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SIMULTANEOUS DETERMINATION OF AMINES AND ISOCYANATES IN WORKING ATMOSPHERES BY GAS–LIQUID CHROMATOGRAPHY

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SUMMARY

A gas–liquid chromatographic method has been developed which permits trace analysis in a single run of amines and isocyanates occurring in relative concentrations of the order of 10,000:1. The amines were determined as free amines after alkalization of the sample and an extractive enrichment into toluene. The isocyanates were hydrolyzed to the corresponding amines during sampling in dilute sulphuric acid. This method gives the total isocyanate concentration. The use of a nitrogen sensitive detector and an alkali-treated packing, Pennwalt 223 with 4% KOH, are important prerequisites. Chromatographic parameters such as column liquid loading, injector impregnation and injector temperature were examined. Good separation between 2,4- and 2,6-toluenediamine isomers was obtained. The enrichment step was studied with respect to the degree of alkalization and to interferences from another amine present in large excess. The method was tested in the working atmospheres of two polyurethane foam factories. The substances determined were N-methylmorpholine, 1,4-diazabicyclo[2,2,2]octane and 2,4- and 2,6-toluenediisocyanates.

INTRODUCTION

Amines and isocyanates often occur simultaneously in working atmospheres, *e.g.*, in polyurethane production where tertiary amines in concentrations of a few per cent are used as catalysts.

Very little attention has been paid to the problem of analyzing amines and isocyanates simultaneously. Measurements of working atmospheres, where isocyanates were used in the production process, have been restricted to these substances. This is probably due to two reasons: the isocyanates were first found to be a serious health risk, even in very low concentrations; and simple methods for trace analysis of amines were not developed until recently. Recent investigations of working atmospheres have shown that asthma can be developed by exposure to amines such as ethylenediamine and piperazine[1,2]. Respiratory problems occur even upon exposure to sub-nanogram levels of amines in air[3]. Thus there is a need to determine amines in working atmospheres.

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At present, isocyanates are usually determined by high-performance liquid chromatography (HPLC) after derivatization during sampling in an organic solvent[4,5]. Amines, on the other hand, are usually determined by gas–liquid chromatography (GLC) after a derivatization step[6,7]. Recently, GLC methods have been developed for direct analysis of free amines at the ng level[8–10]. When sampling is made in acidic aqueous solutions, the isocyanates are converted into their corresponding amine salts[11,12]. This makes it possible to measure both the amine concentration and the total isocyanate concentration in the working atmosphere.

In this paper we describe a method for the simultaneous analysis of amines and isocyanates occurring in working atmospheres at concentrations in the low $\mu g/m^3$ range.

EXPERIMENTAL

Equipment

A Varian 3700 gas chromatograph equipped with a Varian Thermionic Specific Detector (TSD) and a HP 3390A integrator was used for the measurements. The detector parameters were optimized using N-methylmorpholine (2 ppm) and *n*-undecane (2000 ppm) as test substances. Typical parameter adjustments were: bias voltage, −10 V; bead current, five scale divisions; detector temperature, 300°C; air flow, 180 ml/min; hydrogen flow, 3.0 ml/min. The selectivity, measured as the peak to peak ratio for N-methylmorpholine and *n*-undecane, was about 20,000. However, each ceramic bead in the detector has its own characteristics. The injector temperature was 290°C. Two glass columns (1 m × 2 mm I.D.) were used, packed with 1.5 g of 10% and 2.0 g of 28% Pennwalt 223 respectively with 4% KOH on Gas-Chrom R (80–100 mesh)

Solutes were injected directly onto the column using PTFE-faced silicon septa (Microsep F-174-N, Alltech). The carrier gas was nitrogen, 20 ml/min, freed from oxygen and water vapour by use of an "Oxy-trap" (Alltech).

Chemicals

Practical grade 2,4-toluenediamine (2,4-TDA), 2,6-toluenediamine (2,6-TDA) and bis(4-aminophenyl)methane (MDA) and purum grade N-methylmorpholine and 1,4-diazabicyclo[2,2,2]octane (DABCO) were obtained from Fluka (Buchs, Switzerland). AnalaR grade sulphuric acid and aniline were purchased from BDH (Poole, Great Britain). 1,6-Hexamethylenediamine, analysis grade, was obtained from E. Merck (Darmstadt, G.F.R.) and toluene, glass distilled grade, from Rathburn Chemicals (Walkerburn, Great Britain). The amines N,N-dimethylcyclohexylamine (Shell International Chemical Company), bis[2-(N,N-dimethylamino)ethyl] ether (Union Carbide Corporation, New York, NY, U.S.A.), N,N-dimethyl-1,3-propanediamine (BASF AG, Ludwigshafen, G.F.R.) and isophorondiamine (VEBA Chemie AG, Gelsenkirchen-Buer, G.F.R.) were industrial grade.

The GC packings were purchased from Alltech (Arlington Heights, IL, U.S.A.).

Injector impregnation

About 10 μl of a saturated solution of sodium hydroxide were injected into the first part of the column, where about 4 cm were free from packing, at an injector temperature of 300°C. In the subsequent analyses the injector temperature was kept at 290°C.

Substances investigated

Table I shows the amines and isocyanates considered in this investigation. All these substances occur in the working atmospheres of polyurethane industries in mixtures of different compositions depending on the kind of products.

Problems related to large concentration differences between sample components were examined in a model system comprising a solution of N-methylmorpholine, DABCO and the amines 2,4- and 2,6-TDA. The same amines were obtained by sampling air in two factories producing polyurethane foam. One of these investigations is described in ref. 13. The amine concentrations in the model system were chosen according to our experience from the previous investigation.

Sampling

Amines and isocyanates were sampled in glass impingers filled with 10 ml 0.05 *M* sulphuric acid. 30–80 l of air were drawn through the impingers at a flow-rate of 1–1.5 l/min. The samples were then transferred to glass test-tubes and sealed with PTFE-faced screw-caps.

Extraction procedure

In order to obtain sufficient sensitivity in the GC determination of the isocyanates, an approximately ten-fold enrichment step was performed as follows. Five millilitres of the sample solution were transferred to a 7-ml test-tube sealed with a PTFE-faced screw-cap. Toluene (0.5 ml) and 2.5 g of solid NaOH pellets were added in this order. During the addition of hydroxide the test-tube was cooled by tap-water. When most of the hydroxide had dissolved the tube was placed into an ultrasonic bath for about 10 min. The mixture was centrifuged until the toluene layer was clear (*ca.* 3000 *g* for about 5 min). Samples (*ca.* 1 μl) of this layer were then injected directly into the gas chromatograph.

Preparation of standard solutions

Amine standards. The amines (10 mg) were dissolved in 10 ml of 0.05 *M* sulphuric acid and diluted in the same solvent to the required concentrations.

TABLE I

INVESTIGATED AMINES

Amines	*Amines corresponding to hydrolysed isocyanates*
N-Methylmorpholine	2,4-Toluenediamine (2,4-TDA)
1,4-Diazabicyclo[2.2.2]octane (DABCO)	2,6-Toluenediamine (2,6-TDA)
N,N-Dimethylcyclohexylamine	Isophorondiamine (IPDA)
Bis[2-(N,N-dimethylamino)ethyl] ether	Hexamethylenediamine (HMDA)
N,N-Dimethyl-1,3-propanediamine	Aniline
	Bis(4-aminophenyl)methane (MDA)

Isocyanate standards. The corresponding amines were used as standards, *e.g.*, for 2,4-toluenediisocyanate we used 2,4-toluenediamine as standard. These standards were treated in the same way as the amine standards.

The standard solutions were extracted into toluene after alkalization by the same procedure as for the samples.

RESULTS AND DISCUSSION

Sampling

Amines have been sampled in acidified water solutions[10,14,15] as well as on solid adsorbents such as silica gel[16] or on porous polymers such as Tenax[17]. The first procedure is highly reliable for amines and gives almost complete conversion of isocyanates into their corresponding amines[12]. We have tested this sampling technique by connecting two impingers in series glass-to-glass and found only minute amounts of amines in the second impinger. In one experiment we sampled 80 l of air containing 42.6 mg/m^3 N-methylmorpholine at a rate of 1.5 l/min in a solution of 10 ml of 0.05 *M* H_2SO_4, resulting in a solution containing 300 mg/l of the amine. Here we found that less than 1% of the total amine concentration was transferred to the second impinger. Thus a sulphuric acid concentration of 0.05 *M* has sufficient sampling capacity, and it may even be possible to use a still lower concentration.

Air sampling of isocyanates in dilute sulphuric acid yields the total concentration, *i.e.*, of the isocyanates and of amines formed by hydrolysis of isocyanates. Isocyanates *per se* are sampled either in a solution in an impinger[5] or on a solid adsorbent[18] and the isocyanates are derivatized *in situ* prior to liquid chromatographic detection. This procedure only measures non-hydrolyzed isocyanates. The total concentration is perhaps of still greater interest. Some of the hydrolysis products of isocyanates, *e.g.*, 2,4-TDA, are known carcinogens and all probably lead to respiratory problems. Thus, a knowledge of the total isocyanate concentration is needed to decide whether the working atmosphere is safe.

Sample storage

Samples containing less than 1 ng/μl of 2,4- and 2,6-TDA, and higher concentrations of N-methylmorpholine and DABCO, could be stored in the dark for 3 months at room temperature (*ca.* 22°C) without noticeable difference in concentrations.

Optimization of the GLC system

Injector. We have found it important to impregnate the first 4 cm of the bare glass column with alkali to minimize adsorption effects. The favourable effects of impregnation have been mentioned elsewhere[19]. The difference in results obtained before and after impregnation is illustrated in Fig. 1. With the impregnated injector it is possible to use a lower injector temperature. Increasing the injector temperature improves peak shape but to prevent sample decomposition a moderate injector temperature is preferable. We have found 290°C to be suitable for the amines in this investigation.

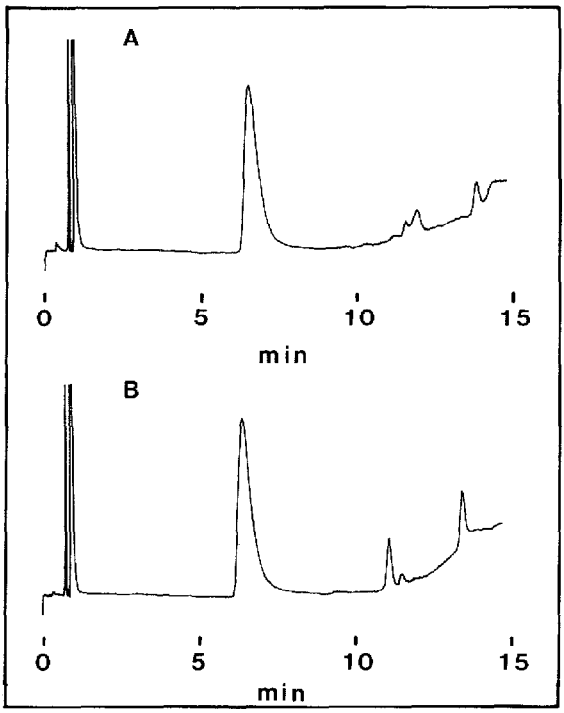


Fig. 1. Effect of injector impregnation with NaOH: A, without impregnation, B, with impregnation. Solutes: N-methylmorpholine (0.9 min, 900 ng/μl); DABCO (6.5 min, 16 ng/μl); impurities in N-methylmorpholine (11 min) and 2,4-TDA (14 min, 2 ng/μl). Injection: 1 μl. Detection: TSD. Packing: 10% Pennwalt 223 with 4% KOH. Column: glass (1 m × 2 mm I.D.), 1.5 g of packing. Attenuation: $2^3 \cdot 10^{-10}$–$2^{-5} \cdot 10^{-10}$ A f.s. Temperatures: injection, 290°C; detection, 300°C; column, 90°C (2 min) to 215°C at 16°C/min. Carrier gas: nitrogen, 20 ml/min. The times given in parentheses are retention times for the respective solutes.

The column

Choice of packing. Different packings were investigated previously[20] with respect to their usefulness in amine analysis. Pennwalt 223 packing with KOH was found to be the most appropriate for general purposes and was therefore used in this investigation. The limited thermal stability of the packing (maximum temperature for isothermal work, *ca.* 200°C; in temperature programming, *ca.* 220°C) makes the packing less suitable for the analysis of very high boiling amines such as MDA. Here a glass capillary column may be an alternative. Recent work on aromatic amines using glass capillary columns with SE-52 as stationary phase and with a nitrogen sensitive detector indicates that it should be possible to analyse high boiling aromatic amines like MDA at concentrations below ng/μl[21].

Amount of packing and liquid loading. The separation between the amines investigated is much better for a Pennwalt packing with 10% liquid loading than for 28% loading, other parameters being the same (Fig. 2). The chromatogram in Fig. 2B was run with temperature programming to illustrate the possibility of separating both low boiling and high boiling components in the same run. An isothermal run at 210°C also gave baseline separation between 2,4-TDA and 2,6-TDA.

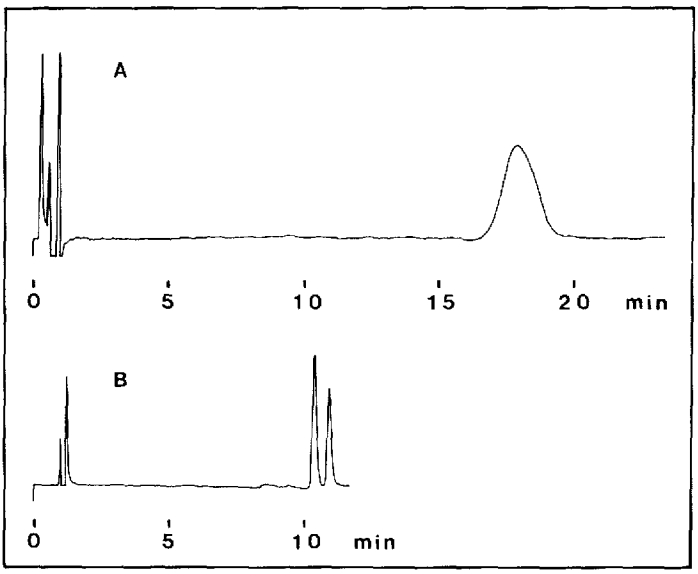


Fig. 2. Influence of liquid loading on column performance. Solutes: 2,4-TDA (10 ng/μl) and 2,6-TDA (10 ng/μl) in both cases. Column packings: 28% (A) and 10% (B) Pennwalt 223 with 4% KOH. Column temperatures: 210°C (A); 70°C (1 min) to 210°C at 20°C/min (B). Attenuations: $2^{-2} \cdot 10^{-10}$ A f.s. (A) and $2^{-4} \cdot 10^{-10}$ A f.s. (B). Other parameters as in Fig. 1.

The best combination of high separation efficiency and low detection limit was obtained with a 10% Pennwalt column (1 m × 2 mm I.D.) with 1.5 g of packing (as in Fig. 2B). When only low boiling amines are present, the 28% packing is preferred because of its better long-term stability.

Isomer separation. Technical toluenediisocyanate (TDI) for polyurethane production always consists of a mixture of the 2,4- and 2,6-isomers. At 10% liquid loading, 2,4-TDA and 2,6-TDA, *i.e.*, the hydrolysis products of the corresponding toluenediisocyanates, can be separated (Fig. 2). Owing to insufficient separation between the isomers, it had previously been necessary to assume certain compositions of the isomeric mixture[12] or to assume that each isomer gave the same detector response. A discrimination between the 2,4- and 2,6-TDI isomers is interesting from a medical point of view as only 2,4-TDA has hitherto been proved to be carcinogenic[22,23].

When the concentrations of amines are increased their retention times decrease wich means that adsorption effects are present, *e.g.*, for DABCO the relative change in retention time was *ca.* 6% when the injected amount was varied from 1 to 20 ng with column temperature programming from 90 to 210°C at 16°C/min. At 28% liquid loading, the corresponding change is only about 0.3% in an isothermal run at 190°C.

The better separation at 10% loading is partly due to a larger contribution from adsorption to solute retention than at 28% liquid loading. The higher number of theoretical plates, because of a thinner liquid film, at 10% liquid loading will not give such a large improvement in resolution, as shown in Fig. 2. This was demonstrated by studying the improvement in resolution for solutes exhibiting very small

adsorption effects on the column. The analysis is favoured by the occurrence of nearly symmetrical peaks of the isomers at low concentrations (ng/μl), indicating linear isotherms in the concentration range considered. These findings are in agreement with those obtained in previous work on mixed retention mechanisms with polar solutes and non-polar columns[24,25]. For solute concentrations of ng/μl the peaks became nearly symmetrical. Thus, the possibility of using adsorption to improve separation in GLC is most favourable in trace analyses, where the adsorption isotherms are usually linear.

Column stability. After prolonged use the column performance deteriorates. It can usually be restored simply by substituting the first 2–3 cm of the column at the injector end with new packing.

Extractive enrichment

In order to achieve sufficient sensitivity for the determination of hydrolysed isocyanates in working environments under Swedish rules for sampling of isocyanates, an extraction procedure was necessary. Toluene behaves well in the chromatographic system and has previously been used for the extraction of amines from strongly alkaline aqueous solutions[12].

Some parameters which could seriously affect the extraction efficiency, *viz.*, concentration of sodium hydroxide in the aqueous phase, volume ratio of aqueous phase to toluene phase, temperature and large excess of one amine, were studied further.

Concentration of alkali. Fig. 3 shows how the extraction recovery varies with sodium hydroxide concentration for some solutes at 21°C, and Table II gives the extraction recovery of amines from solutions saturated with sodium hydroxide and

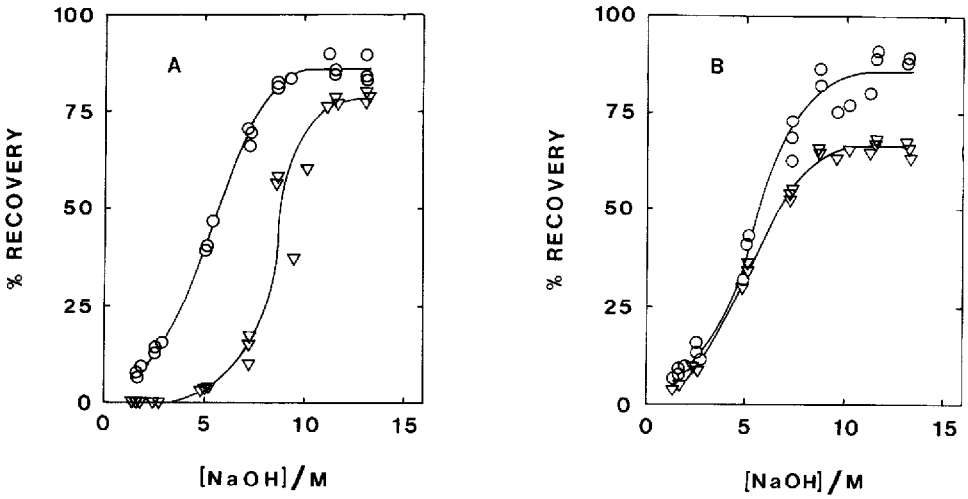


Fig. 3. Variation of extraction recovery with the concentration of sodium hydroxide in the aqueous phase. The extraction was performed with an aqueous to toluene phase ratio of 10:1. Solutes: A, 2,6-TDA (○) and DABCO (▽); B, 2,4-TDA (○) and N-methylmorpholine (▽). Each curve is the result of three different extractions. In each extraction the organic phase was analysed three times by GC. Concentrations in the aqueous phase: 2,6- and 2,4-TDA, 0.5 ng/μl; DABCO, 1 ng/μl; N-methylmorpholine, 370 ng/μl.

TABLE II

EFFECTIVENESS OF EXTRACTION

Volume ratio of aqueous phase to toluene was 10:1. Each recovery value is an average from three extractions. Amine concentrations: 365 ng/μl N-methylmorpholine, 1.0 ng/μl DABCO and 0.5 ng/μl 2,4-TDA and 2,6-TDA.

Amine	*% Recovery*	*Distribution coefficient*
N-Methylmorpholine	70.0	23.3
DABCO	75.3	30.5
2,6-TDA	82.5	47.1
2,4-TDA	90.4	94.2

their distribution coefficients. 5 ml aqueous phase and 0.5 ml toluene phase were used in these experiments. It is concluded that the concentration of sodium hydroxide should be at least 10 *M* in order to obtain maximum recovery. The evaluation of the extraction recovery in this experiment is complicated by the fact that small amounts of sodium hydroxide dissolve together with water in the toluene layer. We have found that this increases the peak areas. To compensate for this the calibration standard solutions must be saturated with sodium hydroxide and water.

Volume ratio of toluene to water. The enrichment factor, F, varies with the volume ratio of toluene to water according to[26]

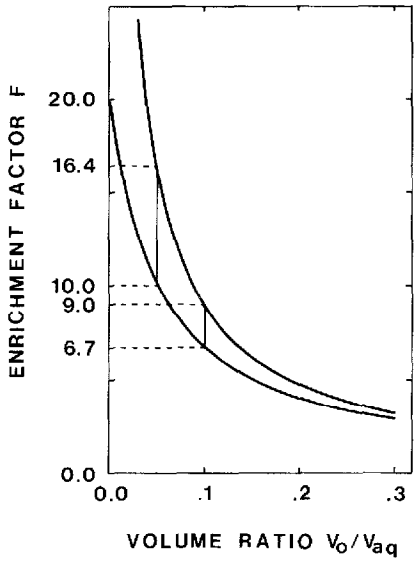
$$F = C_0/C^0_{aq} = \frac{D}{1 + D(V_0/V_{aq})} \quad (1)$$

where C_0 is the concentration in the organic phase at equilibrium, C^0_{aq} is the initial concentration in the aqueous phase before extraction, V_0, V_{aq} are the phase volumes and D is the distribution coefficient, *i.e.*, the ratio of the total concentration in the organic phase to the total concentration in the aqueous phase. For small volume ratios the enrichment factor approaches D.

Fig. 4 shows how the enrichment factor varies with volume ratio of toluene to water for different values of the distribution coefficient, D. For the compounds considered in our model system, N-methylmorpholine, DABCO, 2,4- and 2,6-TDA (distribution coefficients in Table II), the enrichment factor lies between 7 and 9 at a volume ratio of 1:10 and between 10 and 17 at a volume ratio of 1:20. For practical reasons it is difficult to obtain a volume ratio much higher than 1:20 in measurements of working atmospheres with ordinary sampling volumes of 10–20 ml.

The relative error in the extraction, obtained by differentiating eqn. 1, is always less than the relative error in the volume ratio, *e.g.*, with $D = 50$ and a volume ratio of 1:10 a relative error in the volume ratio of 5% results in a relative error in the extraction of 4%.

Temperature. The influence on the analysis of small changes in temperature was unimportant. This was verified by recovery studies as in Fig. 3 at two different temperatures, 21 and 27°C. Within experimental errors, the recovery curves for each solute at the two different temperatures overlapped each other.



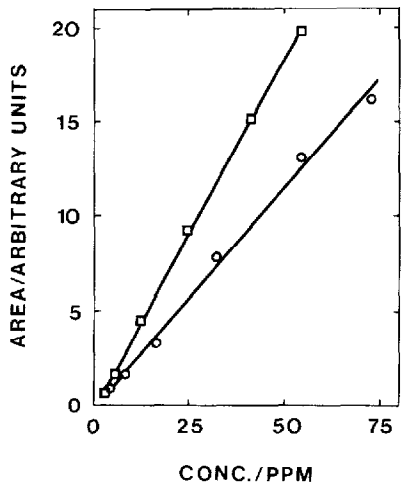


Fig. 4. Variation of enrichment factor with the volume ratio of the toluene phase to the aqueous phase. Upper curve calculated for a distribution coefficient of 90, lower curve for a distribution coefficient of 20.

Fig. 5. Variation of chromatographic peak area with solute concentration in toluene. Solute: DABCO. Lower line: standard prepared in toluene. Upper line: same standard but now treated with sodium hydroxide-saturated water. Extraction ratio of toluene to aqueous phase of 1:10. 1 ppm is equivalent to 1 ng/μl.

TABLE III

INFLUENCE OF EXCESS OF N-METHYLMORPHOLINE ON THE EXTRACTION OF 2,4- AND 2,6-TDA

N-Methylmorpholine concentration in the aqueous phase (ng/μl)	*Normalized peak areas**	
	2,6-TDA	*2,4-TDA*
5	1.0	1.0
10	1.0	1.0
500	0.90	1.0
1000	0.79	0.96

* Corresponding to 0.1 ng/μl of 2,4- and 2,6-TDA in the aqueous phase.

Effect of excess of one amine. The influence of excess concentrations of N-methylmorpholine on the distribution coefficients of 2,4- and 2,6-toluenediamine is shown in Table III. The distribution coefficients decrease at large concentrations of N-methylmorpholine. However, at the concentrations normally present after sampling of amines and isocyanates in the polyurethane industry, the effect of excess of amine on determinations of hydrolysis products of isocyanates can be neglected.

Quantitative analysis

Calibrations. Results are given in Table IV. Good linearity for peak area *versus*

TABLE IV

CALIBRATION CURVES OF PEAK AREA *versus* SOLUTE CONCENTRATION, FOR SOLUTES IN THE MODEL SYSTEM INVESTIGATED

Substance	*Concentration range in toluene phase (ng/μl)*	*No. of points on each curve**	*Correlation coefficient*	*% R.S.D. at 25% of max. concentration*
N-Methylmorpholine	50–1500	6	0.9999	2.3
DABCO	0.8–60	8	0.9998	2.8
2,6-TDA	0.15–10	8	0.9997	3.7
2,4-TDA	0.15–10	8	0.9998	3.4

* Each point is the average value from three injections each of 2 μl.

concentration was obtained over a concentration range of two decades when standard solutions in 0.05 *M* sulphuric acid were extracted and analysed. The extraction recoveries are independent of amine concentration in the concentration ranges considered.

There are two important reasons why amine standards should be treated in the same way as the samples: one is that the recoveries are considerably less than 100% at ten-fold enrichment; the other, as mentioned earlier in connection with the recovery studies, is that the peak areas increase when toluene is in contact with aqueous hydroxide solutions. The latter effect is illustrated in Fig. 5 for DABCO. The upper curve was obtained when saturated hydroxide solution was added to the corresponding toluene standards which give the lower curve. In the calculations, solute partitioning between the two phases has been taken into consideration.

With or without hydroxide the relationship between solute concentration and peak area can be considered as linear. For DABCO, the solute which gave the largest effect, when sodium hydroxide is added, the increase in slope is considerable. Interestingly, the two lines intersect close to zero for all solutes investigated.

Precision. A total relative standard deviation of 5.5% was obtained for four extractions of isocyanates at concentrations of 0.5 ng/μl in 0.05 *M* sulphuric acid with a toluene/water volume ratio of 1:10. The contribution from the chromatographic measurements was determined separately to be 2.5% (about the same as found in ref. 8), which means that the standard deviation in the extraction step is about 5.0% ($\sqrt{5.5^2 - 2.5^2}$). The corresponding value is lower for higher concentrations. For solutions containing *ca.* 5 ng/μl of amines or of isocyanates the standard deviation is 3–3.5% for five determinations.

Detection limit. Generally, for the amines in this investigation, concentrations below 0.1 ng/μl in sample volumes of 1.5 μl can be determined. An exception is MDA where the detection limit is about 2 ng/μl for a 1.5-μl injection. The column has high capacity, so sample volumes of 8–10 μl can be injected and concentrations below 0.03 ng/μl can easily be determined if necessary. The detection limit for the whole procedure including the extraction step is then about 0.003 ng/μl at a volume ratio of 1:10. There is little to be gained by improving the extraction recovery by changing the solvent. The extraction recovery is still as high as 80% even with a phase ratio of 1:20. The sensitivity of our method is generally sufficient to permit

analysis of isocyanates in air at concentrations below 10% of the prevailing Swedish threshold limit values (0.07 mg/m^3) over the prescribed sampling period (5 min). An exception is 4,4'-diphenylmethanediisocyanate, corresponding to MDA, where the detection limit is about 0.10 mg/m^3.

Applications

Two working environments have been investigated for 2,4- and 2,6-toluenediisocyanate and the tertiary amines N-methylmorpholine and DABCO. In both places polyurethane foam was manufactured and the tertiary amines were used as catalysts for the reaction between isocyanates and polyols. The results of the first of these investigations and the possible health hazards were presented in ref. 13. A typical GC analysis from the second investigation is shown in Fig. 6. Twenty samples of air contaminated with amines and isocyanates were collected in 0.05 *M* H_2SO_4 and analysed after extractive enrichment in toluene according to the procedure described.

At different stages of the production process we found air concentrations of isocyanates to be in the order of 0.005–0.025 mg/m^3, of DABCO in the order of 0.1–2 mg/m^3 and of N-methylmorpholine in the order of 20–200 mg/m^3. The amines apparently occur in large excess. These results are similar to those obtained in our first investigation[13], and point to an interesting question recently raised by Tucker and Arnold[27]. They found that the presence in air of DABCO together with toluenediisocyanate led to a significant decrease in the measured toluenediisocyanate concentration probably owing to an increased rate of hydrolysis of isocyanate to the corresponding amine. It is not clear to what extent hydrolysis takes place in the air before sampling or during the sampling procedure. In the latter case any method of determination of unhydrolysed isocyanates in air would give erroneous results.

The problem of high humidity when sampling isocyanates still remains. Chang and Burg[28] recently reported that 90% humidity resulted in 30% losses of isocyanates onto the tube walls, probably by hydrolysis. Such losses can be expected to be con-

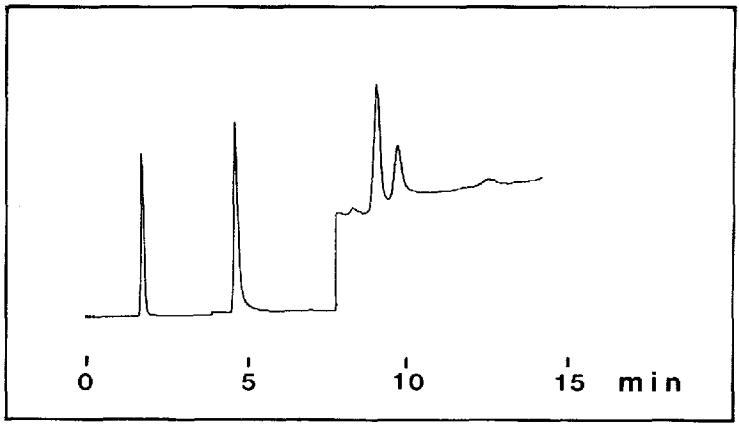


Fig. 6. Chromatogram from a working atmosphere containing N-methylmorpholine (1.75 min, 2600 ng/μl), DABCO (4.7 min, 22 ng/μl), 2,6-TDA (9.2 min, 1.2 ng/μl) and 2,4-TDA (9.9 min, 1.4 ng/μl). Injection volume: 1.6 μl. Attenuation: $2^8 \cdot 10^{-10}$–$2^{-4} \cdot 10^{-10}$ A f.s. Column temperature: 80 to 210°C at 21°C/min. Other parameters as in Fig. 1.

siderably less at 50% humidity as in our applications. A high concentration of amines compared to isocyanates in the atmosphere should improve the recovery when determining the total isocyanate concentration, since these amines would outweigh the amount of hydrolysed isocyanates adsorbed at the tube walls.

The influence of excess amine concentration and humidity on isocyanate sampling need to be investigated further. In these respects the sampling method used by us, which converts isocyanates into their corresponding amines, is less sensitive to sampling parameters than are the derivatization techniques.

Isocyanates and their corresponding amines are both serious health hazards. Thus, in general a method which determines the total isocyanate concentration is preferable.

CONCLUSIONS

We have shown that amines and isocyanates occurring in working atmospheres in polyurethane industries can be simultaneously sampled in dilute sulphuric acid and determined by GLC in a single run. Sample preparation utilizing an extractive enrichment step has made possible determinations in air at concentrations less than 0.01 ng/m^3 with normal sampling procedures.

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