DIISOCYANATES

1,6-HEXAMETHYLENE DIISOCYANATE (HDI)
TOLUENE-2,6-DIISOCYANATE (2,6-TDI)
TOLUENE-2,4-DIISOCYANATE (2,4-TDI)

Method no.: 42

Matrix: Air

Procedure: Samples are collected by drawing a known volume of air through glass fiber filters coated with 0.1 mg of 1-(2-pyridyl)piperazine (1-2PP) which are contained in open-face cassettes. Samples are extracted with 90/10 (v/v) acetonitrile/dimethyl sulfoxide (ACN/DMSO) and analyzed by high performance liquid chromatography (HPLC) using an ultraviolet or fluorescence detector. (The coated filters used in Method 47 for MDI are also acceptable for this procedure. Those filters are coated with 1 mg instead of 0.1 mg of 1-2PP.)

Recommended air volume and sampling rate: 15 L at 1 L/min

Analyte	2,6-TDI	HDI	2,4-TDI
Target concentration, µg/m^3 (ppb):	140(20)	140(20)	140[1](20)
Detection limit of the overall procedure, µg/m^3 (ppb):	1.6(0.23)	2.3(0.32)	1.3(0.17)
Reliable quantitation limit, µg/m^3 (ppb):	2.3(0.32)	2.9(0.43)	2.5(0.36)
Standard error of estimate at target concentration, %: (Section 4.9)	7.63	7.79	6.89

[1]OSHA PEL (Air concentrations are based on 15-L air sample volume.)

Special requirements: It is recommended that coated glass fiber filters be stored at reduced temperature until used for sampling.

Status of method: Evaluated method. This method has been subjected to the established evaluation procedures of the Organic Methods Evaluation Branch.

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1. General Discussion

1.1 Background

1.1.1 History

Some of the earliest procedures to determine atmospheric diisocyanate concentrations were developed by Ranta and Marcali (Ref. 5.1). Both of these procedures are inconvenient because they use a bubbler for sampling and their colorimetric analyses are non-specific. A later sampling procedure uses p-nitrobenzyl-N-n-propylamine (nitro reagent) in toluene bubblers (Ref. 5.2). While this method is specific for diisocyanates, it still retains the use of the bubbler and nitro reagent which is unstable when stored for long periods of time, even if it is kept at reduced temperature. The past couple of years have seen several new derivatizing reagents being used; they include N-methyl-1-naphthalenemethylamine (Ref. 5.3), 9-(n-methylaminomethyl)-anthracene (Ref. 5.4) and 1-(2-pyridyl)piperazine (1-2PP) (Refs. 5.5-5.7). The collection procedure of these new studies all involve the use of toluene bubblers. The purpose of this study was to find a collection system that does not use a bubbler, yet retains the sensitivity, precision and accuracy of the nitro reagent method.

1-2PP is a suitable derivatizing reagent, when coated on a glass fiber filter, for several reasons:

1) The high boiling liquid is retained on a glass fiber filter and stability is not a problem.

2) The rapid and exothermic reaction with both aromatic and aliphatic diisocyanates results in derivatization on the filter (Ref. 5.7).

3) The derivatives have higher molar absorptivities in the UV region than those formed with nitro reagent which allows the extraction volume to be larger without loss of sensitivity (Ref. 5.5).

This procedure compares favorably when tested side-by-side with the nitro reagent method by Cummins (Ref. 5.10) for 2,4-TDI. (Section 4.10) Additional work is being done to study 4,4'-methylenediphenylisocyanate and isophorone diisocyanate using 1-2PP as the derivatizing reagent.

Additional work was performed on this procedure to reflect to change in Title 29 CFR 1910.1000, Table Z-1-A in 1989. The Ceiling PEL of 0.14 mg/m^3 for 2,4-TDI was replaced with an 8-h TWA PEL of 0.04 mg/m^3. The sampling time can be increased to 240 min at a sampling rate of 1 L/min. (Sections 4.6 and 4.12)

1.1.2 Toxic effects (This section is for information only and should not be taken as a basis for OSHA policy.)

Continued inhalation of diisocyanate vapors or mists can cause nausea, headache, coughing, irritation of the nose and throat, shortness of breath and chest discomfort. Massive exposure can cause severe coughing spasms, bronchitis and chemical pneumonitis. Some people can become sensitized to isocyanates and may suffer asthmatic attacks and respiratory distress when subsequently exposed to very low concentrations (Ref. 5.9). Recent studies have produced conflicting results about the mutagenicity of TDI (Refs. 5.1 and 5.9). No data has been found to indicate that diisocyanates are carcinogenic or teratogenic (Refs. 5.1 and 5.9).

1.1.3 Operations where exposure may occur

The manufacture of polyurethane foams, coatings, and elastomers potentially exposes a minimum of 100,000 workers to diisocyanates (Ref. 5.2). Diisocyanates can be found in paints, insulation, adhesives, automobile bumpers, shoe soles, and hundreds of other applications (Refs. 5.2 and 5.8). Over 700 million pounds of diisocyanates were produced in 1975 (Ref. 5.2).

1.1.4 Physical properties

analyte	2,6-TDI	HDI	2,4-TDI
CAS no.:	91-08-7	822-06-0	584-84-9
MW:	174.16	168.20	174.16
bp, °C(mm Hg):	96(1.5)	213(760)	251(760)
mp, °C:	8	-55	22
sp gr(75°C):	NA[1]	1.05	1.22
vp, mm Hg:	NA[1]	0.05	0.025
color:	all colorless to pale yellow		
odor:	all sharp pungent		
flash point(closed cup), °C:	NA[1]	140	127
synonyms and structures:	Figure 1.1.4		

[1]not available

1.2 Limit defining parameters (the analyte air concentrations listed through this method are based on an air volume of 15 L and an extraction volume of 2 mL.)

1.2.1 Detection limit of the analytical procedure

The detection limit of the analytical procedure is the mass of analyte per injection which will result in a peak whose height is about 5 times the amplitude of the baseline noise. (Section 4.1)

Analytical Detection Limit

analyte	2,6-TDI	HDI	2,4-TDI
ng/injection	0.18	0.18	0.18

1.2.2 Detection limit of the overall procedure

The detection limit of the overall procedure is the amount of analyte spiked on the sampling device which allows recovery of an amount of analyte equivalent to the detection limit of the analytical procedure. (Section 4.2)

Detection Limit of the Overall Procedure

analyte	2,6-TDI	HDI	2,4-TDI
ng/sample	24	33	19
µg/m^3	1.6	2.3	1.3
ppb	0.23	0.32	0.17

1.2.3 Reliable quantitation limits

The reliable quantitation limit is the smallest amount of analyte which can be quantitated within the requirements of at least 75% recovery and a precision (1.96 SD) of ±25% or better. The reliable quantitation limits are higher than the detection limits of the overall procedure to satisfy the precision requirement. (Section 4.3)

Reliable Quantitation Limits

analyte	2,6-TDI	HDI	2,4-TDI
ng/sample	34	44	39
µg/m^3	2.3	2.9	2.5
ppb	0.32	0.43	0.36

The reliable quantitation limit and detection limits reported in the method are based upon optimization of the instrument for the smallest possible amount of analyte. When the target concentration of an analyte is exceptionally higher than these limits, they may not be attainable at the routine operating parameters.

1.2.4 Sensitivity

The sensitivity of the analytical procedure is determined by the slope of the calibration curve over a concentration range 0.5 to 2 times the target concentration. The

Sensitivity of the Analytical Procedure

analyte	2,6-TDI	HDI	2,4-TDI
area counts per µg/mL	85600	84300	159000

sensitivity will vary somewhat with the particular instrument used in the analysis. (Section 4.5)

1.2.5 Recovery

The recoveries of the analytes from samples used in the 18-day storage tests remained above the values presented below. These values are determined from the calculated regression lines of the storage graphs. (Section 4.9) The recovery of analyte from the collection medium after storage must be 75% or greater.

Recovery, %			
temp, °C	2,6-TDI	HDI	2,4-TDI
-25	86.3	81.1	81.3
22	86.4	83.0	80.3

1.2.6 Precision (analytical method)

The pooled coefficients of variation obtained from replicate determinations of analytical standards at 0.5, 1 and 2 times the target concentration are presented below. (Section 4.4)

Pooled Coefficients of Variation		
2,6-TDI	HDI	2,4-TDI
0.009	0.013	0.009

1.2.7 Precision (overall procedure)

The overall procedure must provide results at the target concentrations that are ±25% or better at the 95% confidence level. The precisions at the 95% confidence level for the 18-day storage test are presented below. (Section 4.9) The reported values each include an additional ±5% for sampling error.

Precision at the 95% Confidence Level, %		
2,6-TDI	HDI	2,4-TDI
14.9	15.2	13.5

1.2.8 Reproducibility

Five samples, prepared by vapor spiking, and a draft copy of this procedure were given to a chemist unassociated with this evaluation. The samples were analyzed after 6 days of storage at -25°C. The data listed below are corrected for extraction efficiency (Section 4.8).

Recovery, %			
	2,6-TDI	HDI	2,4-TDI
$\bar{X}$	101.5	100.4	105.4
SD	1.6	2.0	2.4

1.3 Advantages

1.3.1 The sampling and analytical procedures are specific and sensitive for several diisocyanates employed in industry (Ref. 5.7).

1.3.2 The collection system is less cumbersome than the use of a bubbler.

1.3.3 1-2PP is more stable and less expensive than p-nitrobenzyl-N-n-propylamine (nitro reagent).

1.4 Disadvantages

The use of peak ratios to confirm low concentrations of diisocyanates is impractical due to the small response at 313 nm.

2. Sampling Procedure

2.1 Apparatus

2.1.1 Samples are collected by use of a personal sampling pump that can be calibrated to within ±5% at the recommended flow rate with the sampling device in line.

2.1.2 A three-piece styrene cassette containing a glass fiber filter coated with 0.1 mg of 1-2PP and a backup pad. (Figure 2.1.2)

2.1.3 Coated filters are prepared by applying 0.5 mL of a solution of 0.2 mg/mL 1-2PP in methylene chloride to each glass fiber filter. The wet filters are allowed to air dry before placing them in a jar. Vacuum is applied to the jar to remove residual methylene chloride. (The coated filters used in Method 47 for MDI are also acceptable for this procedure. These filters are coated with 1 mg of 1-2PP and are prepared as above except a 2.0 mg/mL solution of 1-2PP in methylene chloride is used.)

2.1.4 Coated filters should be stored at reduced temperature as a precaution.

2.2 Reagents

None required.

2.3 Sampling technique

2.3.1 Remove the inlet cover from the three-piece cassette. Save the cover for installation after sampling.

2.3.2 Attach the cassette in the breathing zone of the employee to be monitored.

2.3.3 The recommended flow rate is 1 L/min with a recommended total air volume of 15 L. A longer 240-min sampling time is permissible to comply with the 1989 change of the PEL.

2.3.4 After sampling for the appropriate time, remove the sampling device and reinstall the small plug and inlet cover.

2.3.5 Wrap each sample end-to-end with an OSHA Form 21 seal.

2.3.6 With each set of samples, submit at least one blank sample. The blank should be subjected to the same handling as the samples except that no air is drawn through it.

2.3.7 Bulk samples submitted for analysis must be shipped in sealed vials and in a separate container.

2.4 Retention efficiency

2.4.1 Experimental design

Due to present laboratory limitations, controlled test atmospheres of diisocyanates cannot effectively be generated. However, the following procedure using a vapor spiking technique was used as an alternative to study analyte retention. This was done to approximate the recommended open-face collection of diisocyanates.

A glass syringe barrel equipped with a Luer taper tip was silanized and silanized glass wool was placed into the syringe. The Luer tip was inserted into the inlet part of a cassette so that the tip was flush with the inside surface of the cassette. The other end of the syringe was attached to a sampling port. The outlet of the cassette was attached to a vacuum pump. A critical orifice between the cassette and the pump maintained a constant 1 L/min flow rate.

Dry air samples were prepared by attaching a dry air source to a manifold inlet. Humid air samples were generated by passing air through water in a controlled temperature water bath. The humidity was monitored in the sampling manifold via a humidity probe. The glass wool was spiked with diisocyanate in methylene chloride. The desired quantity of air was then drawn through the glass wool, at a flow rate of 1 L/min, and onto the coated filter, which was analyzed to determine analyte loss.

2.4.2 Retention results

Humidity affects the ability of a glass fiber filter to retain derivatized diisocyanates. When a sample ten times the target concentration is vapor generated and 200 L of dry air (12% humidity) is drawn through the filter, an average of 95.4% of the diisocyanates is found on the coated filter. Only 1.2% is found on the backup pad.

When higher relative humidity (R.H.) is added to the sampling system, a different result is obtained. After samples were vapor spiked at the target concentration using 20 L of dry air, several known volumes of humid air (78% R.H.) pulled through them. The samples showed increasing losses of diisocyanate derivative with increasing volumes of humid air. (Section 4.6)

2.5 Extraction efficiency

The average extraction efficiency for each of the analytes spiked at the target concentration on a coated glass fiber filter is presented below. (Section 4.7)

Average Extraction Efficiency, %		
2,6-TDI	HDI	2,4-TDI
91.2	93.3	90.8

2.6 Recommended air volume and sampling rate

2.6.1 The recommended air volume is 15 L for the OSHA Ceiling PEL.

2.6.2 The recommended air sampling rate is 1 L/min.

2.6.3 To comply with the 1989 PEL changes, the air volume can be increased to 240 L to sample for the OSHA TWA-PEL.

2.7 Interferences (sampling)

Any compound, that could be collected on the glass fiber filter that could react with the 1-2PP or compete with it in the reaction to derivatize the diisocyanate, should be considered as an interference. Potential interferences include anhydrides, amines, alcohols and carboxylic acids.

2.8 Safety precautions (sampling)

The sampling equipment should be attached to the worker in such a manner that it will not interfere with work performance or safety.

3. Analytical Procedure

3.1 Apparatus

3.1.1 High performance liquid chromatograph equipped with UV detector, manual or automatic sample injector, and chart recorder.

3.1.2 HPLC stainless steel column capable of separating diisocyanate derivatives. The column employed in this study was a 25-cm × 4.6-mm i.d. Alltech C_8 (10 µm) stainless steel column.

3.1.3 An electronic integrator, or some other suitable method of determining peak areas.

3.1.4 Vials, 4-mL with Teflon-lined caps.

3.1.5 Syringes, of convenient sizes for sample and standard preparations and injections.

3.1.6 Volumetric pipettes and flasks for preparation of standards.

3.1.7 Suitable glassware for preparation of diisocyanate urea derivatives.

3.1.8 Micro-analytical balance used to weigh standard preparations.

3.2 Reagents

3.2.1 Methylene chloride, hexane, acetonitrile, and dimethyl sulfoxide, HPLC grade.

3.2.2 Water, HPLC grade. Our laboratory employs a commercially available water filtration system for the preparation of HPLC grade water.

3.2.3 1-(2-Pyridyl)piperazine, Aldrich, Milwaukee, WI.

3.2.4 2,6-TDI, Carbolabs, Inc., New Haven, CT.

3.2.5 HDI, Aldrich, Milwaukee, WI.

3.2.6 2,4-TDI, Eastman Chemicals, Rochester, NY.

3.2.7 Ammonium acetate, HPLC grade.

3.2.8 Glacial acetic acid.

3.3 Standard preparation

3.3.1 A solution containing 3.5 g of 2,4-TDI in 25 mL of methylene chloride is slowly added to a stirred solution of 7.25 g of 1-2PP in 100 mL of methylene chloride. The solution is then heated to 35°C for 10 min. Reduce the volume of methylene chloride to about 10 mL with a stream of dry nitrogen. The product is precipitated with hexane, (precipitation may start without adding hexane), filtered, redissolved in a minimal volume of methylene chloride and reprecipitated. The precipitate is filtered and washed with hexane (approximate yield is 9 g of the derivative after being dried by vacuum). This preparation is a modification of the procedure reported by Goldberg et al (Ref. 5.7). Derivatives of the two other diisocyanates are prepared by a similar procedure.

3.3.2 Preparation of working range standards

A stock standard solution is prepared by dissolving the diisocyanate derivatives into DMSO. To express the derivative as free diisocyanate, the amount of 2,4-TDI and 2,6-TDI ureas weighed is multiplied by the conversion factor 0.3479.

$$\frac{\text{MW TDI}}{\text{MW urea}} = \frac{174.16}{500.61} = 0.3479$$

Similarly, the conversion factor for HDI urea is 0.3400.

$$\frac{\text{MW HDI}}{\text{MW urea}} = \frac{168.20}{494.64} = 0.3400$$

All dilutions of the stock solutions are made with acetonitrile to arrive at the working range.

3.4 Sample preparation

3.4.1 The styrene cassette is opened and the glass fiber filter is placed into a 4-mL vial so that the filter is flat against the inside surface of the vial, not folded or crumpled.

3.4.2 Two milliliters of the extracting solution, 90/10 (v/v) ACN/DMSO, are added.

3.4.3 A cap equipped with a Teflon liner is installed.

3.4.4 The vial is shaken to remove large air bubbles from between the filter and the glass. Let the vial set for 1 h.

3.5 Analysis

3.5.1 Reverse phase HPLC conditions

column:	25-cm × 4.7-mm i.d. stainless steel column packed with 10-µm Alltech C_8 or suitable equivalent.
mobile phase:	0.01 M ammonium acetate in 37.5/ 62.5 ACN/water (v/v) adjusted to pH 6.2 with acetic acid
flow rate:	1 mL/min
UV detector:	254 and 313 nm
fluorescence detector:	240 nm excitation 370 nm emission
injection size:	10-25 µL
chromatogram:	Figure 3.5.1

3.5.2 An external standard procedure is used to prepare a calibration curve using at least 2 stock solutions from which dilutions are made. The calibration curve is prepared daily. The samples are bracketed with analytical standards.

3.6 Interferences (analytical)

3.6.1 Any compound having the same retention time as the analyte is a possible interference. Benzaldehyde is an interference for 2,4-TDI urea using the aforementioned analytical conditions but is not normally expected to be found. Generally, chromatographic conditions can be altered to separate an interference.

3.6.2 Retention time on a single column is not proof of chemical identity. Analysis by an alternate column system, ratioing of wavelength response, and mass spectrometry are additional means of identity. (UV spectra for diisocyanate derivatives are shown in Figures 4.11.1-4.11.3)

3.7 Calculations

The concentration in µg/mL of diisocyanate present in a sample is determined from the area response of the analytes as measured by an electronic integrator or peak heights. Comparison of sample response with a least squares curve fit for standards allows the analyst to determine the concentration of diisocyanate in µg/mL for the sample. Since the sample volume is 2 mL, the results in $\mu g/m^3$ of air are expressed by the following equation:

$$\mu g/m^3 = (\mu g/mL)(2\ mL)/(m^3\ \text{of air sampled})(\text{Extraction Eff.})$$

3.8 Safety precautions (analytical)

3.8.1 Avoid skin contact with all solvents.

3.8.2 Wear safety glasses at all times.

3.8.3 Avoid exposure to the diisocyanates standards.

4. Backup Data

4.1 Detection limit of the analytical procedure

The detection limit of the analytical procedure was 0.18 ng/injection for all three analytes. This amount produced a peak whose height was about 5 times the height of the baseline noise. An injection size of 10 µL was used in the determination of the detection limits for the analytical procedure. (Figure 4.1)

4.2 Detection limit of the overall procedure

4.2.1 The following data were obtained by vapor spiking increasing amounts of the analytes onto sampling devices. An injection size of 25 µL was used to determine the detection limits of the overall procedure.

Table 4.2.1
Recoveries Near the Detection Limit

analyte	2,6-TDI		HDI		2,4-TDI	
	spiked	found	spiked	found	spiked	found
ng/sample	16.9	3.5	33.9	3.9	19.3	12.6
	25.4	14.0	44.2	44.9	29.0	21.1
	33.8	27.8	66.2	61.0	38.6	39.0
	42.2	33.9	88.2	82.6	57.9	61.8
	67.6	54.2	132.4	133.7	77.2	68.7
	84.5	61.9			96.6	93.8
	101.4	85.8			115.8	120.8

4.2.2 Graphical presentation of the above data are shown in Figures 4.2.1-4.2.3. The detection limits of the overall procedure determined from the Figures were 24.4 ng/sample for 2,6-TDI, 33.3 ng/sample for HDI, and 19.2 ng/sample for 2,4-TDI.

4.3 Reliable quantitation limit

The following data were obtained by vapor spiking the analytes onto sampling devices. An injection size of 25 µL was used to determine the reliable quantitation limits.

Table 4.3
Extraction Efficiency at the Reliable Quantitation Limit

analyte	2,6-TDI	HDI	2,4-TDI
ng/sample	33.6	44.2	38.6
% recovery	117.4	124.8	82.9
	103.6	114.7	74.6
	103.6	96.8	70.8
	103.6	114.7	82.9
	103.6	114.7	74.6
	103.6	114.7	70.8
	103.6	96.8	82.9
	103.6	96.8	74.6
$\bar{X}$	105.3	109.3	76.8
SD	4.9	10.9	5.3
1.96SD	9.6	21.4	10.4

4.4 Sensitivity and precision (analytical method only)

The following data were obtained from multiple injections of analytical standards.

Table 4.4.1
0.5× Target Concentration

analyte	2,6-TDI	HDI	2,4-TDI
µg/mL	0.700	0.722	0.704
area counts	69054	70015	127935
	69310	70643	127591
	69380	70996	127408
	68824	70340	125457
	68117	68751	124953
	67271	68445	124032
	68701	69385	126054
	68643	69036	125588
	67196	68454	124185
$\bar{X}$	68499.6	69562.8	125911.4
SD	811	967	1454
CV	0.0118	0.0139	0.0115

Table 4.4.2
1× Target Concentration

analyte	2,6-TDI	HDI	2,4-TDI
µg/mL	1.400	1.443	1.407
area counts	127643	129539	236004
	126872	130474	235664
	126332	128313	233651
	127445	128379	234337
	126896	129521	234274
	126037	128186	231355
	127077	129882	234258
	126384	125878	229449
	127033	128370	234524
$\bar{X}$	126857.7	128726.9	233723.7
SD	526	1346	2076
CV	0.0041	0.0105	0.0089

Table 4.4.3
2× Target Concentration

analyte	2,6-TDI	HDI	2,4-TDI
µg/mL	2.800	2.886	2.814
area counts	249771	252219	459331
	244922	249296	457553
	248641	259363	458572
	246677	252678	461448
	246986	252581	461119
	245615	250940	457897
	252601	247011	463557
	248169	249906	460536
	248014	251679	459259
$\bar{X}$	247932.9	251741.4	459919.1
SD	2309	3396	1925
CV	0.0093	0.0135	0.0042

Table 4.4.4
Pooled Coefficients of Variation

2,6-TDI	HDI	2,4-TDI
0.0090	0.0127	0.0087

4.5 Sensitivity

The data in Tables 4.4.1-4.4.3 are presented graphically in Figures 4.4.1-4.4.3.

4.6 Retention efficiency

4.6.1 Two retention studies were conducted, the first at 12% relative humidity and the second at 78% relative humidity. The samples were vapor spiked and removed from the sample generator after a known volume of air had passed through the cassette.

Table 4.6.1.1
Percent Retention at 10× Target Concentration with 200-L Air Volume (12% RH)

analyte	2,6-TDI	HDI	2,4-TDI
µg/sample	27.92	36.44	31.84
filter	96.9	97.2	94.4
backup	1.0	2.0	0.8
filter	95.6	95.6	92.9
backup	0.9	1.8	0.6

Table 4.6.1.2
Percent Retention at 1× Target Concentration (78% RH)

air volume, L	2,6-TDI	HDI	2,4-TDI
5.25	90.8	91.5	85.1
5.25	90.3	88.4	84.0
10.5	91.2	89.8	84.5
15.75	89.7	92.0	82.6
15.75	89.7	86.7	78.9
21.0	89.8	90.0	82.3
21.0	85.1	88.4	77.4
26.25	88.8	93.8	81.7
26.25	84.0	92.4	78.2
31.5	84.5	87.5	77.1
36.75	84.7	89.1	80.0
42.0	86.8	90.3	80.1
42.0	85.9	90.0	79.7
47.25	84.9	84.7	79.2
47.25	84.0	84.4	75.7
52.5	87.4	90.9	80.8
52.5	86.4	87.2	79.4

4.6.2 The following data are presented to show that the diisocyanate derivatives, liquid spiked, are retained on the coated glass fiber filter at the recommended air volume.

Table 4.6.2
Percent retention at 1× Target Concentration with 20-L Air Volume (80% RH)

analyte	2,6-TDI	HDI	2,4-TDI
µg/sample			
% recovery	83.7	79.6	76.0
	93.1	81.4	88.5
	90.1	81.1	86.3
	95.8	81.7	91.4
	89.4	80.8	86.5
	83.6	78.9	78.9
	78.9	75.0	73.0
	88.6	82.3	82.7
$\bar{X}$	87.9	80.1	82.4
SD	5.5	2.3	6.4

4.6.3 Ten liters of 80% R.H. air were drawn through a filter to moisten it and then it was vapor spiked with 20 L of dry air to observe the retention of the derivative on the wet filter.

Table 4.6.3
Recoveries From a Wet Filter

analyte	2,6-TDI	HDI	2,4-TDI
µg/sample	2.792	3.644	3.184
% recovery	100.5	91.6	84.4
	99.6	90.6	79.4
	97.8	88.8	77.8
	104.2	95.9	84.4
	97.8	89.7	81.7
$\bar{X}$	100.0	91.4	81.5
SD	2.6	2.8	3.0

4.6.4 Retention efficiencies at the 1989 TWA-PEL

The following data are presented to show that the diisocyanate derivatives, liquid spiked, are retained on the coated glass fiber filter at the recommended air volume when sampling for the long periods of time needed to determine the TWA exposure. No isocyanate derivative was detected on any of the glass fiber filters placed 0.25 in. behind the coated filters.

Table 4.6.4
Percent Retention at 1× 1989 TWA PEL with 240-L Air Volume (71% RH)

analyte	2,6-TDI	HDI	2,4-TDI
µg/sample	8.412	8.240	8.376
% recovery	103.1	103.5	106.6
	100.3	103.1	106.1
	102.7	102.3	105.9
	98.7	102.6	106.6
	97.1	102.0	105.3
	96.7	102.0	105.4
$\bar{X}$	99.8	102.6	106.0
SD	2.7	0.6	0.6

4.7 Extraction efficiency

The following data represent the analysis of coated glass fiber filters vapor spiked with the analytes at 0.05 and 1 times the target concentrations.

Table 4.7.1
Extraction Efficiency at 0.05× Target Concentration

analyte	2,6-TDI	HDI	2,4-TDI
µg/sample	0.1396	0.1822	0.1592
% recovery	86.0	93.9	98.6
	92.8	90.0	102.1
	80.2	91.7	98.5
	84.2	92.2	100.9
	69.3	91.3	100.1
	89.4	104.9	111.3
	91.7	96.1	96.1
	95.1	91.7	95.6
	77.4	85.6	87.7
	91.7	96.6	101.6
	103.2	107.6	108.2
	94.6	99.6	100.0
$\bar{X}$	88.0	95.1	100.1

Table 4.7.2
Extraction Efficiency at 1× Target Concentration

analyte	2,6-TDI	HDI	2,4-TDI
µg/sample	2.792	3.644	3.184
% recovery	92.0	92.2	93.0
	95.6	98.9	98.1
	92.6	94.1	92.9
	92.4	92.9	94.4
	91.8	92.9	92.0
	93.7	94.9	93.9
	88.3	94.5	85.8
	89.6	92.8	85.5
	90.2	94.3	88.6
	90.8	91.5	90.5
	87.7	88.6	87.5
	89.9	92.3	87.6
$\bar{X}$	91.2	93.3	90.8

4.8 Reproducibility data

Five samples were spiked with the three diisocyanates and had 20 L of humid air drawn through the cassettes. The samples were analyzed by a chemist unassociated with this evaluation after being stored for 6 days at -26°C. The results are corrected for extraction efficiencies.

Table 4.8
Reproducibility Results, % recovery

analyte	2,6-TDI	HDI	2,4-TDI
µg/sample	2.792	3.644	3.184
area counts	102.5	101.3	106.2
	98.8	97.0	103.4
	102.7	102.0	108.6
	102.5	101.3	106.2
	101.2	100.6	102.6
$\bar{X}$	101.5	100.4	105.4
SD	1.6	2.0	2.4

4.9 Storage data

The data in Tables 4.9.2-4.9.4 show the effects of storage at ambient (22°C) and reduced (-20°C) temperatures on vapor spiked cassettes, which were generated with 20 L of dry air followed by 3 L of humid air to moisten the system. Except for day zero, three samples for each of the two storage conditions were analyzed at intervals over an 18-day period. The results are not corrected for extraction efficiency. The data are also presented graphically in Figures 4.9.1.-4.9.6.

Table 4.9.1
Amount Vapor Spiked, µg/Cassette

2,6-TDI	HDI	2,4-TDI
2.792	3.644	3.184

Table 4.9.2
Storage Test of 2,6-TDI

time (days)	percent recovery (ambient)			percent recovery (refrigerated)		
0	77.8	85.5	90.9	77.8	83.5	90.9
	89.5	84.2	87.8	89.5	84.2	87.8
4	89.8	89.0	91.0	84.5	88.3	83.5
7	94.6	86.5	90.5	91.0	92.4	99.0
11	95.1	97.1	87.3	80.9	85.7	81.4
14	103.7	99.4	103.9	89.6	83.7	94.6
18	95.3	95.5	102.0	75.7	85.2	89.7

Table 4.9.3
Storage Test of HDI

time (days)	percent recovery (ambient)			percent recovery (refrigerated)		
0	75.9	82.3	89.7	75.9	82.3	89.7
	91.2	81.9	83.8	91.2	81.9	83.8
4	84.4	83.9	81.1	79.6	80.8	79.3
7	82.1	75.1	81.9	86.9	86.2	95.4
11	82.2	82.5	77.7	76.4	80.0	75.4
14	85.9	82.8	88.4	87.5	81.7	91.2
18	81.8	84.4	85.0	71.4	81.1	83.0

Table 4.9.4
Storage Test of 2,4-TDI

time (days)	percent recovery (ambient)			percent recovery (refrigerated)		
0	74.6	78.6	84.7	74.6	78.6	84.7
	87.7	81.3	82.9	87.7	81.3	82.9
4	83.6	82.7	81.7	80.5	87.8	79.5
7	80.4	72.9	78.6	83.3	84.0	89.3
11	81.4	79.8	72.1	75.1	80.9	76.4
14	84.2	78.4	82.3	83.9	78.4	88.4
18	79.8	82.0	82.9	73.8	82.6	86.2

4.10 Side-by-side sampling

A simple experiment was designed which allowed a bubbler containing nitro reagent and a glass fiber filter coated with 1-2PP to be simultaneously vapor spiked from the same 2,4-TDI atmosphere. This was accomplished by leaching a known amount of 2,4-TDI off a glass wool plug contained in a glass tube with dilution air which is then passed through a "Y" to each sampler. The air flow was controlled by calibrated orifices of similar flow rate down stream from the samplers.

Each sample was analyzed twice and its average was plotted in Figure 4.10. The differences between the bubbler samples and the filter samples appear to be random with no discernible bias between them. The amount of scatter observed in both collection systems was not expected and probably can be attributed to the experimental design. The average line plotted in Figure 4.10 represents the average of all the collected samples and the data is presented below.

Table 4.10
Analysis of Side-By-Side Samples. $\mu g/m^3$

spike	average	collection system	average	collection system
1	192	F	207	F
2	197.5	F	209.5	F
3	164.5	B	162.5	B
4	172.5	B	179	B
5	208.5	F	224.5	B
6	231	F	181	B
7	230	F	244.5	B
8	222.5	F	223	B
9	233.5	F	216	B
10	226	F	250.5	B
11	221.5	F	146.5	B
12	226.5	F	199.5	B
13	212	F	240.5	B
14	212	F	218.5	B
15	223.5	F	245	B
16	225	F	296.5	B
17	202.5	B	230	B
18	219.5	B	176.5	B
19	174	F	248	F
20	331.5	F	269	F

4.11 UV Spectra

Figures 4.11.1-4.11.3 are the UV spectra of the 1-2PP derivatives of the diisocyanates used in this study. The three compounds are named below:

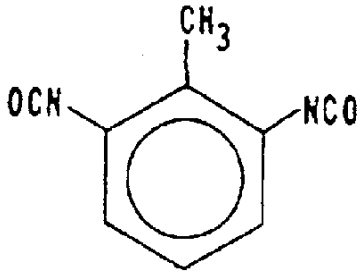
CAS no.	name
	2,6-Bis(4-(2-pyridyl)-1-piperazinylcarbamyl) toluene
72375-27-0	1,6-Bis(4-(2-pyridyl)-1-piperazinylcarbamyl) hexane
72375-21-4	2,4-Bis(4-(2-pyridyl)-1-piperazinylcarbamyl) toluene

4.12 Capacity of an 1-mg coated glass fiber filter

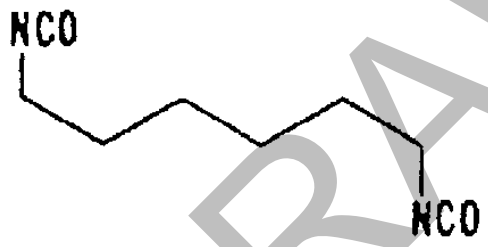
A coated glass fiber filter was challenged with a 65/35 mixture of 2,4-TDI/2-6,TDI. The glass fiber filter coated with 1 mg of 1-2PP was suspended on an adapter ring of a standard 37-mm cassette. Another coated filter was placed on a backup pad in the bottom of the cassette. Four more adapter rings were placed in front of the suspended filter to allow the incoming isocyanate to cover the entire filter face and not just hit the center of the filter. The isocyanate mixture was liquid spiked onto glass wool that had been placed inside a 13-mm stainless steel filter holder. The metal filter holder was inserted into the Luer-Lok fitting of the cassette top. The glass wool was then spiked with 8.52 µg of the TDI mixture. Air was pulled through the cassette and holder at 1 L/min (72% relative humidity). After 15 min, the air flow was stopped and the rear filter was changed and replaced with a new one. The glass wool was spiked again with 8.52 µg of the TDI mixture. This procedure was repeated until a total of 10 rear filters had been removed and a total of 85.2 µg of isocyanate had been spiked onto the glass wool.

When the rear filters were analyzed, none of the showed the presence of any TDI. The front filter, which was not changed during the sampling, had collected a total of 66.1 µg of TDI. The other 19.1 µg of TDI was probably lost on the sides of the adapter rings of the cassette. The 66.1-µg collected represents 7.9 times the 1989 TWA-PEL when sampling for 4 h.

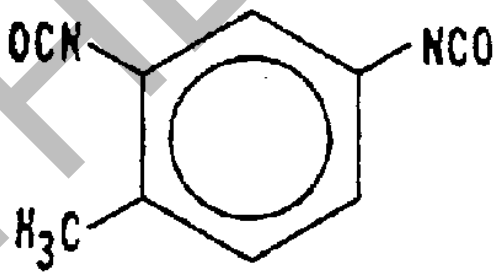
A second cassette containing filters was also tested in the same manner and again none of the rear filters contained any isocyanate. In this test the front filter collected 59.4 µg of TDI or 7.1 times the 1989 TWA-PEL.



toluene-2,6-diisocyanate; 2,6-toluene diisocyanate; 2,6-diisocyanato-1-methylbenzene; isocyanic acid, 2-methyl-1,3-phenylene ester; 2,6-TDI



1,6-hexamethylene diisocyanate; HDI



toluene-2,4-diisocyanate; 2,4-toluene diisoycanate; 2,4-diisocyanato-1-methylbenzene; isocyanic acid, 4-methyl-1,3-phenylene ester; 2,4-TDI

Figure 1.1.4. Structures and synonyms of the diisocyanates.

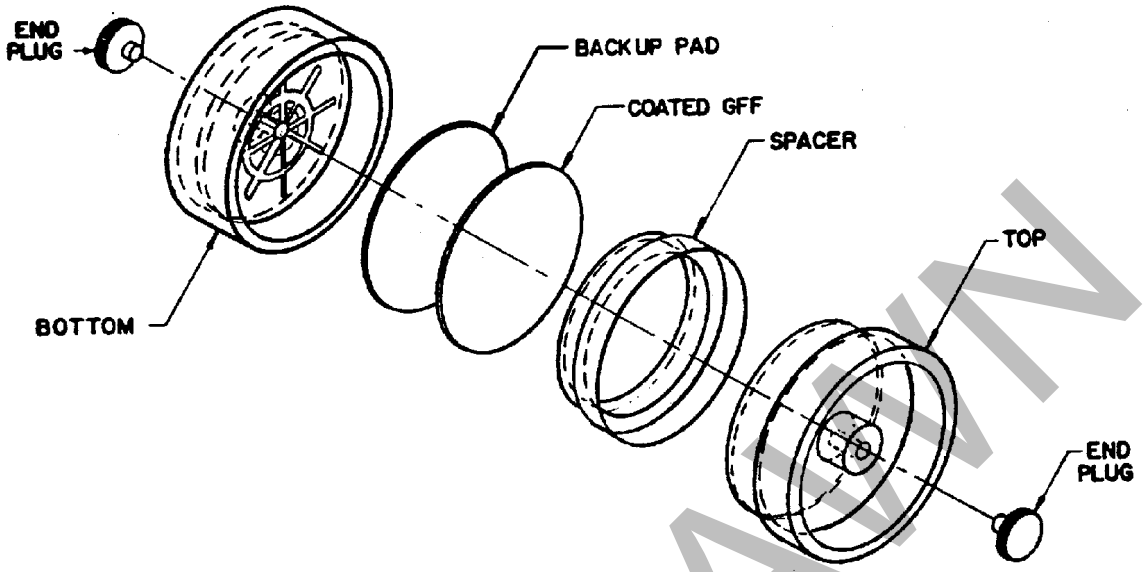


Figure 2.1.2. A drawing of a sample cassette.

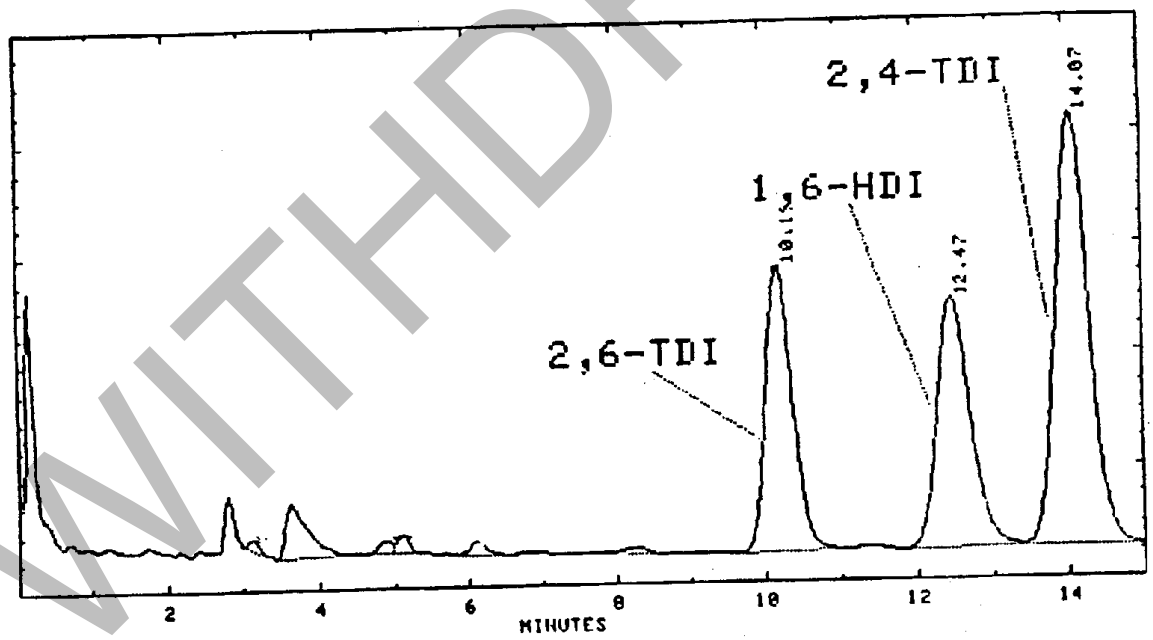


Figure 3.5.1. Chromatogram of standards of the three diisocyanates.

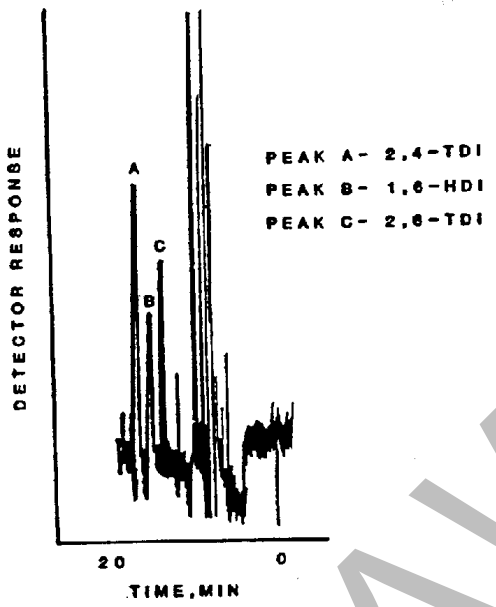


Figure 4.1. Analytical detection limit for the diisocyanates.

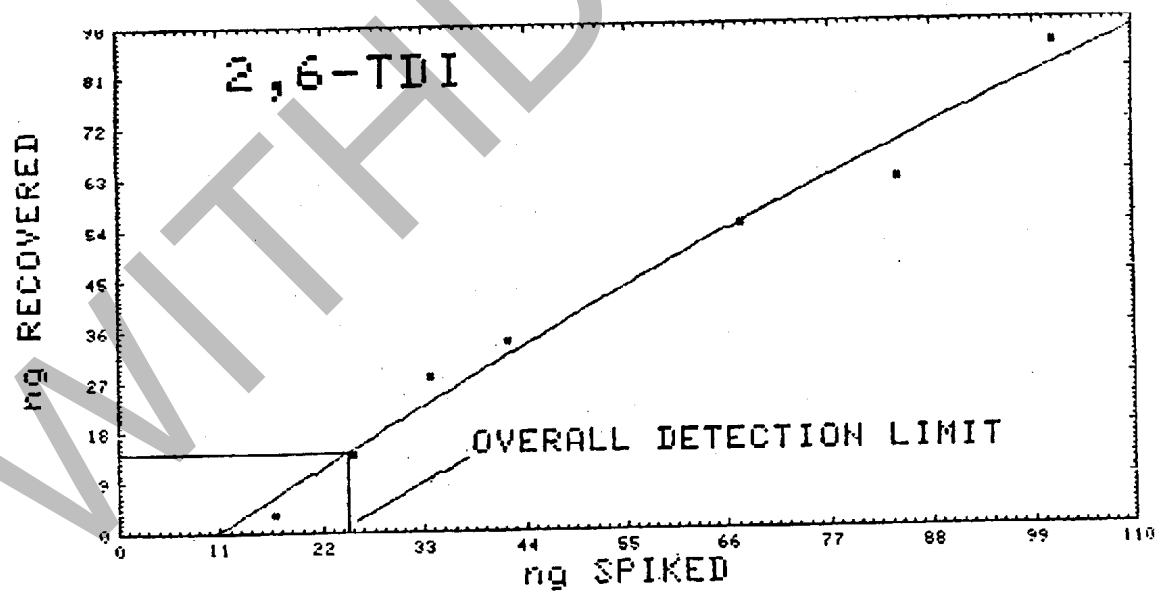


Figure 4.2.1. Detection limit of the overall procedure for 2,6-TDI.

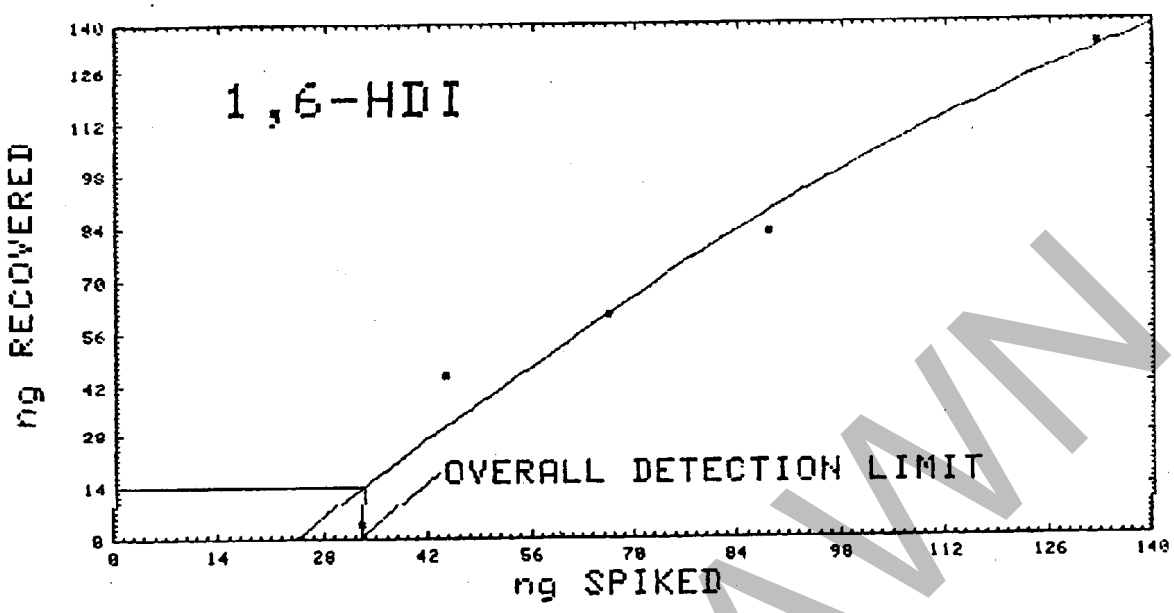


Figure 4.2.2. Detection limit of the overall procedure for HDI.

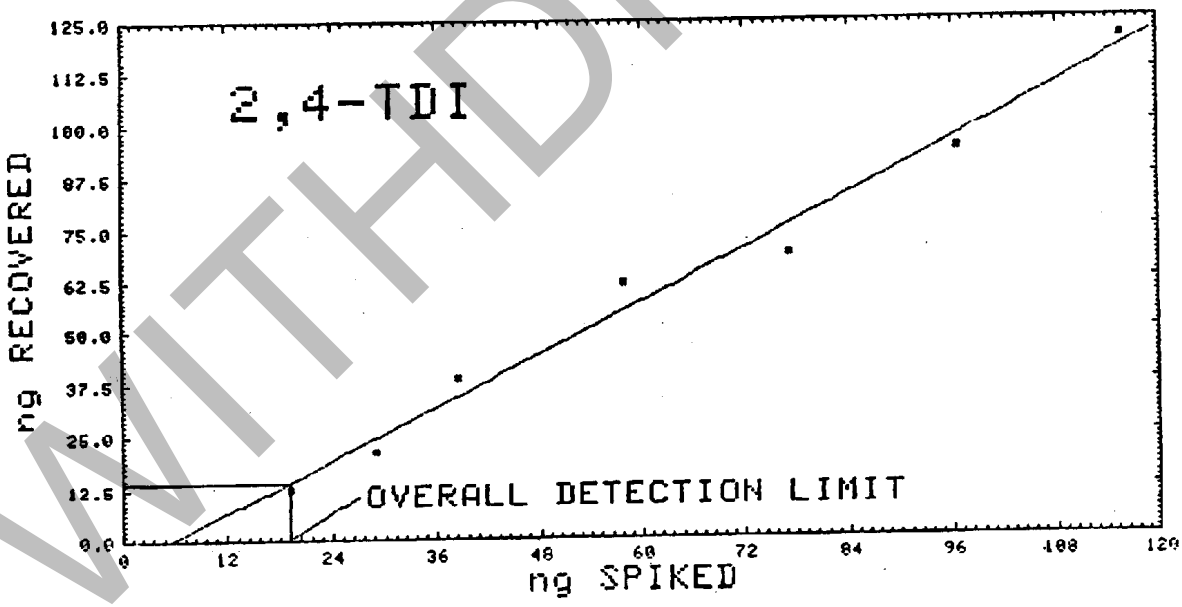


Figure 4.2.3. Detection limit of the overall procedure for 2,4-TDI.

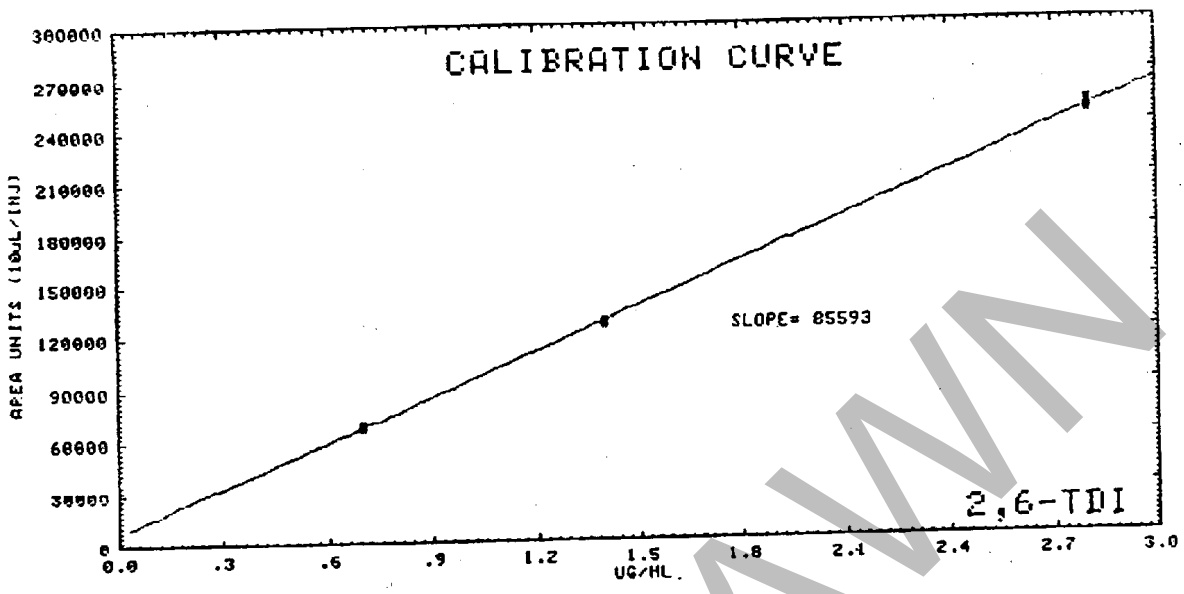


Figure 4.4.1. Calibration curve for 2,6-TDI.

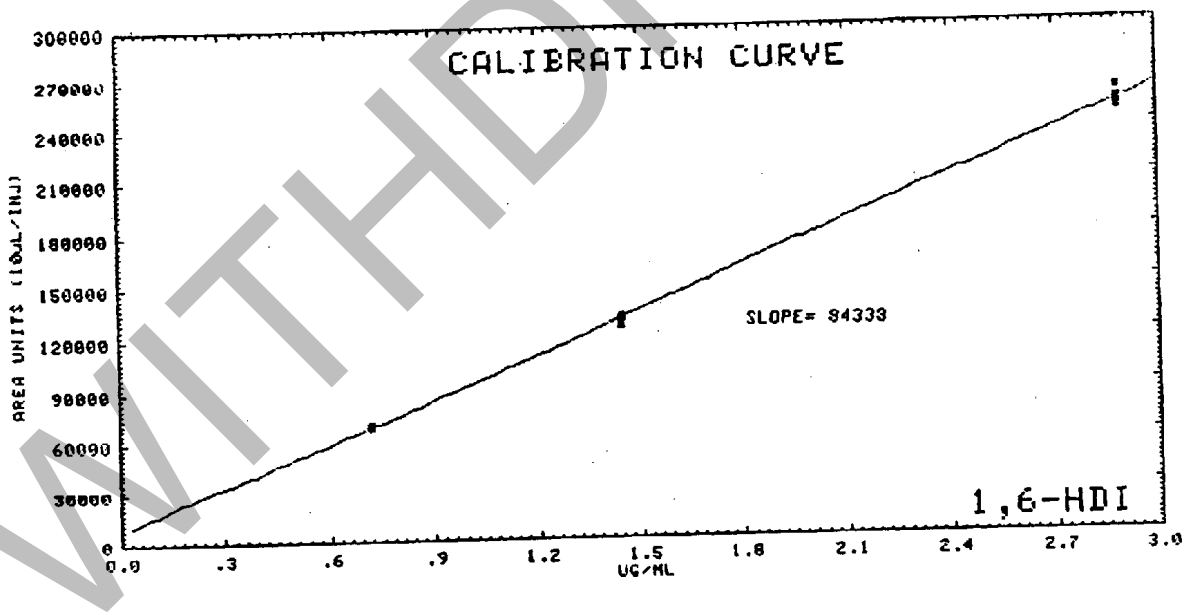


Figure 4.4.2. Calibration curve for HDI.

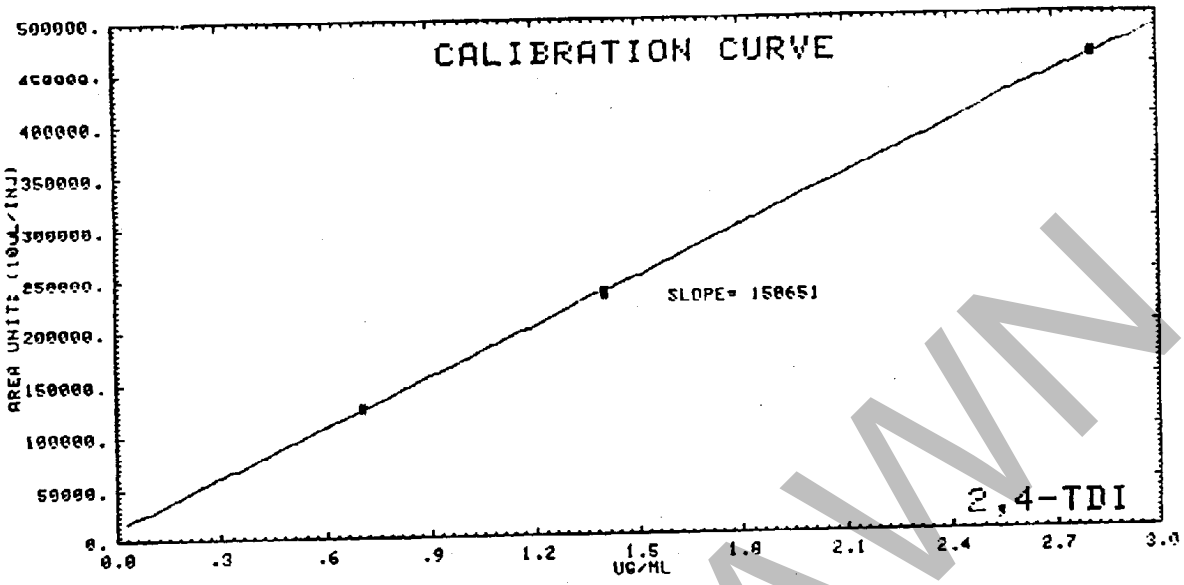


Figure 4.4.3. Calibration curve for 2,4-TDI.

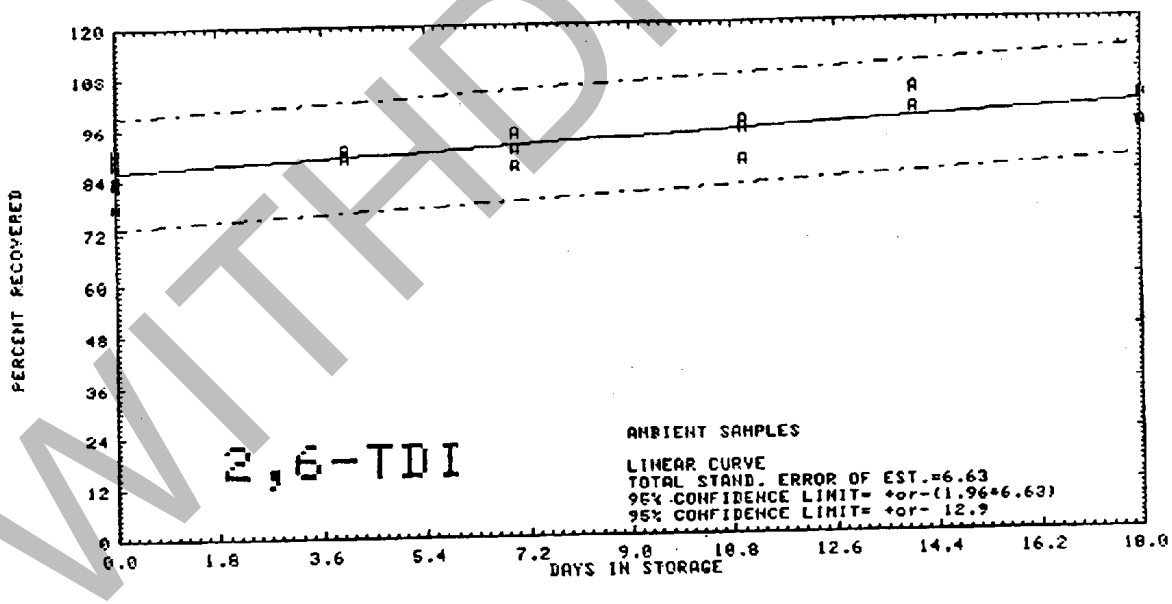


Figure 4.9.1. Ambient storage test for 2,6-TDI.

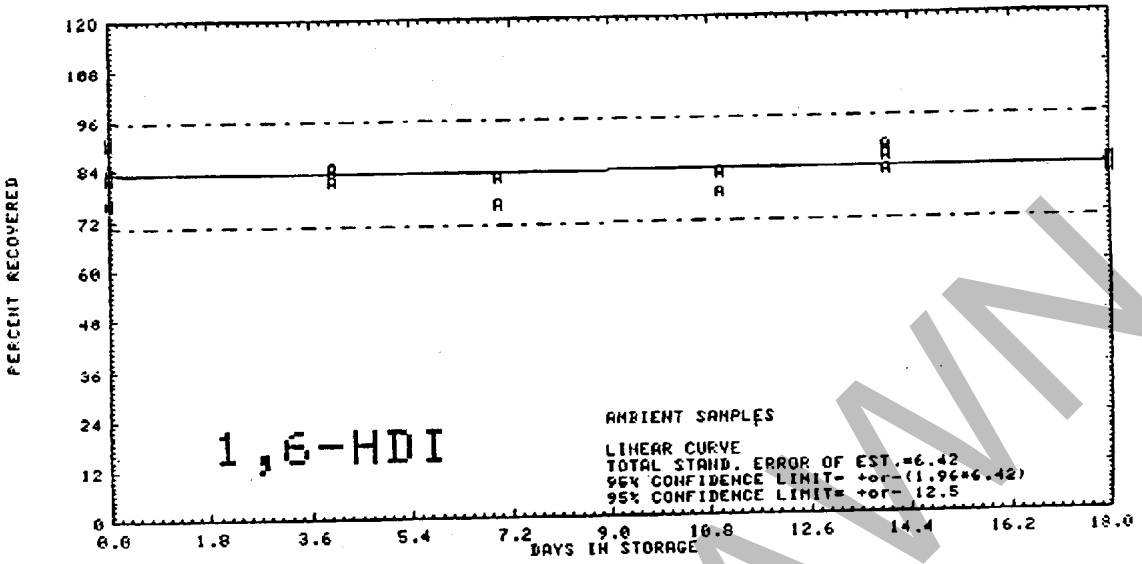


Figure 4.9.2. Ambient storage test for HDI.

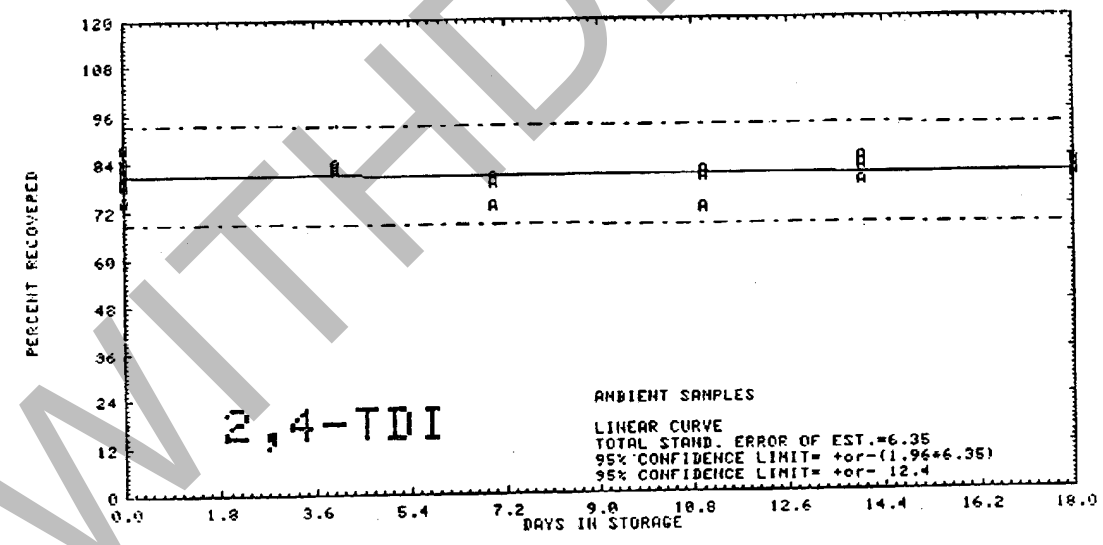


Figure 4.9.3. Ambient storage test for 2,4-TDI.

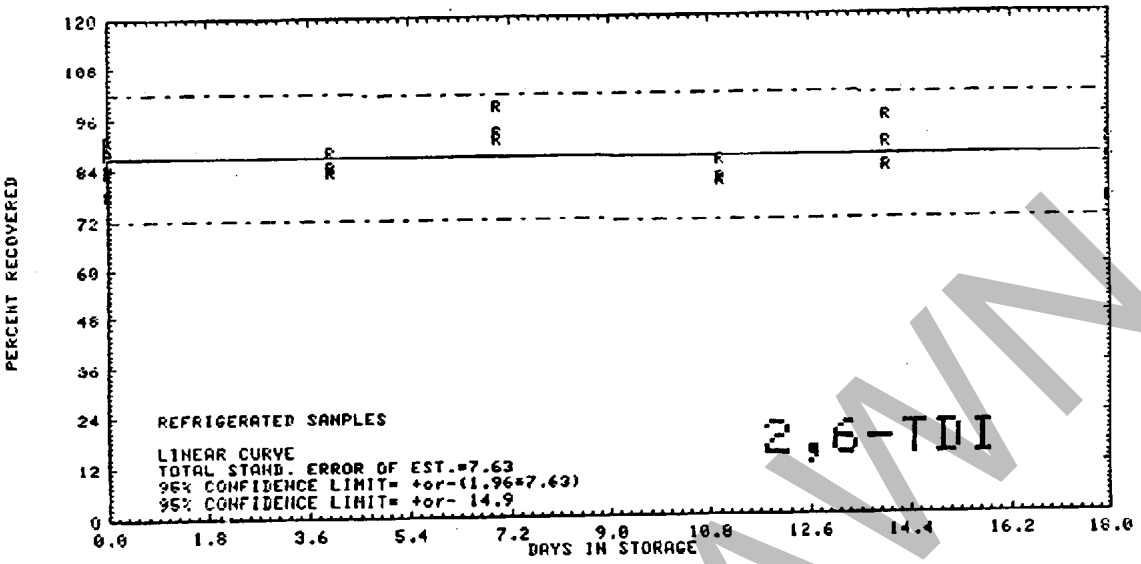


Figure 4.9.4. Refrigerated storage test for 2,6-TDI.

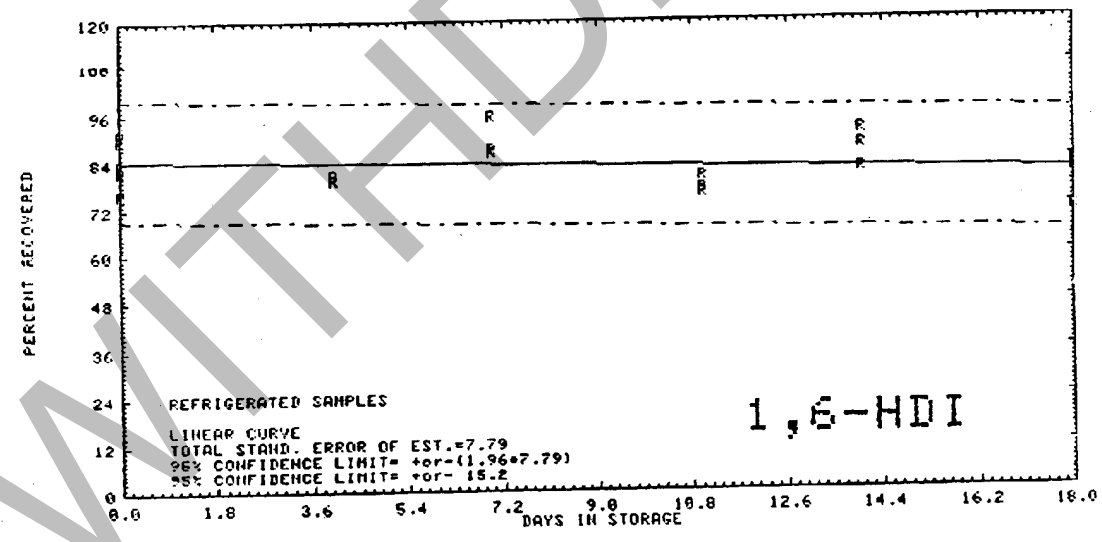


Figure 4.9.5. Refrigerated storage test for HDI.

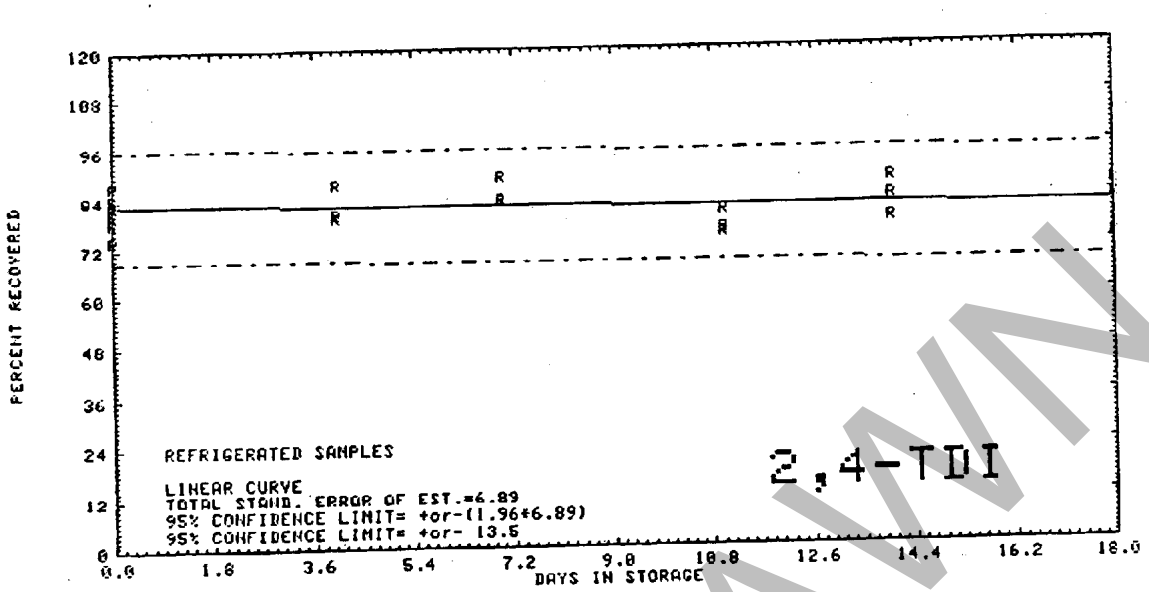


Figure 4.9.6. Refrigerated storage test for 2,4-TDI.

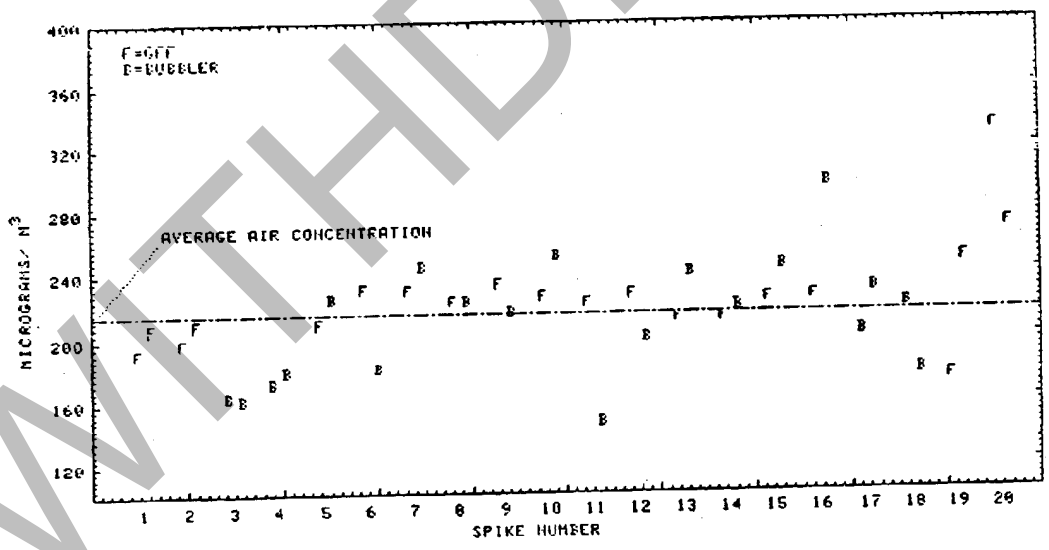


Figure 4.10. Side-by-side comparison of coated filters and bubblers.

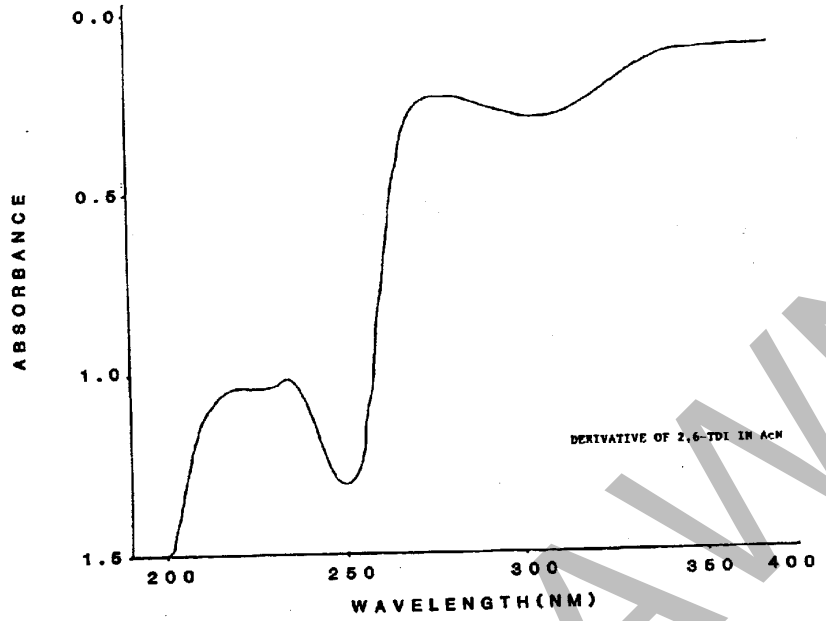


Figure 4.11.1. UV spectrum of 2,6-TDI derivative in acetonitrile.

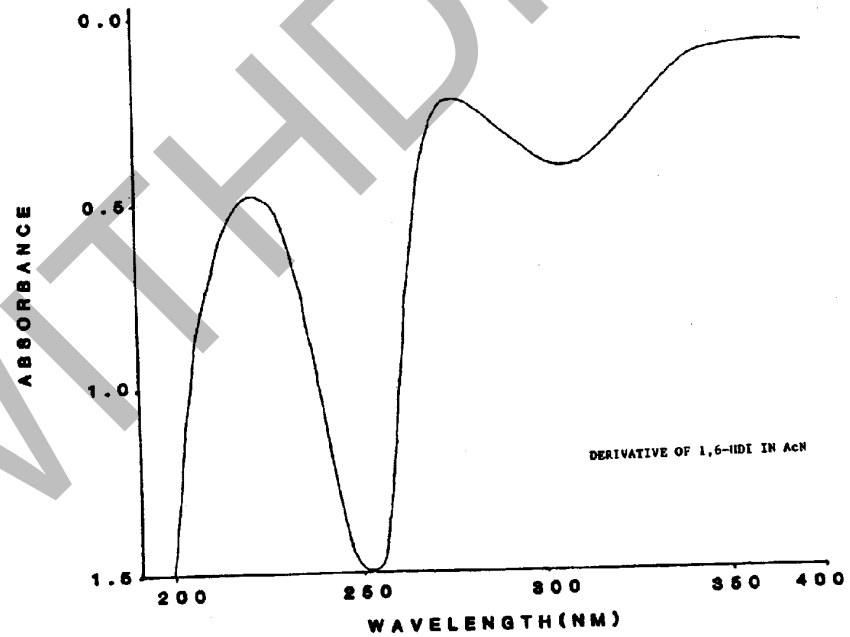


Figure 4.11.2. UV spectrum of HDI derivative in acetonitrile.

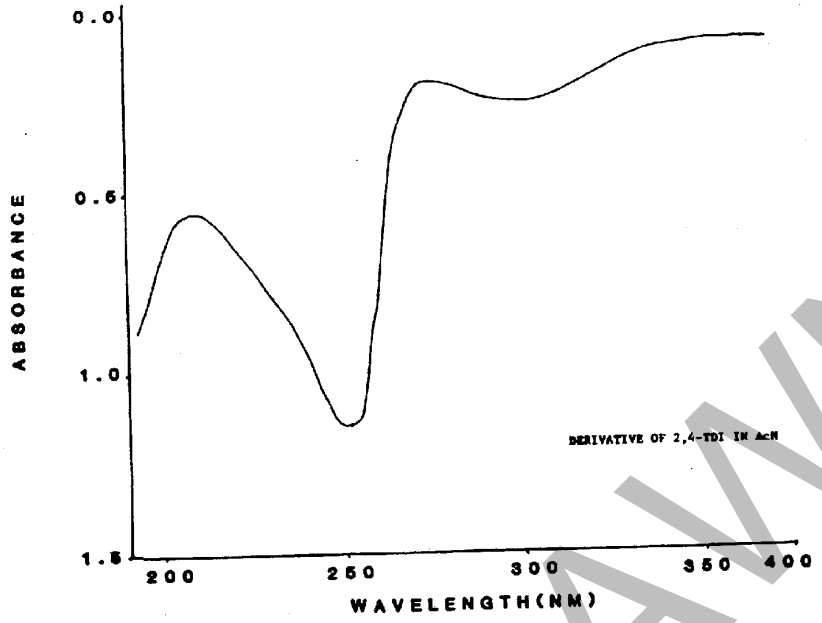


Figure 4.11.3. UV spectrum of 2,4-TDI derivative in acetonitrile.

5. References

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