

Charcoal sampling and gas chromatographic determination of N,N-dimethylformamide in air samples from a polyurethane plant

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RIMATORI V, CARELLI G. Charcoal sampling and gas chromatographic determination of N,N-dimethylformamide in air samples from a polyurethane plant. *Scand j work environ health* 8 (1982) 20—23. A charcoal sampling method and a gas chromatographic determination of N,N-dimethylformamide in the air of a plant producing polyurethane lumps is described. The collection efficiency was checked by drawing standard N,N-dimethylformamide air mixtures through the sampling tube at 0.1 l/min and detecting the organic vapors spectrophotometrically at 215.4 nm. At 1,000 mg/m³, samplings could be carried out for 190 min with negligible N,N-dimethylformamide losses (lower than 1 %). The analysis of N,N-dimethylformamide was performed by gas chromatography on Porapak Q and Tenax GC after extraction with 2 ml of acetone/100 mg of charcoal, with a mean recovery of 90 (SD 2) %, in the range of 0.05—0.5 mg of N,N-dimethylformamide/100 mg of charcoal. The relative standard deviation of the entire procedure was 3.5 %. Because of the good adsorbing efficiency of the charcoal, short-term sampling could be carried out at a relatively high N,N-dimethylformamide concentration. Stationary and personal sampling resulted in mean values ranging between 1.26 and 1.60 mg/m³. The method is particularly suitable in instances where other pollutants are present, and therefore it can be used also for other work areas as well.

Key terms: air pollution, frontal analysis, industrial hygiene.

N,N-dimethylformamide is a widely used solvent in the chemical industry. It is particularly used in the synthesis and spinning of polymeric fibers and in the processing of polyurethane for the production of artificial leather.

Occupational exposure to N,N-dimethylformamide may occur through inhalation or cutaneous absorption. A threshold limit value-time-weighted average (TLV-TWA) of 30 mg/m³ and a threshold limit value-short-term exposure limit (TLV-STEL) of 60 mg/m³ in the ambient air have been recommended by the American

Conference of Governmental Industrial Hygienists (1) with the notation to avoid skin contact, since N,N-dimethylformamide is also readily absorbed cutaneously (8).

Monitoring for monomethylformamide, the major metabolite of dimethylformamide, in the urine of exposed workers has been shown to be a valid method for assessing exposure (11). Measurements of N,N-dimethylformamide in the ambient air remain essential however for the evaluation and control of airborne vapors in the workplace.

In spite of the fact that several analytical methods have been described for the determination of N,N-dimethylformamide in various articles (2, 3, 4, 6, 7), there seems to be insufficient information on air sampling techniques, as well as a lack of data for the evaluation of the efficiency and accuracy of existing procedures. This paper describes a method for sampling air-

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borne N,N-dimethylformamide by adsorption on charcoal and subsequent gas chromatographic determination. Collection efficiency studies have been carried out by drawing air mixtures of known concentrations through charcoal cartridges and by detecting the organic vapors spectrophotometrically at 215.4 nm. The relative standard deviation of the method was 3.5 %.

Materials and methods

Industrial process

Air samplings were carried out in a polyurethane production plant. In the production process N,N-dimethylformamide was used as a solvent. The solution was stratified on a support, washed with water, and dried. The entire process took place in closed cycle machines which had individual extraction facilities, and the workroom was automatically air-conditioned. The workers handled N,N-dimethylformamide only during the sampling of the solution, through a drain valve, for analytical controls. During the sampling the tanks were closed. Now and then the tanks were lowered, and the workers, provided with personal safety devices (waterproof overalls, gas masks, gloves, boots and hats) and operating outside the tanks, disentangled the lumps of polyurethane, when necessary, using proper dipsticks. Every three to four months the tanks underwent cleaning, for which the following procedure was used. After a 12-h washing the solution was drained into a closed reservoir, and the tanks were ventilated with air for 2 h. The tanks were then opened and cleaned by the workers, who were equipped with the aforementioned safety devices.

Air sampling

Air was sampled for one workshift in the breathing zone of the workers (personal samples) and at stationary sites. The personal samplings were interrupted during the workbreaks. A workday comprised three shifts (3×8 h). Model TI 3900/I Casella personal samplers were used for the field samplings. The flowrate was kept at 0.10–0.16 l/min to ensure a pres-

sure drop lower than the maximum permissible value (20 cm of H_2O). The sampler was a glass tube (5 mm inner diameter, 70 mm length) filled with two layers of adsorbent and held by glass wool plugs. The length of the layers was 9 and 5 mm (about 100 and 60 mg), respectively. The adsorbent was charcoal [0.5–0.75 mm, 20/30 mesh, gas chromatography grade (Merck)], which was used without prior physical chemical treatment, except sieving.

Analysis

After the sampling in the workroom, the two charcoal layers were introduced separately into glass stoppered test tubes and extracted with 2 ml of acetone/100 mg of adsorber for at least 1 h. Recovery was 90 (SD 2) % for 0.05–0.5 mg of N,N-dimethylformamide/100 mg of adsorber. The second layer had a control function, ie, traces of N,N-dimethylformamide could be found because of diffusion from the first layer during transport and storage. As a rule, a quantitative sampling should exhibit only slight traces of N,N-dimethylformamide in the control layer. N,N-dimethylformamide losses are negligible if samples are stored in a refrigerator at $-10^\circ C$ for 7 d.

The analyses of the samples were carried out by gas chromatography. N,N-dimethylformamide Uvasol (Merck) was used as the external standard after purification (5).

Models 900 (Perkin-Elmer) and 5700A (Hewlett-Packard) gas chromatographs equipped with flame ionization detectors were used for the analysis. A stainless steel column (inner diameter 32 mm, length 2 m) with 80/100 mesh Porapak Q at $180^\circ C$ and a carrier gas (nitrogen) flowrate of 30 ml/min and a stainless steel column (inner diameter 32 mm, length 0.3 m) with 60/80 mesh Tenax GC at $120^\circ C$ and a carrier gas (nitrogen) flowrate of 25 ml/min were used. The signals were recorded by models 56 (Hitachi) and 7123B (Hewlett-Packard) potentiometric recorders at 1 mV full scale.

The N,N-dimethylformamide air concentration was calculated according to the external standard method, and in the field situation a relative standard deviation (12) of 3.5 % was obtained.

Determination of collection efficiency

The standard N,N-dimethylformamide atmosphere was obtained with the device described by McArthur (9). The air/N,N-dimethylformamide mixture was drawn through the sampling tube at various flow-rates. N,N-dimethylformamide vapors were detected at 215.4 nm in a 12-cm quartz cell by means of a 403 (Perkin-Elmer) atomic absorption spectrophotometer, used as an ultraviolet spectrophotometer. The source was a tin electrodeless discharge lamp run at 8 W. The molecular absorbance signal was recorded by a 56 (Hitachi) potentiometric recorder.

Results and discussion

Calculations made on the basis of the frontal analysis curves at the N,N-dimethylformamide air concentration of 1,000 mg/m³ showed a theoretical plate height of the charcoal tube (100 mg) of 0.45 and 0.1 mm at the flowrate of 0.65 and 0.1 l/min, respectively, at 24°C and 50 % relative humidity. The Freundlich equation

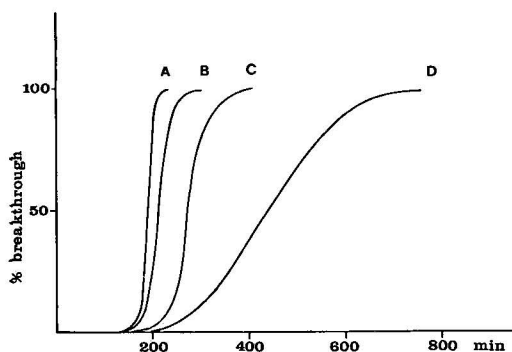


Fig 1. Breakthrough curves for different N,N-dimethylformamide air concentrations (air flowrate 0.1 l/min). (A: 1,000 mg/m³, B: 500 mg/m³, C: 100 mg/m³, D: 3 mg/m³)

Table 1. N,N-dimethylformamide air concentration (mg/m³) in a polyurethane plant.

Shift	Stationary samples (N = 12)		Personal samples (N = 12)	
	Mean	SD	Mean	SD
First	1.27	0.68	1.49	0.64
Second	1.30	0.76	1.76	0.76
Third	1.32	0.67	1.26	0.67

(10) can be applied to the sampling process in the form:

$$t_x = a \cdot c^b,$$

where t_x is the breakthrough time at a given percentage of leakage, c is the N,N-dimethylformamide air concentration (mg/m³), and a and b are constants. The time for a 10 % breakthrough (t_{10}) corresponds to the sampling duration at the N,N-dimethylformamide air concentration at which $c_{\text{output}} = 0.1 c_{\text{input}}$, c_{input} is the N,N-dimethylformamide air concentration of the sampling tube input, and c_{output} is the N,N-dimethylformamide air concentration of the sampling tube output. A maximum sampling duration of t_{10} was chosen because, according to the frontal analysis, the percentage loss (L) of N,N-dimethylformamide is low and can be calculated by the formula

$$L = \frac{c_{\text{input}} \cdot t_{10} - \int_0^{t_{10}} c \cdot dt}{c_{\text{input}} \cdot t_{10}}.$$

At various N,N-dimethylformamide concentrations and at sampling rates of 0.1 l/min, t_{10} was estimated, and a and b were calculated. For example, t_{10} was 440 min at 3 mg/m³ and 190 min at 1,000 mg/m³. The breakthrough curves obtained up to 1,000 mg/m³ show that, for sampling durations of t_{10} , negligible N,N-dimethylformamide losses (lower than 1 %) occur. The Freundlich equation can be expanded on the basis of the calculation of the constants a and b as follows:

$$t_{10} = 514 \cdot c^{-0.1416}.$$

By this equation any maximum sampling duration at concentration c can be calculated. Fig 1 shows breakthrough curves at 0.1 l/min.

Table 1 shows the N,N-dimethylformamide air concentrations measured. The stationary samples ranged between 0.59 and 3.03 mg/m³. A peak level of 9.5 mg/m³ was detected during an unusual operation on open tanks; it was excluded from the table. The personal samples ranged between 0.56 and 4.76 mg/m³.

The short-term personal samplings revealed occasional, but severe, hazardous situations such as the one observed during tank cleaning (230 mg/m³).

Conclusions

The method described has proved to be reliable in the sampling and the analysis of N,N-dimethylformamide in a plant where polyurethane lumps are produced. Hygienic situations could be carefully evaluated from short- and long-term samplings of both the workers' breathing zones and stationary worksites. Since the absorption of this solvent may occur cutaneously as well as through inhalation, the determination of monomethylformamide in the urine of workers has been carried out as an evaluation of the individual exposure to N,N-dimethylformamide. Charcoal showed excellent collection efficiency and was more suitable for personal monitoring than liquid absorption methods. Gas chromatography provided a separative technique that is particularly suitable in the presence of other pollutants.

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