been published. Sampling of formaldehyde in air has been performed using midget impingers containing delute hydrochloric acid containing dinitrophenylhydra-

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zine (DNPH) and chemisorption based on glass-fibre filters impregnated with DNPH. Several advantages has been demonstrated for sampling using the chemisorption technique such as easier handling of the sampling and transportation and the possibility to transporting samples by regular mail. Reported disadvantages include the contamination of the filters of formaldehyde from the general environment during the preparation of the filters and during storage. Larger amounts of the reagent are used in the chemisorption technique than the impinger technique. The removal of the excess of reagent using ion-exchange columns has been effective and lower detection limits have been achieved. Levin *et al.* [3] used LC with UV detection and reported a detection limit of 70 pg/μl of formaldehyde. LC–mass spectrometry via a moving-belt interface gave detection limits in the nanogram range [4].

EXPERIMENTAL

Apparatus

A Varian Model 3500 gas chromatograph equipped with a Varian thermionic specific detector and a Varian Model 8035 automatic on-column injector was employed. The injector was cooled with liquid nitrogen. The injector starting temperature was 110°C for 1.2 s and thereafter the temperature was increased at 150°C/min to a final temperature of 260°C, where it was kept for 6 min. Typical settings for the detector were bead heating current 2.85 A, bias voltage −4.0 V, detector temperature 280°C and gas flow-rates 3 ml/min of hydrogen, 175 ml/min of air and 20 ml/min of nitrogen as the make-up gas. The carrier gas was helium at a flow-rate of 2 ml/min.

Chromatograms were recorded and peaks were evaluated on a Shimadzu C-R3A integrator. A Reacti-Vap evaporator (Pierce) was employed for evaporation of the acetonitrile sample solutions containing the 2,4-dinitrophenylhydrazone derivative. SKC (PA, USA) pumps were used for air sampling.

Columns

CP-Sil 8 CB (Chrompack, Middelburg, Netherlands) fused-silica capillary columns (10 mm × 0.32 mm I.D.) with a film thickness of 1 μm were employed.

Chemicals

Toluene and acetonitrile of HPLC grade were purchased from Lab-Scan (Dublin, Ireland) and ethanol from Kemetyl (Stockholm, Sweden). Formaldehyde, diethyl ether, HCl and NaOH, were from Merck (Darmstadt, Germany) and 2,4-dinitrophenylhydrazine (DNPH), isobutyl chloroformate and the cation-exchange resin Dowex 50W-X8 from Janssen Chimica (Beerse, Belgium). Di-*n*-butylamine (DBA) was purchased from Fluka (Buchs, Switzerland).

Internal standard

The internal standard used was the isobutyl chloroformate derivative of di-*n*-butylamine (1 ng/μl). A solution of toluene containing the internal standard was added to the dry residue from the work-up procedure before the GC analysis. Synthesis of the internal standard was described previously in [9].

Synthesis of the 2,4-dinitrophenylhydrazone derivative

A 1-g amount of 2,4-DNPH · HCl (recrystallized twice from 4 *M* HCl) was added to a solution containing 5 ml of concentrated HCl, 100 ml of ethanol and 0.5 ml of 37% formaldehyde. The solution was heated until all the 2,4-DNPH · HCl had dissolved. The derivative was filtered and washed twice with ethanol and finally recrystallized from ethanol.

Preparation of standard solutions

The 2,4-dinitrophenylhydrazone derivative was dissolved in formaldehyde-free acetonitrile and further dissolved in toluene at the appropriate concentrations.

Preparation of chemisorption filters

A 300-mg amount of DNPH · HCl (recrystallized twice from 4 *M* HCl) was added to 0.5 ml of 85% phosphoric acid and 9 ml of phosphate-free acetonitrile. The mixture was heated with stirring and 13 mm diameter glass filters (Type AE, 0.3 μm pore size) (SKC) were immersed in the hot solution for a few seconds. The filters were dried in a desiccator.

Cation-exchange column

The cation-exchange resin Dowex 50W-X8 was washed three times with water purified in a Milli-Q system (Millipore) and activated with 2 *M* sulphuric

acid for 5 min. This procedure was repeated twice. The resin was washed three times with water and twice with ethanol. Approximately 0.5 g was packed into a glass tube of I.D. 5 mm.

Procedure

Air samples were drawn through the freshly impregnated filters using the SKC pumps at an air flow of 1 l/min. The filters were immersed in 3 ml of acetonitrile and shaken for 1 min. A 2-ml volume of diethyl ether was eluted through a freshly activated cation-exchange column before the sample was eluted through the column. The eluate was evaporated to dryness using an Reacti-Vap evaporator and the residue was dissolved in 1 ml of toluene containing 1 ng/μl of the internal standard. The sample was then ready for injection into the GC system. For each solution three injections were made and the average peak-area ratios of the formaldehyde DNPH derivative and the internal standard were calculated.

RESULTS

Standard

The identity of the formaldehyde DNPH derivative was determined using GC–MS and confirmed by the melting point 166°C. The purity was further checked using GC–thermionic specific detection (TSD).

Choice of reagent

2,4-Dinitrophenylhydrazine was chosen as the derivatization reagent because it reacts rapidly and completely with formaldehyde. The GC–TSD system provides sensitive determination owing to the nitrogen atoms in the hydrazone derivative.

Chromatography

On-column injections of toluene solutions containing the formaldehyde DNPH derivative demonstrated excellent chromatographic performance and well separated formaldehyde DNPH peaks were seen. On injecting samples also containing the DNPH reagent, a tailing DNPH peak interfering with the formaldehyde DNPH peak at low concentrations was observed. Furthermore, repeated injections of DNPH resulted in a much shorter capillary column lifetime.

Repeated split and splitless injections of toluene solutions containing DNPH and formaldehyde DNPH derivative led to a decreased precision. When the injector was rinsed, good performance of the chromatographic system was again established, indicating severe contamination of the injector from the DNPH in the toluene solution. In order to maintian good performance and a long column lifetime, it was found necessary to remove the excess of reagent before injections into the chromatographic system.

A mass spectrometer was also used for detection. In this instance the repeatability and sensitivity were improved by the removal of the excess of reagent due to the lower contamination of the ion source.

A chromatogram of the DNPH derivative diluted

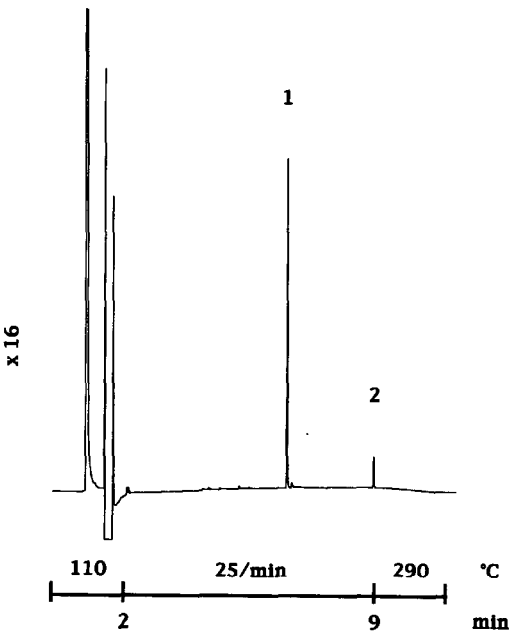

Fig. 1. Chromatogram of a standard solution of the 2,4-dinitrophenylhydrazone derivative of formaldehyde and the isobutyl chloroformate derivative of di-*n*-butylamine (internal standard). On-column injection of 2 μl of a toluene solution containing 1 ng/μl of the internal standard (1) and 112 pg/μl of hydrazone derivative corresponding to 16 pg/μl of formaldehyde (2). Column, CP-Sil 8 CB fused-silica capillary column (10 m × 0.32 mm I.D.) with a film thickness of 1 μm; temperature programming as shown; carrier gas, helium at 2.3 kg/cm^2, thermionic specific detector; bead heating current, 2.85 A; bias voltage, −3.5 V; temperature, 280°C; flow-rates, hydrogen 3, air 180 and make-up (helium), 10 ml/min.

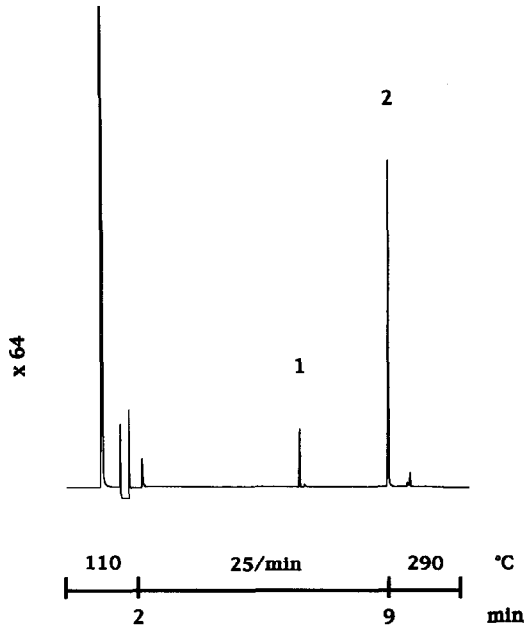

Fig. 2. Chromatogram of the toluene solution obtained from impregnated filters spiked with a concentration of 1 ng/μl of formaldehyde and 1 ng/μl of internal standard and prepared according to work-up procedure giving a concentration of 16 pg/μl of formaldehyde in the toluene solution. Chromatographic conditions and peak identities as in Fig. 1.

in toluene at a concentration of 16 pg/μl with respect of formaldehyde is shown in Fig. 1. In Fig. 2, 1 ng/μl of the same derivative was added to the impregnated filter and the filter was prepared according to the work-up procedure described earlier.

Aldehydes and ketones are well known to react with DNPH to form hydrazones. These hydrazones are well separated from the formaldehyde DNPH peak and elute later in the chromatogram. The proposed method may also be successfully used for these kind of compounds. However, as also described by others [9], when determining higher aldehydes a more complicated chromatographic performance is seen owing to the *syn* and *anti* forms (in thermal equilibrium) of these hydrazones. These are seen in the chromatogram as unresolved double peaks.

Quantitative analysis

Sampling and storage of air samples. Two filters were placed in two filter holders in series and air with *ca.* 60% relative humidity at a flow-rate of 1 l/min was drawn through the filters. The samples were taken in an office with new furniture containing fibreboard. The filters were stored cold and in the dark for 3 weeks and no samples losses were found.

Recovery. The recovery was studied by spiking the filters with 20 μl of a 30 ng/μl formaldehyde solution to five impregnated filters and performing the work-up procedure described earlier. The recovery was found to be 94 ± 7%, within a 95% degree of confidence.

Calibration. Calibration graphs were obtained by adding 20-μl volumes with known concentrations of formaldehyde in ethanol to the 2,4-DNPH-impregnated filters. Seven concentrations of the formaldehyde in ethanol solutions and blanks were used. The work-up procedure described above was then performed. For each concentration three determinations with triple injections of each were made. The calibration graph for 1–6 μg of formaldehyde per chemosorption filter was linear with a correlation coefficient of 0.998.

Detection limit. The detection limit is mainly determined by the formaldehyde content in the chemisorption filters, which normally gives high blank values. The detection limit, defined as three times the filter blanks, was about 300 ng per filter. For a 30-min sampling time with a flow-rate of 1 l/min the detection limit of formaldehyde in air was *ca.* 10 $\mu g/m^3$, corresponding to 1/60th of the present Swedish TLV.

For monitoring lower concentrations of formaldehyde in air, further method development regarding the preparation and storage of both unexposed and exposed filters is required. Sampling of formaldehyde using midget impingers is expected to give lower detection limits, mainly owing to the smaller amount of the DNPH reagent used.

The detection limit for the chromatographic system, defined as three times the noise, was 4 pg of formaldehyde analysed ast he DNPH derivative. This is about fifteen times lower than that of LC methods.

Precision. Ten repeated injections of toluene standard solutions containing the formaldehyde DNPH derivative (40 pg/μl of formaldehyde) and the internal standard were made. The relative standard deviation for the peak-area ratios was 5.0%.

When five filters were spiked with 600 pg of formaldehyde per filter, as described above, the relative standard deviations of the peak-area ratios was 7%.

DISCUSSION

Formaldehyde is widely used in industry, resulting in the exposure of large numbers of workers. The monitoring of formaldehyde in indoor air is also widely applied as it is possibly related to, *e.g.*, the "sick building syndrome". In this instance the concentration of formaldehyde in air is several orders of magnitude lower than that found in, *e.g.*, the fibreboard industry. The present methods for the determination of formaldehyde in air were mainly developed for the determination of formaldehyde at concentrations around TLV levels. When applying these methods to the monitoring of considerable lower concentrations, several problems arise. LC methods do not give satisfactory selectivity and resolution at low formaldehyde concentrations as large amounts volatile compounds also are present in air. Electron-capture detection (ECD) is based on the electron-capturing properties of compounds present in the detector. The best sensitivities are obtained for, *e.g.*, organic halogens and compounds with electron-attracting groups such as positively charged carbon in a carbonyl group. These kind of compounds are known to be present in, *e.g.*, indoor air. The sensitivity for these compounds is much higher compared with DNPH derivatives. The detection principle of ECD is in one way the same as that of GC–TSD. ECD uses the electron-capturing properties of the DNPH and TSD monitors the nitrogen atoms present in DNPH. The choice of detection method is therefore mainly based on more practical considerations and TSD and ECD can be of complementary use.

In this paper, high-resolution GC with TSD has been demonstrated to allow the sensitive determination of formaldehyde in air. Formaldehyde is a low relative molecular mass compound that is difficult to determine as such using GC. Sensitive determinations with detection limits in the picogram range using TSD are achievable when formaldehyde is reacted with a nitrogen-containing reagent. When determining formaldehyde as the DNPH derivative using GC–TSD, the simultaneous determination of other aldehydes and ketones is possible.

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