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Determination of N-methylmorpholine in air samples from a polyurethane foam factory

Comparison between two methods using gas chromatography and isotachopheresis for analysis

by Lars Hansén, MSc,¹ Bengt Åkesson, MSc,² Jan Sollenberg, PhD,¹ Thomas Lundh, MSc²

HANSÉN L, ÅKESSON B, SOLLENBERG J, LUNDH T. Determination of N-methylmorpholine in air samples from a polyurethane foam factory: Comparison between two methods using gas chromatography and isotachopheresis for analysis. *Scand J Work Environ Health* 12 (1986) 66–69. The N-methylmorpholine levels in workroom air in a polyurethane foam factory were determined by two methods in which midget impinger flasks were used for sampling. The analyses were performed by gas chromatography and isotachopheresis. The values obtained by the gas chromatographic method were 19 % higher than those of the isotachopheretic method. Determinations of the amine in samples generated in laboratory experiments showed no statistical difference between the two methods. The mean air concentrations of N-methylmorpholine in different work areas of the factory ranged from 7 to 22 mg/m³. Urine was collected from seven workers and analyzed for N-methylmorpholine by gas chromatography. The amine concentrations and the excretion rates increased considerably during the workday.

Key terms: amine, exposure chamber, impinger, urine excretion.

Amines are widely used as solvents, pH-adjusting agents, and raw materials in chemical syntheses. Tertiary amines are used as catalysts for polymerization reactions. Health effects such as dermatitis (6), throat and eye irritation (4), visual disturbances (7), and asthma (3, 8) caused by industrial amine exposure have been reported.

N-methylmorpholine (MM) is used as a catalyst for the production of flexible and semiflexible polyurethane foam. During the foaming process amine evaporates into the workroom area and can cause health problems such as respiratory irritation and hazy vision (3, 5). The hygienic standard for N-methylmorpholine in the workroom air in Sweden is 20 mg/m³ as a time-weighted average for 8 h of exposure. Audunsson & Mathiasson (2) have described a method for the determination of this substance in air using impinger flasks for the sampling and gas chromatography (GC) for analysis.

As part of the investigations, performed at our institutes, on analytical methods for amines used in industry, we have compared our different methods for the determination of N-methylmorpholine in air. Different sampling equipment was used, and the analysis was performed by GC and isotachopheresis (ITP). The two methods were compared in an exposure chamber experiment and in a study at a polyurethane foam factory. Furthermore urine was collected from occupa-

tionally exposed persons and analyzed for N-methylmorpholine by GC.

Materials and methods

Laboratory experiments

Two concentrations of N-methylmorpholine in air (21°C, 40 % relative humidity) were generated in an exposure chamber as described by Åkesson et al (1). The level of amine in the chamber was monitored continuously by an infrared gas analyzer (Miran 1A; Foxboro Analytical, South Norwalk, Connecticut, United States; wavelength 9.3 µm; pathlength 20.25 m). Series of 10 samples were taken in parallel by the two methods. All the samples were taken inside the chamber within an area of 30 × 30 cm and 1 m above the floor. The sampling time was 60 min.

Polyurethane foam factory study

The collection of air samples for the determination of N-methylmorpholine was done in a polyurethane foam factory where back and cushion pieces of car seats were produced. Stationary samples were taken on two consecutive days in five different work areas [close to the demolding place at a cold-cure molding line, close to the cell cracking machine where the cushion pieces were manually sorted, at two different places of handling the products (drilling and trimming), and at a storing site for freshly made products]. The samples were collected in parallel with the openings of the impinger flasks close to each other and about 1.5 m above the floor on portable stands. The sampling time was 60 min.

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Gas chromatography

Air sampling. The N-methylmorpholine was sampled during 60-min periods (portable sampler pumps; model G; Mine Safety Appliances Co, Pittsburgh, Pennsylvania, United States; 1.0 l/min) in midget impinger flasks of glass containing 10 ml of hydrochloric acid (HCl, 0.1 mol/l). The airflow was controlled by a rotameter (Mechanik Prüfgeräte, Medingen, Federal Republic of Germany), and the loss of sampling solution due to evaporation was adjusted by 6 %, as experimentally determined.

Urine sampling. Urine samples were collected from five women (subjects 1–5) before work at 0500 (sampling from 2300 the previous day). Another sample was taken after the shift at 1515 (sampling from 1130). For another two women (subjects 6 and 7) samples were taken only after the shift. Subjects 1–4 were trimming the cushions. Subject 5 was alternately trimming and sorting cushions coming from the cell cracking machine. Subject 6 was drilling, and subject 7 was sorting freshly cell-cracked cushions. The urine samples were acidified (50 ml of urine and 1 ml of concentrated HCl) and stored in a refrigerator until the analysis. Creatinine was determined in all the samples (11).

Analysis of air samples. The analysis of N-methylmorpholine in the air samples was made according to Audunsson & Mathiasson (2) with minor modifications. To 1 ml of the absorption solution was added 250 μ l of sodium hydroxide (NaOH, 1 mol/l) in a 0.25 % ammonia (NH₃) solution. Analysis was made by a Varian 3700 gas chromatograph (injection volume 2 μ l, injector temperature 170°C, stainless steel column with Carbowax 4000 special and 2 % potassium hydroxide (KOH) on Chrom W AW, column temperature 95°C, nitrogen carrier gas 30 ml/min) with a Varian TSD nitrogen selective detector (detector temperature 190°C, hydrogen flow 4 ml/min, airflow 180 ml/min). For a 60-l sample the detection limit was 0.01 mg/m³.

Analysis of urine samples. To 2 ml of urine was added 0.5 ml KOH (5 mol/l) in a 0.25 % NH₃ solution. The samples were centrifuged 10 min at 3 000 r/min. N-methylmorpholine was analyzed by GC with the same parameters as used for the air samples. The detection limit was 0.1 mg/l of urine. The injection of large numbers (> 200) of urine samples will affect the performance of the GC system, and tailing of the amine peaks may occur. The system can be improved by refilling the first 10 cm of the column after the contaminated packing material has been discarded.

Isotachopheresis

Air sampling. Static gas standards of N-methylmorpholine in air were made in a homemade sack of aluminum-polyester laminate (9).

Samples were taken from the sack by bubbling the amine standard through homemade midget impinger flasks of polystyrene containing 10 ml of HCl (0.05 mol/l). Portable sampler pumps (Anatole J Sipin Co, New York, New York, United States) were used at a flow rate of 0.2 l/min. During the sampling in the laboratory the flow rate was intermittently checked with a soap film meter connected to the outlet of the pump. The loss of absorption solution due to evaporation during sampling was found to be 1.8 % (SD 1.5, N 31).

Concentration of the samples. The possibility to analyze samples containing small amounts of amine can be increased by concentration of the solution from the impinger flasks. This concentration was done by transferring 5 ml of the solution to a polypropylene tube in a thermostated heating block. The solution was evaporated to dryness at 80°C. The process was speeded up by the passing of a gentle stream of nitrogen over the surface of the solution. To avoid losses, probably due to sublimation of the hydrochloride of the amine, the process was stopped when dryness was reached. The evaporation rate of the absorption solution was about 1 ml/h. The residue was dissolved in 500 μ l of distilled water.

Analysis. The analysis was performed with a LKB 2127 Tachophor (LKB-Produkter AB, Bromma, Sweden) with a capillary tube of polytetrafluoroethylene (inner diameter 0.5 mm, length 245 mm). The capillary was thermostated at 15°C, and a conductivity detector was used.

The leading electrolyte was KOH (0.01 mol/l) in 0.4 % (weight/volume) hydroxypropylmethylcellulose (Dow Chemicals, Midland, Michigan, United States). The pH of the solution was adjusted to 7.3 by the addition of cacodylic acid (JT Baker Chemicals NV, Deventer, The Netherlands). The terminating electrolyte was creatinine (0.01 mol/l) in HCl (0.005 mol/l), pH 5.0. The sample volume injected was between 2 and 10 μ l. The migration current was 100 μ A, and the time of analysis was about 15 min.

A calibration graph was made from standard solutions of N-methylmorpholine in water. It was linear in the range tested, namely, 1 to 150 nmol injected into the ITP instrument.

Results and discussion

Laboratory experiments

Nine samples from the laminate sack containing N-methylmorpholine vapor (47 mg/m³) were taken in polystyrene midget impinger flasks, and the "overall recovery" found by ITP analysis was 107 (SD 15) %. In this report we have defined "overall recovery" as the ratio of the N-methylmorpholine concentration determined by the ITP analysis to the calculated value of the concentration in the sack. The uncertainty of

the determinations includes errors from the preparation of the gas standard, from the sampling, from the concentration of the absorption solution, and the final analysis.

The results from the experiments in the exposure chamber are shown in table 1. An analysis of variance gave no significant difference between the results obtained by the two methods ($p > 0.05$).

Table 1. Two different levels of N-methylmorpholine in air (mg/m^3) generated in an exposure chamber as determined by gas chromatography (GC) and isotachopheresis (ITP). (N = number of samples)

	Level 1		Level 2	
	GC (N = 10)	ITP (N = 10)	GC (N = 10)	ITP (N = 10)
Mean	7.6	7.8	19.7	19.2
SD	0.4	0.7	0.8	0.9
Range	7.1–8.3	6.8–8.7	18.5–21.4	18.4–21.0

Table 2. Mean values and range of N-methylmorpholine (mg/m^3) in air from five work areas with different types of work in a polyurethane foam factory, as determined by gas chromatography (GC) and isotachopheresis (ITP). Stationary sampling (60 min) on two consecutive days. (N = number of samples)

Type of work	N	GC		ITP	
		Mean	Range	Mean	Range
Demolding	6	9.2	6.2–11.8	7.1	4.8–9.6
Sorting	4	21.9	18.6–25.1	17.2	15.0–18.7
Drilling	4	17.9	14.7–21.0	15.2	9.6–19.6
Trimming	5	6.8	1.9–8.6	5.4	1.9–7.8
Storing	5	19.6	15.9–23.6	15.0	13.0–22.6

Figure 1. Regression between the results of N-methylmorpholine (MM) in air, obtained by gas chromatography (GC) and isotachopheresis (ITP), on samples taken in a polyurethane foam factory. The equation of the regression line was $\text{ITP} = 0.81 \text{ GC}$, and the correlation coefficient was 0.990.

Polyurethane foam factory study

The results from the sampling of five different work areas in the polyurethane foam factory are shown in table 2. The samples were taken during 60-min periods and illustrate the exposure during various work operations. As the measurements were based only on four to six periods of 60 min during two consecutive days, the study is not to be regarded as an occupational examination of the exposure but as a comparison study of the two methods. Compared to the results given by Belin et al (3) at the same factory, the concentrations of N-methylmorpholine in air are about 30 % lower in the demolding and drilling areas and about 60 % lower in the trimming area. These differences could be due to a rebuilding of the ventilation system which took place after the measurements in 1982 (Rolf Wadlund, personal communication).

Figure 1 shows the regression (calculated with random errors in both variables) between the results obtained by GC and by ITP. The equation of the regression line was $\text{ITP} = 0.81 \text{ GC}$, and the correlation coefficient was 0.990.

To elucidate possible differences in the results, 10 representative samples from the GC sampling method were selected and analyzed by ITP. Correspondingly another 10 samples from the ITP sampling method were selected and analyzed by GC. The regression (calculated with random errors in both variables) for the 20 samples analyzed by both GC and ITP was $\text{ITP} = 0.87 \text{ GC}$, and the correlation coefficient was 0.993. This regression coefficient was not statistically different from the one found between the two methods (including possible differences in sampling).

We found a statistically significant difference of 19 % ($p < 0.05$) between the two methods for samples taken at the factory. We also found a statistically significant difference, 13 %, when comparing only the analytical steps ($p < 0.05$). The difference could not be verified in the laboratory experiments in the exposure chamber.

It is not possible to confirm from our data whether the results measured by GC are too high or those determined by ITP are too low. One standard solution of N-methylmorpholine in water used for the ITP analysis was analyzed by GC, and the result was the same.

The atmosphere in the generation chamber contained pure gaseous N-methylmorpholine in the air, while the atmosphere in the factory also contained other airborne contaminants. We can not exclude the possibility that another contaminant had the same retention time as N-methylmorpholine in the GC analysis or that the amine can react to a reaction product which later splits to the original amine in the hot injector block of the gas chromatograph. Experiments in another investigation on analyses of urine samples seems to indicate that such reversibilities are possible. Such a reaction product can have an electrophoretic

Table 3. N-methylmorpholine levels in urine from subjects from a polyurethane foam factory.

Subject	Estimated exposure (mg/m ³)	Urinary concentration					
		mmol/l		μ mol/mmol of creatinine		Excretion rate (μ mol/h)	
		Before shift	After shift	Before shift	After shift	Before shift	After shift
1	7	0.05	0.22	4	33	3	18
2	7	0.06	0.47	3	81	2	20
3	7	0.11	0.80	6	36	3	17
4	7	0.03	0.29	4	33	2	18
5	14 ^a	0.03	1.1	5	67	3	36
6	18	..	5.2	..	110	..	45
7	21 ^b	..	1.5	..	130	..	19

^a Mean of the sorting, trimming and storing areas.^b Mean of the sorting and storing areas.

mobility other than that of the original compound and thus decrease the ITP response.

We cannot further explain the differences noticed between the two methods. Nevertheless the magnitude of the difference is acceptable if compared to an interlaboratory control in which unknown samples of organic solvent vapors adsorbed on charcoal tubes were analyzed by different laboratories using GC. The relative standard deviations of the reported results were ± 15 –21 % for three solvents (10). Considering these results, the observed difference in our study should not discourage the use of these methods in, for instance, occupational risk evaluations.

Urine samples

The levels of N-methylmorpholine in urine before and after the shift and the estimated exposure (determined as the mean of the concentration of N-methylmorpholine in air of the different work areas) are shown for subjects 1–7 in table 3. An increase of N-methylmorpholine was found in the urine after the end of the shift. A linear correlation seems to exist between the estimated exposure and the urinary N-methylmorpholine as related to both the creatinine levels and the excretion rate. The value of the excretion rate for subject 7 was far off the regression line. This occurrence might be due to an incorrect time registration for the sampling period or incomplete sampling, as the creatinine corrected value for this subject was in accordance with the other creatinine corrected values. Before this relationship for the biological monitoring of N-methylmorpholine can be used, further studies of both industrial and experimental exposures are needed. Such studies have been started.

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