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TRACE ANALYSIS OF AMINES AND ISOCYANATES USING GLASS CAPILLARY GAS CHROMATOGRAPHY AND SELECTIVE DETECTION

V. DIRECT DETERMINATION OF ISOCYANATES USING NITROGEN-SELECTIVE AND ELECTRON-CAPTURE DETECTION

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SUMMARY

The possibilities of direct determination of isocyanates by glass capillary gas chromatography using nitrogen-selective or electron-capture detection was studied in some detail. It was found that only the former method was generally applicable, allowing the quantitative assay of trace isocyanates down to the low picogram range. A comparison with other methods for isocyanate determination, previously developed at these laboratories, was made.

INTRODUCTION

Previous communications in this series have dealt with the determination of amines and isocyanates as perfluoro fatty acid amides using glass-capillary gas chromatography (GC) and electron-capture (ECD) or nitrogen-selective detection (TSD)[1–3]. In the present paper the possibilities of analyzing isocyanates directly by glass capillary GC and TSD or ECD are investigated in some detail.

A GC method for the direct assay of isocyanates is attractive from several points of view and should have certain advantages in comparison with GC methods founded on hydrolysis of the isocyanates to the corresponding amines. Thus, the latter methods determine the sum of isocyanates and primary and secondary amines present in an air sample and the necessity of derivatizing the amines before GC makes these methods more laborious than a direct assay.

The greatest difficulty to surmount in a direct method is connected with the sampling procedure and concerns the instability of isocyanates in the presence of moisture and amines. This would seem to limit the practical use of a direct method

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to instances where the sample is free from interfering substances and where the collected isocyanates can be analyzed fairly rapidly after sampling. However, as demonstrated later, these difficulties can be diminished by the use of a suitable sampling liquid.

We are not aware of any previous investigations utilizing GC in connection with TSD for the assay of isocyanates. However, packed column GC-ECD determinations have been made previously. Thus, in 1967 Wheals and Thomson[4] reported the sensitivity of an isocyanate, *viz.*, 2,4-toluenediisocyanate (2,4-TDI), to ECD, and later Schanche and Hermann[5] developed a method for the assay of 2,4-TDI by means of packed column GC and ECD. The limit of detection was given as 50 pg. Wheals and Thomson also applied GC-ECD to some other aromatic isocyanates, *viz.*, 4,4'-diphenylmethanediisocyanate (MDI) and dianisidine diisocyanate (DADI). However, no detector signal was obtained for these compounds.

EXPERIMENTAL

Apparatus

Chromatographs and detectors. A Varian Model 3700 gas chromatograph equipped with a Carlo Erba on-column injection system and a Varian thermionic specific detector was used for the nitrogen-selective studies. The detector was optimized for maximum sensitivity to nitrogen-containing compouinds. Typical settings for the detector were: gas flow-rates, 4.0 ml/min of hydrogen and 180 ml/min of air; bead heating current, 6.8 scale divisions; bias voltage, −10 V; temperature, 290°C.

For GC-ECD a Carlo Erba Fractovap Model 4160 gas chromatograph equipped with a Model HI-25 electron-capture detector and Control Module 251 was employed in the constant-current mode: voltage, 50 V; pulse width, 0.1 μsec; standing current, 2.0 nA; temperature, 100–300°C. The same instrument with flame ionization detection (FID) was used for GC-FID measurements.

Gases. The carrier gases were helium for TSD and ECD and hydrogen for FID. The inlet pressure was 0.3 kg/cm^2 in all cases. The make-up gas for TSD was nitrogen at a flow-rate of 20 ml/min and for ECD, argon–methane (95:5) at 60 ml/min. These gases were dried over activated molecular sieve 5A and deoxygenated using an "Indicating Oxytrap" (Chrompack, Middelburg, The Netherlands). Hydrogen and air for TSD and FID were used without extra purification. Typical flow-rates for these gases were 4 and 180 ml/min, respectively, for TSD and 30 and 180 ml/min for FID.

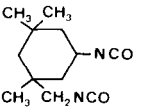
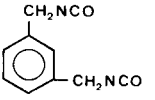
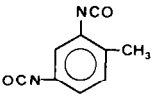
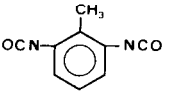
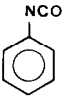
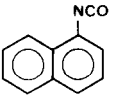
Materials

Chemicals. The isocyanates listed in Table I were obtained from the following suppliers: HDI and PHI from E. Merck (Darmstadt, F.R.G.); TMHDI from ICN Pharmaceuticals (Plainview, NJ, U.S.A.); 2,6-TDI from Aldrich-Europe (Beerse, Belgium) and IPDI, XDI, 2,4-TDI and NI from Fluka (Buchs, Switzerland). The stationary phase OV-73 and deactivation reagent octamethylcyclotetrasiloxane (D_4) were from Ohio Valley Speciality Chemicals (Marietta, OH, U.S.A.).

Solvents and solutions. Isooctane was glass-distilled grade from Rathburn Chemicals (Walkerburn, U.K.). Standard solutions of isocyanates were prepared by dissolving accurately weighed amounts of each isocyanate in isooctane and further dilution in isooctane to appropriate concentrations.

TABLE I

ISOCYANATES INVESTIGATED

Compound	*Abbreviation*	*Formula*
Hexamethylene diisocyanate CA No. 822-06-0*	HDI	$OCN(CH_2)_6NCO$
2,2,4-Trimethylhexamethylene diisocyanate CA No. 28679-16-5	TMHDI	$OCNCH_2C(CH_3)_2CH_2CHCH_3(CH_2)_2NCO$
Isophoron diisocyanate CA No. 4098-71-9	IPDI	
α,α′-Diisocyanato-*m*-xylene CA No. 3634-83-1	XDI	
2,4-Toluenediisocyanate CA No. 584-84-9	2,4-TDI	
2,6-Toluenediisocyanate CA No. 91-08-7	2,6-TDI	
Phenyl isocyanate CA No. 103-71-9	PHI	
1-Naphthyl isocyanate CA No. 30135-65-0	NI	

* CA = Chemical Abstracts Registry Number.

Procedure

Sampling. For sampling isocyanate in industrial air a midget impinger containing 10 ml of isooctane was used. In order to estimate the sampling efficiency and

extent of break-through, two impingers, each with 10 ml of isooctane, were connected in series. A 20-μl volume of an isocyanate solution in isooctane was injected into a silanized glass tube connected to the first impinger. A stream of air with a flow-rate of 1 l/min and a relative humidity of 60% was passed through the absorber chain. The sampling time was 5 min, and in order to ensure complete evaporation the tube was heated to 150°C. All connections were ground-glass joints. The impinger solutions were analyzed by injection directly on to the capillary column.

Column preparation. Duran 50 borosilicate glass capillary columns were drawn, deactivated with D_4 and coated with OV-73 stationary phase as previously described[2].

Quantitative analysis. Quantitative analysis was based on peak-height measurements throughout.

RESULTS AND DISCUSSION

Sampling

Sampling efficiency and break-through. The sampling efficiency was studied for HDI and 2,6-TDI. For both compounds, 98% was absorbed in the first impinger when an isocyanate solution containing 70 ng of isocyanate (7 pg/μl) was evaporated and swep into the impingers for 5 min, using an air flow-rate of 1 ml/min. Although no isocyanate was detected in the second impinger, a small break-through may well take place. When the amount of isocyanate was increased to 700 ng (70 pg/μl), a break-through of 3% was measured for HDI while 93% of it was absorbed in the first impinger. For 2,6-TDI, 99% was absorbed in the first impinger under the same experimental conditions. It thus appears that isooctane is a fairly effective absorption medium for isocyanates, retaining them in a high yield from air streams. The concentrations of isocyanates in the above experiments correspond to one fifth and two times, respectively, the Swedish threshold limit value (5-l sample).

Stability of isocyanate solutions. In order to ascertain the stability of humid isocyanate solutions in isooctane, air with a relative humidity of 60% was drawn through an impinger flask, containing 7 pg/μl of isocyanate, at a flow-rate of 1 l/min for 20 min. The solutions were kept in daylight at room temperature for a specified time and then analyzed. No degradation was observed after 2 days and after storage for 10 days a *ca.* 10% decrease was measured (8% for HDI, 11% for 2,6-TDI). It is concluded that isocyanate solutions in humid isooctane are only slowly degraded. However, in the presence of amines and similar compounds containing active hydrogens the situation may be different. Thus, it is well known that isocyanates easily react with primary and secondary amines forming urea derivatives. As these kinds of amines appear in industrial atmospheres together with isocyanates, interferences are to be expected on sampling.

Schanche and Hermann[5] used toluene for the absorption of 2,4-TDI. They reported that, if the absorption took place for 3 min in the presence of moist air, lower results were obtained, and they gave a formula correlating the results with the humidity of the air. The greater influence of moisture in this case is undoubtedly due to the considerably higher solubility of water in toluene.

TABLE II

DETECTION LIMITS FOR SOME ISOCYANATES USING TSD, ECD AND FID

Isocyanate	*Detection limit (fmol)*		
	TSD	*ECD**	*FID*
HDI	15	–	240
TMHDI	40	–	220
IPDI	35	–	200
XDI	50	40	200
2,4-TDI	10	200	200
2,6-TDI	10	200	200
PHI	30	–	200
NI	30	2000	200

* Measured at ECD maximum response temperature (see Fig. 2).

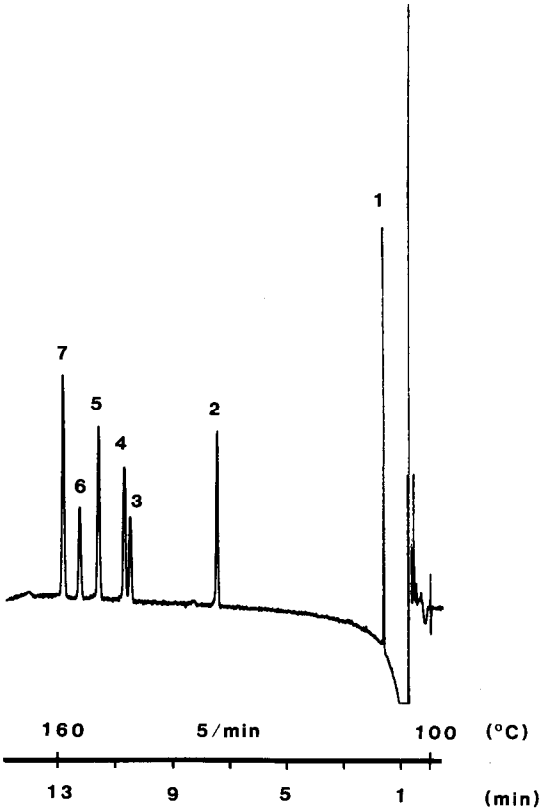


Fig. 1. Chromatogram with TSD of some of the isocyanates investigated. On-column injection of 1 μl of a 0.5 pmol/μl solution of PHI (1), 2,6-TDI and 2,4-TDI (2), NI (3), TMHDI (4 and 5) and IPDI (6 and 7). Column: 10 m × 0.32 mm I.D. Duran 50 glass capillary, D_4-deactivated, with OV-73 stationary phase (film thickness 0.4 μm). Temperature programming as shown. Carrier gas: helium at 0.3 kg/cm^2. Thermionic specific detector: bead heating current, 6.5 scale divisions; bias voltage, −10 V; temperature, 220°C; hydrogen flow-rate, 4 ml/min; air flow-rate, 180 ml/min; make-up gas, nitrogen (flow-rate 20 ml/min). Attenuation: $2 \cdot 10^{-12}$ A.f.s.

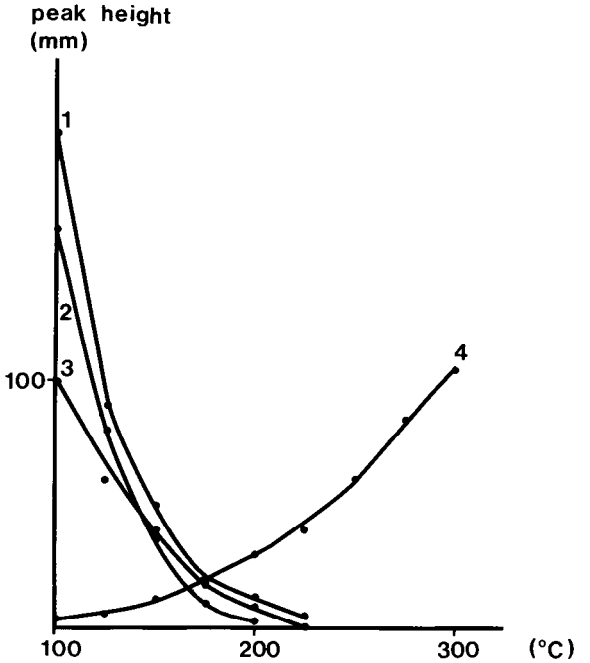


Fig. 2. Variation of the peak height of 2,6-TDI (1), 2,4-TDI (2), NI (3) and XDI (4) with ECD temperature in the range 100–300°C. On-column injection of 1 μl of a 2 ng/μl solution in isooctane, except for NI where a 10 ng/μl solution was used. Column as in Fig. 1. Electron-capture detector: constant-current mode; standing current, 2.0 nA; voltage, 50 V; pulse width, 0.1 μsec; make-up gas, argon–methane (95:5); flow-rate, 60 ml/min.

Gas chromatography

Capillary columns and separation of isocyanates. The choice of capillary column for the separation of isocyanates is not critical. Isocyanates are compounds which behave well on gas chromatography as shown by the symmetrical peaks in the chromatogram in Fig. 1. The two TDIs are not separated on the OV-73 column. TMHDI and IPDI each furnish two peaks. In the first case this is due to the fact that the sample of TMHDI, although labelled 2,2,4-trimethylhexamethylene diisocyanate, is a mixture of this compound and the 2,4,4-isomer. In the second case the two peaks are due to the existence of *cis*- and *trans*-isomers of IPDI.

Choice of detector. The detection limits with three different detectors were established (Table II). TSD and FID are general methods of detection for isocyanates, whereas ECD gives a signal only for certain compounds. This is in agreement with the investigation of Wheals and Thomson[4], who among several investigated isocyanates found only 2,4-TDI to be ECD-positive. TSD is by far the most sensitive of the tested methods; in one instance only, for XDI, was ECD more sensitive.

The importance of ascertaining the nature of the temperature dependence of the ECD is demonstrated in Fig. 2. As can be seen, for ECD-positive isocyanates, the response to 2,4- and 2,6-TDI and NI decreases with temperature, whereas that to XDI increases. This implies different kinds of electron-capture mechanisms for the two groups of isocyanates[6]. In contrast to the isocyanates, perfluoro fatty acid amides

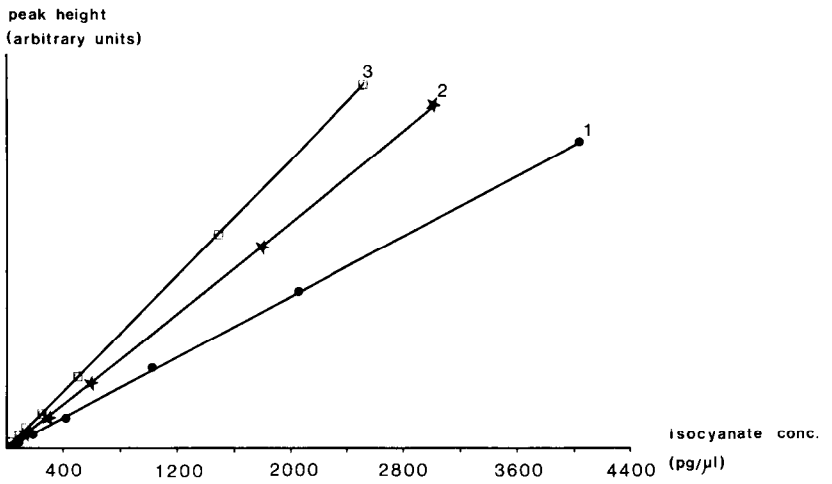


Fig. 3. Calibration curves using TSD for 2,6-TDI (1), HDI (2) and PHI (3). Chromatographic conditions as given in Fig. 1.

of the corresponding amines do not exhibit a temperature-dependent response with the present ECD, but have a more or less constant sensitivity in the temperature range 100–300°C.

Linear range and detection limits. Calibration plots for some isocyanates using TSD are given in Fig. 3, demonstrating a linear response over a wide range. Detection limits for TSD, ECD and FID calculated as the amount giving a signal-to-noise ratio (SNR) of 2:1 are listed in Table II. It is seen that TSD is the best choice for the direct assay of trace isocyanates, showing a high response (detection limits 10–50 fmol) to all kinds of compounds. It is *ca.* 4–20 times more sensitive than FID. ECD is generally less sensitive than TSD and can, furthermore, be applied only to certain isocyanates. Thus, of the eight isocyanates tested only one (XDI) had a higher response to ECD than to TSD. No purely aliphatic isocyanates were ECD positive. For IPDI the detection limits given refer to the most abundant isomer and for TMHDI to peak 5 in Fig. 1.

TABLE III

DETECTION LIMITS OF SOME GC METHODS FOR THE ASSAY OF ISOCYANATES

Isocyanate	*Detection limit (fmol)*			
	Determination as HFBA amides*		*Direct method*	
	ECD	*TSD*	*ECD*	*TSD*
HDI	7	40	–	15
TMHDI	5	50	–	40
IPDI	5	50	–	35
XDI	2	50	40	50
TDI	0.8	80	200	10

* HFBA = Heptafluorobutyric acid.

Comparison with other GC methods for the assay of isocyanates

Previous papers in this series, dealing with the assay of isocyanates, have described their determination as perfluoro fatty acid amides by glass capillary GC after hydrolysis to the corresponding amines and conversion of these into amides. Both ECD and TSD were successfully applied. This method gives the sum of isocyanates and amines present in an air sample, because of the hydrolytic step involved.

The present direct method is specific for isocyanates, but its weakness is the instability of isocyanates in the presence of certain reactive compounds, which can lead to low results. Although the present investigation indicates that the hydrolytic influence of moisture in the air is slight, when isooctane is used as absorption medium, the effect of the simultaneous presence of water and other interfering compounds such as amines has still to be ascertained.

Detection limits for some isocyanates using the various GC methods are collected in Table III. It is seen that the amide method with ECD is the most sensitive general method available, whereas ECD in combination with direct determination can only be applied in isolated cases. TSD is universal with both methods and generally more sensitive with the direct than with the amide method. An advantage of TSD is its wider linear range compared to ECD.

It is concluded that the amide method offers a highly sensitive assay of amines plus isocyanates with ECD and a moderately sensitive one with TSD, whereas the direct method with TSD determines isocyanates with a universally good sensitivity.

The fact that both TSD and ECD are selective is also of importance, since selectivity towards interfering substances often determines the applicability of a certain method.

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