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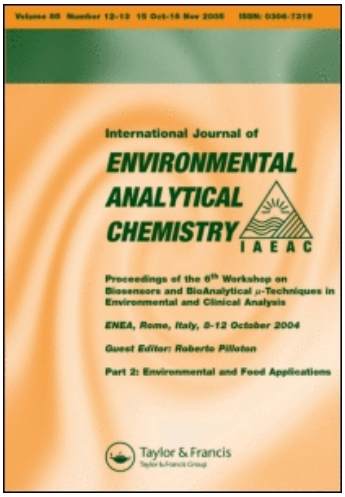

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A Comparison of Methods for the Determination of Isocyanates in Air†

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Isocyanates are in widespread use in certain industries such as in the manufacture of polyurethane products, paints and elastomers. The occupational exposure limit for isocyanates corresponds to 0.3 μg of isocyanate per sample using a 15 minute sampling time.

Airborne isocyanates cause a variety of respiratory problems and workplace monitoring is therefore necessary. Two methods have recently been published by the Health and Safety Executive, one colorimetric and one HPLC using both electrochemical and UV detection. This study has compared these two methods using both field samples and laboratory generated standard atmospheres over a range of concentrations relevant to test the method at occupational exposure levels. The results of the field study showed that the colorimetric method was generally being used at its limit of sensitivity. Although potentially more sensitive, HPLC did show some interference with the field samples, thus limiting its sensitivity. The laboratory study showed good correlation between the two methods down to below half the TLV.

KEY WORDS: Isocyanate air methods, isocyanate method comparison, isocyanate atmosphere generation.

INTRODUCTION

A variety of isocyanates are in widespread use in the chemical industry, such as in the production of polyurethane foams, paints, varnishes, lacquers, adhesives, elastomers, synthetic rubbers, plastics,

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insulation materials etc. Exposure to isocyanates can cause a variety of respiratory problems such as rhinitis, rhinophyngitis and various lung disorders and asthmatic manifestations. They can also cause skin irritations such as eczema and eye problems such as conjunctivitis. It is therefore important to monitor the atmospheric exposure of workers at risk. The British Control Limit for isocyanates is 20 $\mu g/m^3$ (8 hour time weighted average). This is equivalent to 0.3 μg of isocyanate per sample for a 15 minute sampling period at 1 litre/minute. Several methods have been used to determine isocyanate levels in air including colorimetric methods,[1] gas liquid chromatography (GLC),[2,3] high performance thin layer chromatography (HPTLC)[4] and high performance liquid chromatography (HPLC).[5-7] The chromatographic methods tend to measure individual isocyanates whereas the colorimetric method determines isocyanates as a class of compounds. Two "standard methods" have recently been published by the Health and Safety Executive, one colorimetric[8] and one using HPLC.[9] The HPLC method has the advantage of greater sensitivity and is able to discriminate between individual isocyanates, whereas the colorimetric method is simpler, cheaper and requires less skilled operators. The aim of this investigation was to compare the standard HPLC method with the standard colorimetric method for the determination of methylene 4,4-diphenyl-di-isocyanate (MDI) in air using:

a) standard atmospheres generated in the laboratory; and

b) samples from industrial locations.

Both methods were taken from standard publications and were deliberately not modified in any way by the authors.

MATERIALS AND METHODS

Atmosphere generation

Standard atmospheres of MDI were generated in the laboratory using home built apparatus. A nebuliser was used to generate the initial aerosol which was then diluted in a mixing chamber with dry nitrogen and passed into the sampling chamber. Parallel samples were taken isokinetically from the sample chamber to allow direct comparison of the two methods.

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Colorimetric method

Samples were collected in impingers containing a dimethylformamide/hydrochloric acid mixture. Both standard atmospheres and industrial locations were sampled for approximately 15 mins at 1 litre/min using stabilised flow personal sampling pumps. Trapping solutions were stored at 4°C until analysis. On the day of analysis these solutions were added to a solution of sodium nitrite and sodium bromide and then reacted with aqueous sulphamic acid and *N*-(1-naphthyl)ethyl-diamine hydrochloride. The absorbance was then measured at 572 nm and compared with standards. Full details of the procedure are given in the published method.[8]

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HPLC method

Samples were collected in impingers containing 1-(2-methoxyphenyl) piperazine (MPP) in toluene. Both standard atmospheres and industrial locations were sampled at 1 litre/min for approximately 15 mins. Solutions were stored at 4°C until day of analysis, but were left overnight at room temperature to allow derivatisation to run to completion. Samples were then evaporated to dryness and acetylated with acetic anhydride in acetonitrile, before injection onto the HPLC, under the following conditions:

—column: spherisorb ODS 5 μM 25 cm;
—eluant: 60% acetonitrile in sodium acetate buffer pH 6;
—detector: UV at 240 nm and electrochemical at +0.8 volts;
—flow rate: 2.0 ml/min.

Standards were processed using the same procedure as for unknown samples and the response ratio was calibrated from the MDI monomer peak using the formula:

$$\text{response ratio} = \frac{\text{EC response}}{\text{UV response}}.$$

Only samples with a response ratio between 0.75 and 1.5 were counted as isocyanate. The sum of the isocyanate peaks was used to calculate the total isocyanate concentration.

RESULTS

No problems were encountered with the setting up of the colorimetric method. Several problems were encountered with the HPLC method even though this was carried out by experienced operators. The electrochemical detector took a long time to stabilise (which is not uncommon with this type of detector). The purity of the MPP was found to be critical as several spurious peaks were obtained with one particular batch of this reagent. The toluene in which this reagent was dissolved had to be extremely dry. One further problem with the HPLC method was encountered when sampling from one of the industrial locations as a large number of contaminating peaks were found. This limited the sensitivity of the HPLC method and increased the HPLC run times. Specimen chromatograms are shown in Figure 1.

For the field based comparison three factory sites were visited all of which were using MDI in their manufacturing process. Exposure levels were expected to be low and were in fact below the limit of detection of the colorimetric method (0.6 μg of MDI in trapping solution). It was therefore not possible to compare the two methods using the factory air samples.

The results of the method comparison using standard atmospheres generated in the laboratory are shown in Figure 2.

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DISCUSSION

The generation of standard atmospheres to contain an exact concentration of volatile isocyanates is very difficult due to losses attributable to adsorption onto glassware. Due to its low vapour pressure a vapour atmosphere of MDI is particularly difficult to generate at room temperature. Consequently in this experiment the atmosphere was generated as an aerosol using ethyl acetate as a carrier. This solvent was used for three reasons:

a) it does not react chemically with isocyanates;

b) it has a high volatility;

c) it is widely used as a solvent for MDI in industry.

This method of generation proved successful as can be seen from the

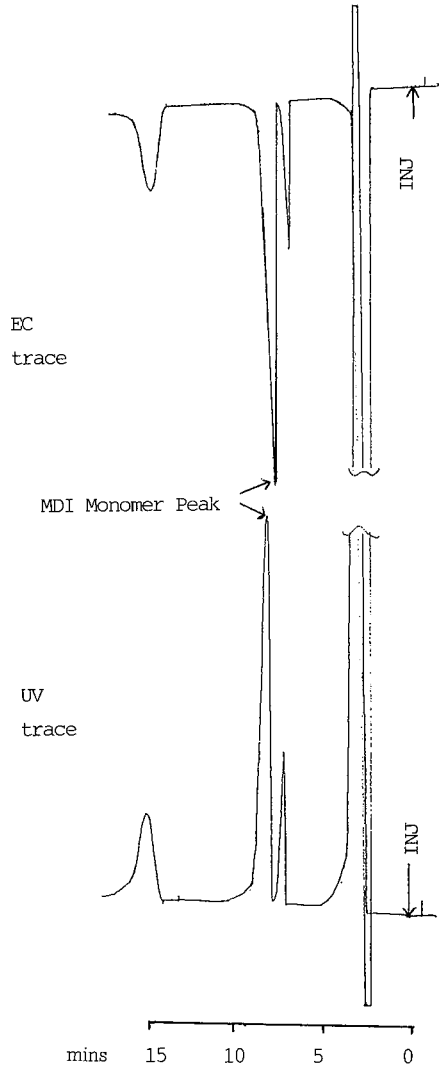

FIGURE 1 Specimen HPLC chromatograms of standard solution.

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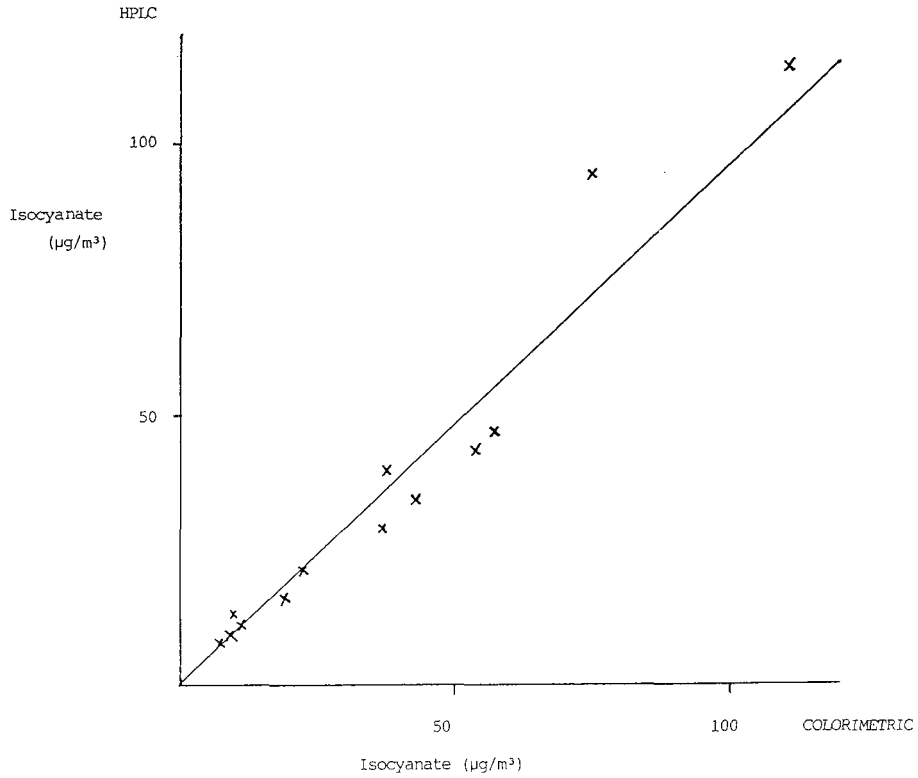

FIGURE 2 Plot of isocyanate levels by HPLC against those found using colorimetric methods.

levels achieved in Figure 2 and allowed a comparison of methods at levels below the British Control Limit for isocyanates.

The results in Figure 2 illustrate that a good correlation ($r = 0.972$, slope $= 1.04$) was shown between the two methods. The agreement was good down to air levels at least half of the British Control Limit. The colorimetric method is close to its limit of detection at the current control limit. The HPLC method was more sensitive using pure standards or at "clean locations" but the sensitivity of this method was no better than the colorimetric method when interfering peaks co-eluted.

We feel that further work is needed on the HPLC method in order to allow its potential for greater sensitivity to be realised.

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References

1. K. Marcali, *Anal. Chem.* **29,** 552 (1957).
2. G. Audunsson and L. Mathiasson, *J. Chromatogr.* **261,** 253 (1983).
3. A. de Pascale *et al.*, *J. Chromatogr.* **256,** 352 (1983).
4. P. A. Ellwood, H. L. Hardy and R. F. Walker, *Analyst* **106,** 85 (1981).
5. D. A. Bagon, C. J. Warwick and R. H. Brown, *Am. Ind. Hyg. Assoc. J.*, **45,** 39 (1984).
6. C. J. Warwick, D. A. Bagon and C. J. Purnell, *Analyst* **106,** 676 (1981).
7. E. H. Nieminen, L. H. Saarinen and J. T. Laaksoi, *J. Liq. Chrom.* **6,** 453 (1983).
8. *Methods for the Determination of Toxic Substances in Air, No. 20, Determination of Organic Isocyanates in Air* (Health and Safety Executive, London).
9. *Organic Isocyanates in Air, Methods for the Determination of Hazardous Substances No. 25* (Health and Safety Executive, London).

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