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/m³ (ppb):	140(20)	140(20)	140[1](20)
Detection limit of the overall procedure, µg/m³ (ppb):	1.6(0.23)	2.3(0.32)	1.3(0.17)
Reliable quantitation limit, µg/m³ (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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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 µg/sample	2,6-TDI 27.92	HDI 36.44	2,4-TDI 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 µg/sample	2,6-TDI	HDI	2,4-TDI
% 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
$\overline{X}$	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 µg/sample	2,6-TDI 2.792	HDI 3.644	2,4-TDI 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
$\overline{X}$	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 µg/sample	2,6-TDI 8.412	HDI 8.240	2,4-TDI 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
$\overline{X}$	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 µg/sample	2,6-TDI 0.1396	HDI 0.1822	2,4-TDI 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
$\overline{X}$	88.0	95.1	100.1

Table 4.7.2
Extraction Efficiency at 1× Target Concentration

analyte µg/sample	2,6-TDI 2.792	HDI 3.644	2,4-TDI 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
$\overline{X}$	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 µg/sample	2,6-TDI 2.792	HDI 3.644	2,4-TDI 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
$\overline{X}$	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. µg/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:

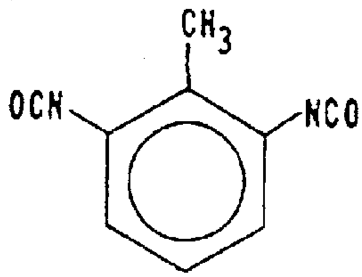
CAS no.	name
	2,6-Bis(4-(2-pyridyl)-1-piperazinylcarbamyl) toluene
72375-27-0	1,6-Bis(4-(2-pyridyl)-1-piperazinylcarbamyl) hexane
72375-21-4	2,4-Bis(4-(2-pyridyl)-1-piperazinylcarbamyl) toluene

4.12 Capacity of an 1-mg coated glass fiber filter

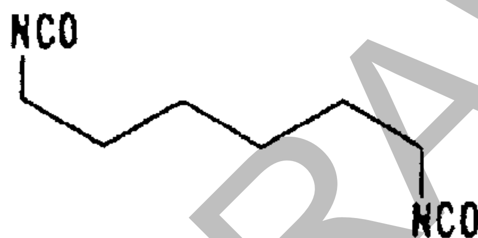
A coated glass fiber filter was challenged with a 65/35 mixture of 2,4-TDI/2-6,TDI. The glass fiber filter coated with 1 mg of 1-2PP was suspended on an adapter ring of a standard 37-mm cassette. Another coated filter was placed on a backup pad in the bottom of the cassette. Four more adapter rings were 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.

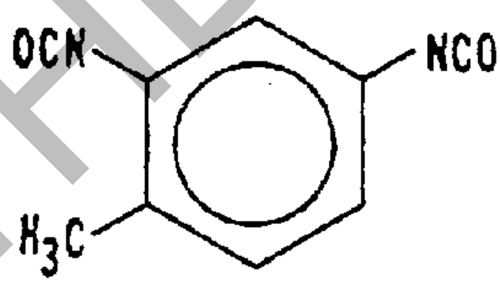
A second cassette containing filters was also tested in the same manner and again none of the rear filters contained any isocyanate. In this test the front filter collected 59.4 µg of TDI or 7.1 times the 1989 TWA-PEL.



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.

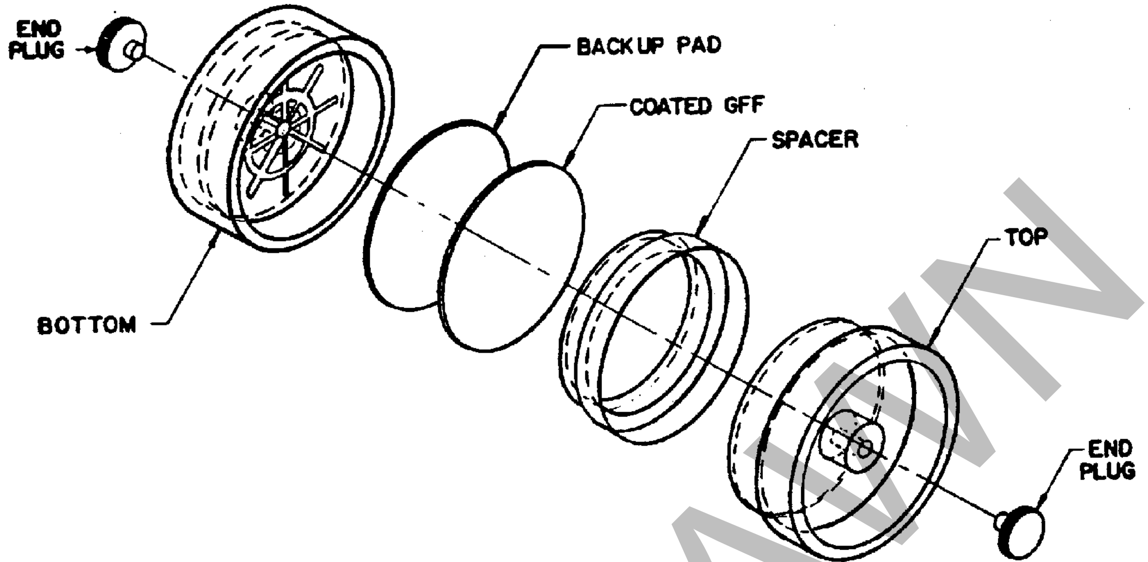


Figure 2.1.2. A drawing of a sample cassette.

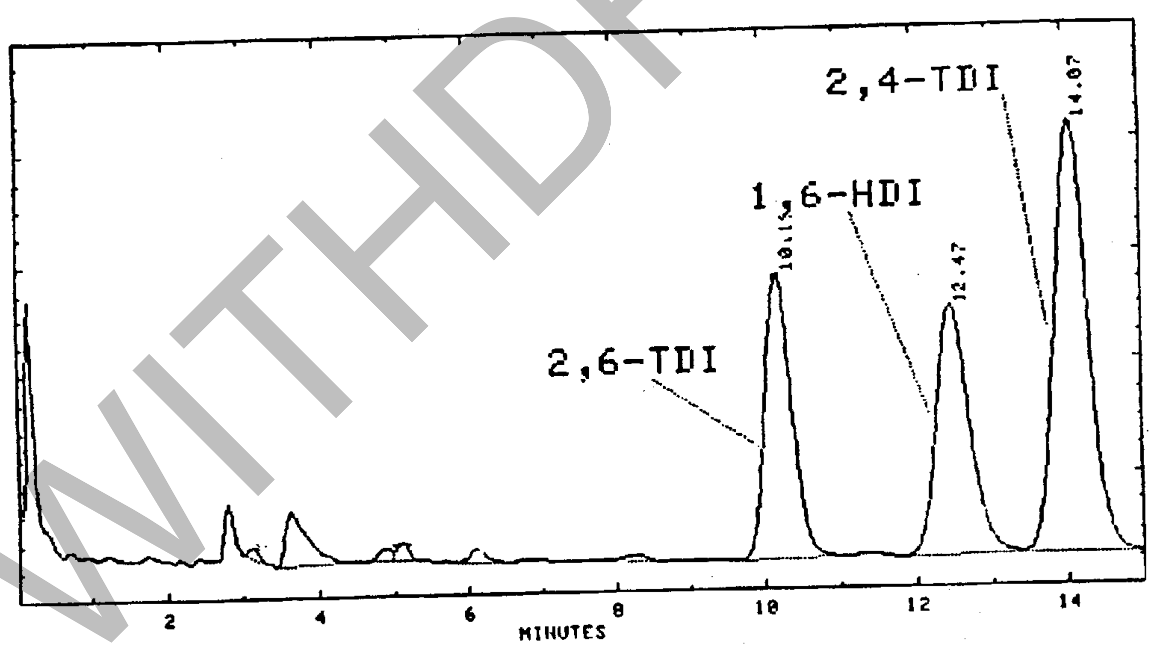


Figure 3.5.1. Chromatogram of standards of the three diisocyanates.

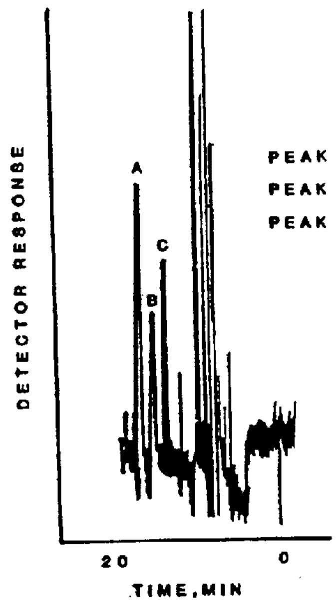


Figure 4.1. Analytical detection limit for the diisocyanates.

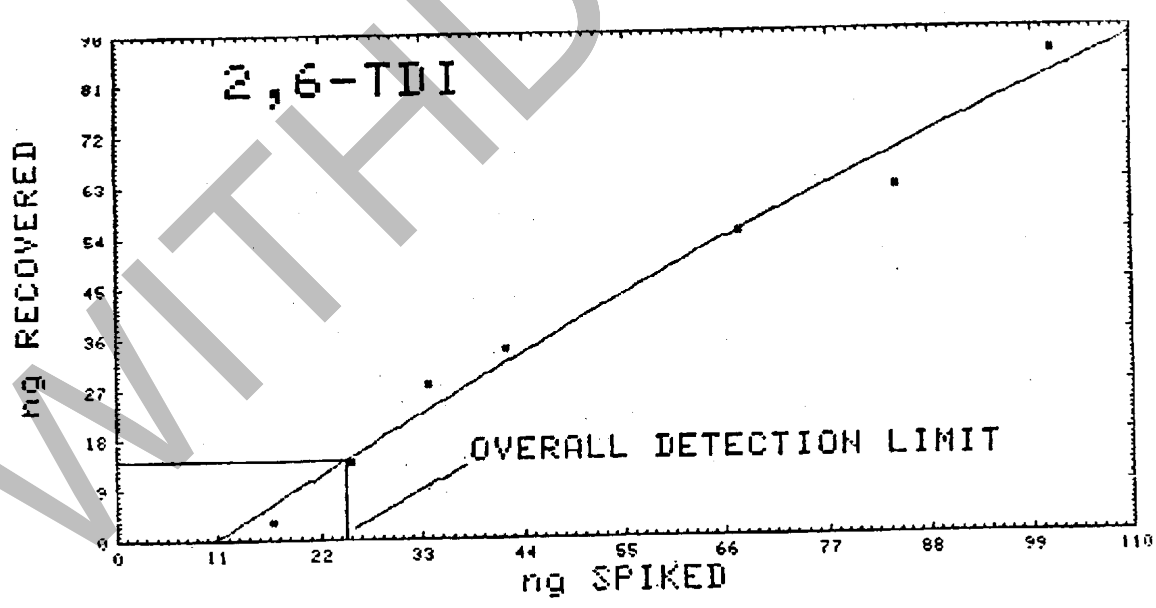


Figure 4.2.1. Detection limit of the overall procedure for 2,6-TDI.

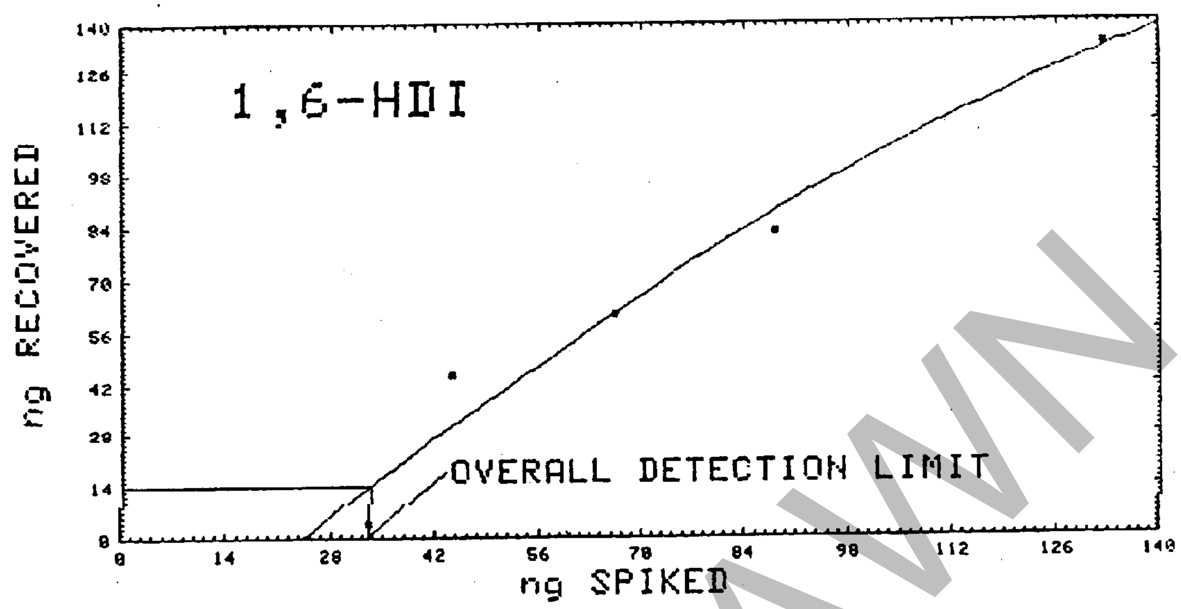


Figure 4.2.2. Detection limit of the overall procedure for HDI.

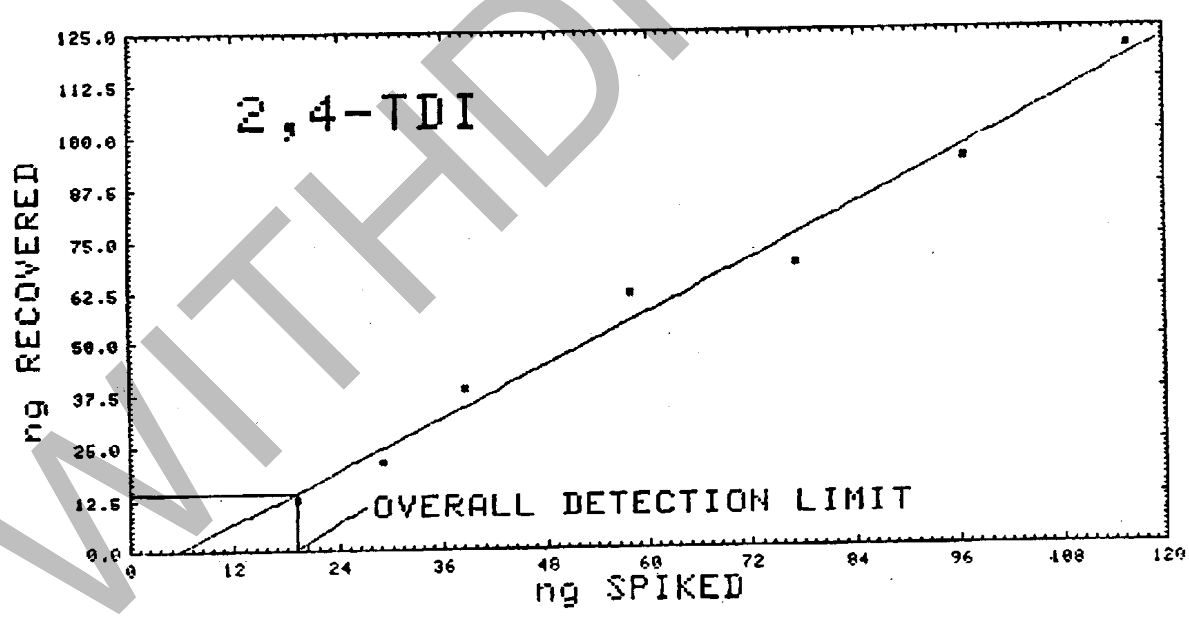


Figure 4.2.3. Detection limit of the overall procedure for 2,4-TDI.

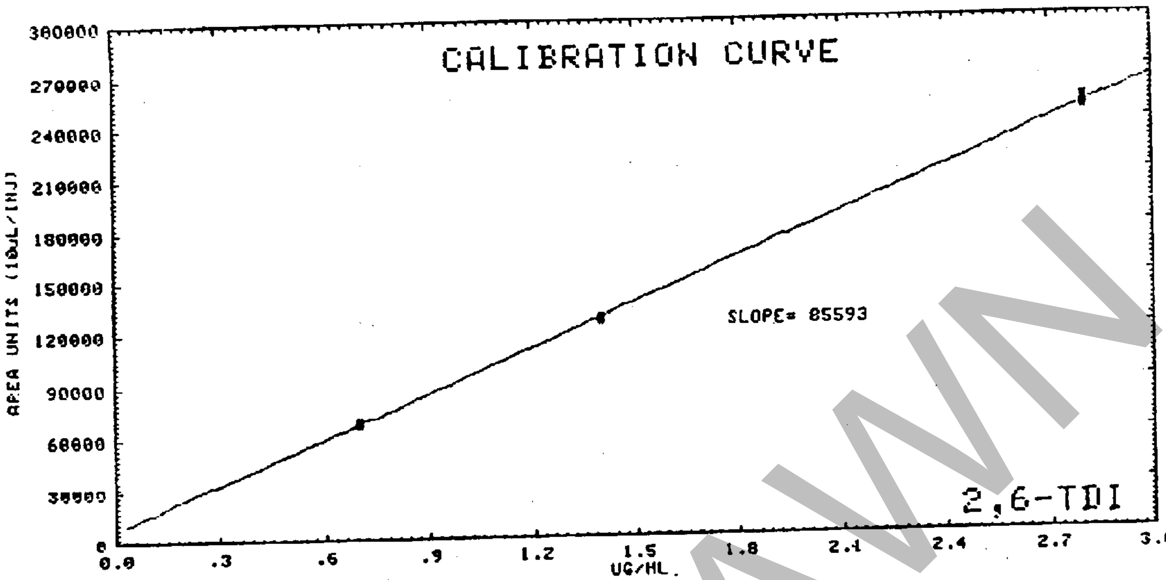


Figure 4.4.1. Calibration curve for 2,6-TDI.

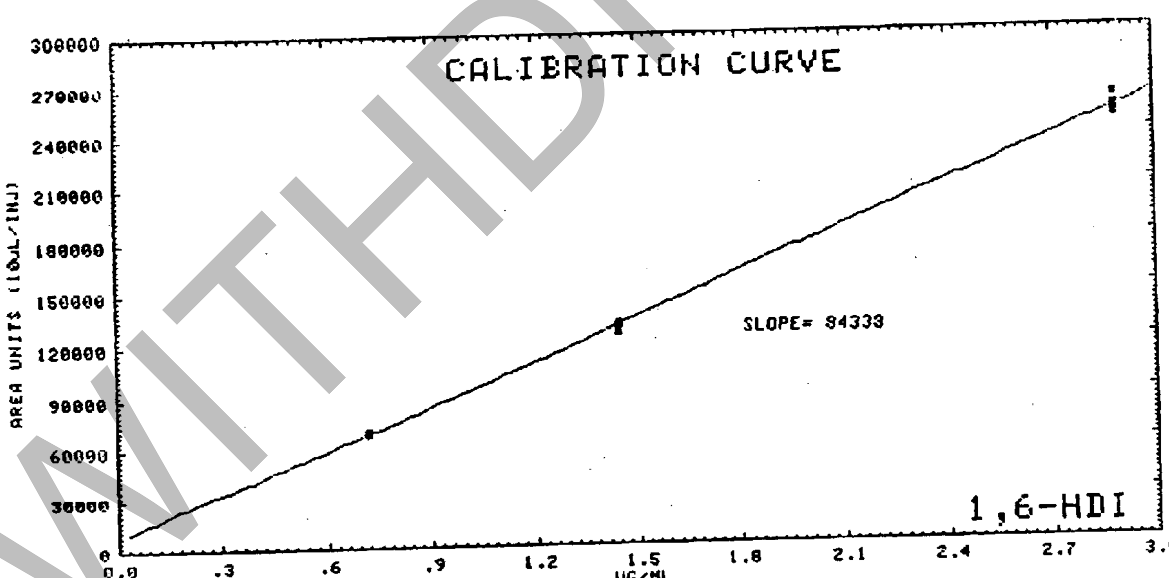


Figure 4.4.2. Calibration curve for HDI.

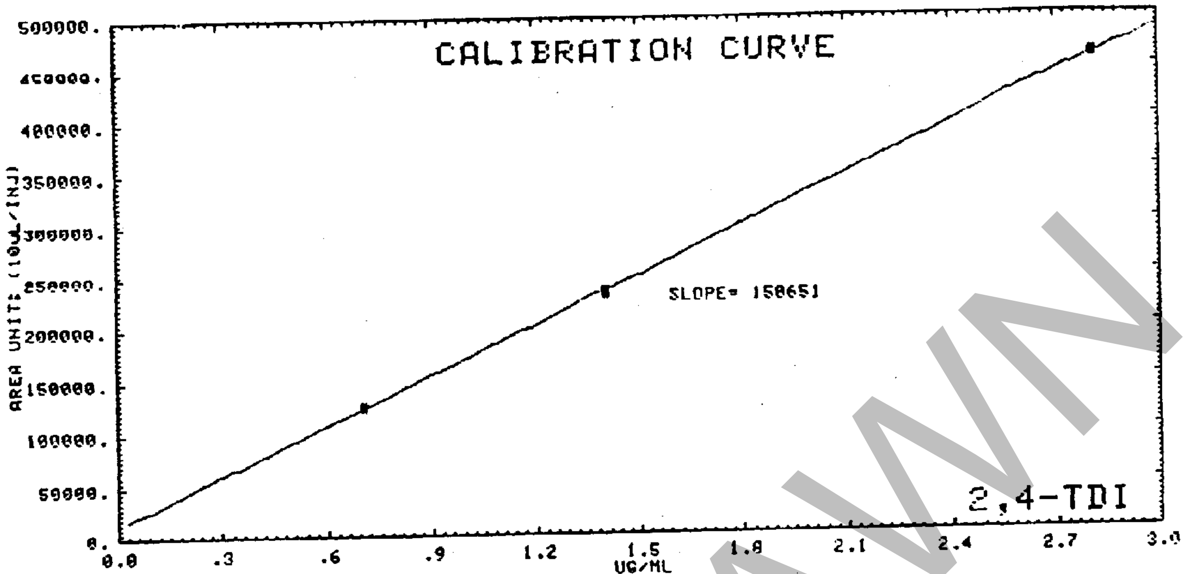


Figure 4.4.3. Calibration curve for 2,4-TDI.

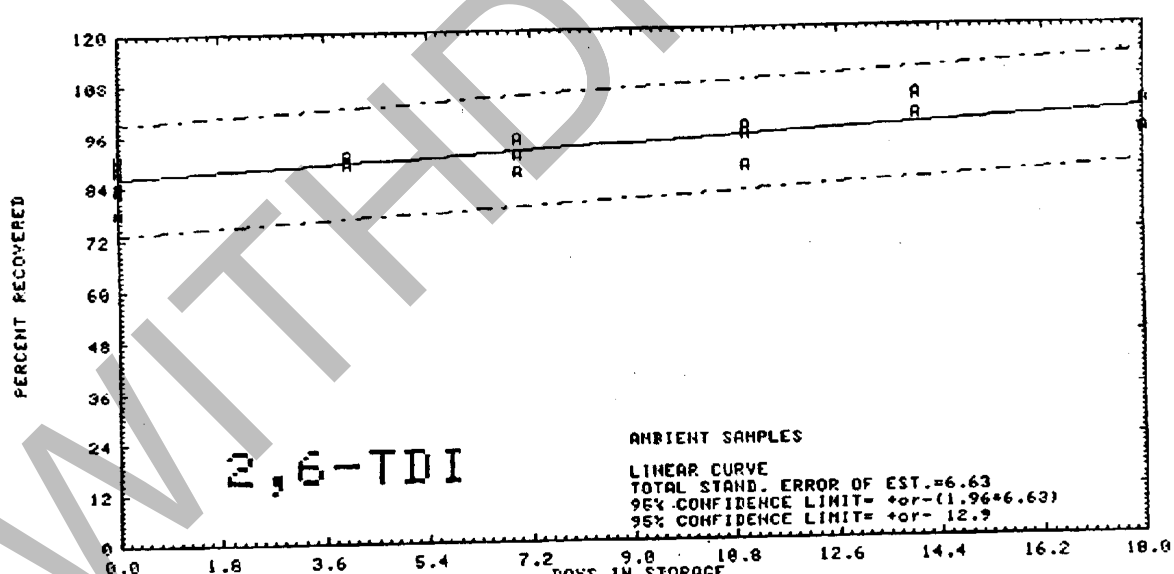


Figure 4.9.1. Ambient storage test for 2,6-TDI.

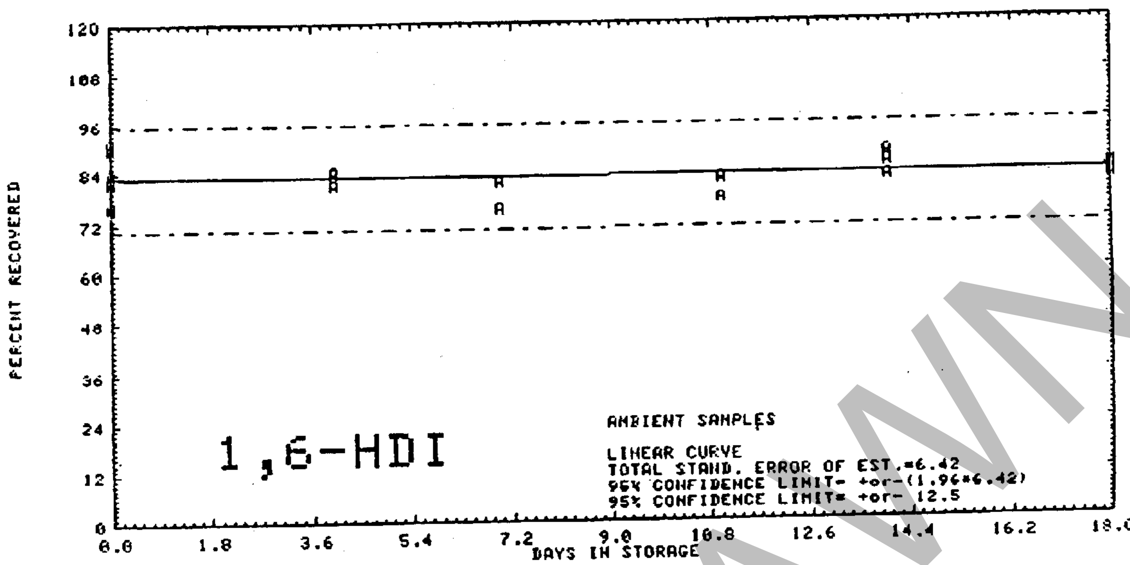


Figure 4.9.2. Ambient storage test for HDI.

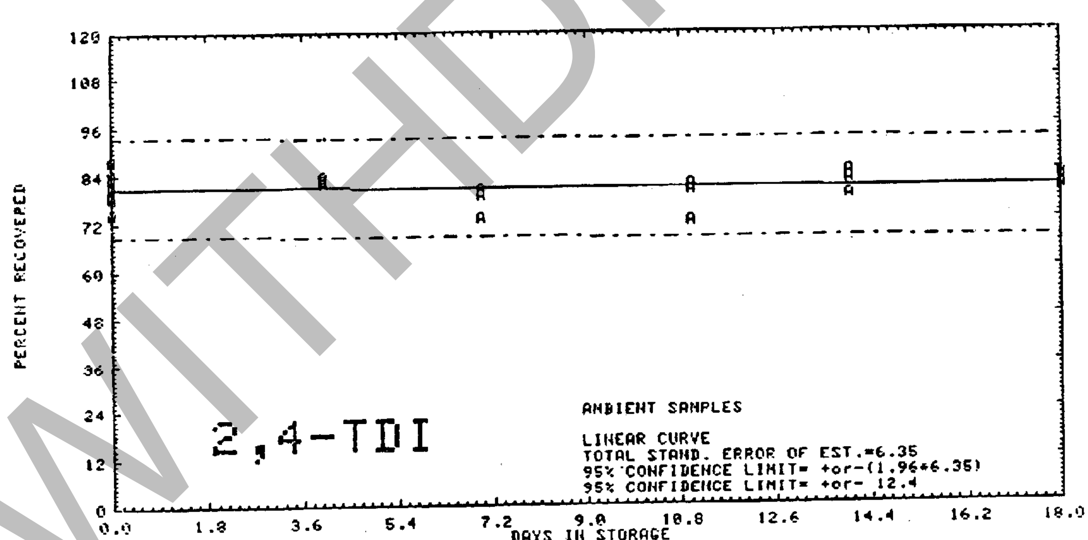


Figure 4.9.3. Ambient storage test for 2,4-TDI.

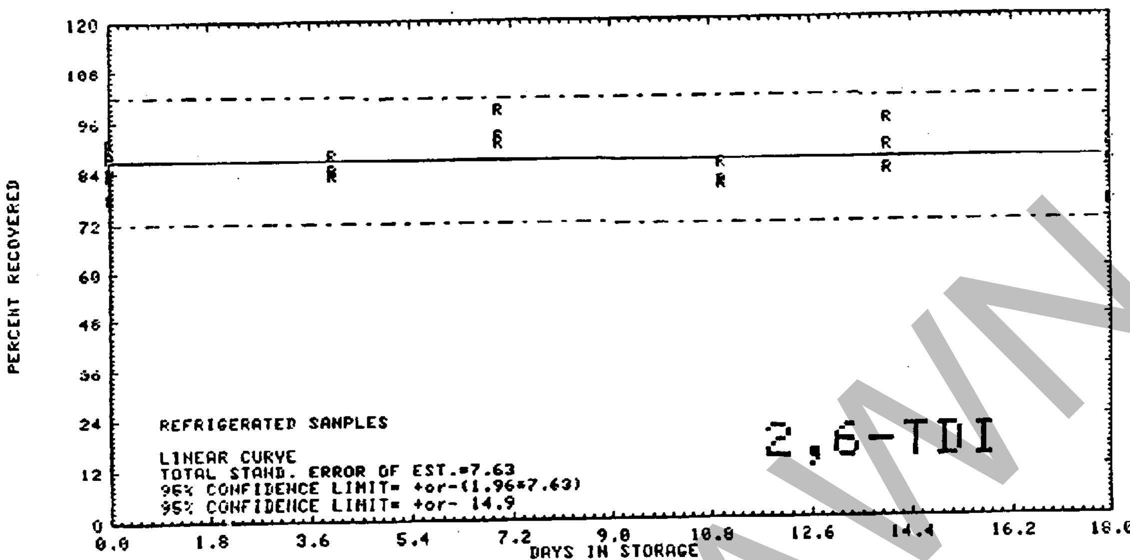


Figure 4.9.4. Refrigerated storage test for 2,6-TDI.

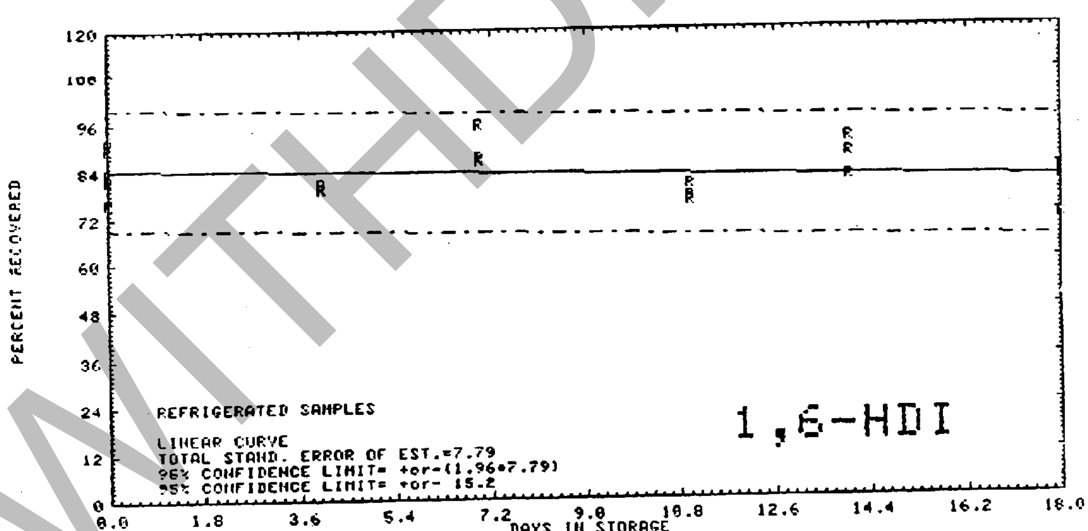


Figure 4.9.5. Refrigerated storage test for HDI.

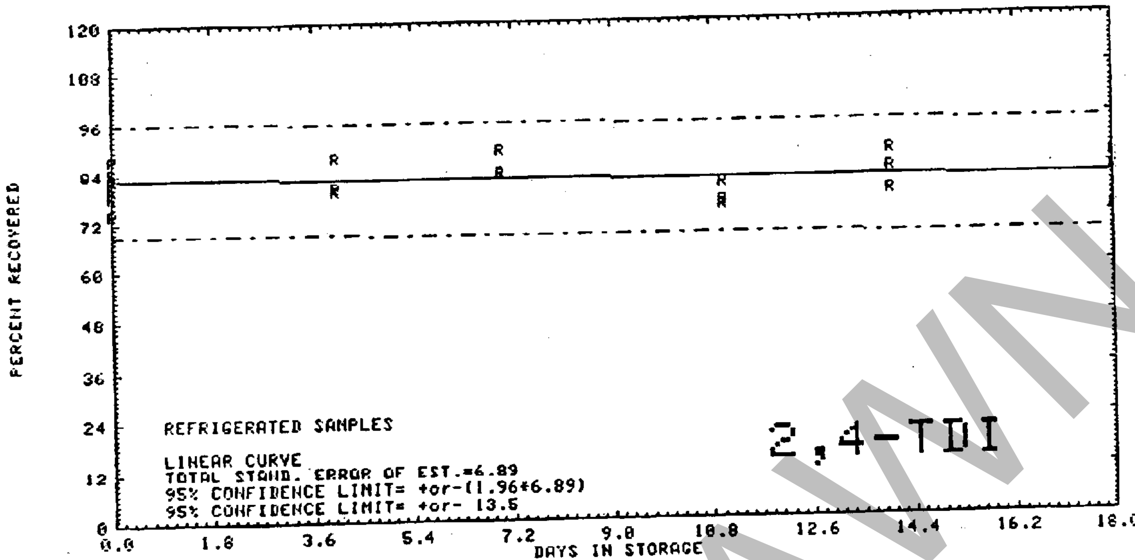


Figure 4.9.6. Refrigerated storage test for 2,4-TDI.

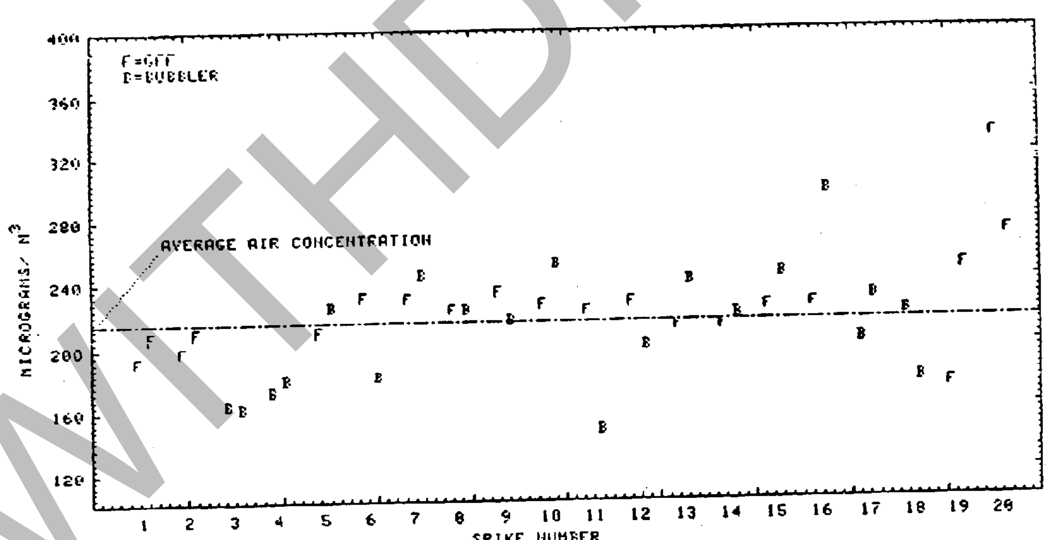


Figure 4.10. Side-by-side comparison of coated filters and bubblers.

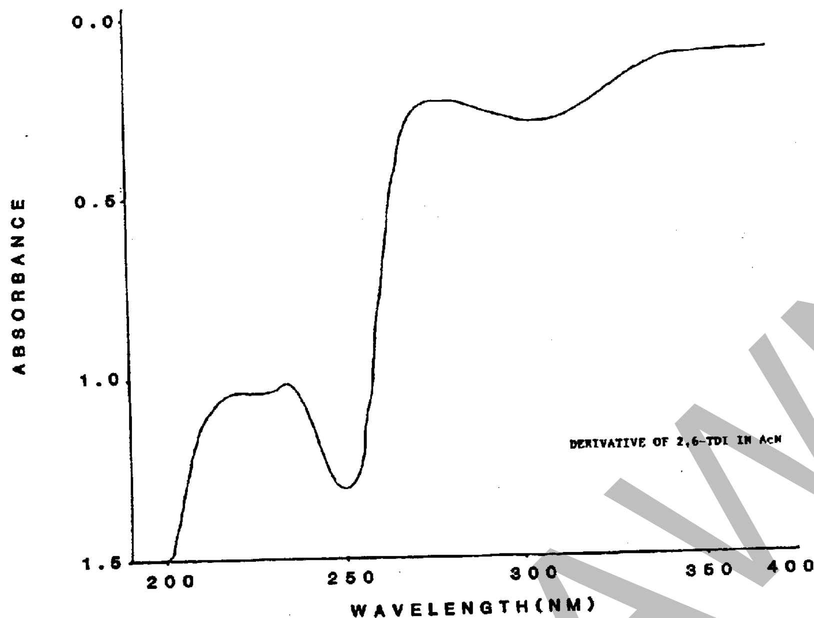


Figure 4.11.1. UV spectrum of 2,6-TDI derivative in acetonitrile.

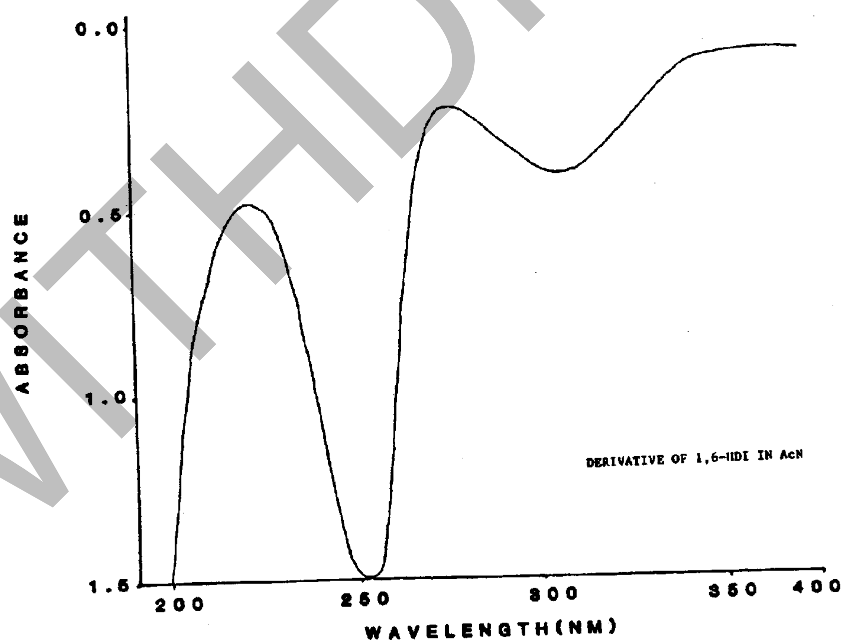


Figure 4.11.2. UV spectrum of HDI derivative in acetonitrile.

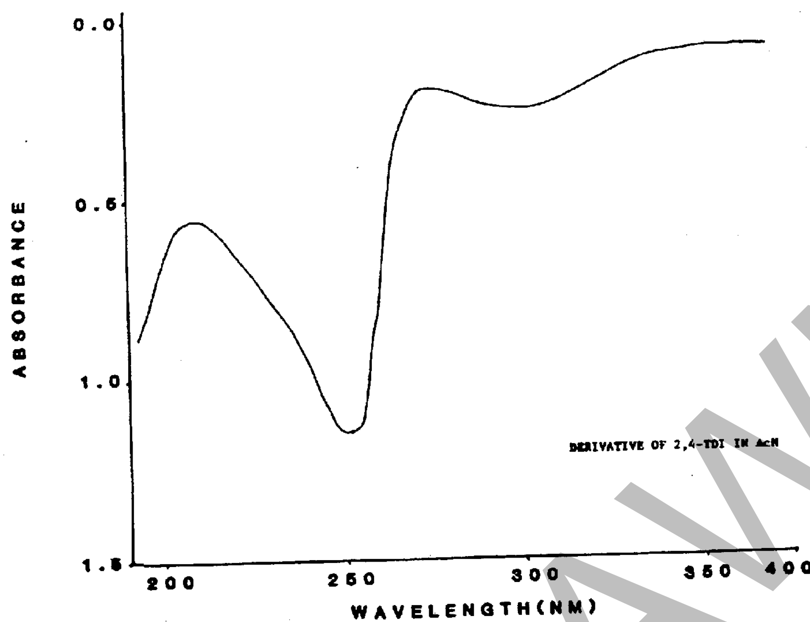


Figure 4.11.3. UV spectrum of 2,4-TDI derivative in acetonitrile.

5. References

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