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TRACE ANALYSIS OF ISOCYANATES IN INDUSTRIAL ATMOSPHERES USING GAS CHROMATOGRAPHY AND ELECTRON-CAPTURE DETECTION

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SUMMARY

A gas chromatographic method for the trace analysis of isocyanates in industrial atmospheres has been developed. It involves absorption of the isocyanates in dilute hydrochloric acid, where they are hydrolyzed to amines which after extraction with toluene react with heptafluorobutyric acid anhydride to form the corresponding amides. These are separated by gas chromatography on an OV-225 stationary phase and monitored by an electron-capture detector.

The method was applied to phenyl isocyanate, 2,4- and 2,6-toluene diisocyanate and to 4,4′-diphenylmethane diisocyanate. The detection limit is *ca.* $1 \cdot 10^{-4}$ mg isocyanate per m^3 air (15 l sample), which means that the sensitivity of the method is of the same order of magnitude as that of our previously developed liquid chromatographic method (C. Sangö and E. Zimerson, *J. Liquid Chromatogr.*, 3 (1980) 971).

INTRODUCTION

A method for the gas chromatographic assay of isocyanates in air was first described in 1965[1] and applied to the determination of 2,4- and 2,6-toluene diisocyanate (2,4- and 2,6-TDI). The air is passed through a short tube packed with a silicone elastomer on celite, on which the isocyanates are retained. They are desorbed by electric heating and analyzed by gas chromatography (GC) on the absorption phase, using a flame ionization detector (FID).

No information is available about the practical application of this method. However, it is evident that a considerable amount of sample is necessary on account of the comparatively low sensitivity of the FID for these compounds in comparison with the electron-capture detector (ECD). It is also recommended that the analysis is performed within 2 h after sampling, which makes it impossible to use a laboratory, elsewhere than at the sampling place, for the analysis.

The first real GC trace analysis method for the assay of isocyanates in air was described by Wheals and Thomson[2] in 1967 and was later used by Schancke and Hermann[3]. It is founded on the observation that 2,4-TDI is a strongly electron-

0021-9673/81/0000–0000/$02 50

capturing substance and hence can be monitored with high sensitivity using an ECD. In addition to 2,4-TDI, 4,4′-diphenylmethane diisocyanate (MDI) and dianisidine diisocyanate were tested but, for unknown reasons, no peaks were obtained. The limit of detection for 2,4-TDI was given as 1 ng per 5 μl of toluene solution, with a linear response in the range 0–30 ng. Schanke and Hermann[3] reported the limit of detection in their experiments with 2,4-TDI to be 0.05 ng per 5 μl of toluene solution. Thus, while it has been demonstrated that the method can be used for the GC trace analysis of 2,4-TDI, it is uncertain whether it can be applied to other kinds of isocyanates. The grade of hydrolysis of the isocyanates in the toluene solution must also be taken into account when using this procedure.

In the present work a more general method is described which permits the GC trace assay of isocyanates common in working atmospheres. The method involves absorption of the isocyanates in dilute hydrochloric acid, where the following reaction takes place

$$RNCO + H_2O + HCl \rightarrow RNH_2,HCl + CO_2 \quad (1)$$

Addition of excess alkali yields the free amine, which is extracted with toluene Acylation of the amine with heptafluorobutyric acid anhydride (HFBAA)[4]

$$RNH_2 + (C_3F_7CO)_2O \rightarrow RNHCOC_3F_7 + C_3F_7COOH \quad (2)$$

affords the corresponding amide and an equivalent amount of heptafluorobutyric acid. This and the excess of HFBAA are removed by shaking with a phosphate buffer solution of pH 7. The toluene solution of the heptafluorbutyric acid amide is then analyzed by GC using an ECD.

EXPERIMENTAL

Apparatus

Chromatograph A Carlo Erba Fractovap Model 2150 gas chromatograph was employed

Detector. A ^{63}Ni (10 mCi) Carlo Erba Model HT-25 ECD with control module 251 was used. The constant-current mode was employed (standing current 1.4 nA, voltage 50 V, pulse width 0.1 μsec).

Column. A circular glass column (2 m × 1/4 in. O.D. × 1.4 mm I.D.) was rinsed first with a chromic acid–sulphuric acid (1:1, w/w) mixture and then with doubly distilled water, and dried in a hot air stream. The column was packed with 3% OV-225 on Chromosorb W HP, 100–120 mesh (Chrompack, Middelburg, The Netherlands).

The column was fastened with vespel graphite ferrules VG2 (Alltech, Arlington Heights, IL, U.S.A.) and conditioned for 24 h at 260°C and a carrier gas flow-rate of 20 ml/min. After conditioning, the column was connected to the detector and the instrument run at 260°C until a stable baseline was attained. During this period, make-up gas (60 ml/min) with the same composition as the carrier gas was fed to the detector.

Carrier gas. The carrier gas was argon–methane (95:5, v/v). It contained a maximum of 5 ppm oxygen and was dried over activated molecular sieve 5A. The instrument was carefully tested for leaks.

Septum and septum flush. In order to minimize contamination from the septum, a septum flush was installed. It was constructed at this laboratory and similar to the septum flush sold by *e.g.* Supelco (Bellefonte, PA, U.S.A.).

Materials

Chemicals. Toluene 2,4- and 2,6-diamine (2,4- and 2,6-TDA), 4,4′-diaminodiphenylmethane (MDA) and aniline were obtained from E. Merck (Darmstadt, G.F.R.). HFBAA was from Pierce (Rockford, IL, U.S.A.). Hydrochloric acid, min. 37% (w/w) (E. Merck) and sodium hydroxide p.a. (tablets) (EKA, Bohus, Sweden) and potassium dihydrogen phosphate (E. Merck) were also used.

Solvents and buffer solutions. The water used was doubly distilled. Toluene was glass-distilled grade (Rathburn Chemicals, Walkerburn, Great Britain). Hydrochloric acid (10%, w/w) was prepared from the 37% acid by dilution with water. Saturated sodium hydroxide solution was obtained by dissolving tablets of sodium hydroxide (*ca.* 50 g) in 100 ml of water.

Phosphate buffer was prepared from potassium dihydrogen phosphate (136 g, 1 mol) and 1000 ml of water. The pH was adjusted to 7.0 with saturated sodium hydroxide.

Procedure

Sampling. A midget impinger (30 ml) was filled with 10 ml of 10% hydrochloric acid and 15 l of air was drawn through the impinger at a rate of 1 l/min using a flow-stable pump (*e.g.* Model P-2500, DuPont, Geneva, Switzerland). The sample solution was transferred to a screw-capped test-tube.

Derivative preparation. A 1-ml volume of the sample solution was transferred to a 5-ml test-tube*. Toluene (1 ml) and saturated sodium hydroxide (2 ml) were added and the test-tube was sealed and shaken for 2 min. The toluene layer, which now contained the free amine was transferred to a 3-ml test-tube, 20 μl of HFBAA were added, and the contents of the tube were shaken and then allowed to stand for 5 min. The excess of HFBAA and the acid formed were removed by shaking with 1 ml of phosphate buffer solution (pH 7). The toluene layer, which now contained the amide, was transferred to a new 3-ml test-tube, ready for injection into the gas chromatograph. It can be kept in a refrigerator for at least 3 months without any noticeable change in composition.

Preparation of standard solutions. The amine (50 mg) was dissolved in 25 ml of 10% hydrochloric acid. A 25-μl volume of this solution was transferred with a Hamilton syringe to 25 ml of 10% hydrochloric acid. This solution contained 2 ng of amine/μl. Standard solutions of the desired composition were made up by transferring the required volume of this solution to 1 ml of 10% hydrochloric acid. The amide was then prepared in the same way as described above.

Gas chromatography. Analyses were made isothermally at such temperatures and flow-rates that the derivatives had retention times of 2–4 min. The following temperatures were used. For the 2,4- and 2,6-TDA derivatives the injector and detector temperatures were 275°C and the column temperature 230°C. For the MDA derivative the corresponding temperatures were 275°C and 260°C, and for the aniline

* All test-tubes used were equipped with ground-glass stoppers

derivative 275°C and 160°C, respectively. The flow-rate was 20 ml/min and the inlet pressure 36 p.s.i. A 2-μl volume of the toluene solution was injected.

Quantitative analysis. The quantitative analysis was based on peak height measurement. The linear range for each derivative was established by injecting standard solutions of the amides and plotting peak height against concentration (Fig. 1).

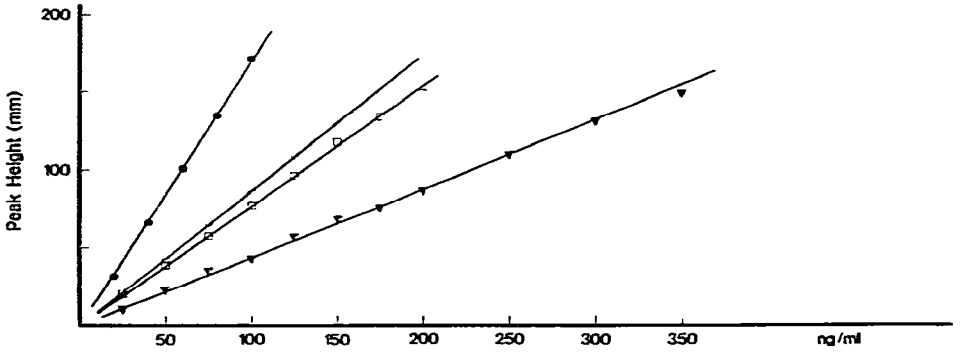

Fig 1. Calibration curves of amine derivatives in toluene. ● = Aniline, ○ = 2,4-TDA; □ = 2,6-TDA; ▼ = MDA

Samples were analyzed using the external standard method. The peaks for the 2,4- and 2,6-TDA derivatives coincide and the sensitivities of the two amides differ somewhat, as shown by Fig. 1. The quantitative evaluation in this case was based on comparison with standards containing 65% of the 2,4-TDA derivative and 35% of the 2,6-analogue, and the results presented as the sum of 2,4- and 2,6-TDI. The content of isocyanate in the air sample is calculated from eqn. 3.

$$\text{concentration of isocyanate (mg/m}^3\text{ air)} = \frac{x \cdot a \cdot M_{\text{isocyan.}}}{v \cdot f \cdot M_{\text{amine}}} \qquad (3)$$

where

x = concentration of the amine in the toluene solution in ng/ml
a = volume of toluene used for extraction (1 ml)
v = volume of air in ml (15,000)
M = molar weight
f = fraction of absorption volume used for analysis (1/10)

RESULTS AND DISCUSSION

Procedure

Losses of isocyanates or the corresponding amines and amides can occur at various stages of the work-up procedure. Of greatest importance are absorption losses at the sampling stage and losses during the following extraction procedures.

Sampling. Experiments with two impinger flasks in series showed that more than 90% of the isocyanates were absorbed in the first flask. However, certain isocyanates, *e.g.* MDI, have a tendency to form aerosols which have a lower degree of absorption in hydrochloric acid. In such cases the use of a gas absorption flask instead of an impinger is recommended.

The amine salt is stable for a long time in the absorption solution when kept in the dark. When it is exposed to light, however, a slow decomposition takes place. However, the nature of the industrial atmosphere can influence the rate of decomposition of the sample.

Extraction of amines from the aqueous phase. On absorption, the isocyanates are converted into the corresponding amine salts, which after alkalizing of the solution were extracted with toluene. On alkalizing with phosphate buffers (1 mol l^{-1}) in the pH range 8–12 it turned out that, while MDA was completely extracted, 2,4- and 2,6-TDA were not, the yield amounting to *ca.* 40%. The yield for aniline was *ca.* 80%.

Only after addition of the double volume of saturated sodium hydroxide solution to the hydrochloric acid were all amines fully extracted from the aqueous phase. Variation of the volume ratio of toluene to the aqueous phase showed that the yield was still nearly 100% with a ratio as low as 1:10.

Formation of amides. Trimethylamine has been recommended as a catalyst in the reaction between amines and HFBAA[4]. We have found that in the present case the reaction proceeds rapidly enough without a catalyst. After 1 min at room temperature the amine is fully converted into the amide. Since the presence of a catalyst such as trimethylamine can complicate the chromatographic separation, it is a definite advantage to be able to dispense with it.

Theoretically several products can be formed on reaction between HFBAA and the amines in question. However, it was shown using GC–mass spectrometry that only one product was obtained, in that just one hydrogen atom at each amino group was replaced by a heptafluorobutyryl group.

Extraction of excess of HFBAA and of heptafluorobutyric acid. These compounds have to be removed from the toluene solution before chromatography. Walle and Ehrsson[4] recommended extraction with 2.5% ammonia. However, it appeared that, using this method, considerable amounts of the TDA derivatives were also extracted while the aniline and MDA derivatives remained in the toluene solution.

Experiments with phosphate buffers (1 mol l^{-1}) proved that in the pH range 6–9 nearly all of the amides remained in toluene solution, while the reagent and the acid were fully removed. With increasing pH more and more of the TDA derivatives were lost (see Table I).

TABLE I
EXTRACTION OF HFBAA AND HEPTAFLUOROBUTYRIC ACID FROM TOLUENE SOLUTION

Phosphate buffer solution (1 mol l^{-1}), pH	*Derivative remaining in the toluene solution after extraction (%)*			
	PhA	*2,4-TDA*	*2,6-TDA*	*MDA*
6	100	99	98	100
7	100	99	100	100
8	97	98	98	100
9	96	101	100	97
10	98	99	97	100
11	95	91	21	100
12	91	8	1	100

Gas chromatography

Choice of stationary phase. Trace analysis of polar compounds on packed columns affords stable, low-bleeding stationary phases. In addition, the support should be carefully deactivated. In this case we have used a moderately polar phase, OV-225, which is a silicone with a cyanopropyl group in addition to methyl and phenyl groups bonded to silicon.

Columns packed with this phase could be used continuously for several months before showing any signs of deteriorating. In order to restore the column properties, it was not always necessary to repack the whole column, but sufficient to change the first 10 cm of the packing. Chromatograms are shown in Fig. 2.

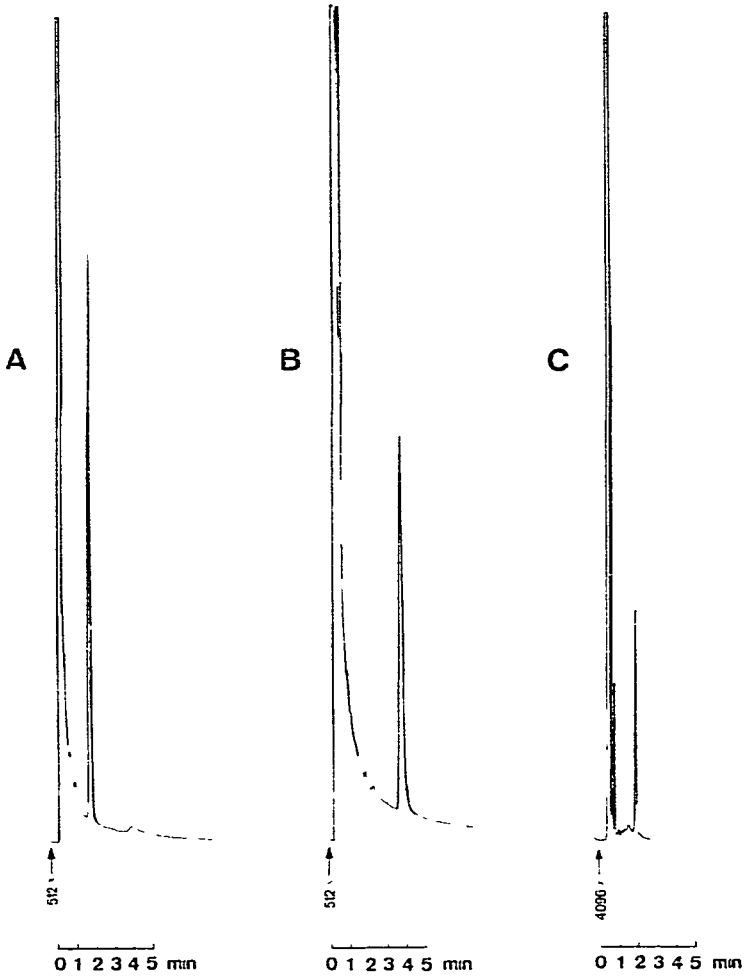

Fig. 2. Chromatograms of amine derivatives corresponding to (A) 25 $\mu g/m^3$ of 2,4-TDI (65%) and 2,6-TDI (35%); (B) 35 $\mu g/m^3$ of MDI; (C) 35 $\mu g/m^3$ of aniline Column, 2 m × 1.4 mm I D. glass column with 3% OV-225 on Chromosorb W HP, 100–120 mesh. Carrier gas, argon–methane (95:5, v/v); flow-rate 20 ml/min. Detector, ECD, constant-current mode; standing current, 1.4 nA; voltage, 50 V; pulse width, 0.1 μsec Temperatures: detector and injector 275°C; column (A) 230°C; (B) 260°C; (C) 160°C

Septum flush. We have found it essential to use a septum flush in order to reduce the contamination caused by the septum. In addition, the lifetime of the septum is considerably increased and the closedown time at the installation of a new septum drastically decreased. The washing and conditioning procedure recommended for new septa in GC manuals is unnecessary when septum flush is used.

Carrier gas. When working with the present ECD in the constant-current mode, 5% methane in argon is recommended as carrier gas for good linearity. This is also promoted by a small pulse width. In the present case the smallest possible, 0.1 μsec, was used. The purity of the carrier gas is also important. The reports concerning the permitted concentration of oxygen differ from 1 to 10 ppm. The argon available contained a maximum of 5 ppm of oxygen and has been used without any adverse effects on the performance of the detector.

Linear range and minimum detectable quantity. Fig. 1 demonstrates the linear range for the investigated amides. The linear range can be increased by diluting the sample or by the use of "make-up" gas as shown in Fig. 3 for the aniline derivative. In this figure the calibration curves without and with "make-up" gas (30 ml/min) are compared. As can be seen, the upper limit of the linear range is increased from 100 to 200 ng/ml. By changing the flow-rate of "make-up" gas, it is accordingly possible to place any sample within the linear range. The minimum detectable quantity (MDQ) is in the present case primarily determined, not by the noise, but by disturbances caused by the solvent. At low concentrations the amide peaks lie on the tail of the solvent peak, as shown by Fig. 4. In this case very small amounts of amides were injected, corresponding to 0.2 pg of TDA and 0.4 pg of MDA. These amounts represent the MDQs of these amides and correspond to air concentrations of $1.0 \cdot 10^{-4}$ and $1.7 \cdot 10^{-4}$ mg/m^3 of TDI and MDI, respectively.

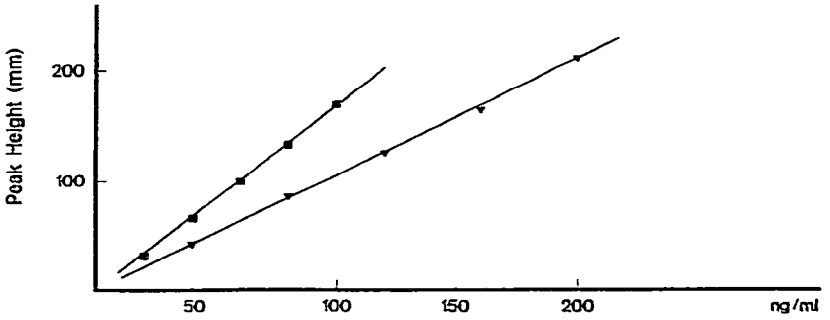

Fig 3. Calibration curves of aniline derivative with (▼) and without (■) "make-up" gas

This means that concentrations down to *ca.* 0.2% of the present Swedish threshold limit values (0.07 mg/m^3 for TDI and 0.1 mg/m^3 for MDI) can be assayed for these isocyanates, using the present method. By changing the experimental conditions, *e.g.* by increasing the air volume and the aliquot of the sample solution taken or by decreasing the volume of toluene used for extraction, the MDQs can be further decreased.

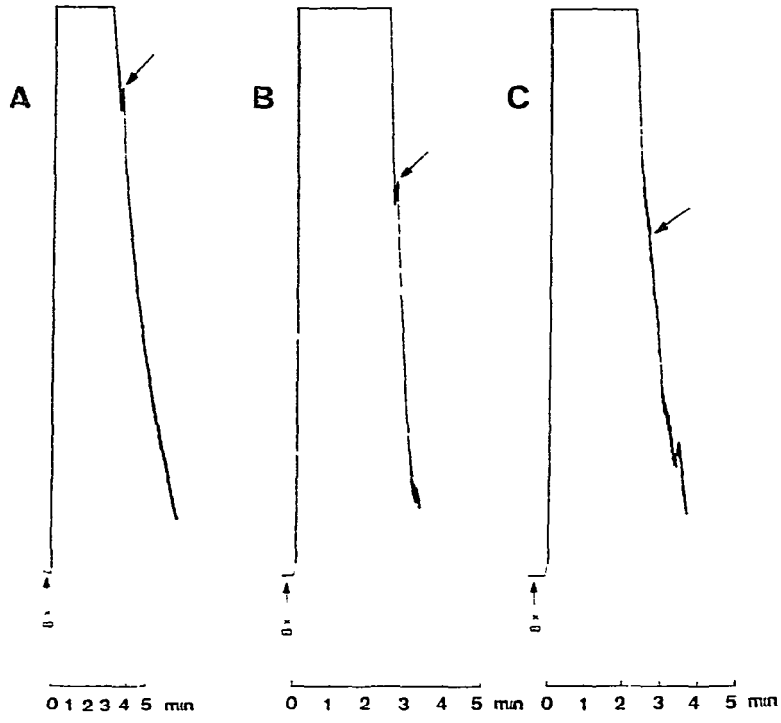

Fig 4 Chromatograms of derivatives of (A) 0.2 pg of TDA and (B) 0.4 pg of MDA; (C) = blank. For conditions see Fig 2.

COMPARISON BETWEEN GC AND HIGH-PERFORMANCE LIQUID CHROMATOGRAPHIC METHODS

Two liquid chromatographic methods for the determination of isocyanates in air were previously developed at this laboratory[5,6]. They involve absorption of the isocyanates in toluene where they react with a UV-absorbing amine to yield a urea derivative which is analyzed by high-performance liquid chromatography (HPLC). For the more sensitive of the two methods[5], utilizing 9-(N-methylaminomethyl)anthracene for derivatization, the detection limit for isocyanates in air is of the same order of magnitude as for the present GC method, *i.e. ca.* $1 \cdot 10^{-4}$ mg/m^3 air.

The LC and GC methods, however, differ in the respect that the LC method measures only the isocyanates, whereas the GC method gives the sum of the isocyanates and the amines formed from them by hydrolysis. Accordingly, by applying both methods it is possible to assay isocyanates as well as amines in the same working atmosphere.

CONCLUSION AND FURTHER WORK

There are now available two sensitive methods for the trace determination of isocyanates in industrial environments. These methods make it possible to assay far

lower concentrations than in the older colorimetric method; because of their selectivity, they also allow the determination of individual compounds.

The present GC method has so far been applied to the analysis of aromatic isocyanates in industrial atmospheres, but should also be suited to the assay of aliphatic isocyanates, which problem is now being studied at this laboratory. Since the method is essentially an amine analysis method, it is, of course, also applicable to the assay of amines. We are also investigating the possibility of applying programmed temperature GC on glass capillary columns, using on column injection and electron-capture detection, in order to be able to assay simultaneously more complex samples of isocyanates and/or amines.

ACKNOWLEDGEMENT

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