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DETERMINATION OF AIRBORNE 2,4-TOLUENEDIISOCYANATE VAPORS

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SUMMARY

An accurate and convenient sampling and analytical method was developed for airborne 2,4-toluenediisocyanate (TDI). A chromophoric derivatizing reagent was used to convert the TDI to a stable urea derivative during collection for subsequent quantification by liquid chromatography. The overall accuracy (at the 95% confidence level) and precision of the method are $\pm 7.9\%$ and $\pm 10.0\%$ respectively under laboratory conditions. Long term stability was observed for both the reagent coated sorbent tube and the TDI urea derivative. A TDI concentration of 1 ppb can be detected by taking a 15-l sample volume.

INTRODUCTION

Diisocyanates are widely used in the production of polyurethane foams, coatings, and elastomers. TDI, which is commercially available as a mixture typically of 80% 2,4- and 20% 2,6-isomers, is generally used in producing flexible polyurethane foams. Accordingly, these compounds occur in many industrial environments. The most troublesome property of many organoisocyanates is the irritating character of their vapors, particularly to the respiratory tract where the organoisocyanates can also act as a respiratory sensitizer. Sensitized individuals show asthma-like symptoms upon further exposure to very low concentrations¹⁻³. Studies of occupational exposure to TDI suggests that the present threshold limit value (TLV) standard for TDI of 0.02 ppm does not adequately protect the workers from becoming sensitized. The National Institute for Occupational Safety and Health (NIOSH) has recently recommended a new standard of 0.005 ppm ($35 \mu\text{g}/\text{m}^3$) as a maximum time-weighted average exposure in working environment with a ceiling value of 0.02 ppm ($140 \mu\text{g}/\text{m}^3$) for any 10-min sample. These proposed changes in the standard create a need for a more sensitive analytical method for the evaluation of the air levels in work areas.

Methods of sampling and analysis of airborne isocyanates include colorimetry⁴⁻⁷, gas chromatography with electron-capture detector⁸, and high-performance

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liquid chromatography (HPLC)⁹⁻¹¹. Colorimetric methods have the drawbacks of low sensitivity, interferences from primary aromatic amines, and not being capable of differentiating among the different isocyanate species. The gas chromatographic method was claimed to be sensitive enough to detect a quantity of 0.05 ng. However, the method seems to have a very narrow linear range which limits its practical usage. The NIOSH method¹¹ employs a HPLC method to separate and quantify the urea derivatives as obtained from reactions between a nitro reagent (N-4-nitrobenzyl-N-propylamine) and the organoisocyanates. The method has two serious disadvantages. The first is the decomposition of the nitro reagent during sampling in an oxidizing or reducing atmospheres¹². The second is the deterioration of the silica column caused by excess nitro reagent in the samples¹².

This paper reports a sampling and analytical procedure for the determination of TDI vapors in work environments. The method employs 1-(2-pyridyl)piperazine as the derivatizing reagent, which forms a stable urea derivative upon exposure to TDI vapors. The urea derivative is then analyzed by a reversed-phase HPLC technique with a UV detector at 254 nm.

EXPERIMENTAL

Apparatus

A HPLC system (Waters Assoc., Milford, MA, U.S.A.) equipped with a Model 440 UV detector set at 254 nm, a Model U6K injector, two Model 6000A solvent-delivery pumps, a Model 660 solvent programmer, and a μ Bondapak C₁₈ column (30 cm \times 3.9 mm) was used.

Chemicals

Practical grade toluene 2,4-diisocyanate and 1-(2-pyridyl)piperazine were obtained from Aldrich (Milwaukee, WI, U.S.A.). Solid support Gas-Chrom Z 60-80 mesh was obtained from Applied Science Labs. (State College, PA, U.S.A.). Methylene chloride, HPLC-grade methanol and acetonitrile were obtained from Fisher Scientific (Cincinnati, OH, U.S.A.). PIC-B5 (pentanesulfonic acid) reagent was purchased from Waters Assoc.

Standard TDI vapor generation system

A TDI vapor generation technique using a PTFE permeation tube was employed in this study to evaluate the sampling and analytical method. A detailed description of the system can be found in the literature and will not be repeated here¹³. The system is capable of generating TDI concentrations from less than 1 ppb* up to 0.3 ppm with an accuracy of $\pm 2\%$. This range covers most of the concentrations that would be encountered in the work areas. For higher concentration, a longer tube or multiple tubes can be used.

HPLC solvents preparation

Dissolve the entire contents of the vial of PIC-B5 reagent in 1 l HPLC-grade methanol or double-distilled water in a 1-l flask as recommended by supplier. Shake

* Throughout this article, the American billion (10^9) is meant.

for 5 min to ensure thorough mixing. A pH value of 3.5 is maintained by glacial acetic acid which is present in the reagent. The solvent was degassed by first purging with nitrogen gas for 10 min and kept at a reduced pressure (25 mmHg) for about 30 min or until no air bubbles were observed. Double-distilled water was filtered through a 0.45- μm Millipore type AA filter and the methanol was filtered through a PTFE filter before degassing.

Preparation of sampling tubes

Glass tubes (6 cm \times 4 mm I.D.) were packed with 100 mg of the coated sorbents and silanized glass wool was placed in both ends of the tubes to contain the sorbents. Gas-Chrom Z was conditioned at 250°C for 8 h under a stream of helium or nitrogen carrier gas to purge adsorbed organics. Dissolve 140 μl piperazine reagent into 20 ml methylene chloride in a 50-ml beaker. Weigh out 3 g of the conditioned solid support and wet it with 5 ml methylene chloride in a 50-ml beaker. Pour the piperazine solution into the beaker and stir the beaker occasionally over a period of 30 min. Pour the mixture into a petri dish and evaporate the solvent at room temperature. The sorbent is now ready for use. The silanized glass wool used as a retaining plug was also coated with the 5% absorbing reagent in the same manner. It was found previously that uncoated silanized glass wool will adsorb TDI in an irreversible manner and thus reduce the sample recovery. Therefore, it is important to coat the glass wool also.

Preparation of TDI derivative for calibration

Add 0.5 ml of TDI to 30 ml toluene in a 50-ml beaker. Add 2 ml of the reagent to 35 ml toluene in a 100-ml beaker. Slowly pour the TDI solution into the reagent solution with stirring. Let the mixtures stand for about 1.5 h with occasional swirling. Filter the solution and dry the precipitate at 80°C until constant weight is obtained. The derivative is further purified by recrystallization in a methanol-water system. Dissolve the derivative in a minimum amount of hot (50°C) methanol and then add distilled water dropwise to the solution to initiate precipitation. Allow the solution to cool slowly to room temperature. Needle-type crystals were obtained on the surface of the glass container. Recrystallization was carried out twice and the purity of the derivative was better than 99.5% as estimated from chromatographic analysis. The melting point of the derivative is 198–199.5°C. A molar extinction coefficient of 60,850 l/mole \cdot cm was measured at 252 nm, which is very close to the reported¹⁴ value of 60,500 l/mole \cdot cm. The purity of this 2,4-TDI derivative was further verified by an elemental analysis performed by outside laboratory. Elemental analysis gives the following compositions: C found 64.6% calculated 64.7%, H found 6.38% calculated 6.39%, N found 22.19% calculated 22.37% and O found 6.15% calculated 6.39%. The purified derivative was then used to prepare standard solutions for calibration.

HPLC operating conditions

The results presented here for 2,4-TDI analysis were obtained using gradient elution from 25% A to 40% B in 15 min at 2 ml/min, where A is methanol with PIC-B5 reagent and B is water with PIC-B5 reagent. The convex gradient programming curve No. 5 of the Model 660 solvent programmer was used.

Procedure

The sampling tubes previously described were used to collect the TDI vapor from the vapor generation system. A hypodermic needle (gauge 21) was used as critical orifice to control the sampling flow-rate and each tube was calibrated with a soap bubble meter for the actual flow-rate before sampling. After sampling, entire contents of the sampling tube were added to a small glass vial for desorption by adding 1 ml methanol to each vial. A 30-min desorption time was allowed with occasional stirring before sample analysis. The injection volume was generally between 10 to 20 μ l and the peak areas were calculated by multiplying the peak height by the peak width at half height.

RESULTS AND DISCUSSION

Representative liquid chromatograms of the reagent blank and the urea derivative with the reagent are shown in Figs. 1 and 2, respectively. As can be seen from Fig. 1, there are several trace impurities present in the derivatizing reagent. These impurities required gradient elution to resolve the peaks of interest.

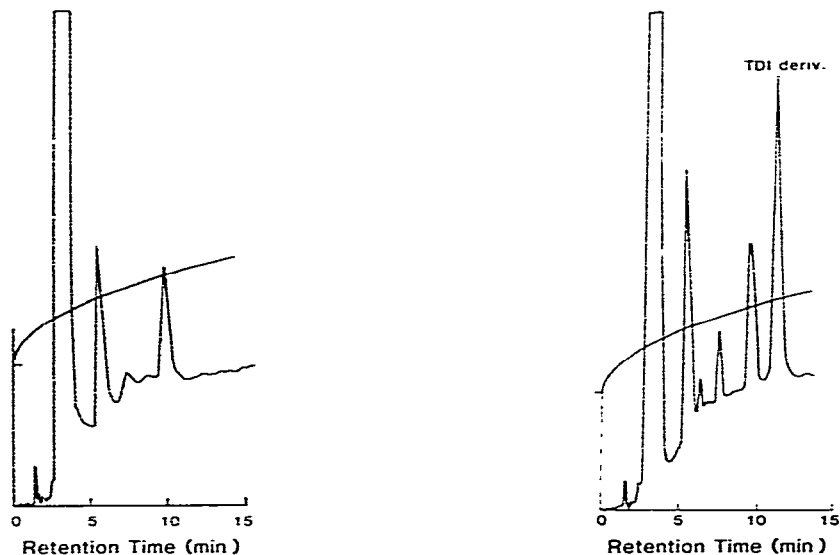


Fig. 1. 1-(2-Pyridyl)piperazine reagent blank. Column: μ Bondapak C_{18} ; solvent: methanol-water-PIC-B5, 25 to 40% methanol in 15 min. curve No. 5; 0.02 a.u.f.s.

Fig. 2. Chromatogram of TDI urea derivative with derivatizing reagent. Conditions as in Fig. 1; amount of TDI derivative, 100 ng.

Fig. 3 presents the calibration curve obtained with solutions of the purified 2,4-TDI urea derivative. A minimum of 5.82 ng of the urea derivative or an amount equivalent to 2.02 ng of TDI was detected in this study. The error bars shown in Fig. 3 are the range of replicate measurements. The calibration curve is essentially linear over the range of from 5.82 ng to 145.5 ng of the urea derivative. The calibration was checked again after a period of three months to assure that the system was performing consistently. Virtually no deviation from the original calibration was observed. The

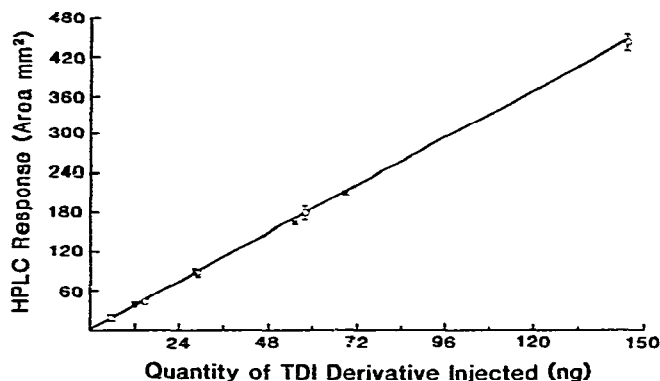


Fig. 3. TDI Derivative calibration curve; ○, initial values, ×, subsequent verification.

calibration curve thus obtained was used as working standards for the evaluation of sampling and analytical methodology developed.

The sampling and sample recovery efficiency of the entire method was first investigated by collecting samples from the vapor generation system at different concentration levels, which ranged from 0.99 ppb (one fifth of the proposed standard) up to 42.3 ppb (twice the proposed ceiling value). A set of six samples were collected at each of five concentration levels and each set of samples was analyzed and compared with the concentrations obtained from gravimetrically calculated values of the vapor generation system. The total sampling and analytical recovery average for the entire method was 106.3%. Fig. 4 shows the relationships between the measured concentration and the calculated concentration using regression analysis. The correlation coefficient is 0.997 and the percent relative standard deviation of the slope is 1.60%. Lower concentrations could be quantified by using a larger air sample or by injecting a larger volume of sample. The precision of the method expressed as percent relative standard deviation is $\pm 10.0\%$, which is an average of the five sets of samples analyzed. The accuracy of the method is $\pm 7.9\%$ calculated at a 95% confidence level.

Stability of the desorbed samples was tested for a period of 28 days. Six samples collected at 20.3 ppb were desorbed and stored at room temperature for the first seven days and then stored in a refrigerator for the rest of the test period. The results are shown in Fig. 5, where the range indicates two standard deviations from the mean. The differences among the means from these analyses were insignificant by Student *t*-test ($p \leq 0.05$).

The stability of the reagent coated sampling tubes were studied by storing six blank tubes for a period of 45 days under ordinary laboratory conditions. Another set of six tubes were made from freshly prepared sorbent. These two sets of sampling tubes were then used to collect samples at the same time and under the same conditions. A *t*-test was made on the results of analyses, which showed that the difference between the means was not significant ($p \leq 0.05$). Therefore, the reagent coated sorbents appear to be stable during storage at room temperature for as long as one and a half months. This property makes it very convenient in that the reagent coated sorbents can be prepared in a large batch and stored for a period of time.

An important aspect of a method is the effect of storage time upon sample

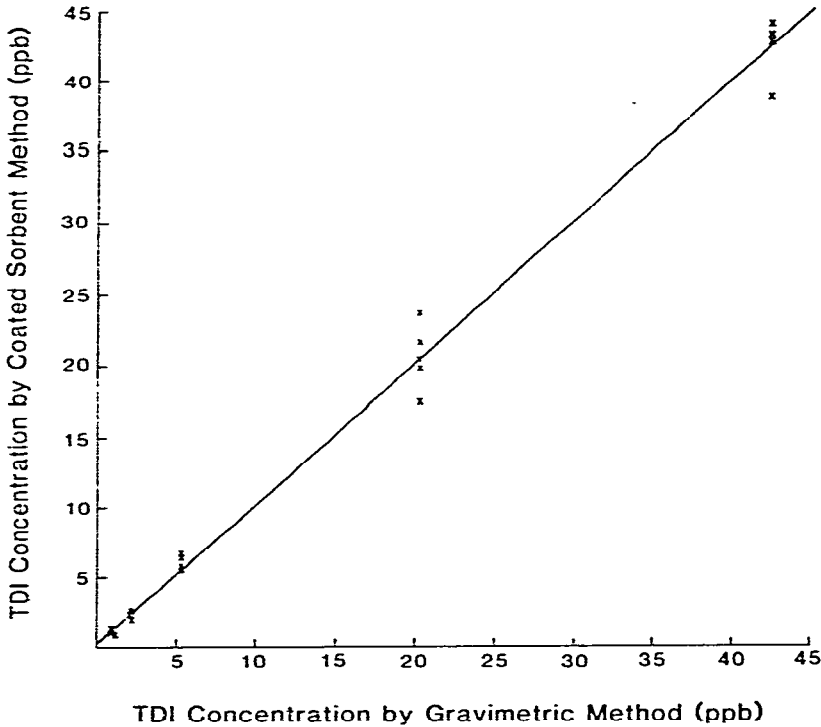


Fig. 4. Gravimetric calibration vs. HPLC method for TDI measurement.

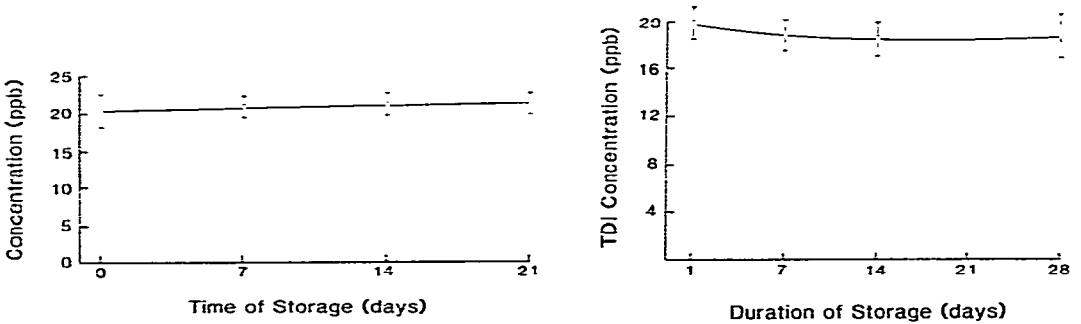


Fig. 5. Stability of TDI derivative in methanol solution.

Fig. 6. Recovery of TDI after sample storage under dry condition.

recovery. A study was made to test the effect of prolonged sample storage upon the recovery efficiency of the method. Experiments were carried out under two different conditions, the first used TDI vapors diluted with dry air and the second used humidified air (90% relative humidity) for dilution.

Four sets of samples with six samples in each set were collected at the same time and under the same conditions in the dry dilution air system. One set of samples was analyzed at the day of collection. A second set of samples was stored at room temperature and analyzed at day 7. The rest of the samples were then stored under

refrigeration. The third set of samples was analyzed at day 14 and the last set at day 28. The results of the test are shown in Fig. 6, again, the range indicates two standard deviations from the mean. It appears that there may be some sample loss during storage at room temperature over a period of seven days. No further loss was found after seven days with samples stored in the refrigerator. However, the differences among the means are all less than 7% which lies within the range of accuracy of the method. This may imply that the differences observed are due to variations in sample analysis.

The samples collected under humid conditions were used to simulate the actual field sampling situations where water vapor is always present. Eighteen samples were collected at the same time from the vapor generation system which was humidified to about 90% relative humidity by bubbling dilution air through a saturated salt solution. A set of six samples was analyzed at the day of collection and the rest of the samples were stored under room temperature. A second set of six samples was analyzed at day 7 and the remaining samples were stored in a refrigerator and analyzed at day 14. It was found that approximately 30% losses of TDI molecules occurred in the flow dilution system before it reached the sampling manifold at this humidity level. The losses are believed to be due to wall adsorption. This is supported by the fact that similar concentrations were consistently observed when the system was monitored by the Marcali method, continuous tape monitor; and this method¹⁵. Essentially complete sample recovery was observed after one week storage by comparing the results from the first and the second sets of samples. Approximately 7% loss was found for samples stored more than one week. The results from this experiment are somewhat different from the previous one in which a decrease in sample recovery was found for one week storage under room temperature. The effect of storage for a period of longer than seven days was found to be the same in both dry and humid sampling conditions. The results of this humidity study indicate that (1) the water vapor does not displace the TDI collected, (2) the water vapor does not inhibit the derivatization reaction, (3) no hydrolysis of the derivative once it was formed, (4) the moisture has no effect on the desorption efficiency.

Finally the capacity of the sampling tubes was studied to see if the method is suitable for long term 8-h sampling at concentration levels that might be expected in the work environments. Two concentration levels were studied in this experiment, one at 40.4 ppb and the other at 5.1 ppb. Two tubes were connected in series and the second tube was changed at certain time intervals during the sampling process. The sampling flow-rate was set to about 160 ml/min by using a gauge 27 hypodermic needle. The first tube serves as sample collection tube and the second tube serves as back-up tube to trap the break-throughed TDI molecules, if there is any. The back-up tubes were analyzed first to see if break-through has occurred and the front tube was then analyzed to confirm the observation. No detectable amount of TDI derivative was found in any of the back-up tubes. This means that no break-through has occurred after 8-h sampling at concentrations of 5.1 and 40.4 ppb. It is also confirmed by the quantitative recovery of TDI derivative from the front tubes. The deviations of the recovered TDI from the calculated values were 0.7% and 2.1% for 40.4 and 5.1 ppb levels, respectively. These deviations are well within the experimental error. Therefore, the sampling tubes should be capable of 8-h sampling at concentration levels normally encountered in the industrial environments for compliance study.

A separation scheme has also been worked out to separate the 2,4- and 2,6-TDI isomers. A linear gradient elution from 100% A to 100% B in 15 min at a flow-rate of 2 ml/min was used, where A is acetonitrile-methanol-water (5:15:80) buffered with PIC-B5 reagent and B is acetonitrile-methanol-water (15:25:60) buffered with PIC-B5 reagent. The retention times are 8.9 min and 11.1 min for 2,6-TDI and 2,4-TDI derivative, respectively. We were unable to differentially crystallize the 80:20 mixtures of 2,4- and 2,6-TDI derivatives at this time to obtain a pure 2,6-TDI derivative. No further study was made to characterize the performance of the method for 2,6-TDI isomer.

CONCLUSIONS

The analytical method developed is sensitive enough to detect a TDI concentration of 1 ppb in a 15-l sample volume, which is one fifth of the new proposed standard. Concentrations lower than 1 ppb can also be detected by increasing the sample volume and/or increasing the sample injection volume of HPLC. The derivatizing reagent used has the advantages of that it is a stable liquid, high boiling point (b.p. 283°C), completely miscible with water, soluble in several solvents, and commercially available. In general, interferences for the method would be any compound that would reduce the adsorption efficiency of the coated sorbents for TDI or any compound that would have the same retention time as the TDI derivative in the HPLC analysis. Toluene diamine, a hydrolysis product of TDI, was tested for its retention time under the same HPLC condition and was found not to interfere with the analysis. Once TDI was collected, it does not appear to be affected by water vapor. The reagent coated sorbents can be effectively used within a period of one and a half months after its preparation. The sampling tube developed for TDI collection is convenient to use in the field because no fragile glassware was used and problems associated with the spill of the sampling solutions is avoided.

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