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CHARACTERIZATION OF ATMOSPHERIC EMISSIONS FROM POLYURETHANE RESIN MANUFACTURE

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CHARACTERIZATION OF ATMOSPHERIC EMISSIONS FROM POLYURETHANE RESIN MANUFACTURE

by

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Approved for:

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29 August 1974

SUMMARY AND CONCLUSIONS

Midwest Research Institute arranged for and conducted tests at a polyurethane resin facility to help answer the question as to whether or not this industry has an air pollution problem. Requirements for conducting meaningful tests include:

1. Adequate analytical methods,

2. Adequate sampling techniques,

3. Accurately monitored process variables,

4. Raw data for dispersion modeling, and

5. Scrubber efficiency data.

After the necessary negotiations, literature and laboratory work were completed, a mobile laboratory was taken to the test site where samples were analyzed both on-site and on a delayed basis at MRI. In the process studied, nitrogen continuously sweeps through the reactor containing alkyd resin, toluene diisocyanate (TDI) and mineral spirits. Samples were taken of the "sweep" gas as it left the reactor and also after it had passed through a scrubber whose major function was to hydrolyze TDI to amines. On the inlet side of the scrubber, a manifold was inserted to take samples through an impinger for colorimetric measurement of TDI; cryogenic traps and an MDA-tape analyzer for TDI were also inserted. The outlet sampling manifold was the same as the inlet manifold, except evacuated bulbs were used in place of the cryogenic traps. Cryogenic traps could not be used in the outlet system because of the high moisture content.

Emissions are greatest during the first part of the reaction when an exotherm occurs (from 150 to 200°F) and TDI concentration is the highest. Analytical data show both the inlet and outlet scrubber streams contain mainly nitrogen, mineral spirits, and TDI. The aqueous scrubber removed very little TDI during these tests. Scrubber outlet composition during the peak 1-hr emission period averaged:

Nitrogen	97.5% by vol
Mineral spirits	2.5% by vol
TDI	1.2 ppm by vol

Applying the Gaussian plume dispersion model presented in EPA workbook AP-26 to these analytical data, one can predict that the maximum ground-level concentration of TDI and mineral spirits should be only about 0.1% of the maximum allowable value for an 8-hr averaging period. Total emission of TDI was about $\frac{1.8 \times 10^{-8} \text{ lb TDI}}{\text{Pounds Product}}$.

Based on this study, one can draw the following major conclusions:

1. The maximum ground-level concentration of both TDI and mineral spirits is about 0.1% of the maxima allowable for an 8-hr averaging period, thus indicating that no hazard existed at the test site under the conditions studied.

2. Statement No. 1 is true in spite of the fact that the TDI scrubber was operating poorly* at the time of sampling. This would indicate that scrubbers are not needed for TDI removal <u>if the specific process and conditions</u> which were studied are kept under control.

3. Should several such plants be clustered in or around a common community, as is frequently the case in the chemical processing industry, a problem could result.

From the conclusions, it is recommended that:

1. Other test sites be studied under a broader range of operating conditions to determine air emissions.

2. At present, caution should be exercised in extrapolating the data presented herein to the entire polyurethane coatings industry, since it is specific to one plant.

3. Priorities should be extended to other areas of the plastics industry having potentially high hazardous/toxic emissions.

4. A search for possible clustered polyurethane sites might be in order; this might also apply to other plastics processes.

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* Reported by plant site personnel subsequent to MRI sampling.

SECTION I

INTRODUCTION

The Environmental Protection Agency (EPA) recognizes the plastics industry as a potentially serious source of air pollution. In a recent study, Foster D. Snell, Inc., determined the most likely resin manufacturing processes that contribute to hazardous/toxic objectionable emissions. Through a series of semiquantitative calculations they used a "priority decision model" to show that the four industries, listed in decreasing order of priority below, were at the top of the list insofar as potential air pollution is concerned:

1. Polyurethanes

2. Acrylics

3. Alkyds

4. Phenolics

The priority ratings were arrived at by including only resin manufacturing considerations and not such factors as monomer synthesis, polymer fabrication, etc. In the case of polyurethanes, foams were specifically excluded.

As the above-described findings were being made, MRI was contracted through Task No. 38 of EPA Contract No. 68-02-0228 to conduct the field work associated with the task under consideration. On 8 November 1973, a joint meeting of EPA, Foster D. Snell, Inc., and MRI personnel was held to initiate the field-testing phase of the program. Consistent with mutual agreement Snell was to be contacted before making industrial contacts; it was also agreed to limit early contacts to polyurethanes. In compliance with these agreements, MRI personnel proceeded to contact the following companies suggested by Foster D. Snell, Inc.: Ashland Chemical Company, Diamond Shamrock Company, and Witco Chemical Company. Ashland Chemical Company management reported that it used only a low level of toluene diisocyanate (TDI) as a viscosity builder and believed its operation to be atypical for study. Diamond Shamrock had sold its operations to Stephan Chemical Company; only know-how, and not facilities, was sold. Witco Chemical

Company admitted to being a producer of polyurethane coatings and promised some stack composition data as soon as it had a chance to make the proper analyses. Witco did not seem willing to admit anyone for tests, and its own analyses have not been forthcoming.

As the next approach, MRI obtained permission from Foster D. Snell, Inc., and EPA to contact other companies for potential emission studies. At this point, MRI was allowed to guarantee complete anonymity to the company where the tests were to be run. This approach was ultimately successful and was the way admittance was obtained to the test site described in this report.

Midwest Research Institute also asked EPA to contact Mobay Chemical Company as a potential test site. Mobay seemed willing to cooperate; however, project funds did not permit testing at a second polyurethane plant at this time. The approach used with Mobay might well be the easiest way to obtain admittance to test sites in the future.

As soon as MRI received word that studies <u>might</u> be permitted at an "anonymous" location, a meeting was held with the industrial concern involved and the potential test site was visited. While negotiations were uncertain at this point, a formal proposal (in writing) by MRI solidified admittance to the final test site which must remain anonymous. The actual testing and necessary preparatory data were obtained on 20, 21 and 22 May 1974, during a typical run producing a urethane coating resin.

The following section gives several further comments on site selection, before the overall schedule of the project is discussed in Section III. All aspects of experimental details including a description of the test site, technical considerations of both an equipment and analytical nature, and test schedule are present in Section IV. The process studied and analyses are given in Section V, followed by Conclusions and Recommendations, which are given respectively in Sections VI and VII.

SECTION II

SITE SELECTION

Foster D. Snell, Inc., provided MRI with a list of companies producing urethane coating resins for either captive use, or for sale, or both. This information is given in Appendix A; locations of plants are also listed. The companies have been alphabetized for easy reference. The first thing one notes is that there is a large variety of companies--large and small--producing urethane coating resins. Obviously, there is no typical recipe and no typical set of operating conditions, because each producer has his own group of proprietary products made in his own equipment. This makes it very difficult to extrapolate data from one plant and caution indeed needs to be exercised in this regard. On the other hand, it was felt that information from one carefully selected plant might give an indication of whether there is a problem with polyurethanes in general.

From conversations with producers of polyurethane resins and from MRI's own technical information (see Section IV), we know that the most dangerous chemical used during the manufacture of polyurethane coating resins is toluene diisocyanate. Furthermore, no major producer of such resins is known to operate without a closed reaction system. The task's goal thus becomes fairly simple: to run tests at a site where major quantities of TDI are handled in a closed system producing urethane resins.

SECTION III

EXPERIMENTAL PLAN

TEST REQUIREMENTS

Several requirements were necessary to help answer the basic question: "Does the polyurethane coatings industry have an air pollution problem?" Among them were:

1. Adequate analytical methods for quantifying the major constituents of polyurethanes air emissions were needed. This required some literature searching as well as considerable laboratory work to check out the methods to be used.

2. Adequate sampling techniques needed to be worked out which would yield representative samples. Considerable experience at MRI on related programs assisted in this area which is described in detail later in this section of the report.

3. Temperature, pressure and stack velocity had to be monitored to define process variables and calculate results.

4. Sufficient chemical, process and geometric data were needed to determine the dispersion of air emissions.

5. Some idea of the efficiency of the cleanup or scrubber system (if used) was desired.

6. Before any test of this type can be successful, the proper mix of personnel and talents was needed. Thus, a blend of chemical engineers, mechanical engineers, analytical chemists, polymer chemists and technologists were used to adequately pursue the goals of the project.

TEST SITE

The analyses were conducted partially on-site and partially on a delayed basis by collecting samples to bring back to MRI. Delayed analyses were

required for some analyses which could not be performed in the field. A photograph showing the general test area with the MRI mobile laboratory parked at the test site, and a schematic of the test site are given in Figure 1. The schematic shows the location of the scrubber system, stack, unloading station, etc. Because of the complexity of the roof line, several simplifications have been made. Although not immediately obvious from the drawing, the TDI unloading inlet is located near the entrance to the reaction area where the scrubber is also located. The interior of the mobile laboratory is shown in Figure 2.

Figure 3 shows a block diagram of the process itself. Charge components for the urethane resin reactor consist of alkyd resin, mineral spirits and TDI. The alkyd resin (previously diluted with mineral spirits) is charged to the reactor first and then preheated to about 150°F. Nitrogen pressure (about 2 oz) is maintained on the reactor at all times, with the vented gases going through the scrubber system. At 150°F, TDI is added and reaction commenced; an exotherm to about 200°F usually occurs during the period subsequent to TDI addition. The reaction is followed by withdrawal of aliquot portions directly from the reactor which are checked for viscosity. As soon as the proper viscosity is reached, the reaction is considered ready to terminate through a quench of alcohol and water. The quench removes the last traces of TDI. During the tests conducted in this study, gas stream samples were taken at the points indicated in Figure 3 at Sample Points Nos. 1 and 2. Samples from the former have no meaning insofar as air emission is concerned, but are needed to calculate scrubber efficiency. Ambient samples were also taken near the scrubber.

TECHNICAL CONSIDERATIONS

Pertinent Variables

In the reaction under study, the major process variables influencing gas emissions to the atmosphere are:

1. Reaction temperature,
2. Nitrogen purge rate,
3. Reaction rate (uptake of TDI),
4. Scrubber design and efficiency,
5. Diluent type and amount,
6. Alkyd type and amount, and
7. TDI amount.

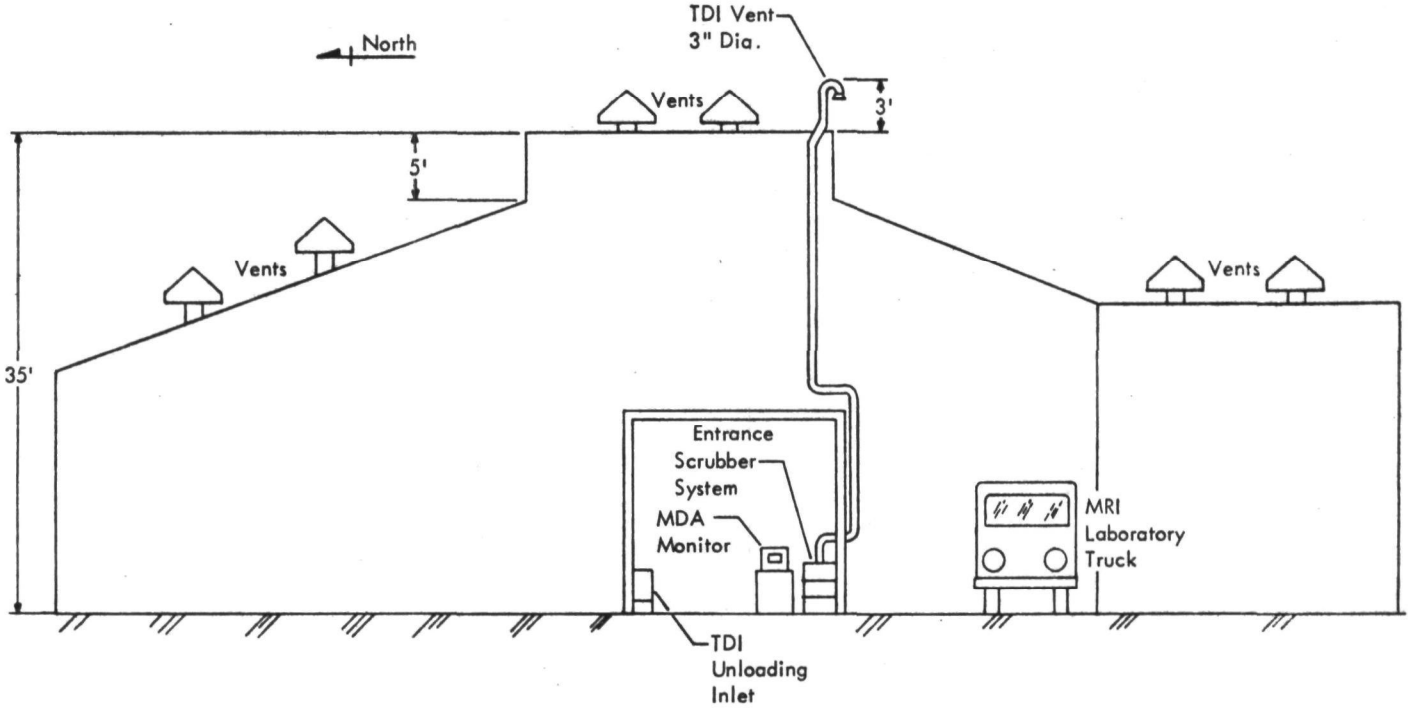
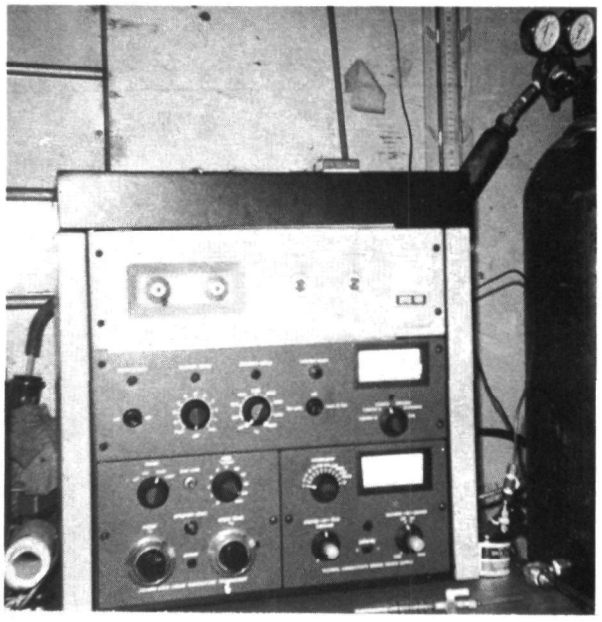


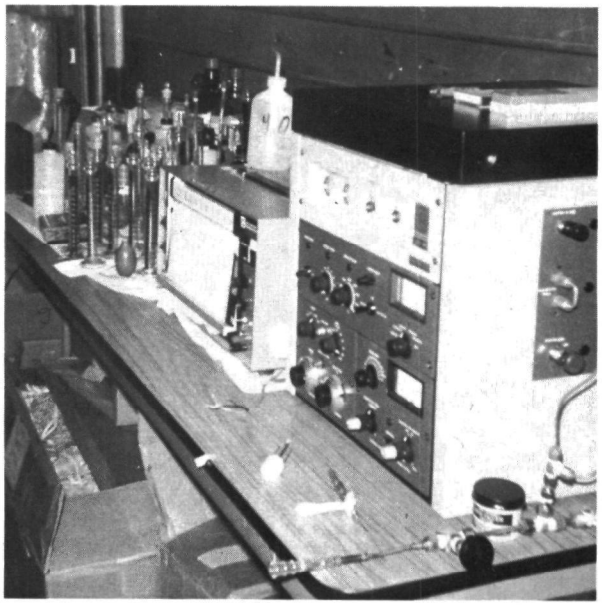
Figure 1. Photograph of general test area and mobile laboratory and schematic of the test site.

Photograph A. Colorimetric test equipment



Photograph B. Gas chromatograph

Photograph C. Colorimetric test equipment



Photograph D. Combined colorimetric equipment and gas chromatograph

Figure 2. Mobile laboratory interior.

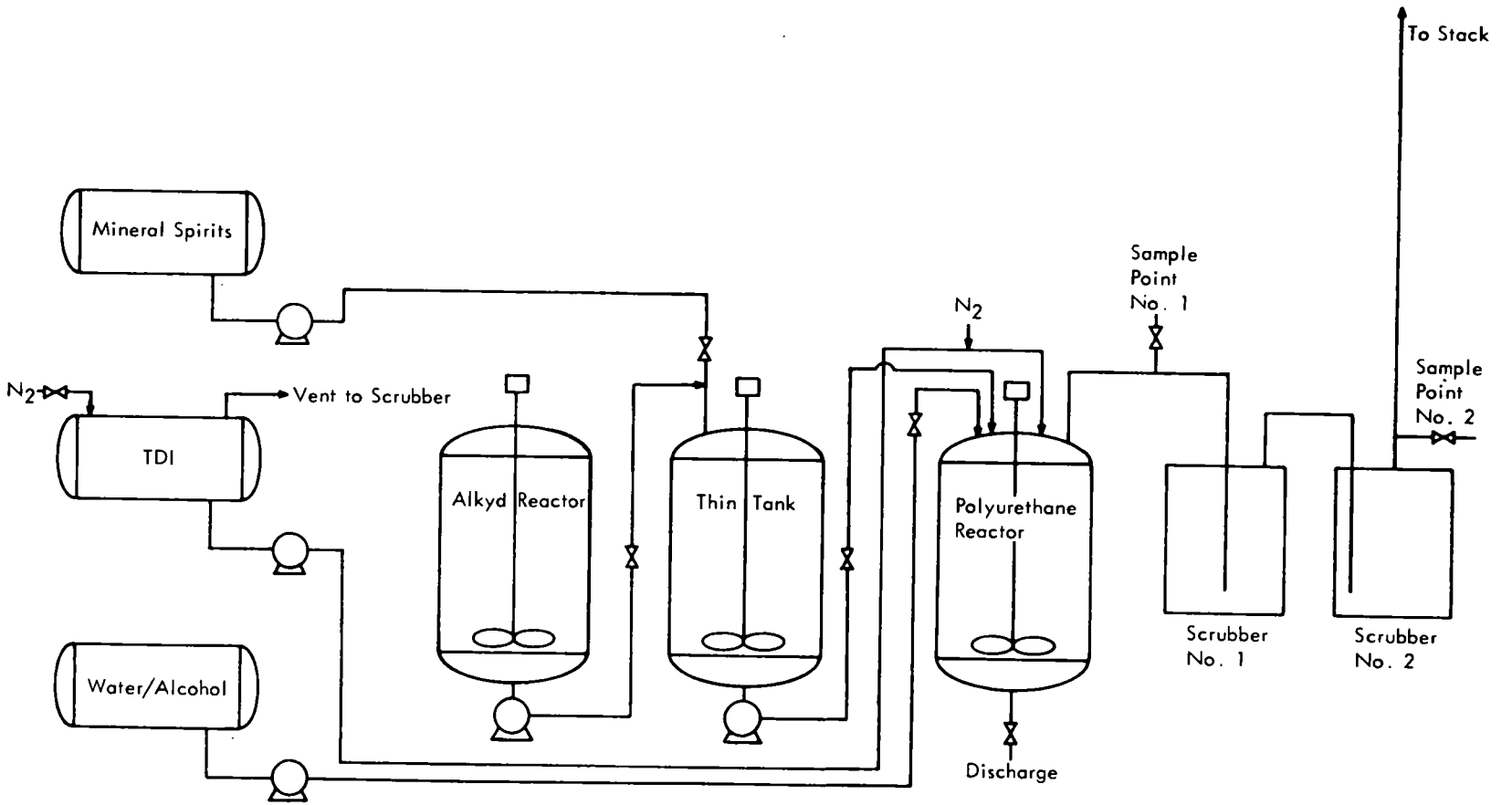


Figure 3. Flow diagram for polyurethane reaction system.

It would appear that all of these factors are easy to establish and control. In actuality, the exotherm that occurs after the addition of TDI varies somewhat depending on how "old"* or "new"** the TDI is when it is added. Thus, a "hot" reaction normally results from "new" TDI, while some coaxing (heat input) of the reaction is needed whenever "old" TDI is used. The amount of TDI that is free to escape obviously varies between "old" and "new" TDI. Test data reported herein were obtained using "new" TDI and, thus, the reaction period was somewhat shorter than the 24-hr period obtained using the older TDI.

Constituents and Their Behavior

Of the major charge components, the alkyd resin can vary greatly in composition; however, the one used in this study was made using glycerine, linseed, pentaerythrytol, phthalic anhydride, xylene, and mineral spirits. It recently came to our attention that alkyd resin plant emissions were studied in detail under Contract No. 68-02-0259. While that information is not readily available to MRI, data from a private source show that the major component coming from an alkyd plant is xylene. The behavior of this solvent is well documented.

Turning more to the urethane resin process under study, it is informative to look at TDI itself. First of all, selected characteristics of chemicals used in polyurethane resin manufacture are given in Table 1. TDI has a relatively high boiling point (250°C), a low odor threshold (0.4 ppm), and an even lower maximum allowable exposure concentration (8-hr weighted average) of 0.02 ppm. It is obviously of far greater toxicity at low concentrations than mineral spirits, which have a maximum allowable exposure (8 hr) of 500 ppm.

Chemical Analyses

From a presurvey of the process under study, it was evident that TDI (plus its hydrolysis products) and mineral spirits would probably be the major constituents in the streams analyzed. Thus, the best and most reliable means for determining low to moderate concentrations of these components were sought. Insofar as TDI is concerned, it can be detected at 0.0035-0.070 ppm levels on 40-liter air samples using a method first reported by Marcali[1/] and presently sanctioned by the Department of Health, Education, and Welfare. The only apparent shortcoming of this method is that it is not specific to TDI but determines both TDI and amines.

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* Presumably part of the isocyanate has already reacted.

** Recently received from supplier.

1/ Marcali, Anal. Chem., 29, 552-558 (1957).

Table 1. SELECTED CHARACTERISTICS OF CHEMICALS USED IN POLYURETHANE RESINS MANUFACTURE

	Odor Threshold	Maximum Allowable Exposure (8-hr weighted avg)[a]	Physical Data
Toluene diisocyanate (TDI)	0.4 ppm	0.02 ppm 0.14 mg/m^3	250°C boiling point < 1 mm Hg vapor pressure
4,4'-Diphenylmethane diisocyanate (MDI)	N.A.	0.02 ppm 0.2 mg/m^3	194-199°C boiling point N.A.
Hexamethylene diisocyanate	N.A.	N.A.	N.A.
4,4',4"-Triphenylmethane triisocyanate	N.A.	N.A.	N.A.
Mineral spirits	N.A.	500 ppm	150-210°C boiling point

a/ Values reported in Threshold Limit Values of Airborne Contaminants and Intended Changes, adopted by American Conference of Governmental Industrial Hygienists (1970).

A continuous tape apparatus manufactured by MDA Scientific of Park Ridge, Illinois, apparently overcomes this shortcoming and detects TDI at levels as low as 20 ppb while meeting OSHA criteria. In the present study both methods were used to complement one another.

Mineral spirits were analyzed by gas liquid chromatography, mass spectrometry and infrared spectroscopy. The goal was not to identify individual components of the mineral spirits, but rather to identify the mixture of hydrocarbons on a "fingerprint" basis. A further goal was to make certain that other major organics were not hidden in the complex mixture.

Details of the various analyses are given in Appendix B.

SAMPLING

Equipment

A block diagram showing the overall sampling scheme is shown in Figure 4. On the inlet side of the scrubber, the manifold was connected to the MDA monitor, a cryogenic trap and a bubbler. Temperature and pressure in the gas stream were also monitored. A photograph of the inlet sampling system is shown in Figure 5-D. Outlet gases were sampled through a similar manifold shown in Figures 5-A, 5-B, and 5-C. The main difference between the inlet and outlet manifolds was the substitution of a preevacuated bulb for the cryogenic trap at the outlet; this was necessary because a cryogenic trap could not be used on the water vapor-saturated outlet side.

Procedures

TDI-Colorimetric Bubbler Trains - The impinger or bubbler (Figure 6-B) was rinsed with absorbing reagent and filled with 15 ml of the same reagent. For analysis, the bottom of the first impinger only was removed. A complete discussion of this procedure is given in Appendix B.

TDI-MDA Tape - Two MDA tape monitors were mounted in enclosed, air-purged boxes. Approximately 3-ft lengths of 1/4-in. Teflon tubing connected each monitor to the manifold valve (Figure 4). A complete discussion of this procedure is given in Appendix B.

Cryogenic Traps - Stainless steel traps (Figure 6-C) were cleaned with chloroform, the open ends were capped, and then the traps were pumped down. The traps were shipped to the test site evacuated. At the test site, each trap was numbered, uncapped and a reducing fitting (1/2 in. x 1/4 in.) attached to the valve outlet.

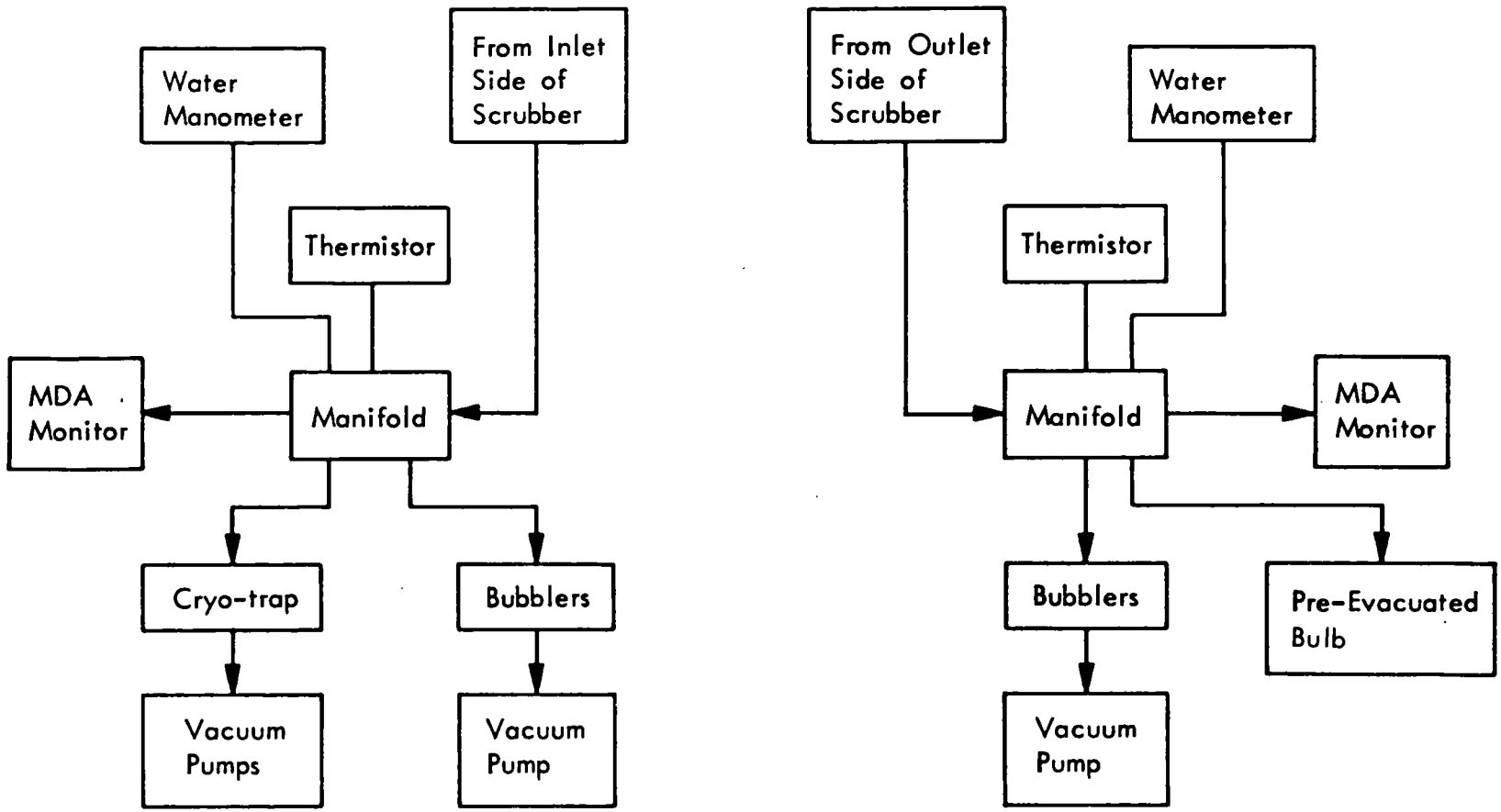
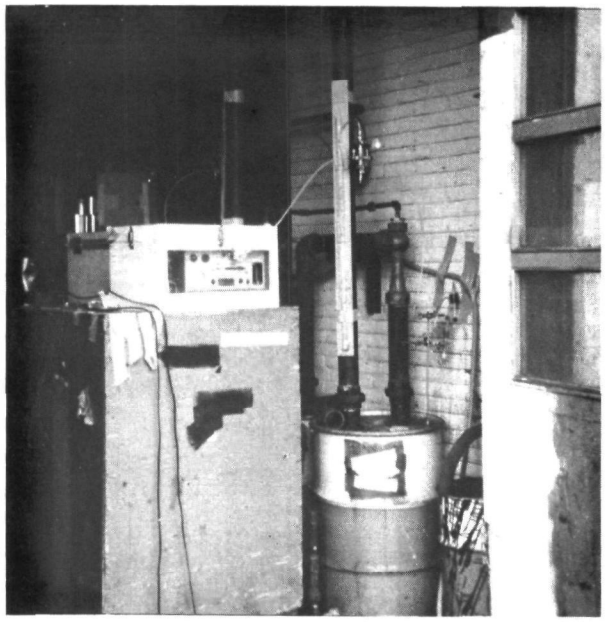
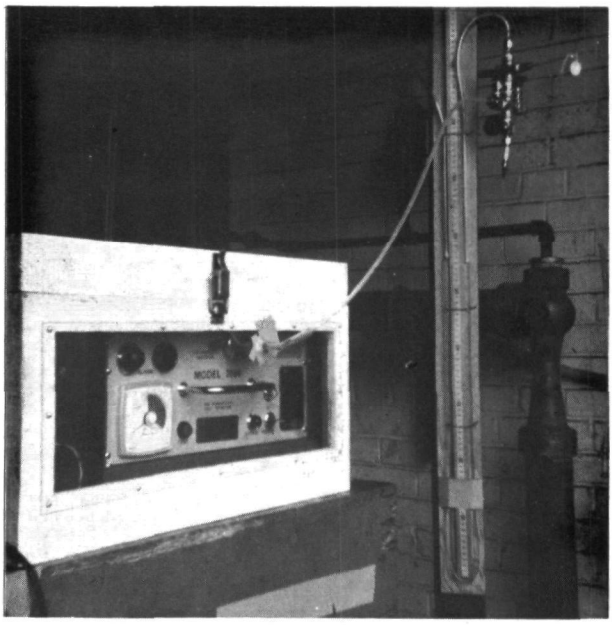


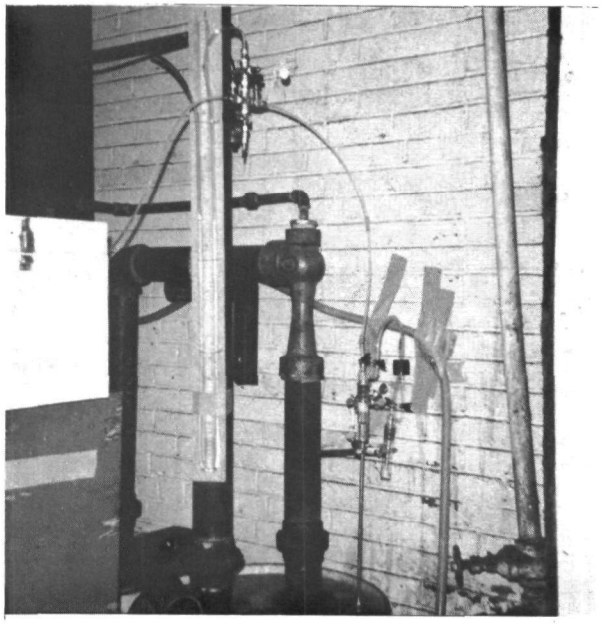
Figure 4. Inlet and outlet sampling manifolds.



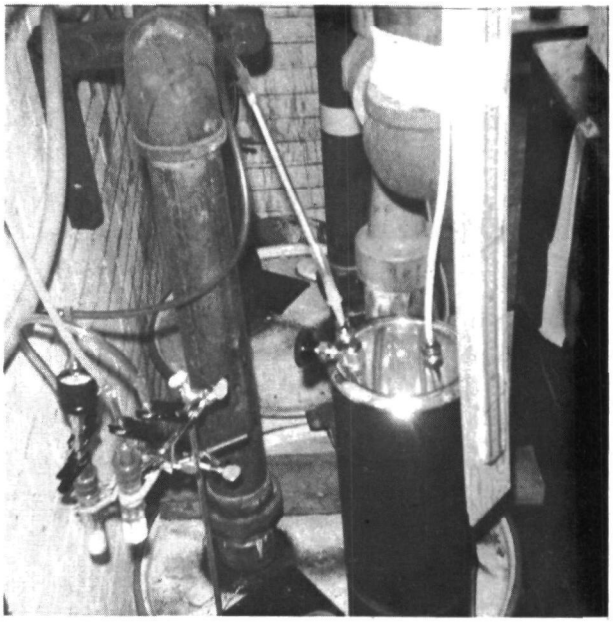
Photograph A



Photograph B



Photograph C



Photograph D

Figure 5. Sampling system at test site.

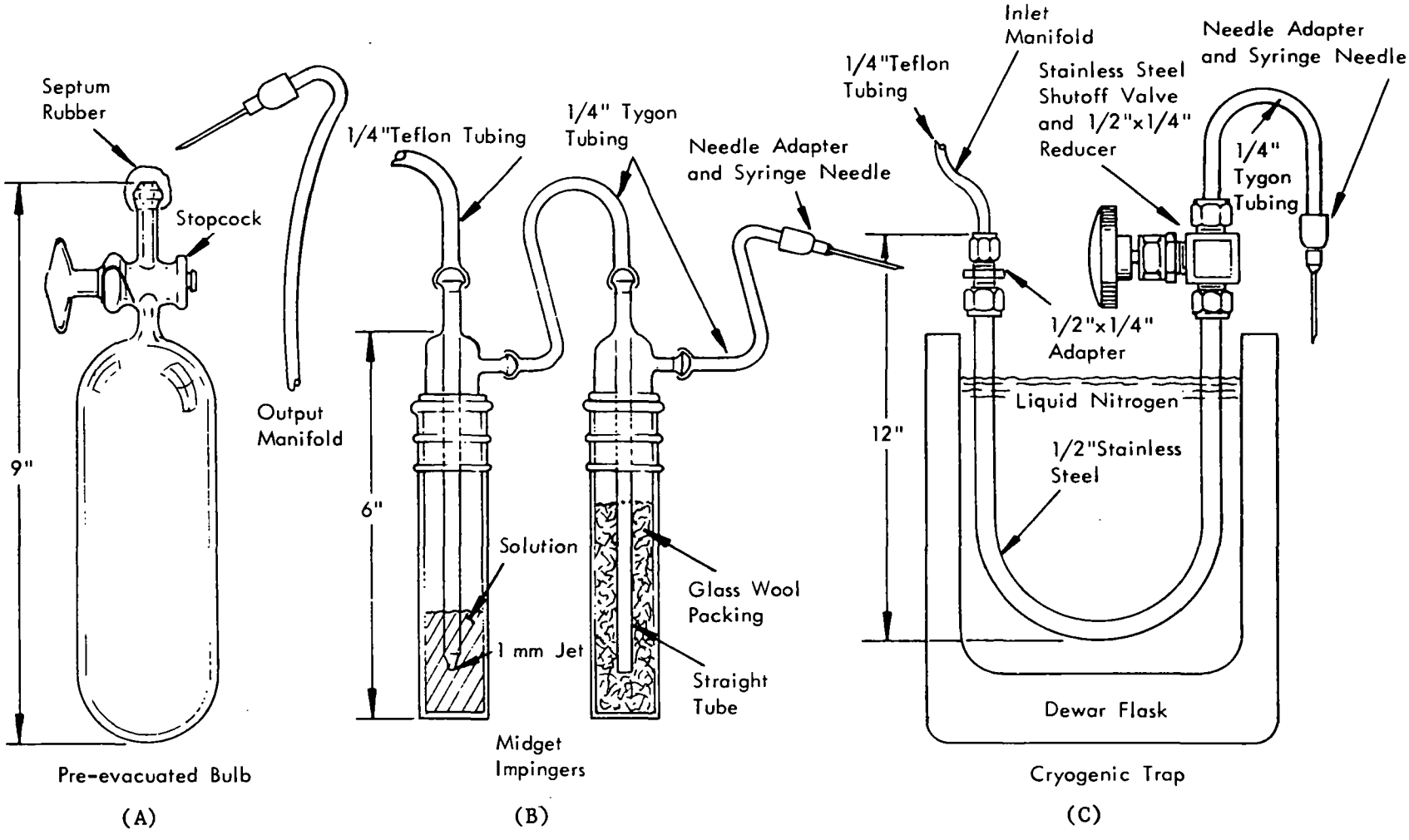


Figure 6. Sampling equipment.

The same needle flow control orifice--standardized at 1 liter/min--was used for all tests. The uncapped end was fitted to the manifold via a 1/2 in. x 1/4 in. reducing union attached to the trap. A short section of Teflon tubing between the manifold valve and the reducing union provided thermal isolation to prevent excessive condensation.

For each test, the manifold and trap valves were opened, a rotameter inserted on the outlet side of the trap, and the needle orifice inserted through the wall of 1/2 in. I.D. rubber tube which was connected to a vacuum pump. After obtaining the proper flow reading, the rotameter was removed and the sample period started by immersing the trap into liquid nitrogen. At the end of sampling the valves were closed and the trap removed and capped.

Evacuated Bulbs - Prior to shipment, new septa were installed on the bulbs (Figure 6-A) and the bulbs were pumped down to a stable high vacuum. Each bulb was again pumped down immediately before sampling. For sampling, a 22-gauge hypodermic needle connected to the manifold valve (Figure 7) was inserted through the septum. The valve was opened for 30 sec, then closed and the bulb removed for analysis.

TEST SCHEDULE

The test schedule in relation to related activities is shown in Figure 8. Before the test actually began, it was necessary to install monitoring equipment including manifolds and to make a "dry run" to insure that all equipment was functioning properly. TDI was delivered to the plant just prior to the run, and, since the TDI storage tank is vented through the scrubbers, it was possible to check out the concentration of TDI. During this time it was discovered that the nitrogen plus TDI coming from the storage tank was not moving at the desired velocity. In addition, water was not flowing properly through the scrubber system. Once these and several other preliminaries were taken care of, the actual tests were begun without further difficulties.

A copy of the sampling schedule is shown in Table 2. The time scale was compressed when compared to the one presented in the "work plan" because reaction time was about 5 hr rather than the anticipated 24 hr. As mentioned previously, shorter reaction times are frequently observed with fresh or "new" TDI, as was used in this particular run. As a result of the decrease in reaction time, far fewer samples were taken (or needed) than originally thought necessary to define the system.

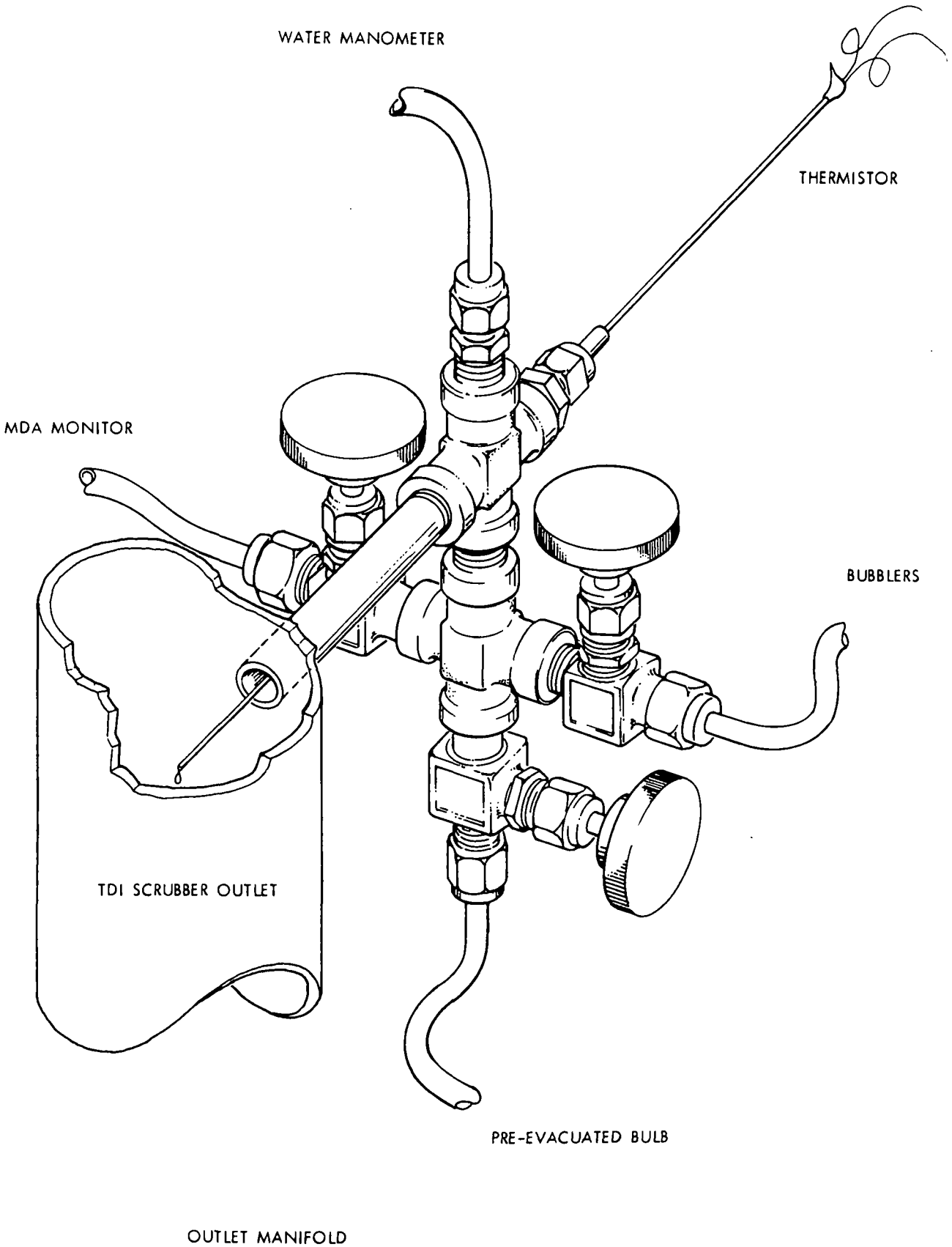
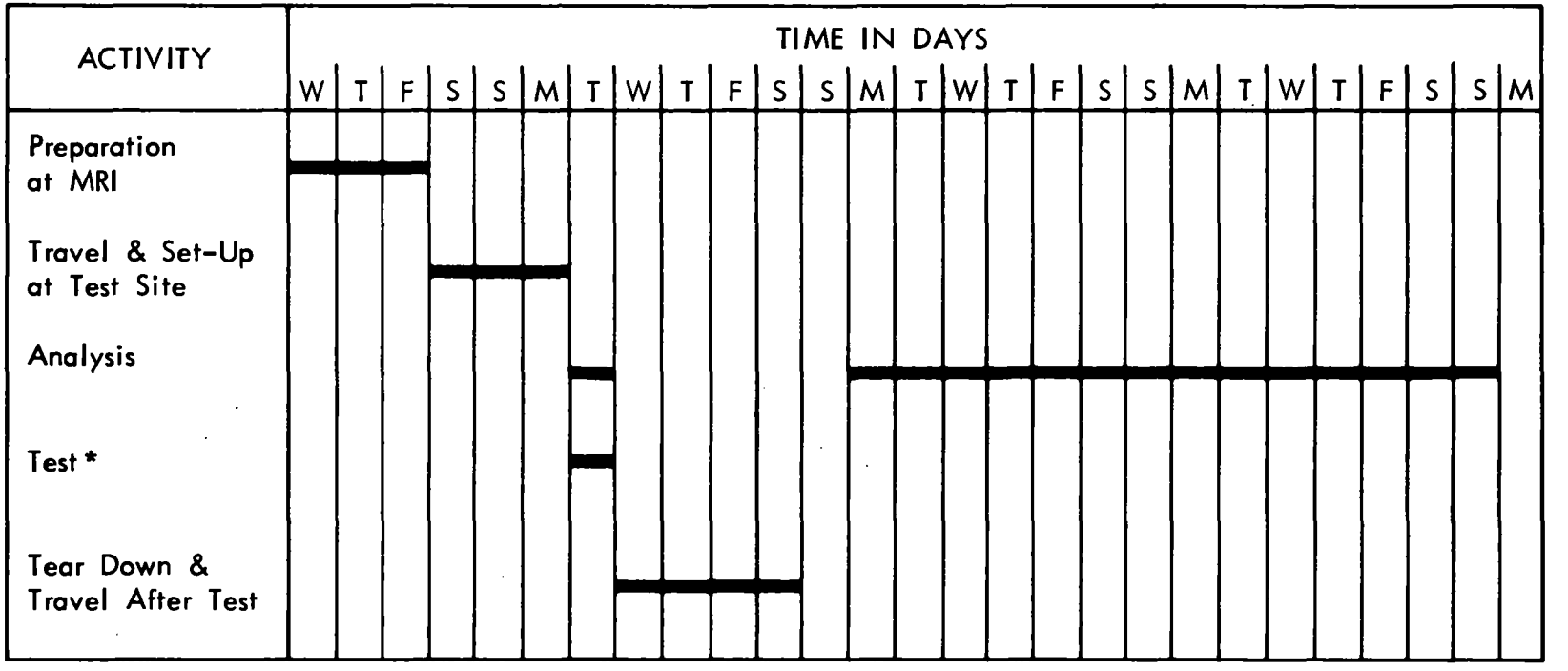


Figure 7. Scrubber outlet manifold.



* 5 hrs., 18 min

Figure 8. Test schedule and related activities.

Table 2. SAMPLE SCHEDULE

Sample Point	Components Sought	Time (min)	Total No.	Sample Train	Analytical Method
Inlet to scrubber	Major organics	+9,[a] +32, +71, +161, +173	5[b]	Cryogenic	GC
	TDI and related amines (through hydrolysis)	-12,[a] +5, +18, +73, +118, +223	6	Impinging solution	Colorimetric
	TDI	Continuous	--	Heated line	MDA tape analyzer
Outlet to scrubber	Major organics	-12, +3, +16, +62, +107, +211	6[b]	Evacuated bulb	GC
	TDI and related amines (through hydrolysis)	-9, +3, +23, +73, +118, +223	6	Impinging solution	Colorimetric
	TDI	Continuous	--	Heated line	MDA tape analyzer

a/ Time is relative to onset of TDI charging at 1747; times are medians of sampling periods.
b/ Includes duplicates.

SECTION IV

PROCESS DATA AND THEIR ANALYSIS

PROCESS DATA

A compilation of raw process data taken during the run is given in Table 3. Samples were labeled from 0 to 7 in order of increasing time. Pressures, temperatures, times and flowrates are given for outlet and inlet samples, as required.

MATHEMATICAL FORMULAE

TDI-Colorimetric

Concentration of TDI (plus amines) in the effluent stream were computed from the equation:

$$\text{TDI (plus amines), ppm (V/V)} = \frac{\text{TDI (plus amines), } \mu g}{\text{Sample Volume, } \ell} \; \frac{22.4\ \ell/\text{mole}}{174\ \text{g/mole}}$$

$$\times \frac{760\ \text{mm Hg}}{738\ \text{mm Hg}} \times \frac{273 + T}{273} \quad .$$

Micrograms (μg) of TDI were obtained colorimetrically according to the accepted procedure in Appendix B; sample volume was measured by flowmeter. Grams of TDI (plus amines) emissions for each sample period were calculated from:

$$\text{TDI (plus amines), g} = \frac{\text{TDI (plus amines), } \mu g}{\text{Sample Volume, } \ell} \times \text{Effluent Flow, } \ell/\text{min}$$

$$\times \text{ Sample Time, min} \times 10^{-6} \quad .$$

Table 3. RAW DATA

Process Parameters	Sample No. 0	1	2	3	4	5	6[a]	7[a]
Kettle temperature, °F	146	145	150	176	190	202	--	--
Time	1735	1750	1800	1850	1930	2115	2140	2240
Inlet pressure, mm H_2O	7	11	12	13	18	18	--	--
Outlet pressure, mm H_2O	2	3	8	8	8	13	--	--
Inlet temperature, °C	28	43	44	55	43	44	--	--
Outlet temperature, °C	28	28	29	34	34	18	--	--
Room temperature, °C	37	34	34	32	30	19	--	--
Barometric pressure, mm Hg	738	738	738	738	738	738	--	--
Cryogenic Samples								
Time on	--	1752	1810	1813	1939	2123	--	--
Time off	--	1801	1848	1934	2118	2157	--	--
Flow at start, cm^3/min	--	940	940	940	940	940	--	--
Flow at stop, cm^3/min	--	--	--	--	900	900	--	--
Evacuated Bulb Samples								
Time on	1735	1750	1803	1849	1934	2118	--	--
Pump down pressure, monthly	707	707	707	707	707	707	--	--
MDA Tape Monitor								
Inlet TDI ppm	0.038	0.027	> 0.08	> 0.08	> 0.08	> 0.08	0.02	0.008
Flow, inlet, cm^3/min	400	400	400	400	400	400	--	--
Outlet TDI, ppm	0.0055	0.000	0.000	> 0.08	--	> 0.08	--	--
Flow, outlet, cm^3/min	400	450	450	450	--	400	--	--
Impinger Samples								
Time start, inlet	1738	1747	1801	1848	1933	2117	--	--
Time end, inlet	1738	1752	1807	1908	1953	2137	--	--
Flow, start, inlet, cm^3/min	940	940	940	940	940	940	--	--
Volume, inlet, ℓ	4.7	4.7	5.6	18.8	18.8	18.8	--	--
Volume, outlet, ℓ	11.6	8.4	21.0	23.1	21.0	21.0	--	--
Time start, outlet	1733	1747	1801	1848	1933	2117	--	--
Time end, outlet	1744	1755	1821	1910	1953	2137	--	--
Flow start, outlet, cm^3/min	1050	1050	1050	1050	1050	1050	--	--

a/ Only inlet TDI levels were recorded.

Sample time is the time from the beginning of the sample period until the beginning of the next period.

TDI-MDA Tape

No special calculations are needed to obtain parts per million of TDI using the MDA tape apparatus; levels are recorded on a continuous tape and "spot" checked by reading a precalibrated card.

Cryogenic Traps

No special calculations required.

Evacuated Bulbs

No special calculations required.

Dispersion Model

A Gaussian plume dispersion model, presented in EPA workbook AP-26, was used. Pertinent information from this workbook is included in Appendix C for reference purposes.

RESULTS

TDI-Colorimetric

Colorimetric data for both outlet and inlet samples as a function of sample time are given in Tables 4 and 5. Note that TDI plus amine concentration was low, between 0.070 (inlet) and 0.033 (outlet) ppm, before the actual run began. TDI was in the system as a result of vapor vented during unloading of a tank truck of TDI just prior to run time. As reaction time and temperature increased, the concentration of TDI initially increased, as would be expected. Smoothed plots showing the TDI (plus amines) in inlet and outlet scrubber streams are shown in Figure 9. The TDI concentration built to a maximum during the first 30 min of the run; experimental maxima were 2.43 ppm (inlet) and 1.45 ppm (outlet) at medium times of 1805 and 1848, respectively. The run began at 1747 and it took less than 10 min to add about 3,000 lb of TDI.

Table 4. TEST RESULTS - TDI ANALYSES
(Samples Nos. 0-3)

	Sample Number							
	0		1		2		3	
Sample Point	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet
TDI and amines, ppm	0.070	0.033	1.62	1.07	2.43	0.831	1.19	1.45
TDI, colorimetric, μg	2.24	2.61	49.6	61.3	89.0	119	141	225
TDI, MDA tape, ppm[a]	0.038	0.005	0.02	0.0	Limit	Limit	Limit	Limit
Time, start[b]	1733	1733	1747	1747	1801	1801	1848	1848
Time, median	1735	1738	1750	1750	1805	1810	1900	1900
Total sample time, min	5	11	5	8	6	20	20	22
Gas flowrate, cm^3/min[c]	940	1050	940	1050	940	1050	940	1050
Gas volume, ℓ	4.7	11.5	4.7	8.4	5.64	21.0	18.8	23.1
Temperature, °C	28	28	43	28	44	29	55	34
TDI and amines, g	0.002	0.001	0.041	0.028	0.20	0.073	0.093	0.120

a/ 15-20 min delay on MDA monitor readings; range of the MDA instrument was 0.0-0.08 ppm.

b/ With tests 6 and 7, TDI concentration was read visually at time indicated.

c/ Flowrate from exhaust was 160-240 ft/min from 3-in. I.D. pipe; 200 ft/min rate was used. Total flow = 9.8 ft^3/min = 275 ℓ/min.

Notes: Cumulative process discharge of TDI and amines for entire process cycle (1747-2305 hr):
inlet - 0.36 g
outlet - 0.25 g
TDI charging began at 1747 hr. Test 0 was prior to reactor startup.
Outlet TDI concentration on monitor was > 0.08 ppm from 1800 to 2130 (corrected for time delay).

Table 5. TEST RESULTS - TDI ANALYSES
(Samples Nos. 4-7)

	Sample Number							
	4		5		6		7	
Sample Point	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet
TDI and amines, ppm	0.31	0.32	0.0	0.023	--	--	--	--
TDI colorimetric, μg	38.0	44.4	0.0	3.4	--	--	--	--
TDI, MDA tape, ppm[a/]	Limit	Limit	Limit	Limit	0.02	0.004	0.008	0.0
Time, start[b/]	1933	1933	2117	2117	--	--	--	--
Time, median	1945	1945	2130	2130	2140	2140	2240	2240
Total sample time, min	20	20	20	20	--	--	--	--
Gas flowrate, cm^3/min[c/]	940	1050	940	1050	--	--	--	--
Gas volume, ℓ	18.8	21.0	18.8	21.0	--	--	--	--
Temperature, °C	43	34	44	18	--	--	--	--
TDI and amines, g	0.024	0.026	< 0.001	0.005	--	--	--	--

a/ 15-20 min delay on MDA monitor readings; range of the MDA instrument was 0.0-0.08 ppm.

b/ With tests 6 and 7, TDI concentration was read visually at time indicated.

c/ Flowrate from exhaust was 160-240 ft/min from 3-in. I.D. pipe; 200 ft/min rate was used. Total flow = 9.8 ft^3/min = 275 ℓ/min.

Notes: Cumulative process discharge of TDI and amines for entire process cycle (1747-2305 hr):
inlet - 0.36 g
outlet - 0.25 g
TDI charging began at 1747 hr. Test 0 was prior to reactor startup.
Outlet TDI concentration on monitor was > 0.08 ppm from 1800 to 2130 (corrected for time delay).

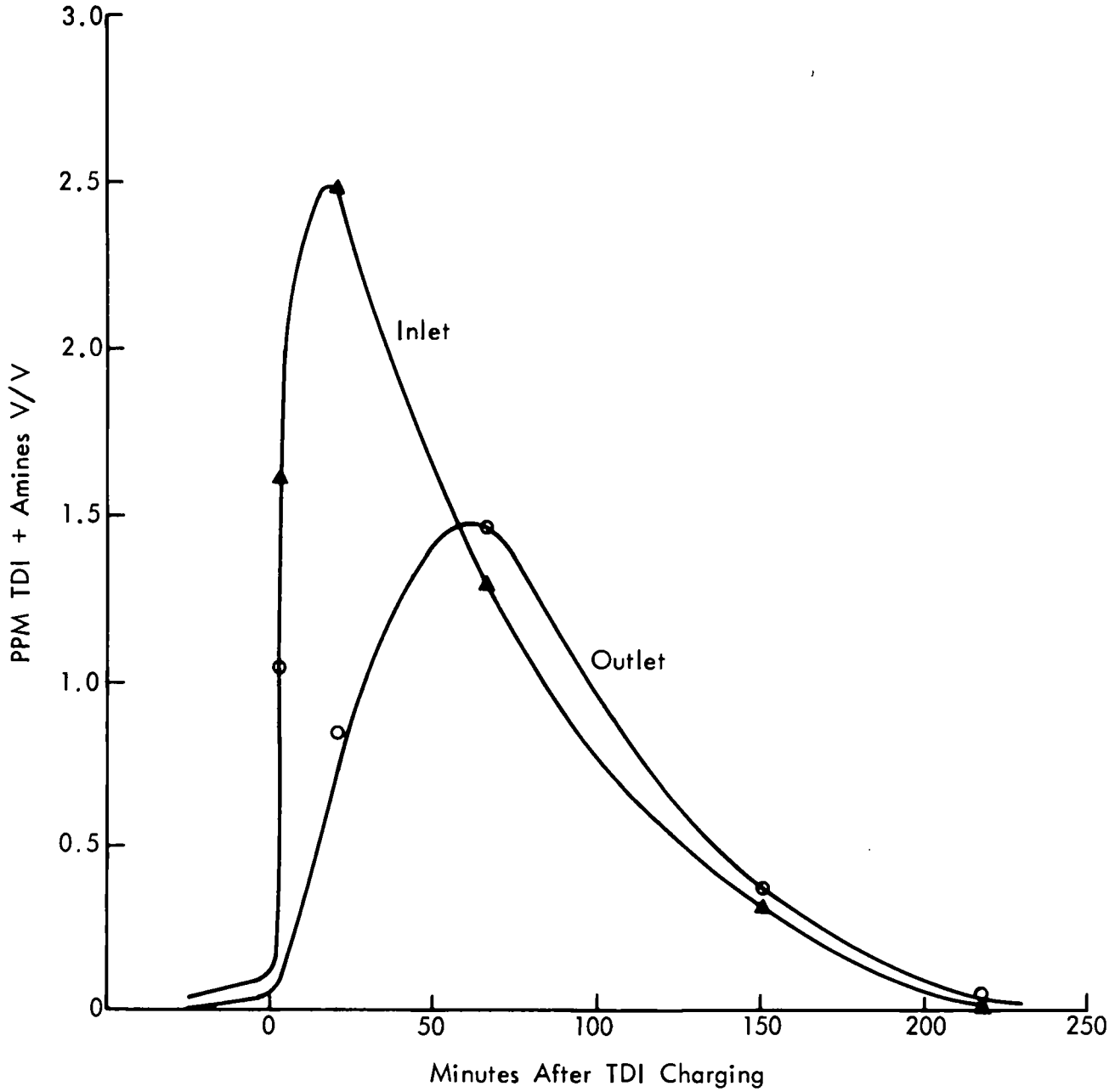


Figure 9. TDI + amine concentration (colorimetric) versus time.

TDI-MDA Tape

The MDA tape apparatus reportedly determines only TDI. Measurements taken with this apparatus are given in Tables 4 and 5. MDA data are limited because the instrument can detect a maximum level of 0.08 ppm; there is also an 18-min delay in the printout. Nevertheless, the MDA data parallel colorimetric data in that a "limit" (> 0.08 ppm) reading was obtained about 18 min after the colorimetric method indicated TDI readings above 0.08 ppm. Also, MDA readings dropped below 0.08 ppm at 2140, or about 10 min after the colorimetric method showed 0.0 and 0.023 ppm in the inlet and outlet streams, respectively.

One of the MDA tape instruments was used to monitor ambient air in front of the scrubbers at 1920; it showed no detectable TDI.

Cryogenic Traps

Only two of the cryogenic traps from the inlet to the scrubber (Nos. 4 and 5 of Table 5) contained any significant amount of condensibles. Chromatographic data on these samples were typical of mineral spirits No. 302 as covered in the next section on "Evacuated Bulbs." Because of the greater relative importance of the outlet stream with respect to air emissions, no more work was done to analyze inlet components.

Evacuated Bulbs

The evacuated bulbs contained gas and a small amount of liquid which condensed in the line leading from the sampling manifold. The liquid was compared by infrared spectroscopy, gas chromatography and mass spectrometry with the mineral spirits added to the alkyd resin as a diluent. The results showed:

Infrared Spectroscopy: No discernible difference is detected between the spectrum of the liquid phase of the No. 5 outlet sample (Figure 10) and that of the No. 302 mineral spirits (Figure 11). The spectra indicate a preponderance of saturated hydrocarbons similar to those in mineral spirits. Levels of extraneous organic materials of about 1% or greater would have shown up, if present.

Gas Chromatography: Retention times for 23 peaks obtained from No. 302 spirits matched retention times for 23 peaks from the No. 5 outlet sample (see Table 6). Peak No. 2 in the outlet sample is not present in the mineral spirits, but represents less than 0.1% of the sample volume.

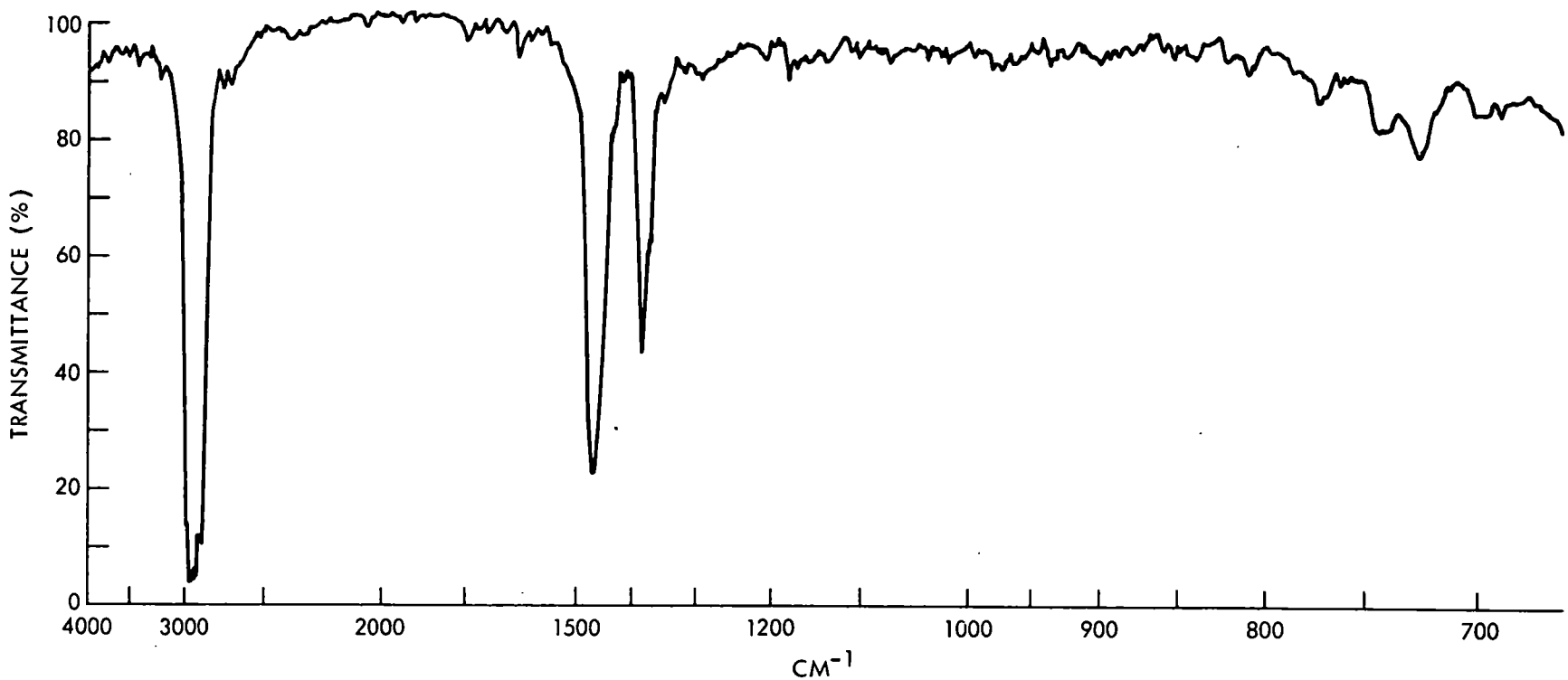


Figure 10. Infrared spectrum of liquid from No. 5 outlet.
Conditions: Perkin-Elmer Infracord NaCl cell.

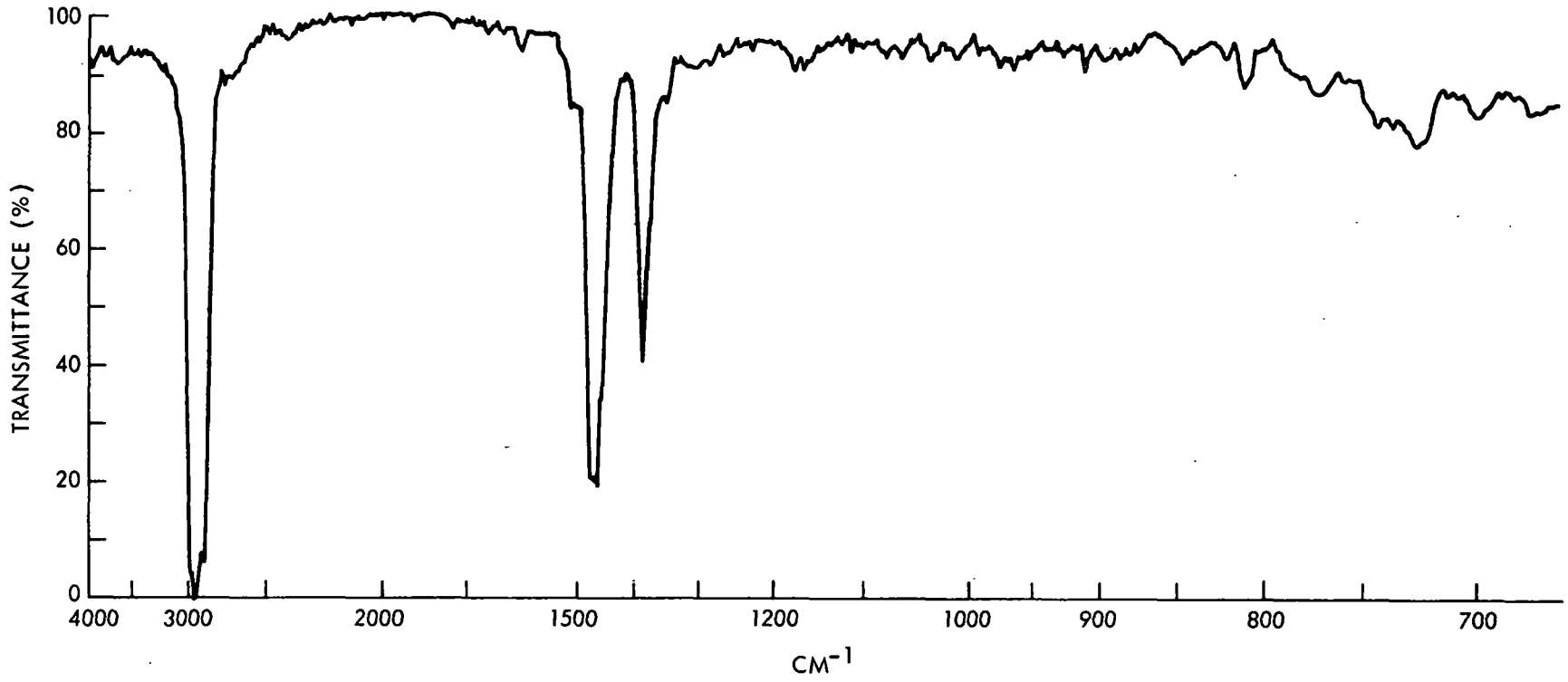


Figure 11. Infrared spectrum of No. 302 mineral spirits.
Conditions: Perkin-Elmer Infracord NaCl cell.

Table 6. GAS CHROMATOGRAPH RETENTION TIMES

Conditions: Varian Aerograph Gas Chromatograph, Model 1420, equipped with dual columns, dual high-sensitivity thermal conductivity detectors and 6-port gas sample valve.
Sample volume: gas, 5 ml; liquid, 3 µl.
Column: 6.5 ft x 1/8 in. Porapak Q.
Flow rate: 60 ml/min.
Column temperature: 50-250°C at Δ t20°C/min.
Sensitivity: 50 µg/ml.

Peak Number	No. 5 Outlet (min)	No. 302 Mineral Spirits (min)
1	1.75	1.75
2	2.63	Not present
3	2.88	2.88
4	3.69	3.74
5	4.75	4.69
6	5.56	5.61
7	6.19	6.16
8	6.44	6.38
9	7.34	7.38
10	7.85	7.88
11	8.54	8.38
12	8.69	8.73
13	9.0	9.0
14	9.19	9.23
15	9.60	9.51
16	10.38	10.39
17	10.92	10.95
18	11.53	11.53
19	11.86	11.86
20	12.43	12.50
21	13.25	13.19
22	14.43	14.06
23	15.75	15.73

Mass Spectrometry: Mass spectrometry was utilized to examine the 10 major peaks of the gas chromatogram. These peaks represented over 99% of the sample. These mass spectra, included as Appendix D, show that there were probably no unresolved materials in these peaks of a nature different from mineral spirits.

The gas phase of the evacuated bulb samples was saturated with mineral spirits which condensed both in the bulbs and in the line connected to the bulbs. Vapor pressure measurements at experimental conditions showed 2.5 vol % mineral spirits present at saturation.

Dispersion Model

The data that have been presented describe gas emissions (vol %), emission rates, stack configuration, stack diameter, and stack surfaces. To make the information meaningful from an environmental standpoint, the ground-level concentrations of the toxic gases must be determined. In order to do this, the following source characteristics were used:

Internal diameter of vent = 3 in.

Volumetric discharge rate = 275 ℓ/min

Composition of discharge during the peak 1-hr period:

Nitrogen	97.5% (vol)
Mineral spirits	2.5% (vol)
TDI	1.2 ppm (vol)

For the wind speeds greater than about 10 mph, aerodynamic downwash, which would be greatest on the leeward side of the building (from which emissions emanate), is the dominant factor in the atmospheric dilution process. Emissions would be swept into the region of induced turbulence and quickly mixed over the cross-section of the building normal to the wind direction. In this case, the dilution factor (DF) is simply:

$$\text{(Downwash) Dilution factor (DF)} = \frac{\text{Volume rate of pollutant emission}}{\text{Wind speed x building cross section}}$$

For wind speeds less than about 10 mph, the TDI vent may be treated as an elevated point source which is unaffected by the presence of the building. The location and magnitude of the maximum ground-level pollutant concentration vary with the atmospheric stability and wind speed, as shown in Table 7.

Table 7. RESULTS OF DISPERSION CALCULATIONS

Atmospheric Condition		Point of Max. Ground-Level Concentration		Residential Area	
Stability	Wind Speed	Distance From Source	DF[a]	Ground Level DF[a]	Plume Centerline DF[a]
--	> 10 mph	< 100 m	1.1×10^5		
Extremely Unstable	5 mph	50 m	2.8×10^5	1.4×10^8 2.5×10^7[b]	1.4×10^8
Unstable	5 mph	70 m	3.2×10^5	2.5×10^8 1.8×10^7[b]	2.5×10^8
Slightly Unstable	5 mph	110 m	3.4×10^5	1.0×10^7	1.0×10^7
Neutral	5 mph	160 m	3.7×10^5	3.4×10^6	3.6×10^6
Slightly Stable	5 mph	220 m	3.9×10^5	1.8×10^6	2.0×10^6
Stable	5 mph	390 m	4.2×10^5	9.2×10^5	1.1×10^6

a/ Dilution factor = $\frac{\text{Concentration in Flue Gases}}{\text{Concentration in Ambient Air}}$

b/ With inversion at 100 m; for more stable atmosphere, DF is unaffected by 100 m inversion.

Dilution factors are given for the points of maximum ground-level concentration and for the residential receptor distance of approximately 3,000 ft. The evaluation was made by considering the location of the residential area as shown in Figure 12, and the general plant area shown in Figure 13.

If one assumes the worst possible case (a DF of 10^5), the following holds true:

Component	Maximum ground-level concentrations, ppm	Maximum allowable 8-hr concentrations, ppm
TDI	1.2×10^{-5}	0.02
Mineral spirits	0.25	500

The ground-level concentrations of both TDI and mineral spirits are only about 0.1% of the maximum allowable values for an 8-hr averaging period under such adverse conditions. One should remember that these numbers assume that none of the TDI is converted to amines; in all likelihood, most of the TDI is hydrolyzed, thus increasing the safety factor further.

Each run contains about 30,000 lb of resin and emits about 0.25 g (5.5×10^{-4} lb) of TDI as a maximum. Based on these numbers,

$$\frac{5.5 \times 10^{-4}}{3.0 \times 10^{4}} \times \frac{1.8 \times 10^{-8} \text{ lb TDI}}{\text{lb product}}$$

is emitted into the atmosphere.

DISCUSSION OF RESULTS

Considerable caution is necessary in evaluating the graph of TDI-plus-amines versus time (Figure 9). Since the MDA monitor was off scale for most of the process run, no continuous measure of TDI levels is available. The colorimetric method is not sensitive enough for shorter sample periods than those used during testing. Due to the rapid reaction rate during this process run, sufficient colorimetric analyses were not obtainable to properly describe the curve.

Thus, the exact shape of the inlet and outlet curves is not determinable with the present information. Since the sample periods are fairly long, the actual maxima may be higher than shown in the graph and the error limits for the calculated totals of TDI from the process are estimated to be approximately -50% to +100%. The lag in the outlet concentration is expected, since the internal volume of each scrubber is about 200 liters with turbulent flow. Several minutes will therefore be required to sweep the "old" gas from the scrubber.

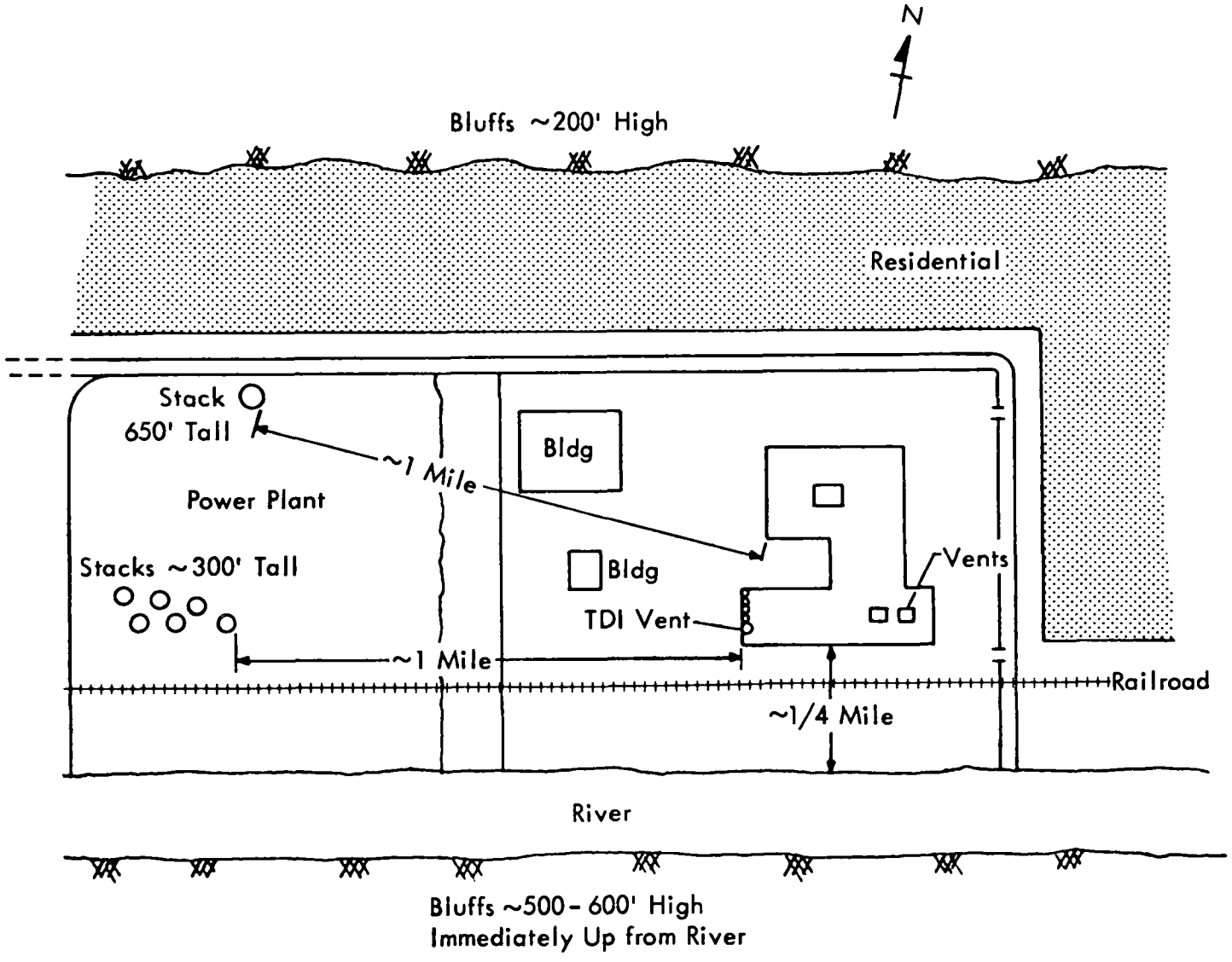


Figure 12. Simplified view of test site and vicinity (not to scale).

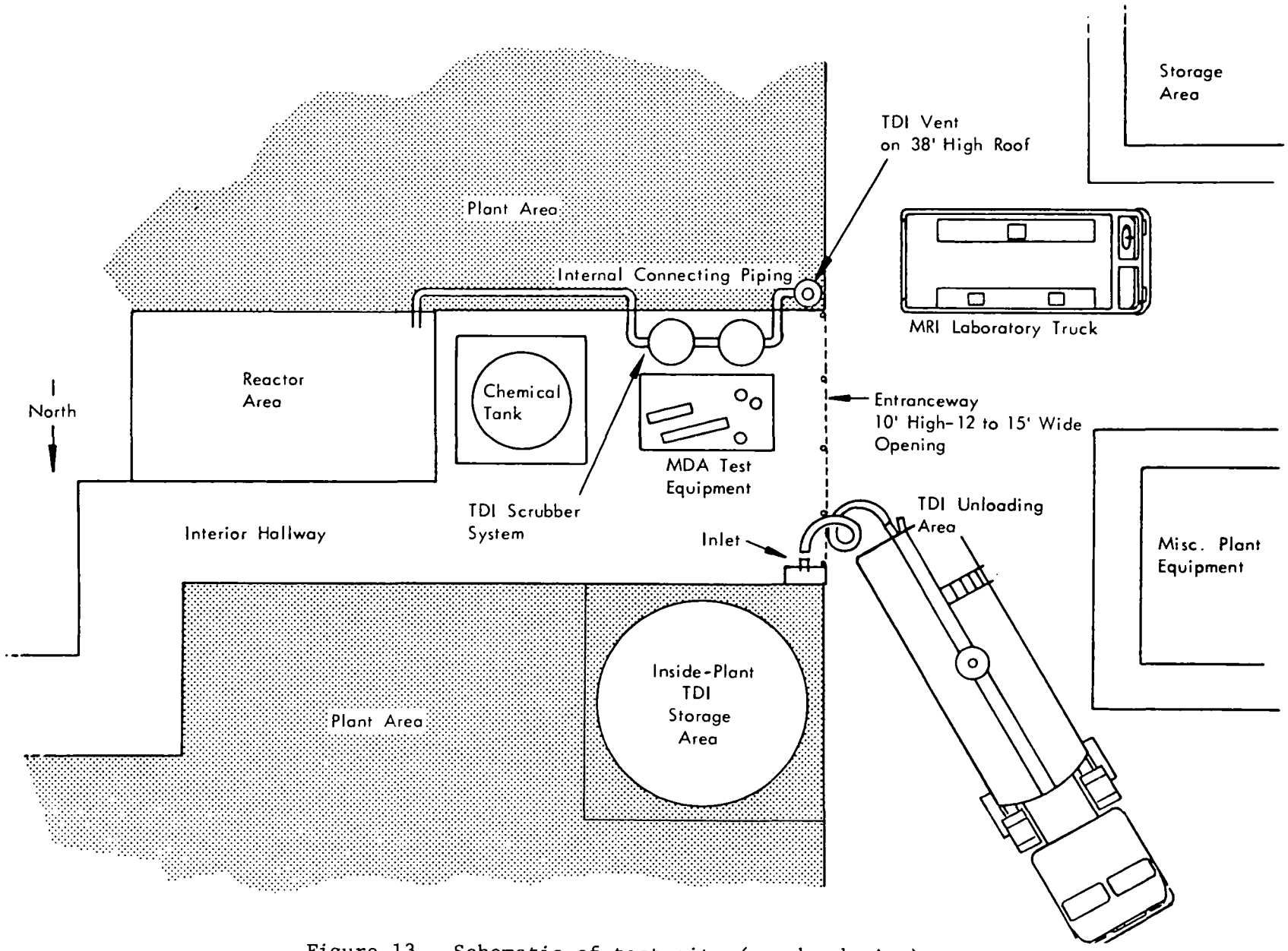


Figure 13. Schematic of test site (overhead view)

With the information gained from this test, the response of the MDA monitors could be modified by a gas dilution technique to allow the instruments to measure the levels of TDI present.

From the analytical results for total organics, it is reasonably certain that the only significant toxic materials from this particular process are TDI and mineral spirits. It is interesting to note that, while the permissible exposure level for mineral spirits is 25,000 times higher than TDI, the concentration of the mineral spirits is also 25,000 times greater than that of the TDI. The TDI concentration rises rapidly to a peak and then falls to zero by the end of the reaction. The concentration of the mineral spirits is at a constant level throughout the process, since condensation in the lines of mineral spirits was observed from a few minutes after the start of the reaction until the end. Thus, the mineral spirits emissions could far exceed the levels found during this test if the temperature of the exiting gas stream were higher than 25°C. At higher temperatures the mineral spirits would be emitted instead of condensing out in the piping.

Thus, if the process conditions of the plant studies are representative of the industry and if other plants exist with less favorable diffusion conditions from the stack or much higher total flowrates, the toxic level of mineral spirits could be reached well before that for TDI.

SECTION V

CONCLUSIONS

The major conclusions to be drawn from the results of this study are:

1. The maximum ground-level concentration of both TDI and mineral spirits is about 0.1% of the maxima allowable for an 8-hr averaging period, thus indicating that no hazard existed at the test site under the conditions studied.

2. Statement No. 1 is true in spite of the fact that the TDI scrubber was operating poorly* at the time of sampling. This would indicate that scrubbers are not needed for TDI removal <u>if the specific process and conditions</u> which were studied are kept under control.

3. Should several such plants be clustered in or around a common community, as is frequently the case in the chemical processing industry, a problem could result.

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* Reported by plant site personnel subsequent to MRI sampling.

SECTION VI

RECOMMENDATIONS

Based on the conclusions drawn in this report, it is recommended that:

1. Other test sites be studied under a broader range of operating conditions to determine air emissions.

2. At present, caution should be exercised in extrapolating the data presented herein to the entire polyurethane coatings industry, since it is specific to one plant.

3. Priorities should be extended to other areas of the plastics industry having potentially high hazardous/toxic emissions.

4. A search for possible clustered polyurethane sites might be in order; this might also apply to other plastics processes.

APPENDIX A

LIST OF COMPANIES PRODUCING URETHANE COATING RESINS FOR EITHER CAPTIVE USE OR FOR SALE OR BOTH: COMPANIES AND PLANT LOCATIONS

A&H Paint Company	Columbus, Ohio
Absolute Coatings, Inc.	Bronx, New York
Acron Chemical Company	--
Acro Chemical Products Corporation	Long Valley, New Jersey
Adelphi Paint & Color Works, Inc.	Carlstadt, New Jersey Ozone Park, New York
Adhesive Products Corporation	Bronx, New York
Admiral Paint Company	--
Advance Process Supply Company	Brooklyn, New York Chicago, Illinois
American Herberts Corporation	Woodside, New York
Amercoat Corporation	Brea, California
John L. Armitage & Company	Newark, New Jersey Elk Grove, Illinois Richmond, California
Ashland Oil, Inc.	Los Angeles, California Newark, New Jersey
The Baker Castor Oil Company	Bayonne, New Jersey
Ball Chemical Company	Glenshaw, Pennsylvania
Beatrice Foods Company	Wilmington, Massachusetts
The Biggs Company	Santa Monica, California
Cargill, Inc.	Carpentersville, Illinois Lynwood, California Philadelphia, Pennsylvania
Celanese Corporation	Los Angeles, California Louisville, Kentucky Newark, New Jersey

Chem-Seal Corporation of America	Los Angeles, California
Chemical Coatings & Engineering Company	Media, Pennsylvania
Commercial Solvents Corporation	Carpentersville, Illinois Chicago, Illinois
CONCHEMCO, Inc.	Baltimore, Maryland Kansas City, Missouri
Continental Polymers Corporation	Santa Ana, California
Cook Paint & Varnish Company	Detroit, Michigan Houston, Texas North Kansas City, Missouri
Desoto, Inc.	Berkeley, California Chicago Heights, Illinois Garland, Texas
The Dexter Corporation	El Monte, California Olean, New York Cleveland, Ohio Hayward, California Los Angeles, California Rocky Hill, Connecticut Waukegan, Illinois
Diamond Shamrock Corporation	Harrison, New Jersey
E. I. du Pont de Nemours & Company, Inc.	Chicago, Illinois Fort Madison, Iowa Parlin, New Jersey Philadelphia, Pennsylvania South San Francisco, California Toledo, Ohio Tucker, Georgia
Emerson & Cuming, Inc.	Canton, Massachusetts
The Epoxylite Corporation	El Monte, California
Farnow, Inc.	South Kearny, New Jersey

France, Campbell & Darling, Inc.	Kenilworth, New Jersey
Freeman Chemical Corporation	Ambridge, Pennsylvania Saukville, Wisconsin
Furane Plastics, Inc.	Los Angeles, California
General Latex and Chemical Corporation	Ashland, Ohio Cambridge, Massachusetts
The P. D. George Company	St. Louis, Missouri
The Goodyear Tire & Rubber Company	Akron, Ohio
Hoover Ball and Bearing Company	Ann Arbor, Michigan
Interplastic Corporation	Minneapolis, Minnesota
Isochem Resins Company	Lincoln, Rhode Island
Jewel Paint & Varnish Company	Chicago, Illinois
Kohler-McLister Paint Company	Denver, Colorado
Lu-Sol Corporation	El Monte, California
The Master Mechanics Company	Cleveland, Ohio
McCloskey Varnish Company	Los Angeles, California Philadelphia, Pennsylvania Portland, Oregon
Midwest Manufacturing Corporation	Burlington, Iowa
Minnesota Mining and Manufacturing Company	Decatur, Alabama
Minnesota Paints, Inc.	Fort Wayne, Indiana
Mobay Chemical Company/Naftone, Inc.	New Martinsville, West Virginia
National Lead Company	Philadelphia, Pennsylvania
Norris Paint & Varnish Company, Inc.	Salem, Oregon

Northeastern Laboratories Company, Inc.	Melville, New York
C. J. Osborn Chemicals, Inc.	Pennsauken, New Jersey
Poly Resins, Inc.	Sunn Valley, California
PPG Industries, Inc.	Circleville, Ohio Houston, Texas Milwaukee, Wisconsin Springdale, Pennsylvania Torrance, California Cleveland, Ohio
Preservative Paint Company	Seattle, Washington
Prime Leather Finishes Company	Milwaukee, Wisconsin
Raffi and Swanson, Inc.	Wilmington, Massachusetts
Reichhold Chemicals, Inc.	Azusa, California Detroit, Michigan Elizabeth, New Jersey Houston, Texas South San Francisco, California Tacoma, Washington
Schenectady Chemicals, Inc.	Schenectady, New York
SCM Corporation	Chicago, Illinois Cleveland, Ohio Reading, Pennsylvania San Francisco, California
The Sherwin-Williams Company	Chicago, Illinois Cleveland, Ohio Emeryville, California Garland, Texas Los Angeles, California Newark, New Jersey
Sta-Crete, Inc.	San Francisco, California
A. E. Stanley Manufacturing Company	Marlboro, Massachusetts

Textron Inc., Spencer Kellogg Division	Bellevue, Ohio
Thiokol Chemical Corporation	Trenton, New Jersey
Francoa Chemical Corporation	Reading, Massachusetts
Union Carbide Corporation	Institute, West Virginia
Westinghouse Electric Corporation	Manor, Pennsylvania
Wilmington Chemical Corporation	Wilmington, Delaware
Witco Chemical Corporation	Chicago, Illinois Lynwood, California New Castle, Delaware
Woburn Chemical Corporation	Harrison, New Jersey
Wyandotte Chemical Corporation	Wyandotte, Michigan

APPENDIX B

ANALYTICAL METHODS FOR TDI

A. Analysis of TDI in Air (Modified Marcal: Method)

Principle

TDI is hydrolyzed by the absorbing solution to the corresponding toluene diamine derivative.

The diamine is diazotized by the sodium nitrite-sodium bromide solution.

The diazo compound is coupled with N-(1-Naphthyl)ethylenediamine to form a colored complex.

The amount of colored complex formed is in direct proportion to the amount of TDI present. The amount of colored complex is determined by reading the absorbance of the solution at 550 nm.

Toluene diamine is formed on a mole for mole basis from TDI. This amine is used in place of TDI for standards. This accomplishes two things. First, the amine is not as toxic as TDI. Second, TDI is semisolid at room temperature. Weighing the semisolid is more difficult than weighing the dry amine. Both compounds have been tested by this method and the results compare favorably.

Range and Sensitivity

The range of the standards used is equivalent to 1.0-20.0 μg TDI. In a 40-liter air sample, this range converts to 0.0035-0.070 ppm. The sensitivity can be increased by using longer path length spectrophotometer cells.

If the sample is so concentrated its absorbance is greater than the limits of the standard curve, it can be diluted with absorber solution and the absorbance reread. This extends the upper limit of the range. The upper limit can also be extended by taking a smaller air sample.

A single bubbler absorbs 95% of the diisocyanate if the concentration is below 2 ppm. Above 2 ppm, about 90% is recovered.

Interferences

Any free organic amine will interfere, including any that may be present in detergents.

Methylene-di-(4-phenylisocyanate) (MDI) will form a colored complex in this reaction. However, its color development time is about 1-2 hr compared with 5 min for TDI. Therefore MDI is not a serious problem, if color density is determined within 10 min of the addition of coupling reagent.

Apparatus

Beckman Model B spectrophotometer or equivalent

Cells, 1-cm, 4-cm, 5-cm, or 10-cm matched cells

Several (each) volumetric flasks: 50 ml, 100 ml, 1-liter, glass-stoppered

Balance capable of weighing to at least three decimal places

Pipettes: 0.5 ml, 1 ml, 15 ml

Graduated cylinders: 25 ml, 50 ml

Reagents

All reagents must be ACS reagent grade or better.

Double distilled water
2, 4-diaminotoluene
Hydrochloric acid, concentrated, 11.7 N
Glacial acetic acid, concentrated, 17.6 N
Sodium bromide

Sodium nitrite solution: Dissolve 3.0 g sodium nitrite and 5.0 g sodium bromide in about 80 ml double distilled water. Adjust volume to 100 ml with double distilled water.

Sulfamic acid

Sulfamic acid solution, 10% w/v: dissolve 10 g sulfamic acid in 100 ml double distilled water.

N-(1-Naphthyl)ethylenediamine dihydrochloride

N-(1-Naphthyl)ethylenediamine solution: Dissolve 50 mg in about 25 ml double distilled water. Add 1 ml concentrated hydrochlorid acid and dilute to 50 ml with double distilled water. Solution should be clear; any coloring is due to contamination by free amines, and if the solution is colored it should not be used.

Absorber solution: Add 35 ml concentrated hydrochloric acid and 22 ml glacial acetic acid to approximately 600 ml double distilled water. Dilute the solution to 1 liter with double distilled water. Use 15 ml in each sample-collecting impinger.

Standard solution A: Weigh out 140 mg of 2,4-toluenediamine (equivalent to 200 mg of 2,4-toluene diisocyanate). Dissolve in 660 ml of glacial acetic acid, transfer to a 1-liter glass-stoppered volumetric flask, and make up to volume with double distilled water.

Standard solution B: Transfer 10 ml of standard solution A to a glass-stoppered 1-liter volumetric flask. Add 27.8 ml of glacial acetic acid so that when solution B is diluted to 1 liter with double distilled water, it will be 0.6N with respect to acetic acid.

Procedure

Cleaning Equipment: Wash all glassware in a hot amine-free detergent solution, or soak in a 1% aqueous trisodium phosphate (analytical reagent) solution at room temperature, preferably overnight, to remove any oil.

Rinse well with hot tap water.

Rinse well with double distilled water. Repeat this rinse several times. Any amines from organic detergents must be removed to prevent interferences.

Analysis of Samples: Remove impinger tube taking care not to lose any absorber solution.

Start blank at this point by adding 15 ml fresh absorber solution to a clean impinger cylinder. To each bubbler add 0.5 ml of 3% sodium nitrite solution, gently agitate, and allow solution to stand for 2 min.

Add 1 ml of 10% sulfamic acid solution, agitate and allow solution to stand about 2 min to destroy all the excess nitrous acid present.

Add 1 ml of 0.1% N-(1-Naphthyl)ethylenediamine solution. Agitate and allow color to develop. Color will be developed in 5 min. A reddish-blue color indicates the presence of TDI.

Add double distilled water to adjust the final volume to 20 ml in the cylinder. Mix.

Transfer each sample and blank to 1-cm or longer spectrophotometer cell.

Using the blank, adjust the spectrophotometer to 0 absorbance.

Determine the absorbance of each sample at 550 nm.

From the previously prepared calibration curve (see below) read the micrograms TDI corresponding to the absorbance of the sample and calculate the parts per million TDI.

Calibration and Standards

To each of a series of eight 25-ml graduated cylinders add 5 ml of 1.2N hydrochloric acid.

To these cylinders add the following amounts of 0.6N acetic acid: 10.0, 9.5, 9.0, 8.0, 7.0, 6.0, 5.0, and 0.0 ml, respectively.

To these cylinders add standard solution B in the same order as the acetic acid is added: 0.0, 0.5, 1.0, 2.0, 3.0, 4.0, 5.0, and 10.0 ml, so that the final volume is 10 ml. None (0.0 ml) of the standard is added to the 10 ml acetic acid; 0.5 ml of the standard is added to the 9.5 ml acid; and so on. The cylinders now contain the equivalent of 0.0, 1.0, 2.0, 4.0, 6.0, 8.0, 10.0, and 20.0 µg TDI, respectively. The standard containing none of the standard solution is the blank.

Add 0.5 ml of the 3.0% sodium nitrite reagent to each cylinder. Mix. Allow to stand for 2 min.

Add 1 ml of the 10% sulfamic acid solution. Mix. Allow to stand for 2 min.

Add 1 ml of the N-(1-Naphthyl)ethylenediamine solution. Mix. Let stand for 15 min.

Make up to exactly 20 ml with double distilled water.

Transfer each solution to 1 cm or longer spectrophotometer cell. (At the lower end of the calibration curve, 5 cm cells give an 11% relative instrumental error for the 1.0 µg TDI standard. For smaller path lengths, the error is greater.)

Using the blank, adjust the spectrophotometer to 0 absorbance at 550 nm.

Determine the absorbance of each standard at 550 nm.

A standard curve is constructed by plotting the absorbance against micrograms TDI.

Calculations

$$ppm = \frac{\text{micrograms} \times 24.45}{174.15 \times 40} = \text{micrograms} \times 0.00351$$

micrograms - micrograms TDI taken from standard curve

mol wt = wt TDI = 174.15

V = volume of air sample in liters (40 liters)

B. Analysis of the TDI in Air (MDA TDI Monitor, Model 7000)

Principle

The MDA apparatus is based on a chemical reaction which takes place on a special test paper which has been impregnated with suitable chemicals. The result of this reaction is to produce a colored stain which is monitored photoelectrically. The test paper is in the form of a continuous reel of paper tape contained in a cassette. A motor drive pulls the tape past a sensing head at a slow, constant speed. A metered air sample is drawn into the instrument by a small pump. This air sample passes through a portion of the tape. An equivalent section of the tape width is shielded from the gas and is used as a reference. The TDI concentration of the gas sample is proportional to the density of the color stain. The outputs of the photocell detectors are amplified to drive the meter, recorder and alarm system.

Range and Sensitivity

The instrument range is from 0-0.08 ppm with logarithmic response. The sensitivity limit is approximately 0.002 ppm.

Interferences

Methylene-di-(4-phenylisocyanate) will also form a colored complex, but the development time is 1-2 hr; the sensor reads the stain after an 18 min delay.

Apparatus

MDA Model 7000 monitor was used in this study. Each tape cassette will run for 168 hr. Shelf life is 3 months for the unopened tape. Specially printed recorder charts, available from MDA, were used.

Calibration and Standards

The instrument is supplied with a calibration card with zero and 0.02 ppm level stains.

APPENDIX C

REFERENCE MATERIAL ON GAUSSIAN PLUME DISPERSION MODEL FROM EPA WORKBOOK AP-26

Chapter 1 — INTRODUCTION

During recent years methods of estimating atmospheric dispersion have undergone considerable revision, primarily due to results of experimental measurements. In most dispersion problems the relevant atmospheric layer is that nearest the ground, varying in thickness from several hundred to a few thousand meters. Variations in both thermal and mechanical turbulence and in wind velocity are greatest in the layer in contact with the surface. Turbulence induced by buoyancy forces in the atmosphere is closely related to the vertical temperature structure. When temperature decreases with height at a rate higher than 5.4°F per 1000 ft (1°C per 100 meters), the atmosphere is in unstable equilibrium and vertical motions are enhanced. When temperature decreases at a lower rate or increases with height (inversion), vertical motions are damped or reduced. Examples of typical variations in temperature and wind speed with height for daytime and nighttime conditions are illustrated in Figure 1-1.

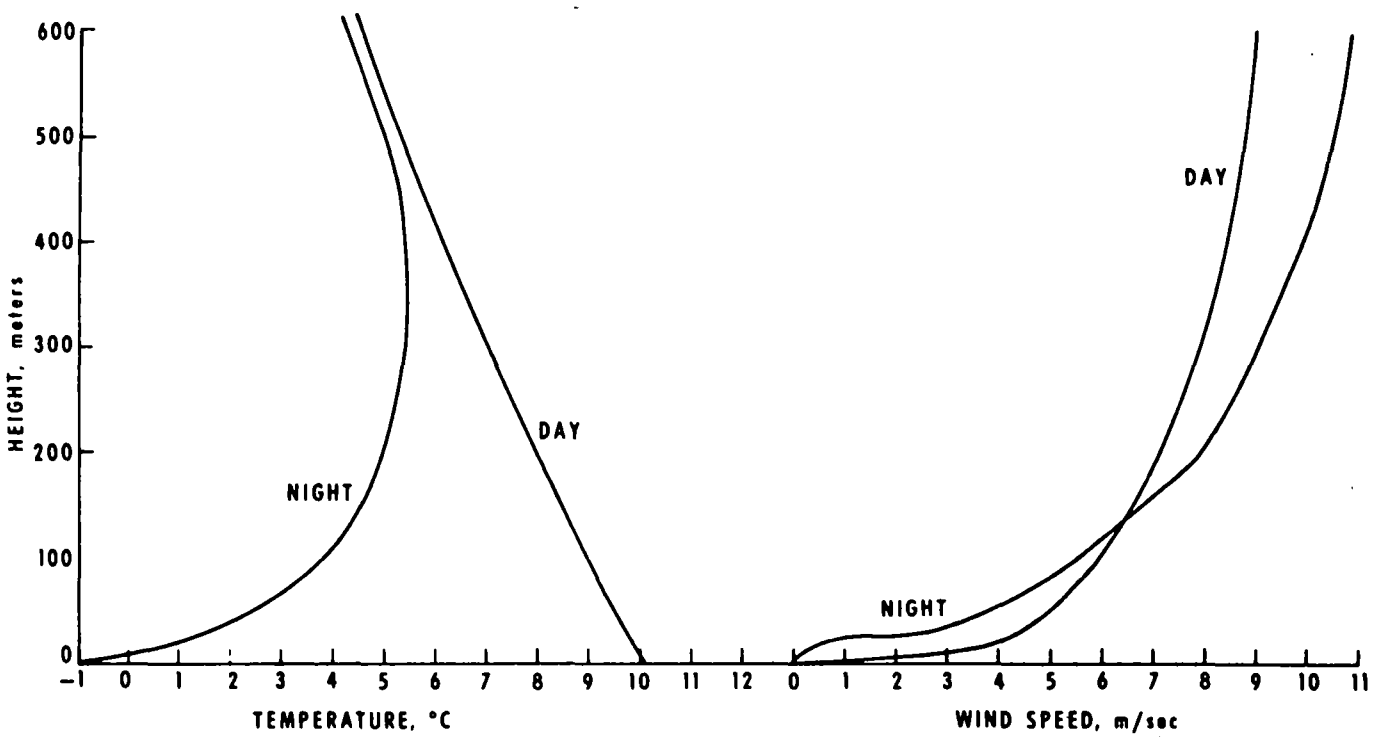

Figure 1-1. Examples of variation of temperature and wind speed with height (after Smith, 1963).

The transfer of momentum upward or downward in the atmosphere is also related to stability; when the atmosphere is unstable, usually in the daytime, upward motions transfer the momentum "deficiency" due to eddy friction losses near the earth's surface through a relatively deep layer, causing the wind speed to increase more slowly with height than at night (except in the lowest few meters). In addition to thermal turbulence, roughness elements on the ground engender mechanical turbulence, which affects both the dispersion of material in the atmosphere and the wind profile (variation of wind with height). Examples of these effects on the resulting wind profile are shown in Figure 1-2.

As wind speed increases, the effluent from a continuous source is introduced into a greater volume of air per unit time interval. In addition to this dilution by wind speed, the spreading of the material (normal to the mean direction of transport) by turbulence is a major factor in the dispersion process.

The procedures presented here to estimate atmospheric dispersion are applicable when mean wind speed and direction can be determined, but measurements of turbulence, such as the standard deviation of wind direction fluctuations, are not available. If such measurements are at hand, techniques such as those outlined by Pasquill (1961) are likely to give more accurate results. The diffusion param-

eters presented here are most applicable to ground-level or low-level releases (from the surface to about 20 meters), although they are commonly applied at higher elevations without full experimental validation. It is assumed that stability is the same throughout the diffusing layer, and no turbulent transfer occurs *through* layers of dissimilar stability characteristics. Because mean values for wind directions and speeds are required, neither the variation of wind speed nor the variation of wind direction with height in the mixing layer are taken into account. This usually is not a problem in neutral or unstable (e.g., daytime) situations, but can cause over-estimations of downwind concentrations in stable conditions.

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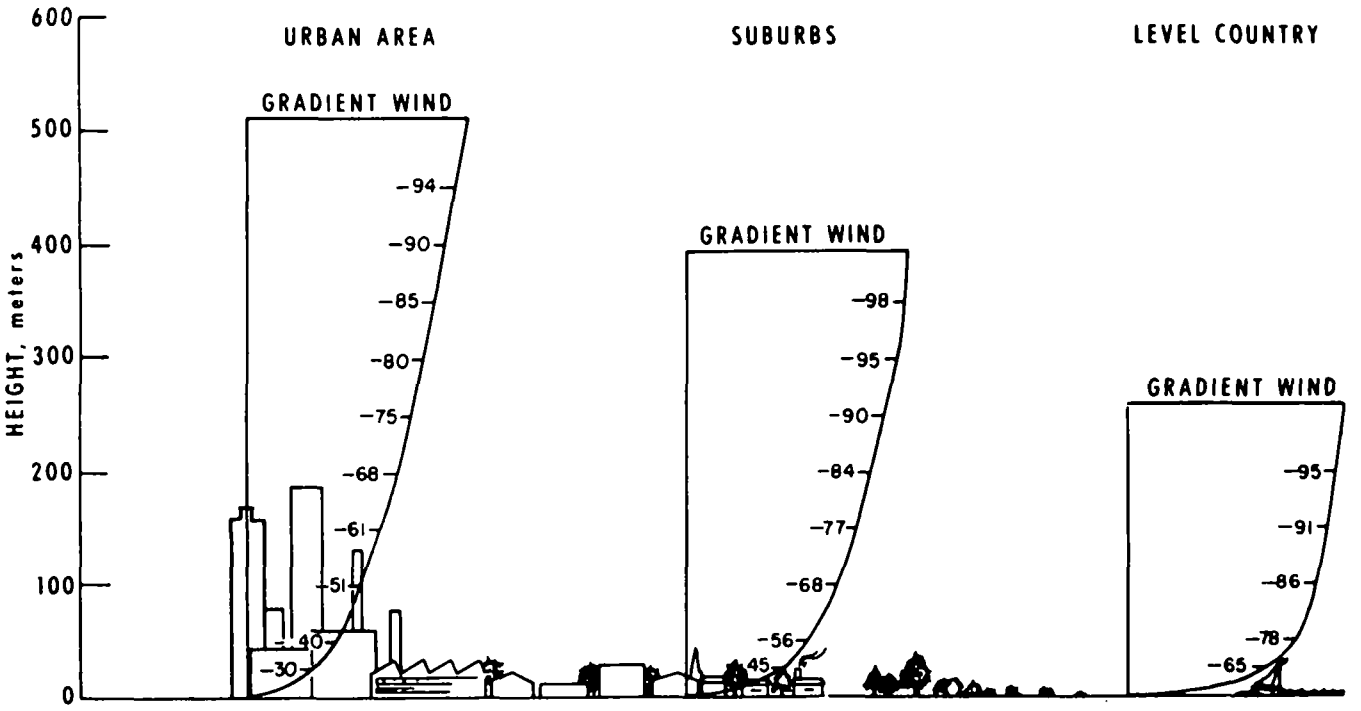

Figure 1-2. Examples of variation of wind with height over different size roughness elements (figures are percentages of gradient wind); (from Davenport, 1963).

For a number of years estimates of concentrations were calculated either from the equations of Sutton (1932) with the atmospheric dispersion parameters C_y, C_z, and n, or from the equations of Bosanquet (1936) with the dispersion parameters p and q.

Hay and Pasquill (1957) have presented experimental evidence that the vertical distribution of spreading particles from an elevated point is related to the standard deviation of the wind elevation angle, σ_E, at the point of release. Cramer (1957) derived a diffusion equation incorporating standard deviations of Gaussian distributions: σ_y, for the distribution of material in the plume across wind in the horizontal, and σ_z for the vertical distribution of material in the plume. (See Appendix 2 for properties of Gaussian distributions.) These statistics were related to the standard deviations of azimuth angle, σ_A, and elevation angle, σ_E, calculated from wind measurements made with a bi-directional wind vane (bivane). Values for diffusion parameters based on field diffusion tests were suggested by Cramer, et al. (1958) (and also in Cramer 1959a and 1959b). Hay and Pasquill (1959) also presented a method for deriving the spread of pollutants from records of wind fluctuation. Pasquill (1961) has further proposed a method for estimating diffusion when such detailed wind data are not available. This method expresses the height and angular spread of a diffusing plume in terms of more commonly observed weather parameters. Suggested curves of height and angular spread as a function of distance downwind were given for several "stability" classes. Gifford (1961) converted Pasquill's values of angular spread and height into standard deviations of plume concentration distribution, σ_y and σ_z. Pasquill's method, with Gifford's conversion incorporated, is used in this workbook (see Chapter 3) for diffusion estimates.

Advantages of this system are that (1) only two dispersion parameters are required and (2) results of most diffusion experiments are now being reported in terms of the standard deviations of plume spread. More field dispersion experiments are being conducted and will be conducted under conditions of varying surface roughness and atmospheric stability. If the dispersion parameters from a specific experiment are considered to be more representative than those suggested in this workbook, the parameter values can be used with the equations given here.

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Chapter 3 — ESTIMATES OF ATMOSPHERIC DISPERSION

This chapter outlines the basic procedures to be used in making dispersion estimates as suggested by Pasquill (1961) and modified by Gifford (1961).

COORDINATE SYSTEM

In the system considered here the origin is at ground level at or beneath the point of emission, with the x-axis extending horizontally in the direction of the mean wind. The y-axis is in the horizontal plane perpendicular to the x-axis, and the z-axis extends vertically. The plume travels along or parallel to the x-axis. Figure 3-1 illustrates the coordinate system.

DIFFUSION EQUATIONS

The concentration, χ, of gas or aerosols (particles less than about 20 microns diameter) at x,y,z from a continuous source with an effective emission height, H, is given by equation 3.1. The notation used to depict this concentration is χ (x,y,z;H). H is the height of the plume centerline when it becomes essentially level, and is the sum of the physical stack height, h, and the plume rise, ΔH. The following assumptions are made: the plume spread has a Gaussian distribution (see Appendix 2) in both the horizontal and vertical planes, with standard deviations of plume concentration distribution in the horizontal and vertical of σ_y and σ_z, respectively; the mean wind speed affecting the plume is u; the uniform emission rate of pollutants is Q; and total reflection of the plume takes place at the earth's surface, i.e., there is no deposition or reaction at the surface (see problem 9).

$$\chi\,(x,y,z;H) = \frac{Q}{2\pi\,\sigma_y\,\sigma_z\,u}\,\exp^{*}\left[-\frac{1}{2}\left(\frac{y}{\sigma_y}\right)^2\right]\left\{\exp\left[-\frac{1}{2}\left(\frac{z-H}{\sigma_z}\right)^2\right]+\exp\left[-\frac{1}{2}\left(\frac{z+H}{\sigma_z}\right)^2\right]\right\} \qquad (3.1)$$

*Note: exp $-a/b = e^{-a/b}$ where e is the base of natural logarithms and is approximately equal to 2.7183.

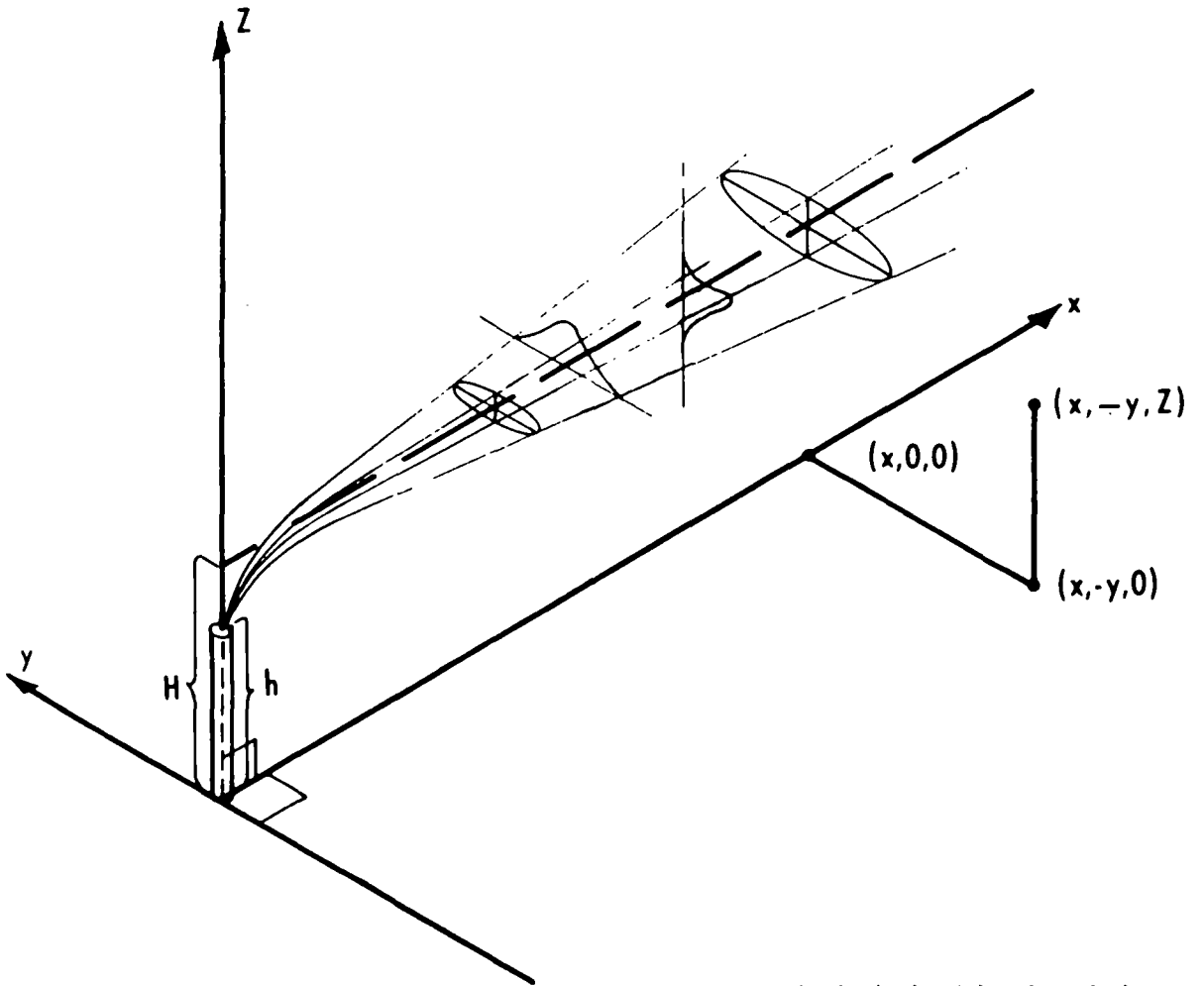


Figure 3-1. Coordinate system showing Gaussian distributions in the horizontal and vertical.

Any consistent set of units may be used. The most common is:

χ (g m^{-3}) or, for radioactivity (curies m^{-3})
Q (g sec^{-1}) or (curies sec^{-1})
u (m sec^{-1})
σ_y, σ_z, H,x,y, and z (m)

This equation is the same as equation (8.35) p. 293 of Sutton (1953) when σ's are substituted for Sutton's parameters through equations like (8.27) p. 286. For evaluations of the exponentials found in Eq. (3.1) and those that follow, see Appendix 3. χ is a mean over the same time interval as the time interval for which the σ's and u are representative. The values of both σ_y and σ_z are evaluated in terms of the downwind distance, x.

Eq. (3.1) is valid where diffusion in the direction of the plume travel can be neglected, that is, no diffusion in the x direction.

This may be assumed if the release is continuous or if the duration of release is equal to or greater than the travel time (x/u) from the source to the location of interest.

For concentrations calculated at ground level, i.e., z = 0, (see problem 3) the equation simplifies to:

$$\chi\,(x,y,0;H) = \frac{Q}{\pi\,\sigma_y\,\sigma_z\,u}\,\exp\left[-\frac{1}{2}\left(\frac{y}{\sigma_y}\right)^2\right]\exp\left[-\frac{1}{2}\left(\frac{H}{\sigma_z}\right)^2\right] \qquad (3.2)$$

Where the concentration is to be calculated along the centerline of the plume (y = 0), (see problem 2) further simplification results:

$$\chi\,(x,0,0;H) = \frac{Q}{\pi\,\sigma_y\,\sigma_z\,u}\,\exp\left[-\frac{1}{2}\left(\frac{H}{\sigma_z}\right)^2\right] \qquad (3.3)$$

For a ground-level source with no effective plume rise (H = 0), (see problem 1):

$$\chi\,(x,0,0;0) = \frac{Q}{\pi\,\sigma_y\,\sigma_z\,u} \qquad (3.4)$$

EFFECTS OF STABILITY

The values of σ_y and σ_z vary with the turbulent structure of the atmosphere, height above the surface, surface roughness, sampling time over which the concentration is to be estimated, wind speed, and distance from the source. For the parameter values given here, the sampling time is assumed to be about 10 minutes, the height to be the lowest several hundred meters of the atmosphere, and the surface to be relatively open country. The turbulent structure of the atmosphere and wind speed are considered in the stability classes presented, and the effect of distance from the source is considered in the graphs determining the parameter values. Values for σ_y and σ_z are estimated from the stability of the atmosphere, which is in turn estimated from the wind speed at a height of about 10 meters and, during the day, the incoming solar radiation or, during the night, the cloud cover (Pasquill, 1961). Stability categories (in six classes) are given in Table 3-1. Class A is the most unstable, class F the most stable class considered here. Night refers to the period from 1 hour before sunset to 1 hour after sunrise. Note that the neutral class, D, can be assumed for overcast conditions during day or night, regardless of wind speed.

Table 3-1 KEY TO STABILITY CATEGORIES

Surface Wind Speed (at 10 m), m sec^{-1}	Day			Night	
	Incoming Solar Radiation			Thinly Overcast or ≥4/8 Low Cloud	≤3/8 Cloud
	Strong	Moderate	Slight		
< 2	A	A-B	B		
2-3	A-B	B	C	E	F
3-5	B	B-C	C	D	E
5-6	C	C-D	D	D	D
> 6	C	D	D	D	D

The neutral class, D, should be assumed for overcast conditions during day or night.

"Strong" incoming solar radiation corresponds to a solar altitude greater than 60° with clear skies; "slight" insolation corresponds to a solar altitude from 15° to 35° with clear skies. Table 170, Solar Altitude and Azimuth, in the Smithsonian Meteorological Tables (List, 1951) can be used in determining the solar altitude. Cloudiness will decrease incoming solar radiation and should be considered along with solar altitude in determining solar radiation. Incoming radiation that would be strong with clear skies can be expected to be reduced to moderate with broken (⅝ to ⅞ cloud cover) middle clouds and to slight with broken low clouds. An objective system of classifying stability from hourly meteorological observations based on the above method has been suggested (Turner, 1961).

These methods will give representative indications of stability over open country or rural areas, but are less reliable for urban areas. This difference is due primarily to the influence of the city's larger surface roughness and heat island effects upon the stability regime over urban areas. The greatest difference occurs on calm clear nights; on such nights conditions over rural areas are very stable, but over urban areas they are slightly unstable or near neutral to a height several times the average building height, with a stable layer above (Duckworth and Sandberg, 1954; DeMarrais, 1961).

Some preliminary results of a dispersion experiment in St. Louis (Pooler, 1965) showed that the dispersion over the city during the daytime behaved somewhat like types B and C; for one night experiment σ_y varied with distance between types D and E.

ESTIMATION OF VERTICAL AND HORIZONTAL DISPERSION

Having determined the stability class from Table 3-1, one can evaluate the estimates of σ_y and σ_z as a function of downwind distance from the source, x, using Figures 3-2 and 3-3. These values of σ_y and σ_z are representative for a sampling time of about 10 minutes. For estimation of concentrations for longer time periods see Chapter 5. Figures 3-2 and 3-3 apply strictly only to open level country and probably underestimate the plume dispersion potential from low-level sources in built-up areas. Although the vertical spread may be less than the values for class F with very light winds on a clear night, quantitative estimates of concentrations are nearly impossible for this condition. With very light winds on a clear night for ground-level sources free of topographic influences, frequent shifts in wind direction usually occur which serve to spread the plume horizontally. For elevated sources under these extremely stable situations, significant concentrations usually do not reach ground level until the stability changes.

A stable layer existing above an unstable layer will have the effect of restricting the vertical diffusion. The dispersion computation can be modified for this situation by considering the height of the base of the stable layer, L. At a height 2.15 σ_z above the plume centerline the concentration is one-tenth the plume centerline concentration at the same distance. When one-tenth the plume centerline concentration extends to the stable layer, at height L, it is reasonable to assume that the distribution starts being affected by the "lid." The following method is suggested to take care of this situation. Allow σ_z to increase with distance to a value of L/2.15 or 0.47 L. At this distance x_L, the plume is assumed to have a Gaussian distribution in the vertical. Assume that by the time the plume travels twice this far, 2 x_L, the plume has become uniformly distributed between the earth's surface and the height L, i.e., concentration does not vary with height (see Figure 3-4). For the distances greater than 2 x_L, the concentration for any height between the ground and L can be calculated from:

$$\chi\,(x,y,z;H) = \frac{Q}{\sqrt{2\pi}\,\sigma_y\,L\,u}\,\exp\left[-\frac{1}{2}\left(\frac{y}{\sigma_y}\right)^2\right] \qquad (3.5)$$

for any z from 0 to L
for x >2 x_L; x_L is where $\sigma_z = 0.47$ L

(see problem 6). Note that Eq. (3.5) assumes normal or Gaussian distribution of the plume *only* in the horizontal plane. The same result can be obtained from the following equation where σ_{zL} is an effective dispersion parameter because $\sqrt{2\pi}$ L = 2.5066 L and 0.8 πL = 2.51 L.

$$\chi\,(x,y,z;H) = \frac{Q}{\pi\,\sigma_y\,\sigma_{zL}\,u}\left[\exp -\frac{1}{2}\left(\frac{y}{\sigma_y}\right)^2\right] \qquad (3.6)$$

for any z from 0 to L
for x >2 x_L; x_L is where $\sigma_z = 0.47$ L
The value of $\sigma_{zL} = 0.8$ L

EVALUATION OF WIND SPEED

For the wind speed, u, a mean through the vertical extent of the plume should be used. This would be from the height H — 2 σ_z through H + 2 σ_z. Of course, if 2 σ_z is greater than H then the wind can be averaged from the ground to H + 2 σ_z. However, the "surface wind" value may be all that is available. The surface wind is most applicable to surface or low-level emissions, especially under stable conditions.

PLOTS OF CONCENTRATIONS AGAINST DISTANCE

To gain maximum insight into a diffusion problem it is often desirable to plot centerline concentrations against distance downwind. A convenient procedure is to determine the ground-level centerline concentrations for a number of downwind distances and plot these values on log-log graph paper. By connecting the points, one may estimate concentrations for intermediate downwind distances (see problem 6).

ACCURACY OF ESTIMATES

Because of a multitude of scientific and technical limitations the diffusion computation method presented in this manual may provide *best estimates* but not infallible predictions. In the unstable and stable cases, severalfold errors in estimate of σ_z can occur for the longer travel distances. In some cases the σ_z may be expected to be correct within a factor of 2, however. These are: (1) all stabilities for distance of travel out to a few hundred meters; (2) neutral to moderately unstable conditions for distances out to a few kilometers; and (3) unstable conditions in the lower 1000 meters of the atmosphere with a marked inversion above for distances out to 10 km or more. Uncertainties in the estimates of σ_y are in general less than those of σ_z. The ground-level centerline concentrations for these

APPENDIX D

MASS SPECTROMETRY DATA FOR NUMBER 5 OUTLET SAMPLE AND NUMBER 302 MINERAL SPIRITS SAMPLE

Instrument: (1) Atlas CH-4B medium resolution mass spectrometer equipped with a Varian 620/i computer;

(2) GC/MS system consisting of a Microtek 220 Gas Chromatograph interfaced to the Atlas CH-4B mass spectrometer via a two-stage helium separator.

The mass spectra in this appendix show the strong similarity between a major gas chromatographic peak from the No. 5 outlet sample and a comparable peak from the No. 302 mineral spirits. No attempt was made to identify the specific compound.

Ten peaks representing over 99 vol % of the sample were chosen for comparison. The mass spectrometer was run at higher than normal sensitivity so that minor variations would be magnified.

Two spectra are paired for comparison under each figure. Thus, Figure D-1A is to be compared to Figure D-1B, etc.

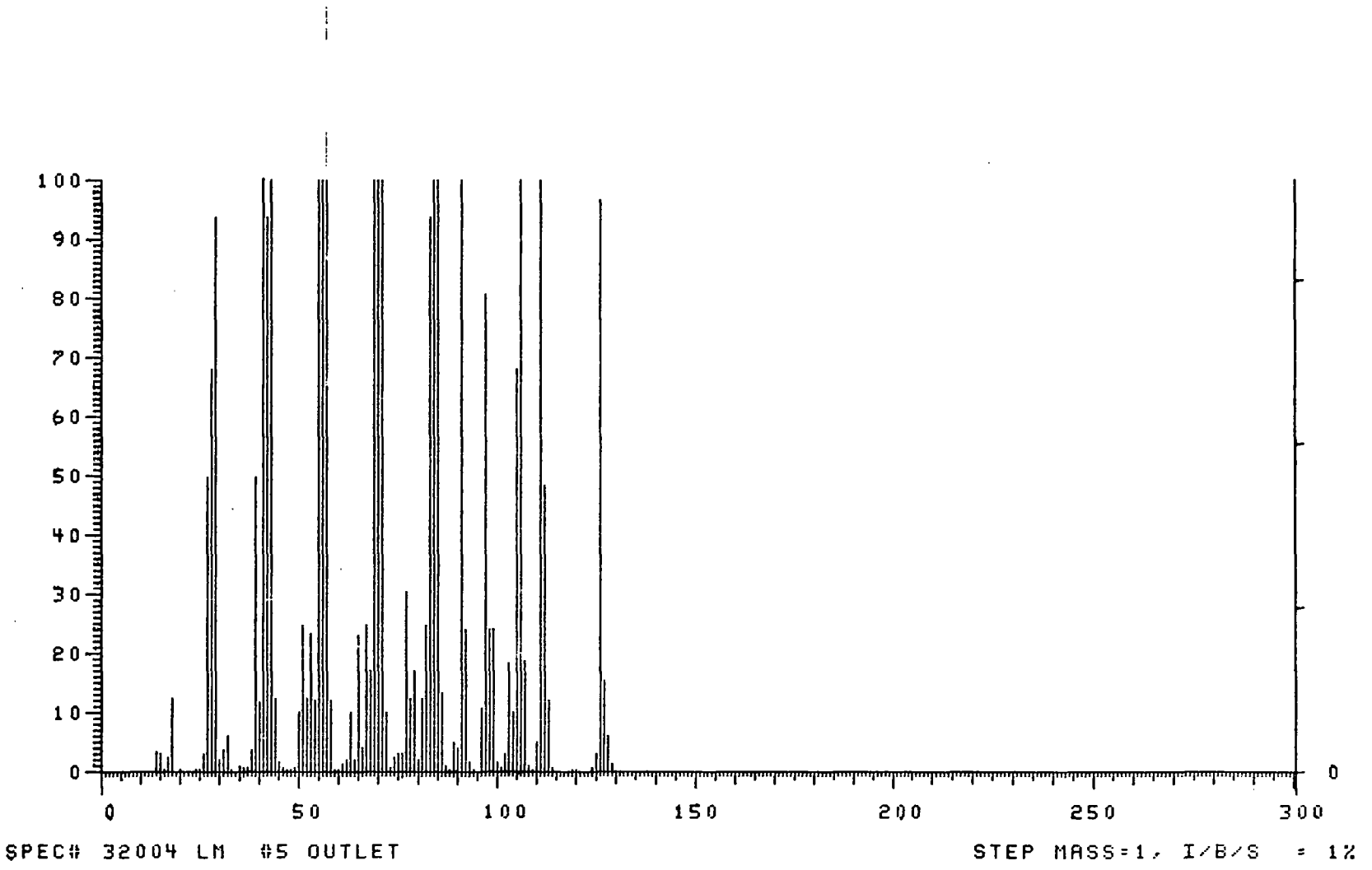
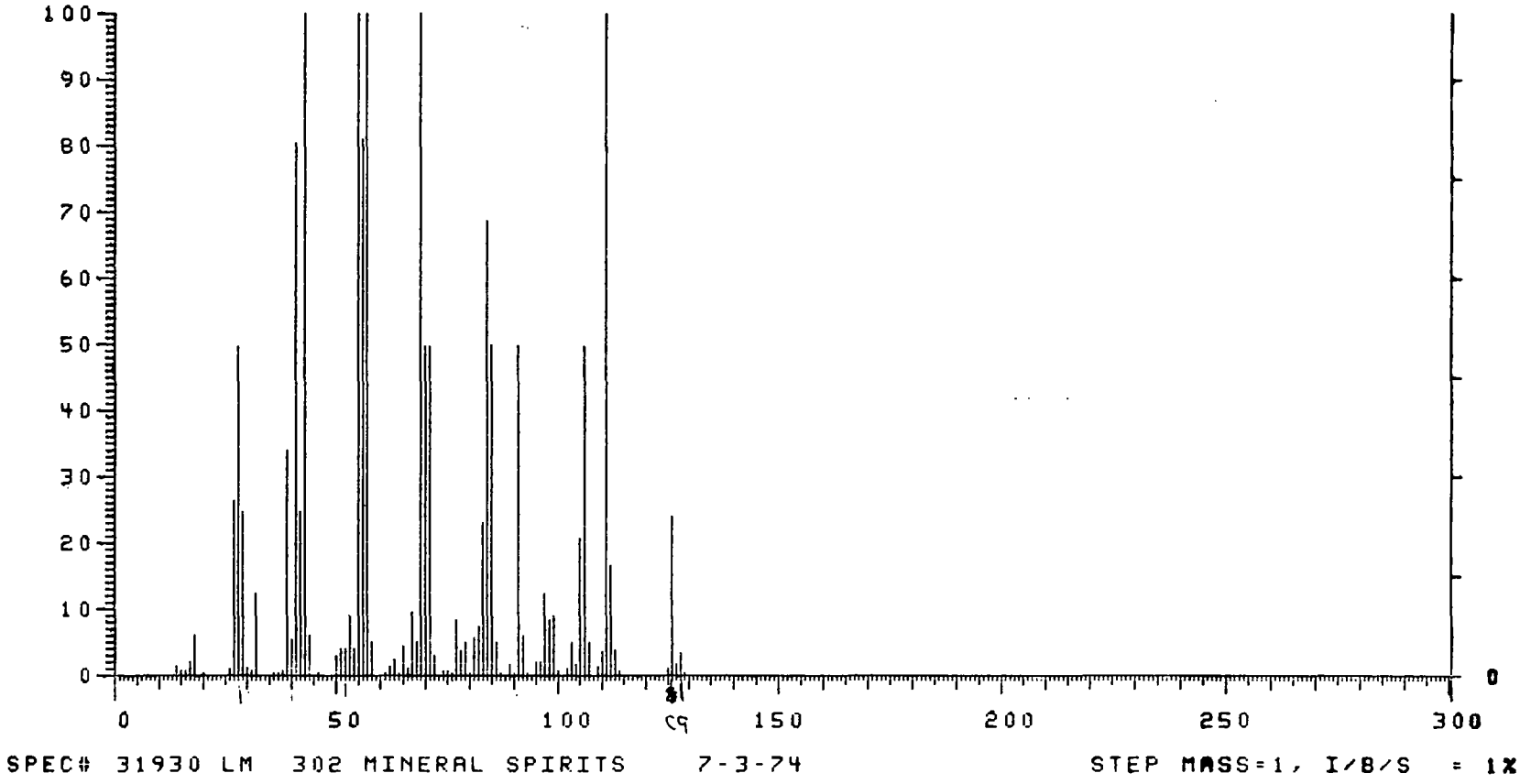

100
90
80
70
60
50
40
30
20
10
0
0
50
100
150
200
250
300
0
SPEC# 32004 LM #5 OUTLET
STEP MASS=1, I/B/S = 1%

Figure D-1A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10
0
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50
100
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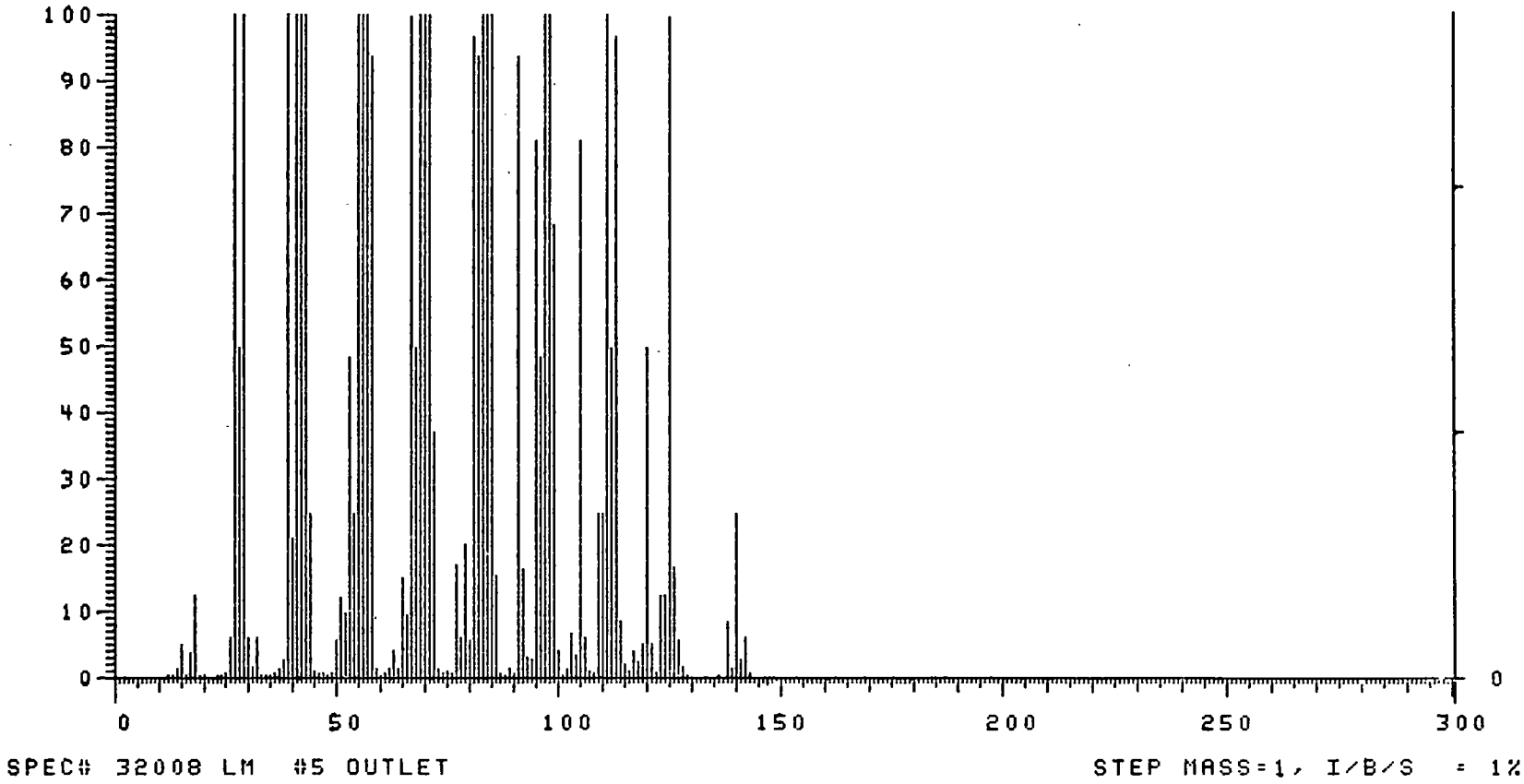
200
250
300
SPEC# 31930 LM 302 MINERAL SPIRITS 7-3-74
STEP MASS=1, I/B/S = 1%

Figure D-1B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80
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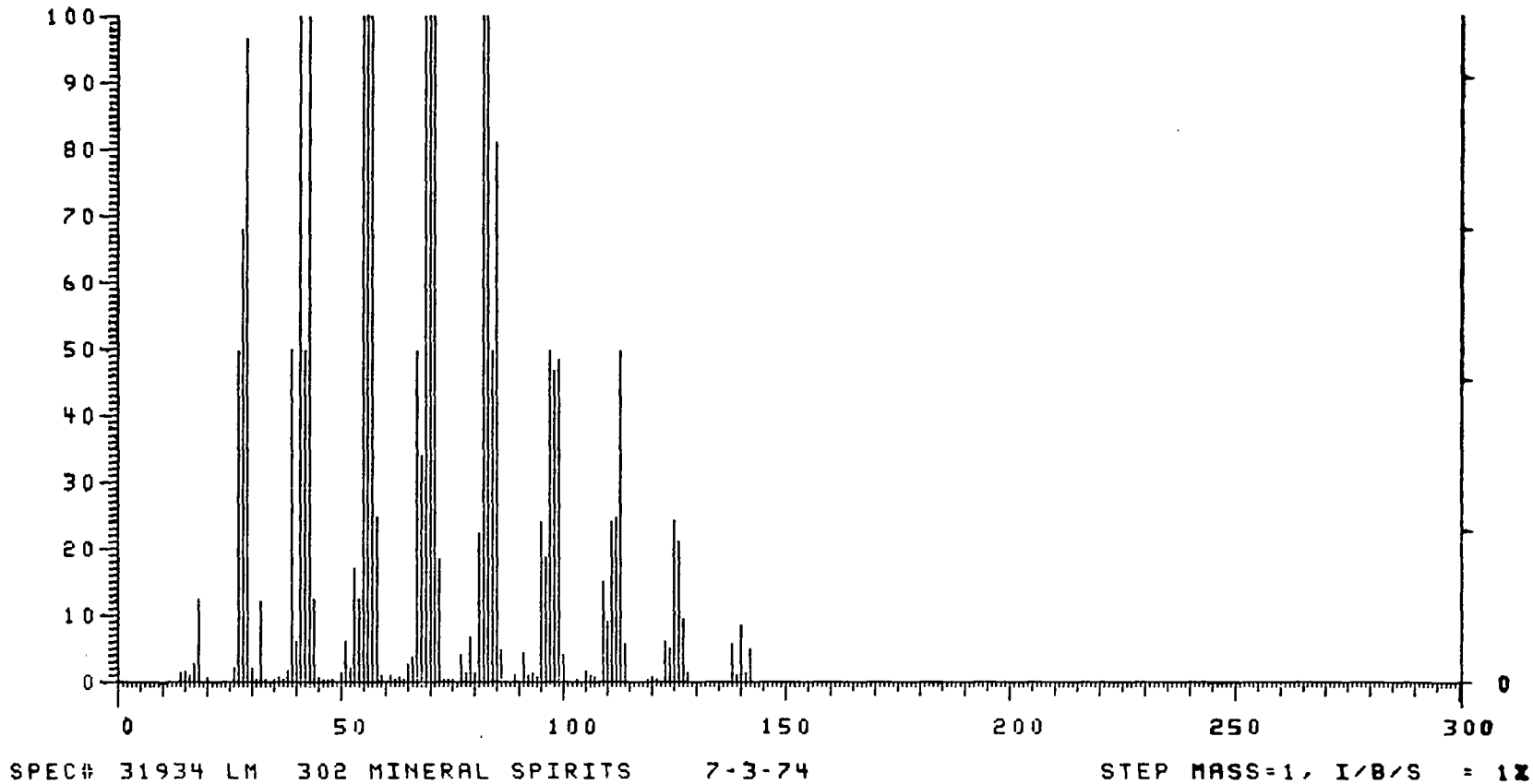
60
50
40
30
20
10
0
0
50
100
150
200
250
300
0
SPEC# 32008 LM #5 OUTLET
STEP MASS=1, I/B/S = 1%

Figure D-2A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10
0
0
50
100
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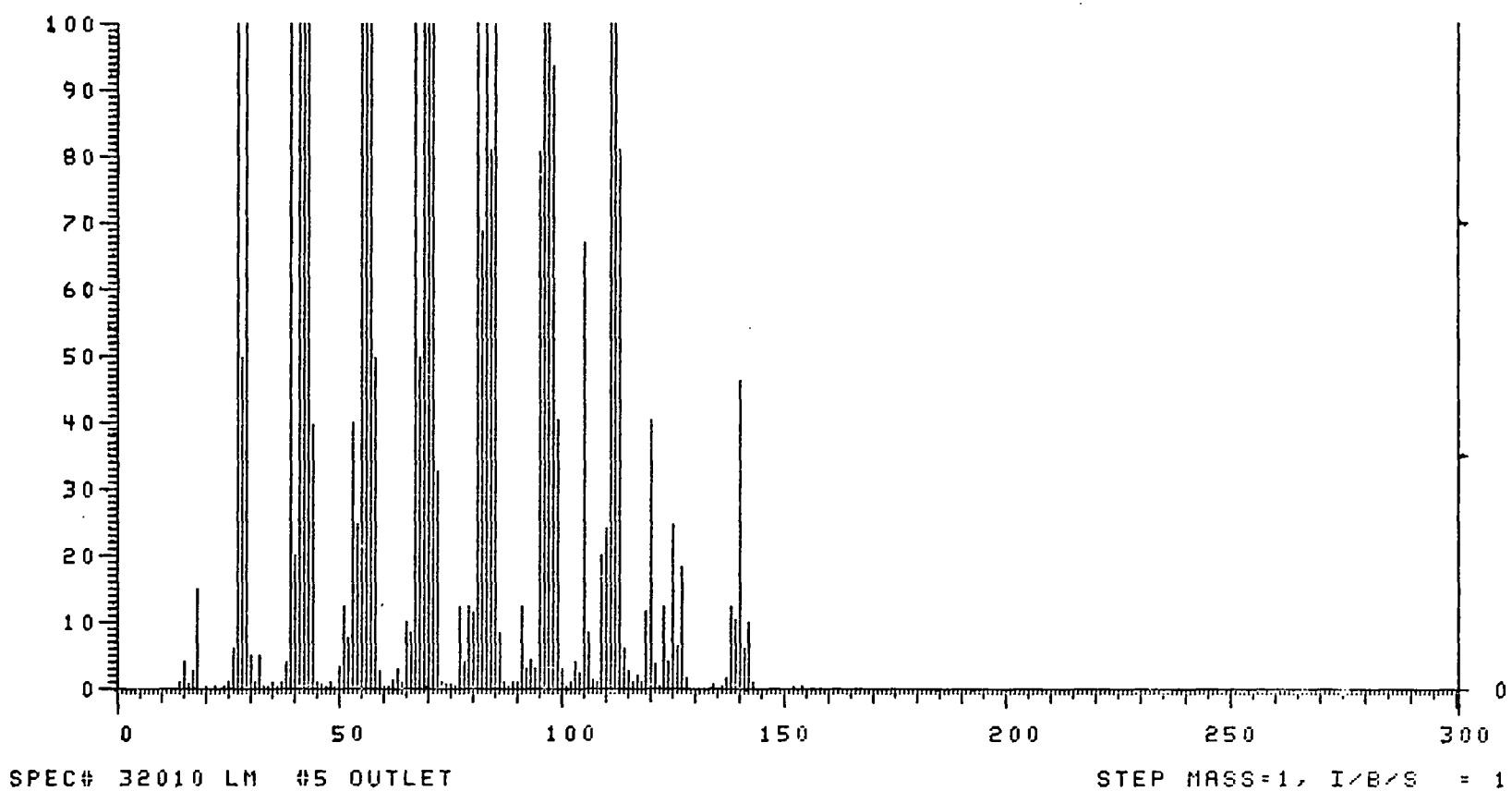
STEP MASS=1, I/B/S = 1%

Figure D-2B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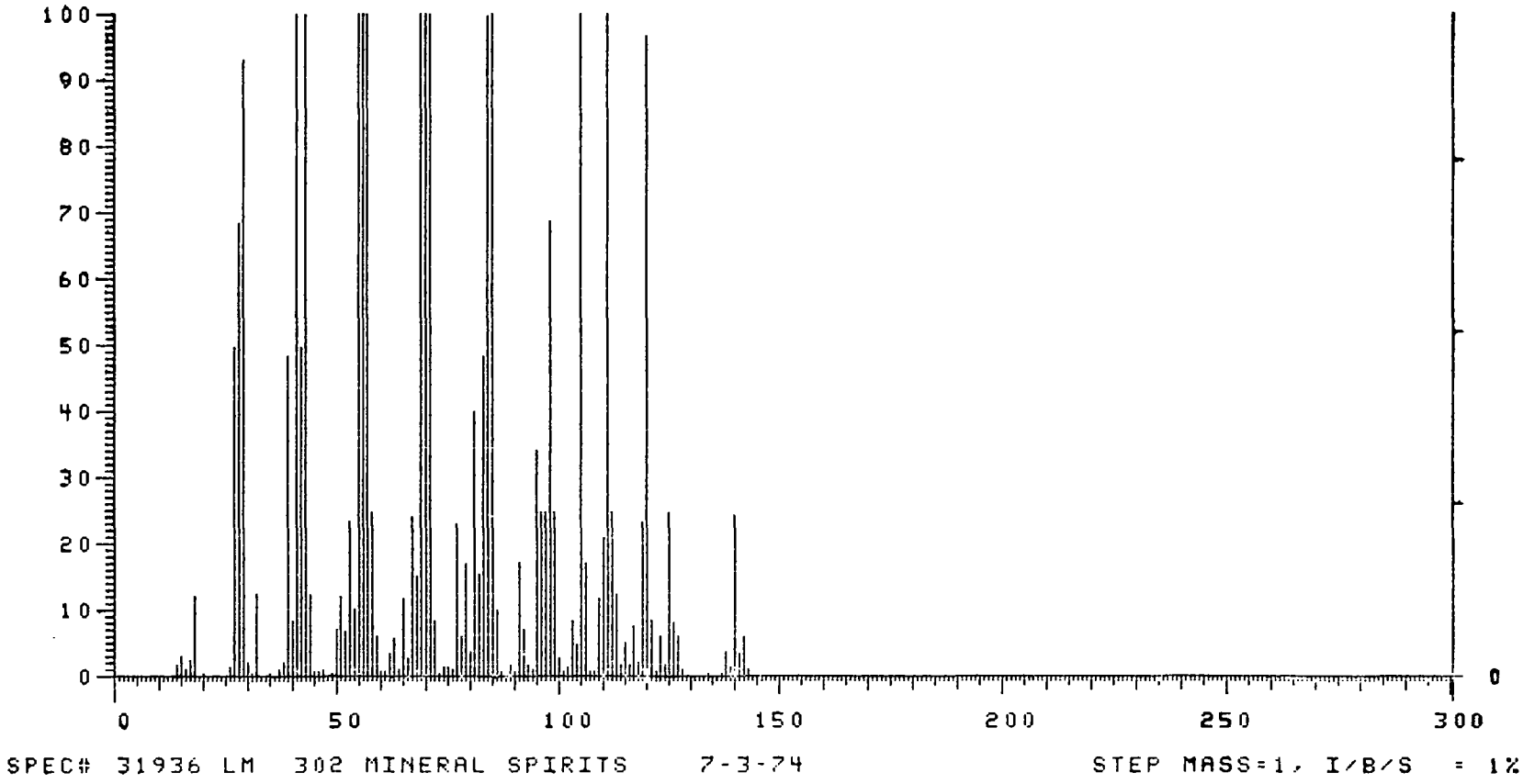
50
40
30
20
10
0
0
50
100
150
200
250
300
0
SPEC# 32010 LM #5 OUTLET
STEP MASS=1, I/B/S = 1%

Figure D-3A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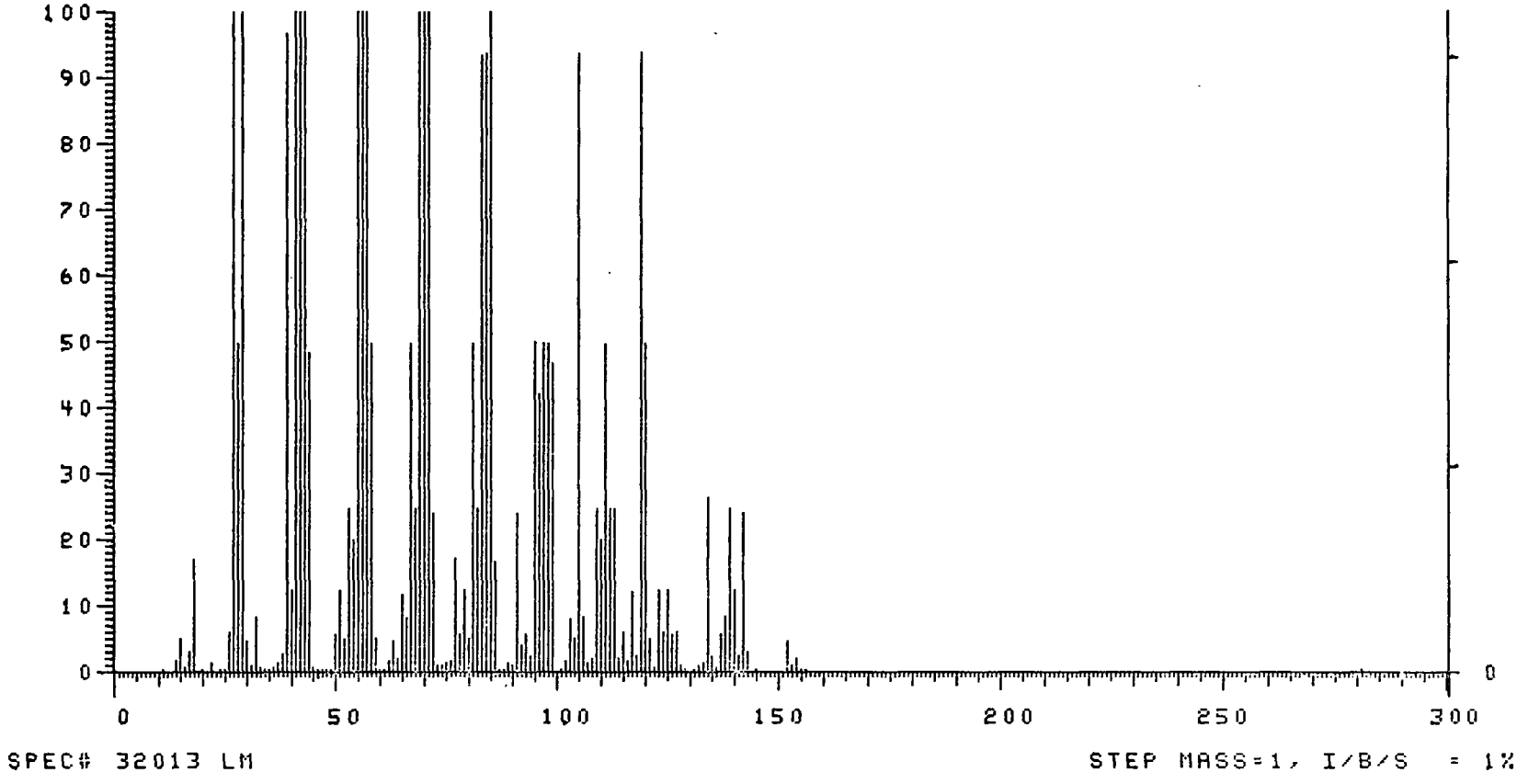
SPEC# 31936 LM 302 MINERAL SPIRITS 7-3-74
STEP MASS=1, I/B/S = 1%

Figure D-3B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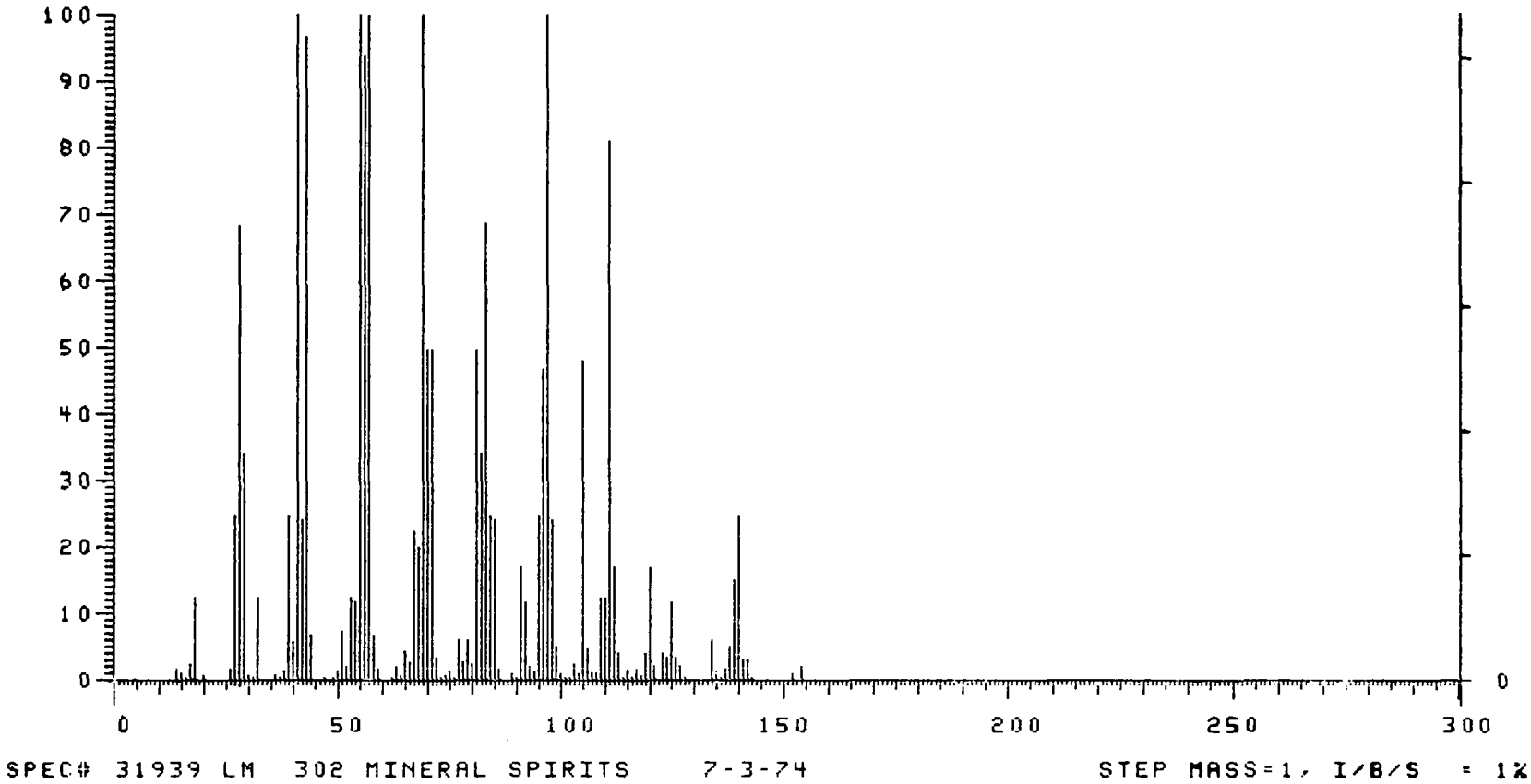
SPEC# 32013 LM
STEP MASS=1, I/B/S = 1%

Figure D-4A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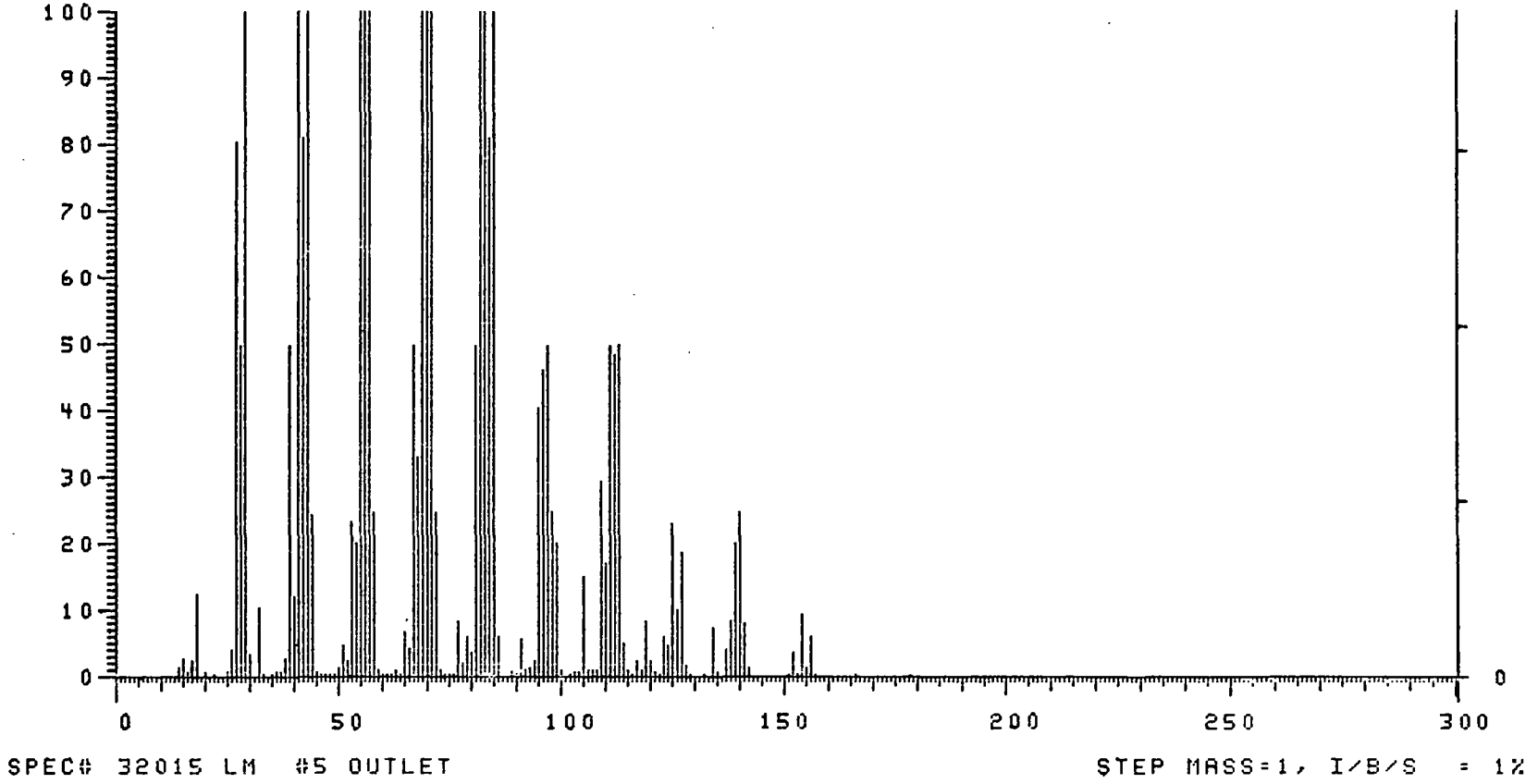
SPEC# 31939 LM 302 MINERAL SPIRITS 7-3-74
STEP MASS=1, I/B/S = 1%

Figure D-4B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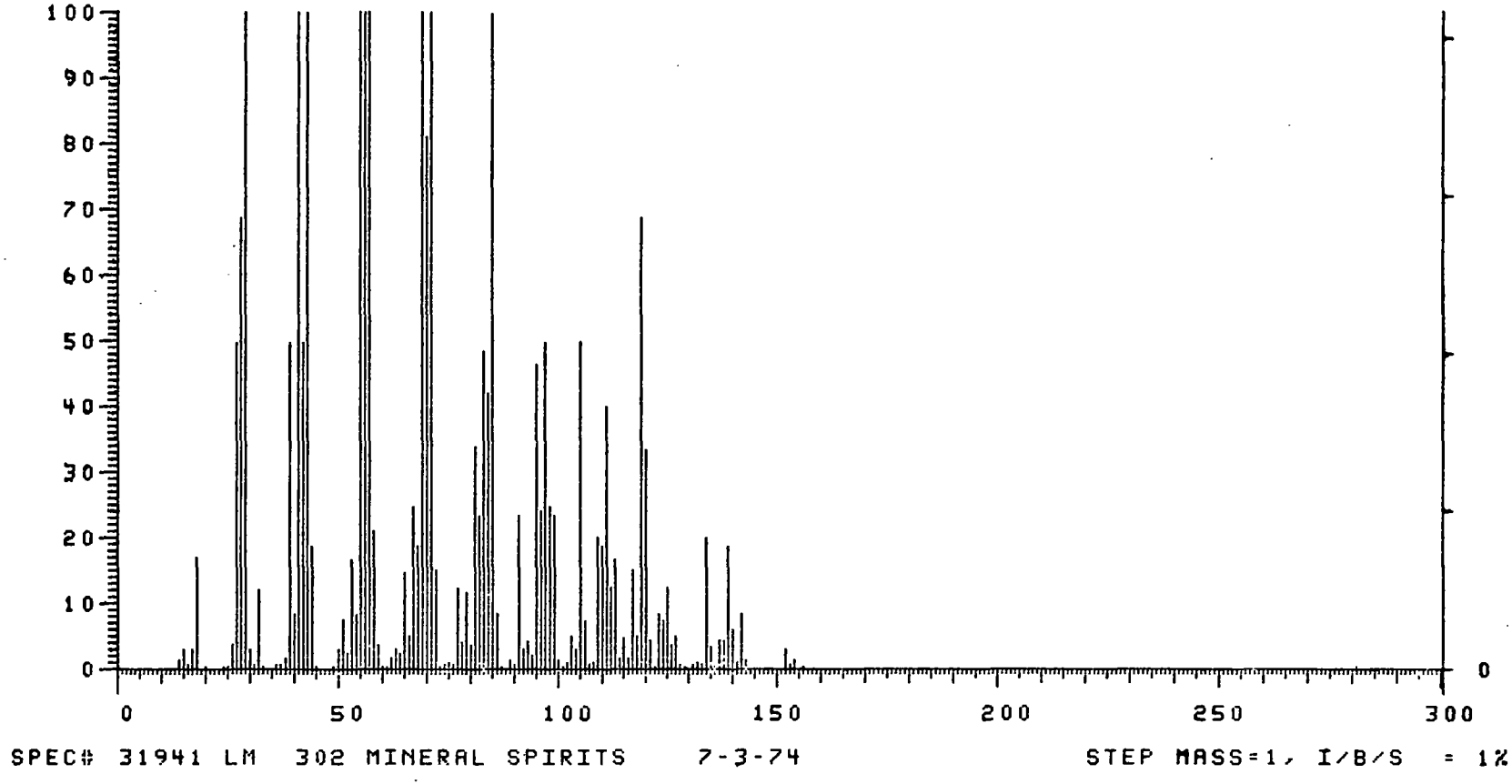
SPEC# 32015 LM #5 OUTLET
STEP MASS=1, I/B/S = 1%

Figure D-5A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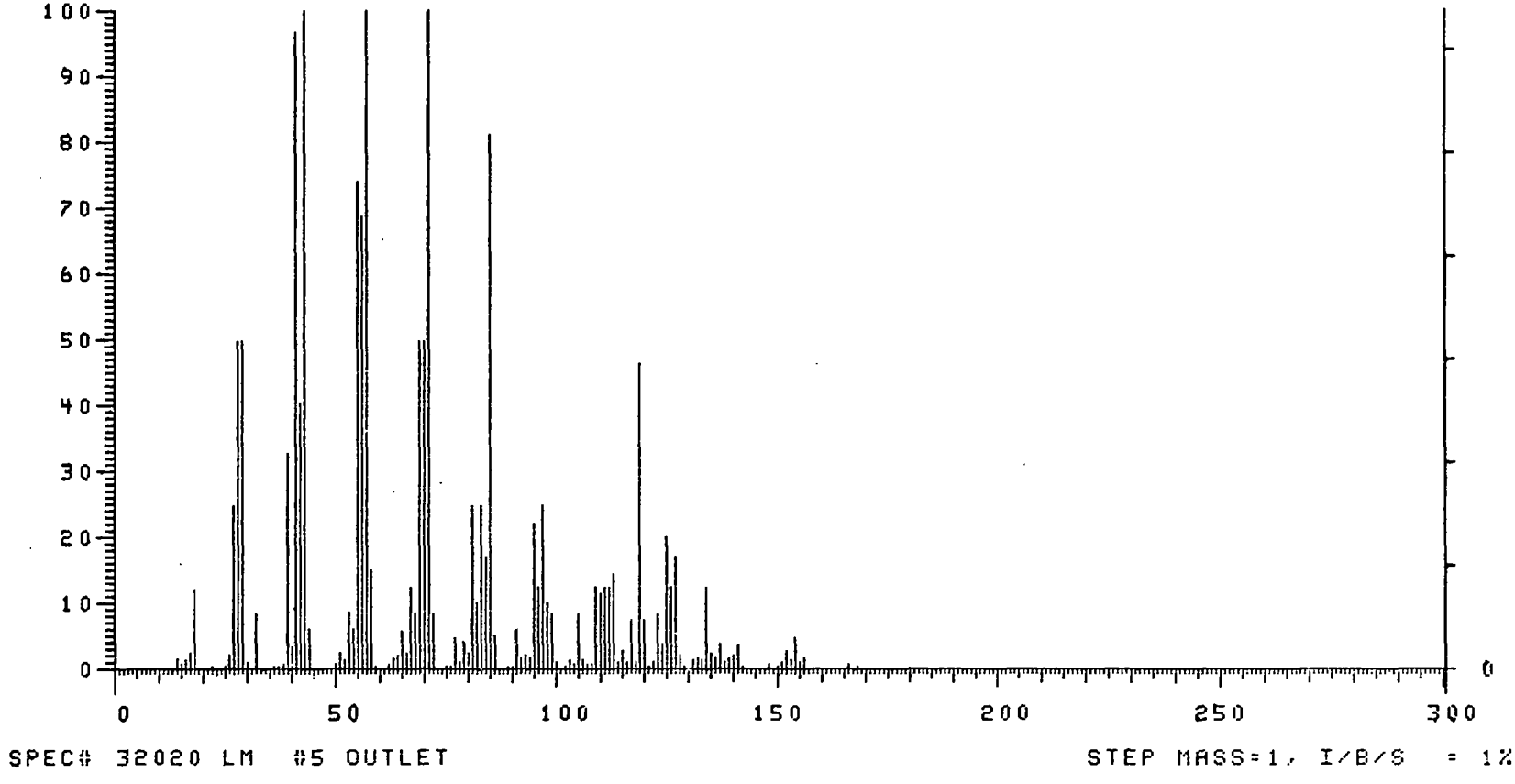
SPEC# 31941 LM 302 MINERAL SPIRITS 7-3-74
STEP MASS=1, I/B/S = 1%

Figure D-5B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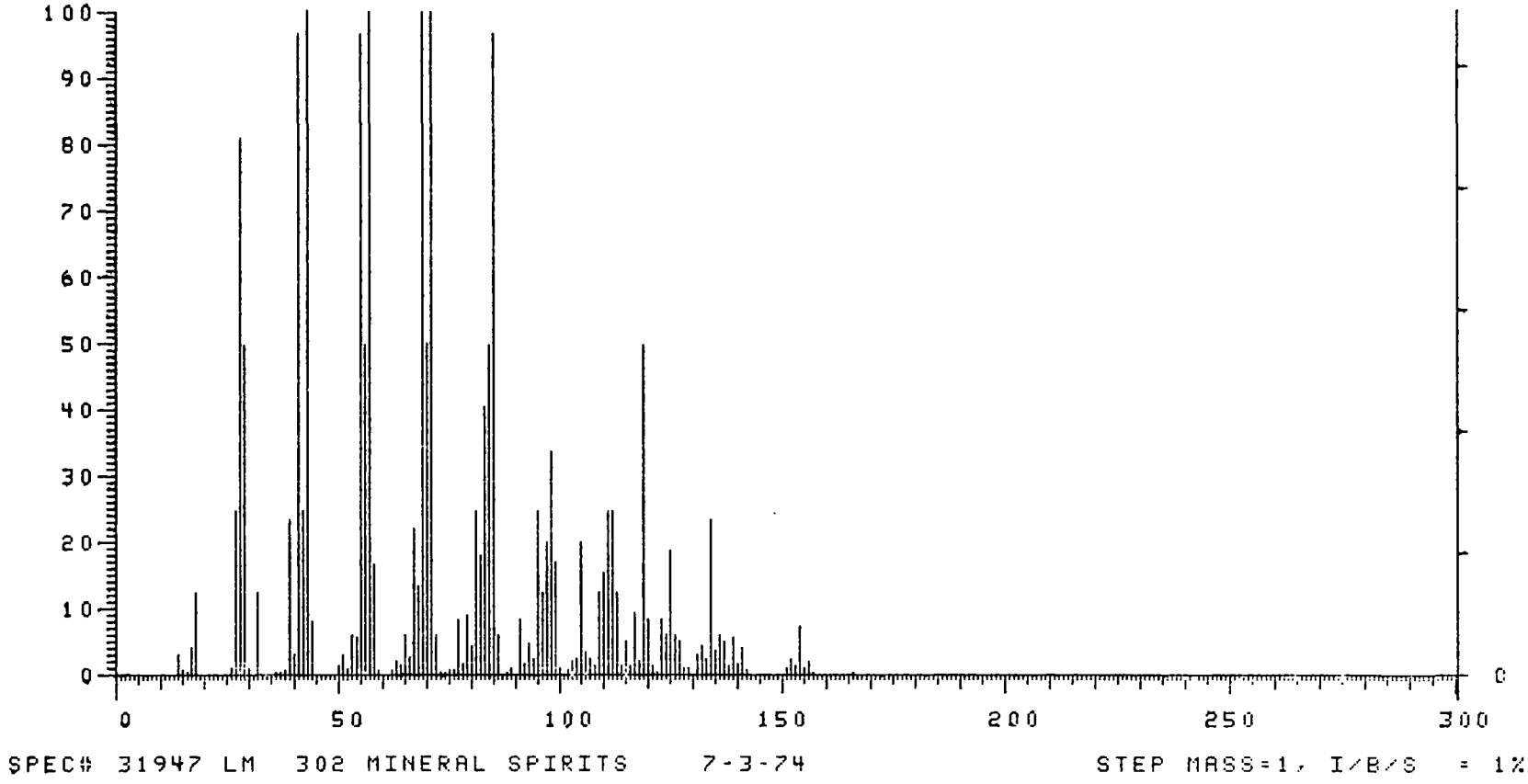
SPEC# 32020 LM #5 OUTLET
STEP MASS=1, I/B/S = 1%

Figure D-6A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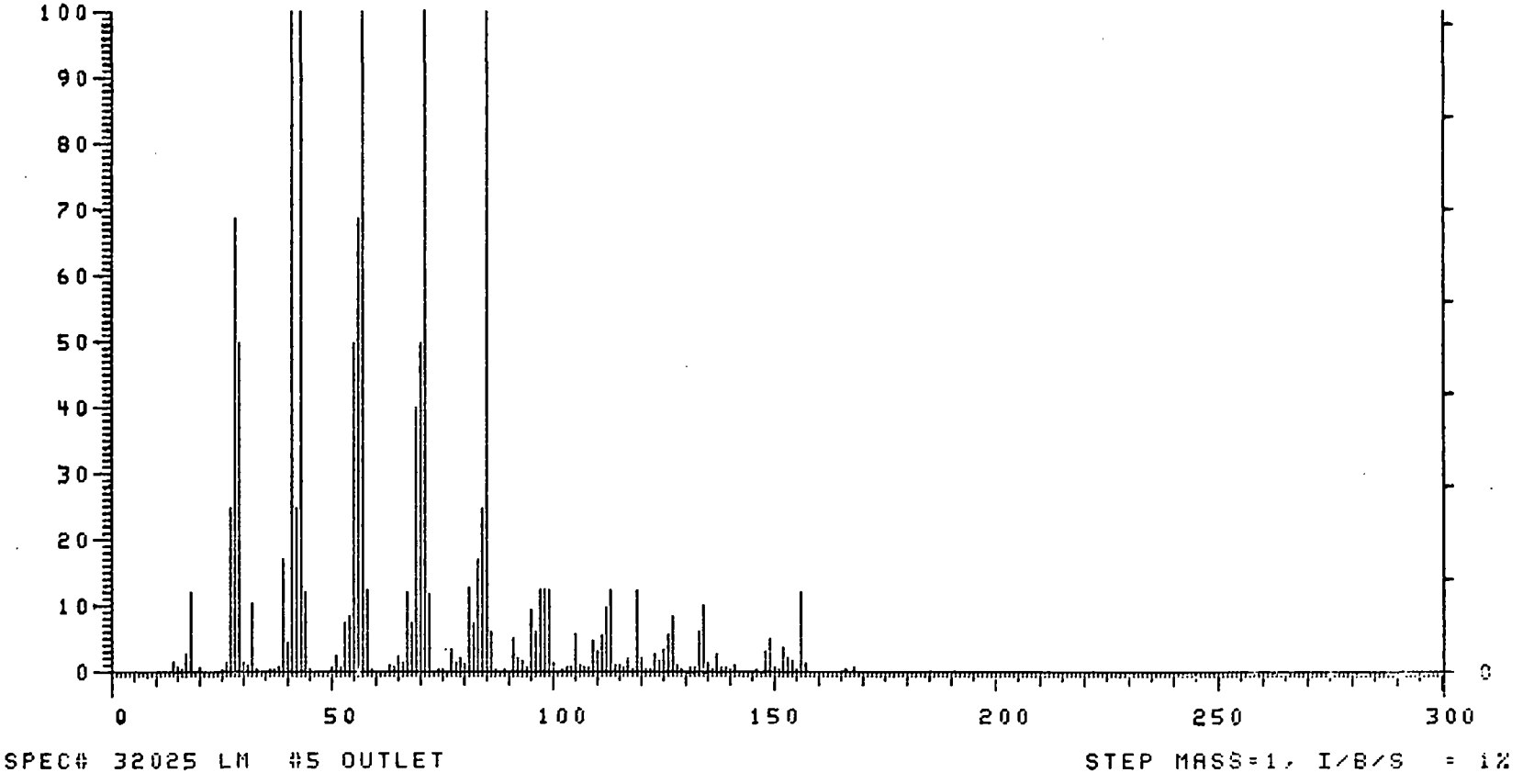
SPEC# 31947 LM 302 MINERAL SPIRITS 7-3-74
STEP MASS=1, I/B/S = 1%

Figure D-6B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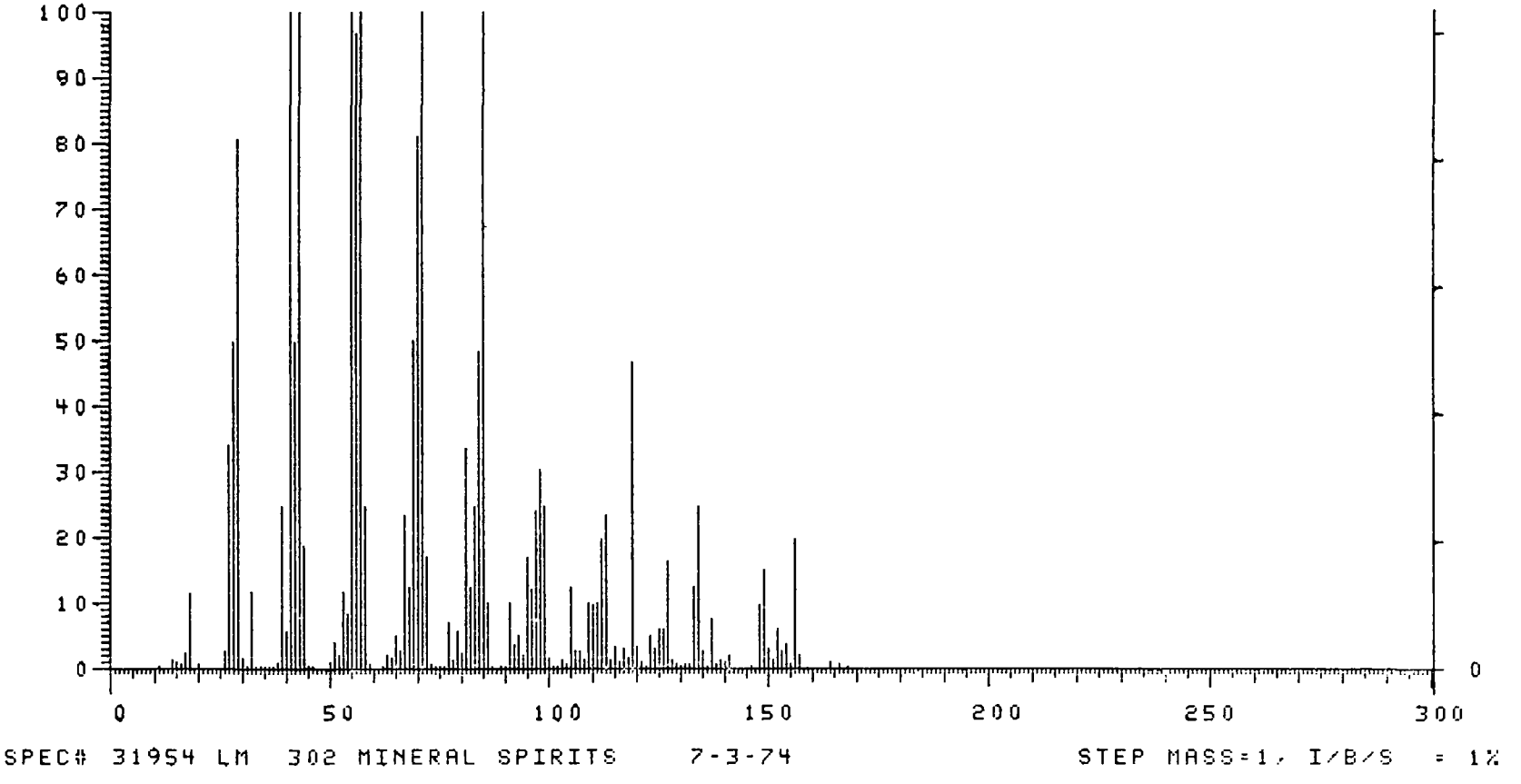
SPEC# 32025 LM #5 OUTLET
STEP MASS=1, I/B/S = 1%

Figure D-7A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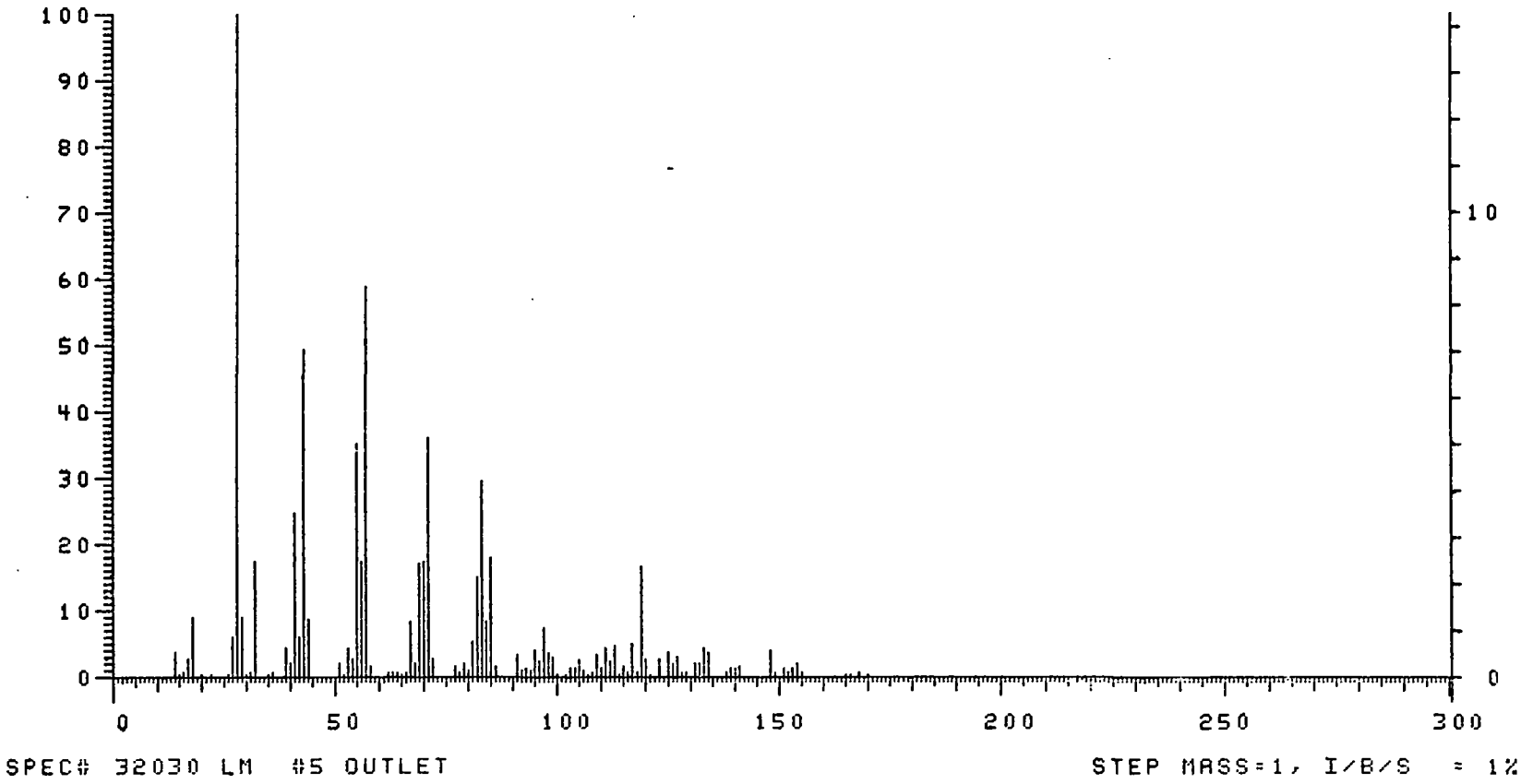
SPEC# 31954 LM 302 MINERAL SPIRITS 7-3-74
STEP MASS=1, I/B/S = 1%

Figure D-7B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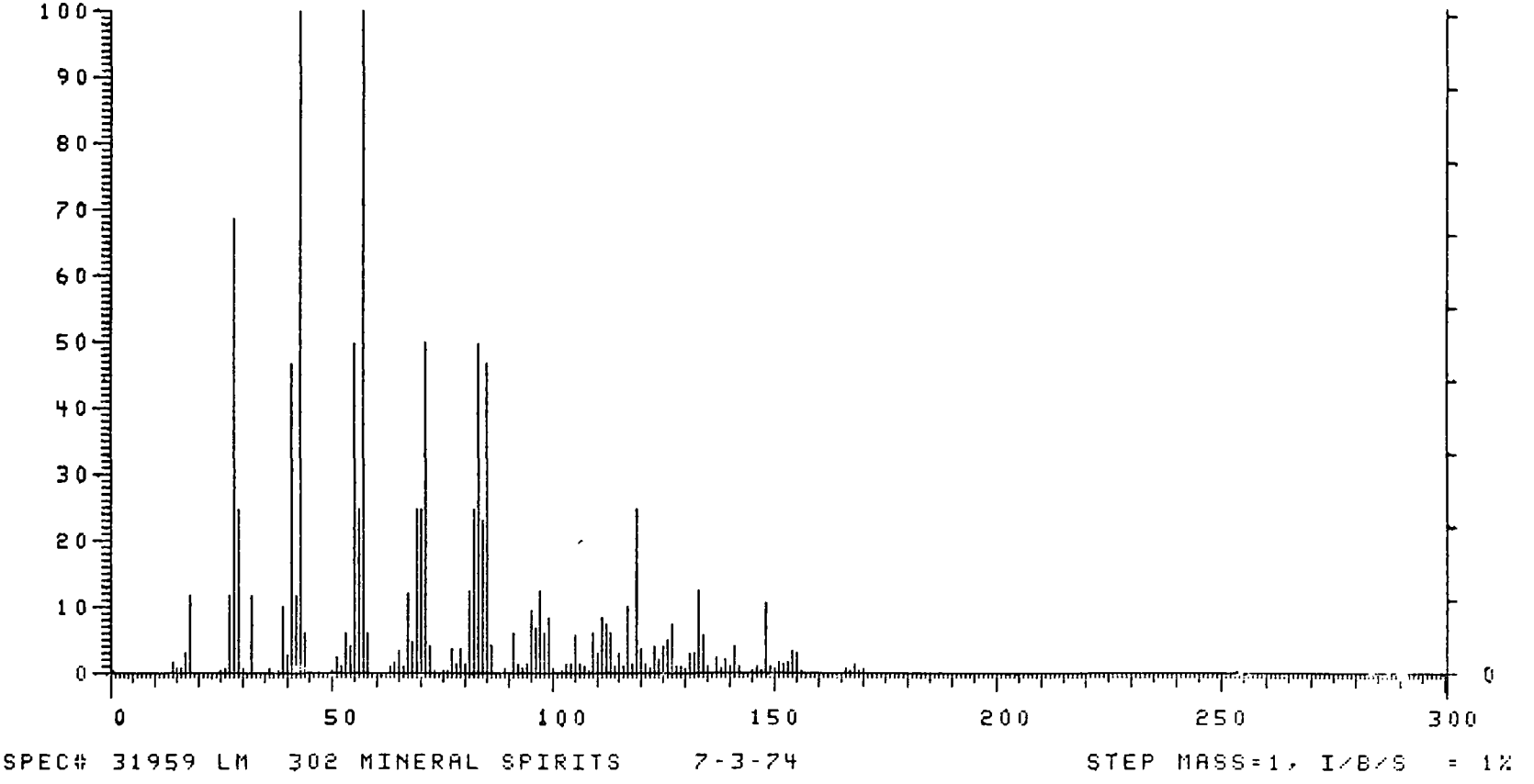
SPEC# 32030 LM #5 OUTLET
STEP MASS=1, I/B/S = 1%

Figure D-8A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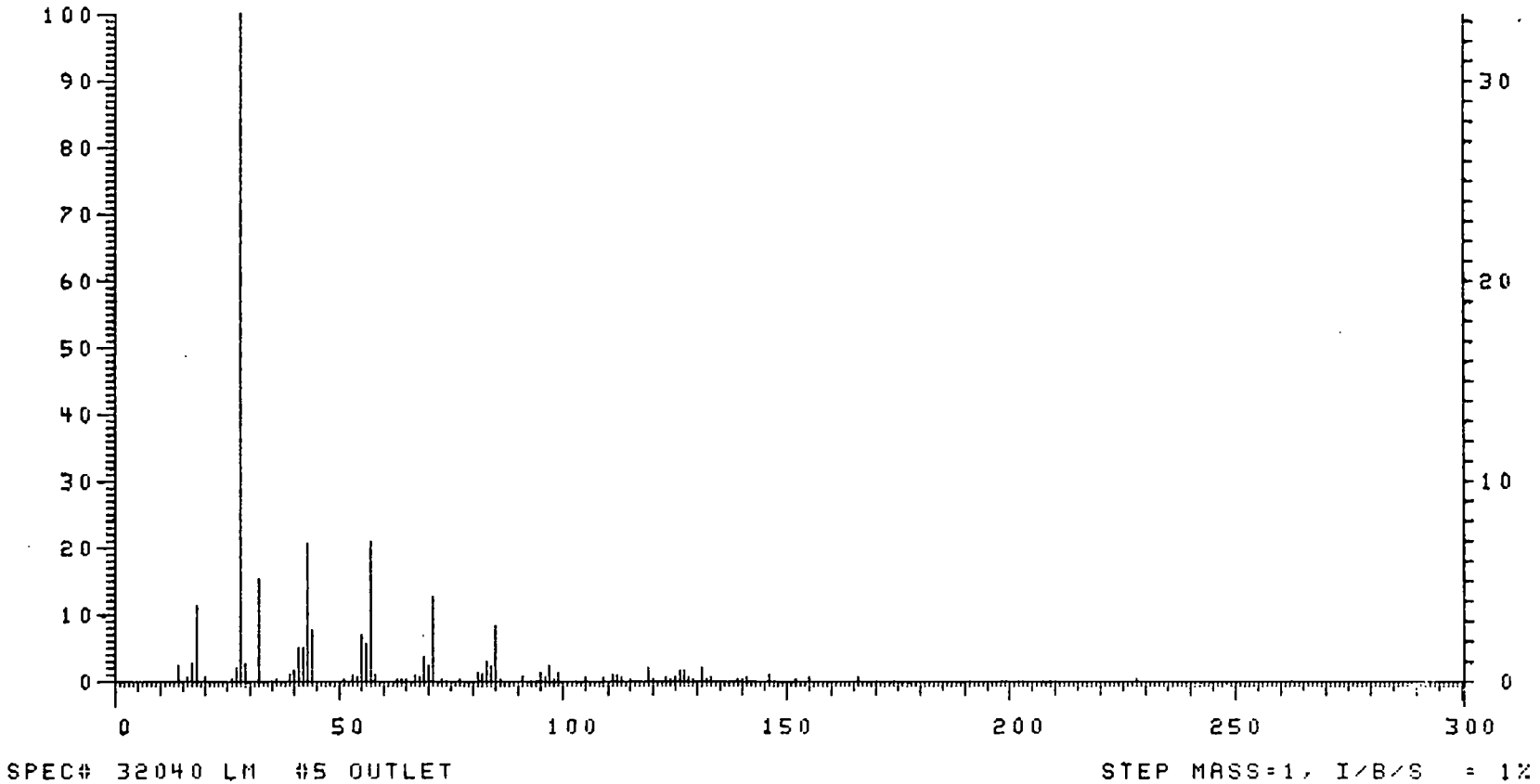
SPEC# 31959 LM 302 MINERAL SPIRITS 7-3-74
STEP MASS=1, I/B/S = 1%

Figure D-8B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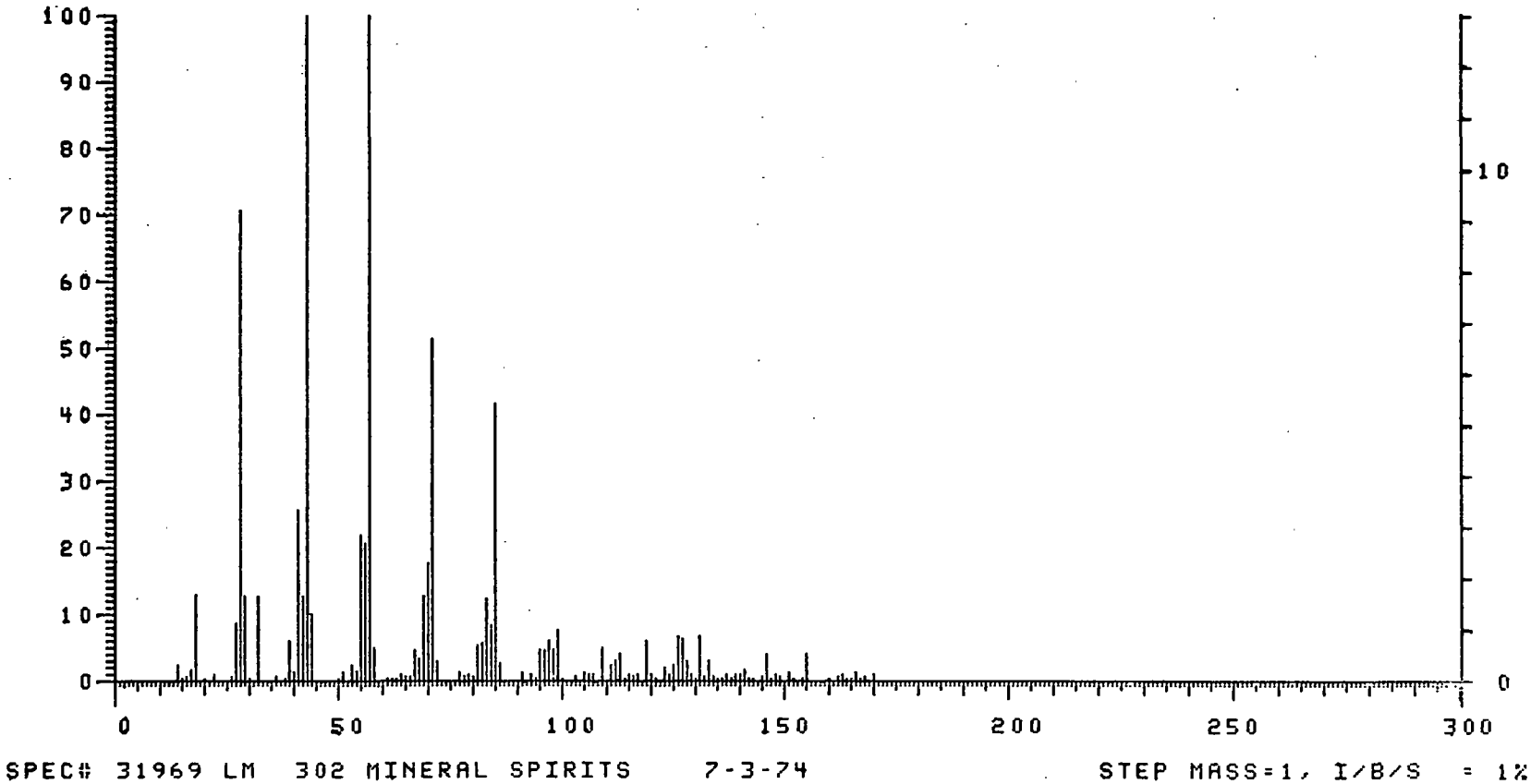
SPEC# 32040 LM #5 OUTLET
STEP MASS=1, I/B/S = 1%

Figure D-9A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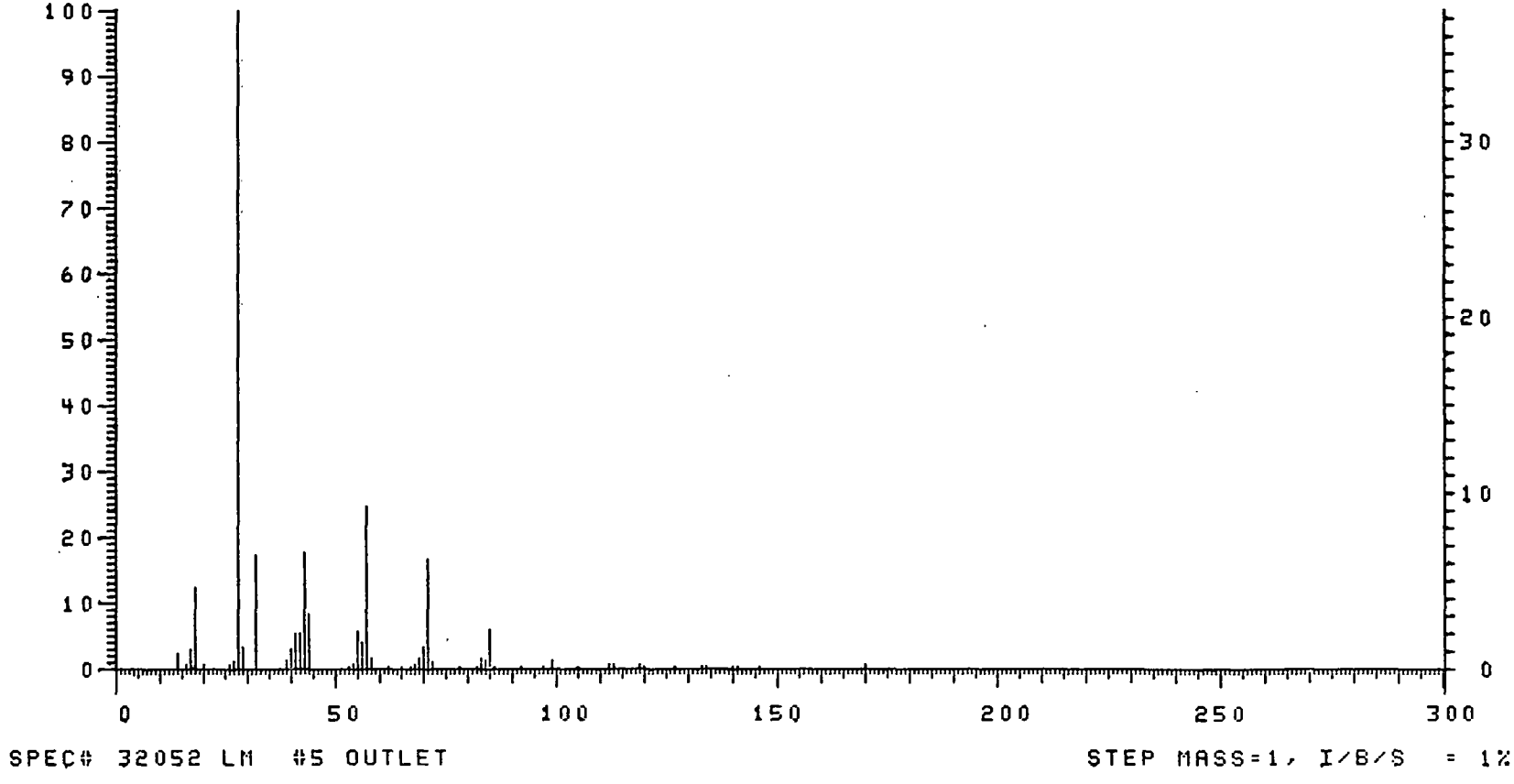
SPEC# 31969 LM 302 MINERAL SPIRITS 7-3-74
STEP MASS=1, I/B/S = 1%

Figure D-9B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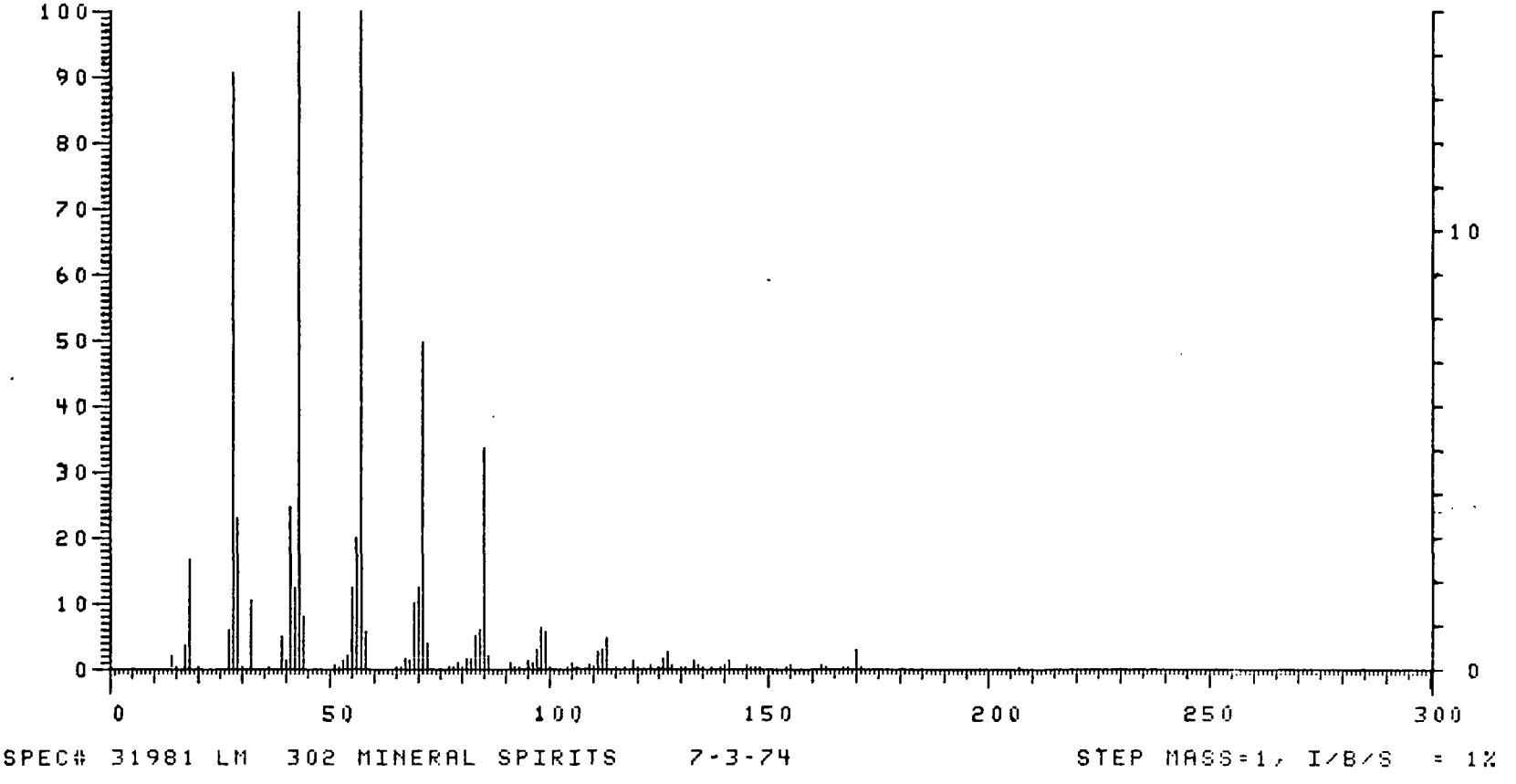
SPEC# 32052 LM #5 OUTLET
STEP MASS=1, I/B/S = 1%

Figure D-10A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SPEC# 31981 LM 302 MINERAL SPIRITS 7-3-74
STEP MASS=1, I/B/S = 1%

Figure D-10B

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

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4. TITLE AND SUBTITLE Characterization of Atmospheric Emissions from Polyurethane Resin Manufacture		5. REPORT DATE October 1974
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Wayne E. Smith and John R. LaShelle		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Midwest Research Institute 425 Volker Boulevard Kansas City, Missouri 64110		10. PROGRAM ELEMENT NO. 1AB015; ROAP 21AXM-060
		11. CONTRACT/GRANT NO. 68-02-0228 (Task 38)
12. SPONSORING AGENCY NAME AND ADDRESS EPA, Office of Research and Development NERC-RTP, Control Systems Laboratory Research Triangle Park, NC 27711		13. TYPE OF REPORT AND PERIOD COVERED Final; 10/73-10/74
		14. SPONSORING AGENCY CODE
15. SUPPLEMENTARY NOTES		

16. ABSTRACT The report describes the characterization of air pollutant emissions from a polyurethane resin manufacturing plant. Samples were taken before and after the air pollution control device (scrubber). Analysis for toluene di-isocyanate (TDI) and amines was conducted both on site and on a delayed basis. The sampling train included an impinger for colorimetric measurement of TDI. Cryogenic traps and a tape sampler for TDI were also used for the scrubber inlet samples. The outlet sampling manifold consisted of evacuated bulbs in place of the cryogenic traps because of the high moisture content. TDI emissions were found to be maximum in the first part of the resin formation reaction. Total emissions consisted of 0.000 000 018 lb TDI per lb of product. The scrubber had negligible effect on the TDI emissions.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Air Pollution	Air Pollution Control	13B
Polyurethane Resins	Stationary Sources	11I, 11J
Manufacturing	Characterization	13H
Analyzing	Toluene Di-Isocyanate	14B
Cyanates		07C
Amines		
Scrubbers		07A

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