

Determination of dimethylethylamine in air samples from iron foundries by isotachophoresis

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HANSÉN L, SOLLENBERG J, UGGLÄ C. Determination of dimethylethylamine in air samples from iron foundries by isotachophoresis. *Scand J Work Environ Health* 11 (1985) 307–310. A method for the determination of dimethylethylamine in workroom air has been developed. Static gas standards of the amine in air were used to evaluate different sampling techniques. The analysis was performed by isotachophoresis. The sampling equipment of choice was midjet impinger flasks of glass or polystyrene containing 10 ml of hydrochloric acid (50 mmol/l). The method was used in a field study of three different iron foundries where air samples were taken. The dimethylethylamine concentration found was in the range 0.5–155 mg/m³. No pretreatment of the samples was necessary, and no interfering substances from the air in the foundries affected the analysis.

Key terms: cold-box, gas standard, mold core, polyurethane catalyst.

In the production of mold cores in the foundry industry the cold-box technique is of increasing importance. The mold cores are made of fine granular sand, 4,4'-diphenylmethane diisocyanate (MDI), and a liquid phenolic resin. The reaction is catalyzed by a gaseous tertiary amine which is pressed through the mixture. Triethylamine (TEA) has thus far been the dominating amine catalyst. But for the last few years the use of the more volatile dimethylethylamine (DMEA) seems to be increasing in Sweden.

DMEA is a liquid with a strong ammoniacal odor. It has a boiling point of 35°C and is very flammable with a flashpoint of –36°C (8). In animal experiments it has been indicated that DMEA is very irritating to the eyes, remarkably irritating to the mucous membrane in the respiratory organ, and slightly irritant to the skin (8). The hygienic standard for DMEA in workroom air is 75 mg/m³ in Denmark, whereas no corresponding value has been adopted in Sweden.

Gas chromatography is generally used for the analysis of DMEA. Two such methods using aromatic polymers or ethylene glycols as stationary phases have been described by Lindsay Smith and co-workers (6, 7) for the analysis of DMEA and some other aliphatic amines. Casselman & Bannard (1) have indicated the problems connected with the gas chromatographic analysis of amines. Recently Dalene et al (2) published a method for the analysis of TEA and other aliphatic amines by gas chromatography. Volpi (10) has described a colorimetric and a gas chromatographic method for DMEA in workroom air. Schütz & Wolf (9) have used a gas chromatographic

method to measure DMEA and several other compounds in exhaust gases from different processes in foundries, among them cold-box core-making.

In connection with an extensive study on the occupational environment in foundries and as part of our investigations on analytical methods for amines used in industry (3, 4, 5), we have developed an alternative method for the analysis of DMEA in air samples by isotachophoresis (ITP). The method has been used in a field study of three different foundries and is presented in this report.

Materials and methods

Preparation of gaseous standards

Static gaseous standards of DMEA in air were made in home-made sacks, as shown in figure 1. A sheet of aluminum laminated with a 12-μm thick polyester layer (Åkerlund & Rausing, Lund, Sweden) was folded to form a sack (125 × 80 cm) with the polyester layer inside. The edges were affixed with tape adhesive on both sides. The inlet system for the diluting air was a polytetrafluoroethylene (PTFE) tube (inner diameter 4 mm) fastened with PTFE nuts directly on the wall of the sack. Purified diluting air (charcoal filter) was introduced into the sack, and the volume (generally 100 l) was registered on a gas meter. DMEA was injected directly through the laminate by a microliter syringe. In this step the DMEA and the syringe had to be chilled to avoid losses due to evaporation. A gentle tapping of the sack was used to mix the gas. Concentrations between 15 and 75 mg/m³ were generated.

Air sampling

Laboratory experiments. Samples were taken from the sack by different techniques. Sampling in 10 ml

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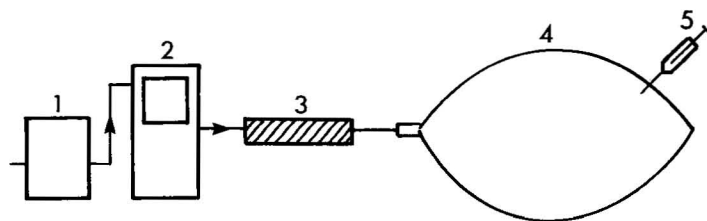


Figure 1. A static system for the production of gaseous standards of dimethylethylamine in air. (1 = pump, 2 = gas meter, 3 = charcoal tube, 4 = aluminum-laminated polyester sack, 5 = microliter syringe)

of hydrochloric acid (HCl) (50 mmol/l) was compared by bubbling the gaseous amine standard through home-made midjet impinger flasks of polystyrene, spill-proof midjet impinger flasks of glass (Svenska labglas AB, Stockholm, Sweden), and gas washing bottles of glass. Sampling was also performed on silica gel tubes [6 mm outer diameter $\times$ 70 mm, no 226-10, SKC Inc, Eighty Four, Pennsylvania, United States (USA)]. When comparisons were made with glass flasks or silica gel tubes, they were run in parallel with the polystyrene flasks. Portable sampler pumps (Anatole J Sipin Co, New York, New York, USA) were used at a flow rate of 200 ml/min. During the sampling the flow rate was intermittently checked with a soap film meter connected to the outlet of the pump.

For desorption of the amine from the silica gel the following solvents were used: water, HCl (50 mmol/l), and HCl (100 mmol/l) : ethanol (1 : 1). Each gel section was transferred to separate glass vials, 1.0 ml of the desorption solvent was added to the vial with the sorbent layer, and 0.5 ml of the the same solvent was added to the back-up sorbent layer vial. The vials were then shaken for 30 min in a laboratory shaker.

Foundry study. Air samples were taken in three different iron foundries. Foundry A had several small and rather old machines in the area where small mold cores (< 1 kg) were produced. Five persons were exposed. Foundry B had two modern machines which were fully enclosed. Mold cores of small and medium sizes (1–4 kg) were produced, and four persons were exposed. Foundry C had one modern large machine (enclosed), and one old machine in which large and medium-sized mold cores (5–15 kg) were produced. Three persons were exposed. In all three foundries the core machines were ventilated, and in foundries B and C the exhaust gases were burned in a butane flame.

Both personal and stationary samples were collected. The stationary samples were taken about 1.5 m above the floor level close to the machines and in the area where newly made cores were stored. At all sampling sites polystyrene flasks were used. When the samples were collected in glass flasks or on silica gel tubes, they were run in parallel with the polystyrene flasks. The sampling occurred on 2 d when the production was said to be normal.

Concentration of the samples

The sensitivity of the analysis can be increased by concentration of the absorption solution from the impinger flasks. The procedure involves transferring 5 ml of the solution to a polypropylene tube, which was put in a thermostated heating block, and evaporating the solution to dryness at 80°C. The process was speeded up by passing 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 in the tubes. The evaporation rate for the absorption solution was 1 ml/h. The residue was dissolved in 500 μ l of distilled water. An aliquot of the solution was injected directly into the isotachophoretic instrument for analysis.

Analysis

The analysis was performed by isotachopheresis with an LKB 2127 Tachophor (LKB-Produkter AB, Bromma, Sweden) equipped with a conductivity detector and a capillary tube (PTFE, inner diameter 0.5 mm, length 230 mm). The capillary was thermostated at 15°C. The leading electrolyte was potassium hydroxide (10 mmol/l) in 0.4 % (weight/volume) hydroxypropylmethylcellulose (90 HG 15 Pas, Dow Chemicals, Midland, Michigan, USA). The pH of the solution was adjusted to 8.8 by the addition of L-Valine (solid) (Sigma, St Louis, Missouri, USA). The terminating electrolyte was tris(hydroxymethyl)aminomethane (20 mmol/l) in HCl (5 mmol/l), pH 8.5. The sample volume was between 2 and 10 μ l, the migration current was 100 μ A, and the time of analysis was about 12 min. DMEA was quantified from measurements of the zone lengths on the graph through a pocket lens, magnifying 10 times, with a graduated scale.

Results and discussion

Laboratory experiments

An analytical separation of DMEA and TEA is shown in figure 2. A calibration graph for DMEA analyzed by isotachopheresis was made from standard solutions of DMEA in water. It was linear in the range tested (1 to 150 nmol). The practical detection

limit for DMEA in this system was about 1 nmol. (This value corresponds to 7.3 μmol of amine in a sample concentrated 10 times, which can be obtained from 4 l of air containing a DMEA content of 2 mg/m^3 .)

The results of the laboratory experiments of sampling DMEA from a sack with two different impinger flasks are shown in table 1. By "overall recovery" we mean the quotient of the DMEA concentration determined by the isotachophoretic 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, sampling, concentration of the absorption solution, and the final analysis. The recoveries were similar for the two types of impinger flasks.

If necessary the absorption solution can be concentrated 10 to 20 times with negligible loss of DMEA.

In one experiment gas washing bottles of glass with sintered glass filters were used for sampling about 400 μg of DMEA from gas standards. The recoveries had a slightly greater variation in comparison to those obtained when impinger flasks were used (recovery = 96 %, SD = 13, N = 5).

The experiments with adsorption tubes gave unsatisfying recoveries with the desorption solutions used. However, the use of solid sorbents for the sampling of amines will be dealt with in another work.

Foundry study

The results of the determinations of DMEA in three different foundries are shown in table 2. The figures indicate that the personal samples are slightly higher than the stationary ones taken in the vicinity of the

machine. However the samples taken under the cover show very high concentrations of DMEA. Consequently the worker who takes the mold cores out of the machine will have a higher exposure than the stationary samples indicate.

All samples in the field study were taken at random, and the investigation is not to be regarded as an occupational examination of the exposure to DMEA in

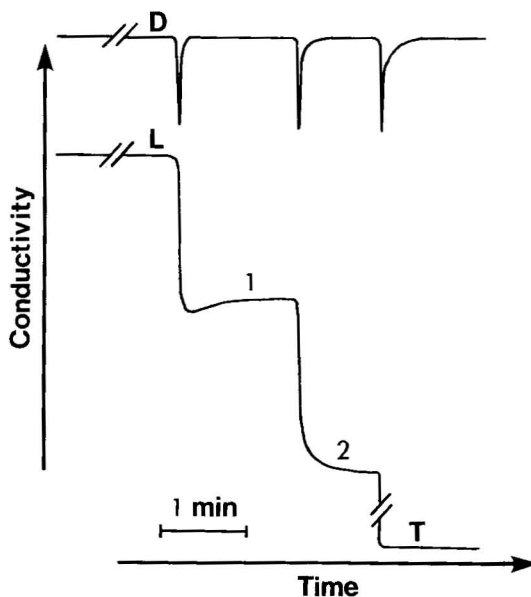


Figure 2. Isotachopheric separation of dimethylethylamine (23 nmol, 1) and triethylamine (20 nmol, 2). The migration current was 50 μA , and the scale indicates 1 min of recording. (L = leading electrolyte, T = terminating electrolyte, D = differential signal)

Table 1. Analysis of dimethylethylamine (DMEA) from static gas standards in an aluminum-laminated polyester sack. Comparison between sampling in midjet impinger flasks of polystyrene and glass at three different concentration levels.

DMEA generated (mg/m^3)	DMEA sampled (μg)	Overall recovery (%)											
		Polystyrene						Glass					
		Unconcentrated			Concentrated 10 times			Unconcentrated			Concentrated 10 times		
		Number of samples	Mean	SD	Number of samples	Mean	SD	Number of samples	Mean	SD	Number of samples	Mean	SD
14	200	4	103	6	4	90	17	7	100	6	7	101	5
35—47	250—350	15	104	9	7	97	4	12	99	4	9	97	6
63—70	340—420	12	104	10	—	—	—	6	97	7	—	—	—

Table 2. Analysis of dimethylethylamine (DMEA) during cold-box core-making in three different iron foundries.

Type of sampling	Foundry A		Foundry B		Foundry C	
	Number of samples	DMEA (mg/m^3)	Number of samples	DMEA (mg/m^3)	Number of samples	DMEA (mg/m^3)
Personal	5	4.5—34	4	1.8—7.1	3	7.4—15
Stationary (at the machine)	8	0.7—14	8	0.5—3.5	9	1.8—10
Stationary (under the cover)	1	155	—	—	2	77—95
Stationary (far from the machine)	—	—	5	0.5—0.9	—	—

iron foundries but as a test of the sampling and analytical method.

The results of samples analyzed directly by isotachophoresis (x) were compared with those of the same samples that were concentrated up to 20 times (y). The equation of the regression line obtained was: $y = 1.02x - 1.11$, and $r = 0.997$ for 22 samples. The samples originated from two of the foundries, and most of them were from stationary sampling sites close to the machines. The concentration range of DMEA in air was 2 to 155 mg/m³. Schütz & Wolf (9) report the range 19–185 mg/m³ for DMEA in foundries during cold-box core-making.

The present method can be used to determine DMEA in air at a concentration of 2 mg/m³ in iron foundries when sampling 4 l of air. No pretreatment of the samples before analysis is necessary, and no interference affects the analysis.

The unique quality of the isotachophoretic analysis to discriminate interfering substances which are not charged at the prevailing pH of the system makes the evaluation of the separation rational and convenient.

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