

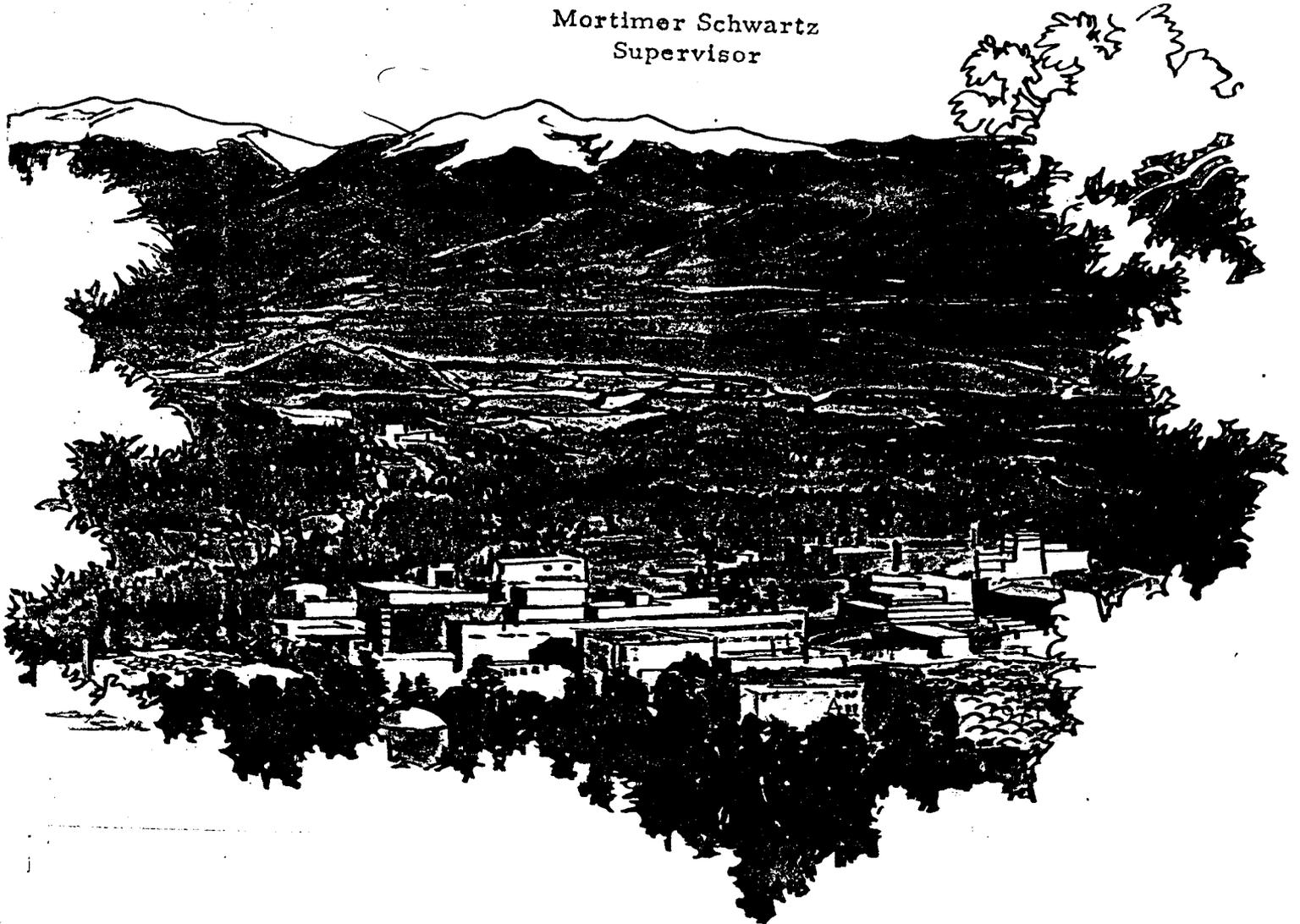
ENVIRONMENTAL STUDIES AT S-SITE

Water and Soil Analyses for RDX-HMX, Barium, TNT, and Boron

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The overall studies were to determine the level of RDX-HMX, barium, TNT, and boron contamination placed in the water effluent, to determine the concentration of these elements and compounds that might build up in the soil, and to determine the source and travel distance of these species throughout the S-Site drainage system. Methods of analyses for RDX, HMX, TNT, barium, and boron in water and soil are also discussed.

ENVIRONMENTAL STUDIES AT S-SITE

Water and Soil Analysis for RDX-HMX, Barium, TNT, and Boron

During the summer of 1971, environmental studies were carried out in the Analytical Laboratory of Group GMX-3. The overall studies were made to determine the level of RDX-HMX, barium, TNT, and boron contamination placed in the water effluent, to determine the concentration of these elements and compounds that might build up in the soil, and to determine the source and travel distance of these species throughout the S-Site drainage system.

The drainage system at S-Site makes use of two major canyons in this area; Water Canyon and Del Valle Canyon. Small feeder canyons and several drainage ditches pour all of the waste water from S-Site operations into one of these major canyons. It was from the drainage floor of these two canyons that soil and water samples were taken for analyses. Samples for analyses were taken from the canyons at S-Site, K-Site, Magazine Area C, and Frijoles Mesa Site (Figure 1). In addition, water samples were removed at the outlets of settling basins adjacent to operating buildings

Information on the precipitation in the area was obtained from the LASL Weather Summary-LASL Bulletin (Tables 1 and 2).

TABLE 1
MONTHLY PRECIPITATION
(inches)

	<u>1971</u>	<u>1970</u>	<u>1969</u>	<u>1968</u>
June	0.60	1.56	3.29	0.03
July	4.25	2.49	4.44	6.60
August		5.60	2.91	6.39



Figure 1

Map of Environmental Study Area

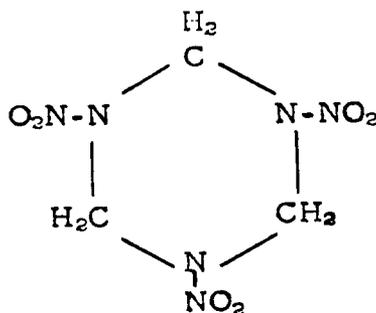
TABLE 2

YEARLY PRECIPITATION
(inches)

<u>1965</u>	<u>1966</u>	<u>1967</u>	<u>1968</u>	<u>1970</u>	<u>1971</u>
23.70	17.48	20.80	19.55	14.93	2.48 (to 6/30/71)

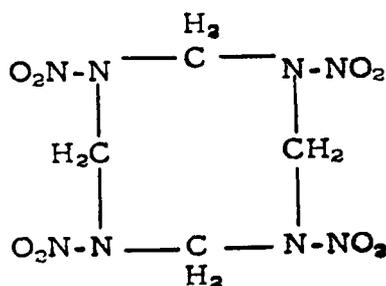
A literature search revealed no method for the analysis of RDX or HMX in water. Walter Selig, LLL, had done a considerable amount of work on the analysis of the solid samples of RDX and HMX, but none of these methods could be adapted to water solutions.

RDX, Cyclotrimethylenetrinitramine, is a compound having the structure:



It is soluble in water to the extent of only 76 parts per million at 25°C.

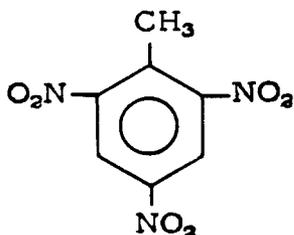
HMX, Cyclotetramethylenetetranitramine, has the structure:



It is soluble in water to the extent of only 50 parts per million at 25°C. The extremely low solubility of both compounds demanded a method of analysis that would be able to detect very small amounts of the compounds in the parts-per-million range. Several methods were attempted.

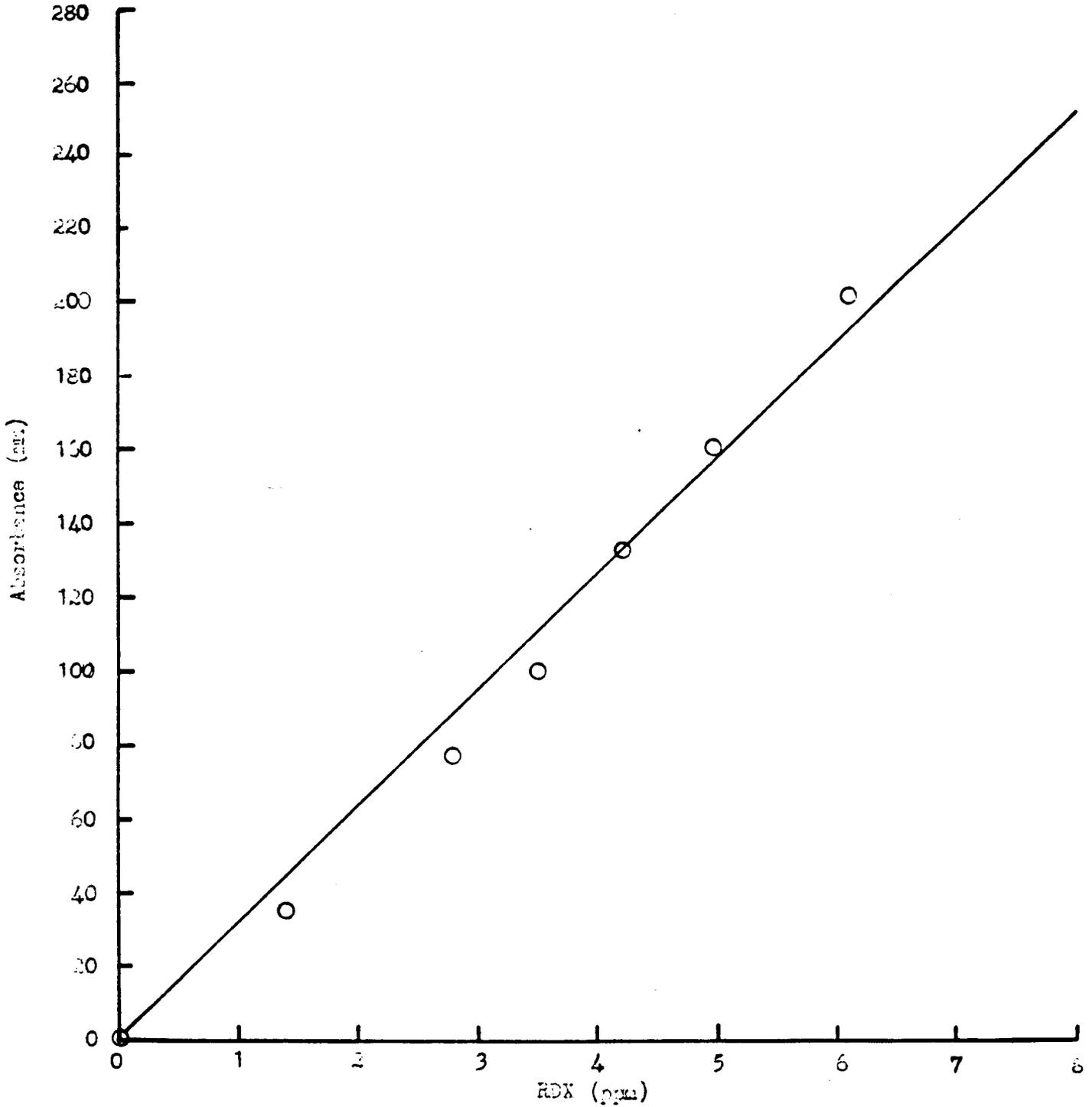
The first attempt was to determine the RDX and HMX concentration in water by using the ultraviolet region of the spectrum. Standard curves were run for varying concentrations of RDX versus water with major absorptions appearing at 230 m μ and 195 m μ . This relationship for RDX was shown to follow Beer's Law. Standard curves were also run for HMX and it too followed Beer's Law with major absorptions appearing at 230 m μ and 195 m μ (Figures 2 and 3).

TNT, 2,4,6-trinitrotoluene, is very slightly soluble in water, 0.013 gram per 100 grams of water at 20°C. It is an aryl nitrocompound having the structure:



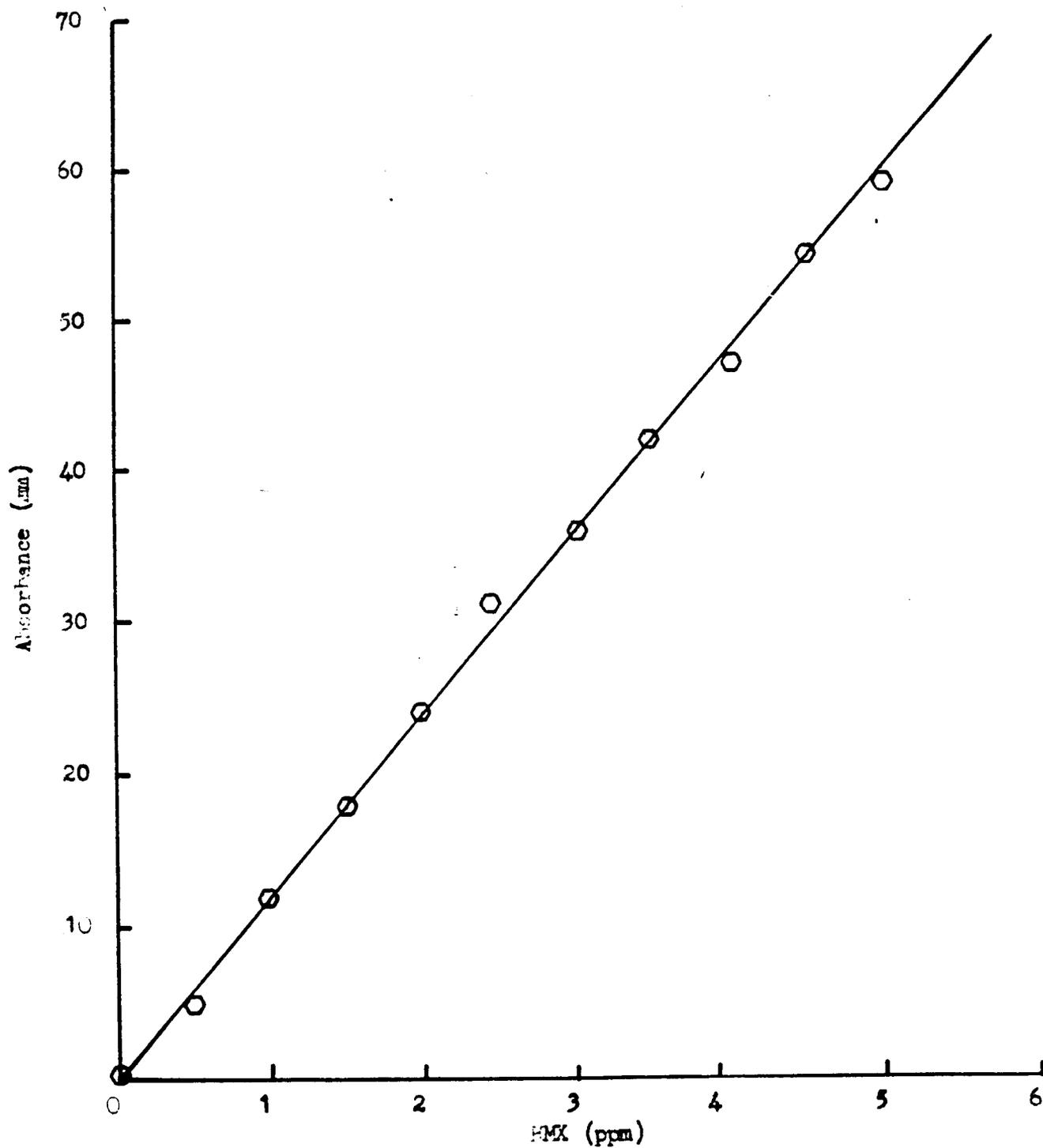
TNT also absorbs in the ultraviolet region with maximum absorption at 230 m μ . This absorption follows Beer's Law (Figure 4).

An attempt was made to compensate for two of the compounds by saturation of the solvent in the reference cell and measuring the third, but the presence of other absorptions from undetermined contaminants in this region made this fruitless. The direct ultraviolet analysis of water solutions was dropped.



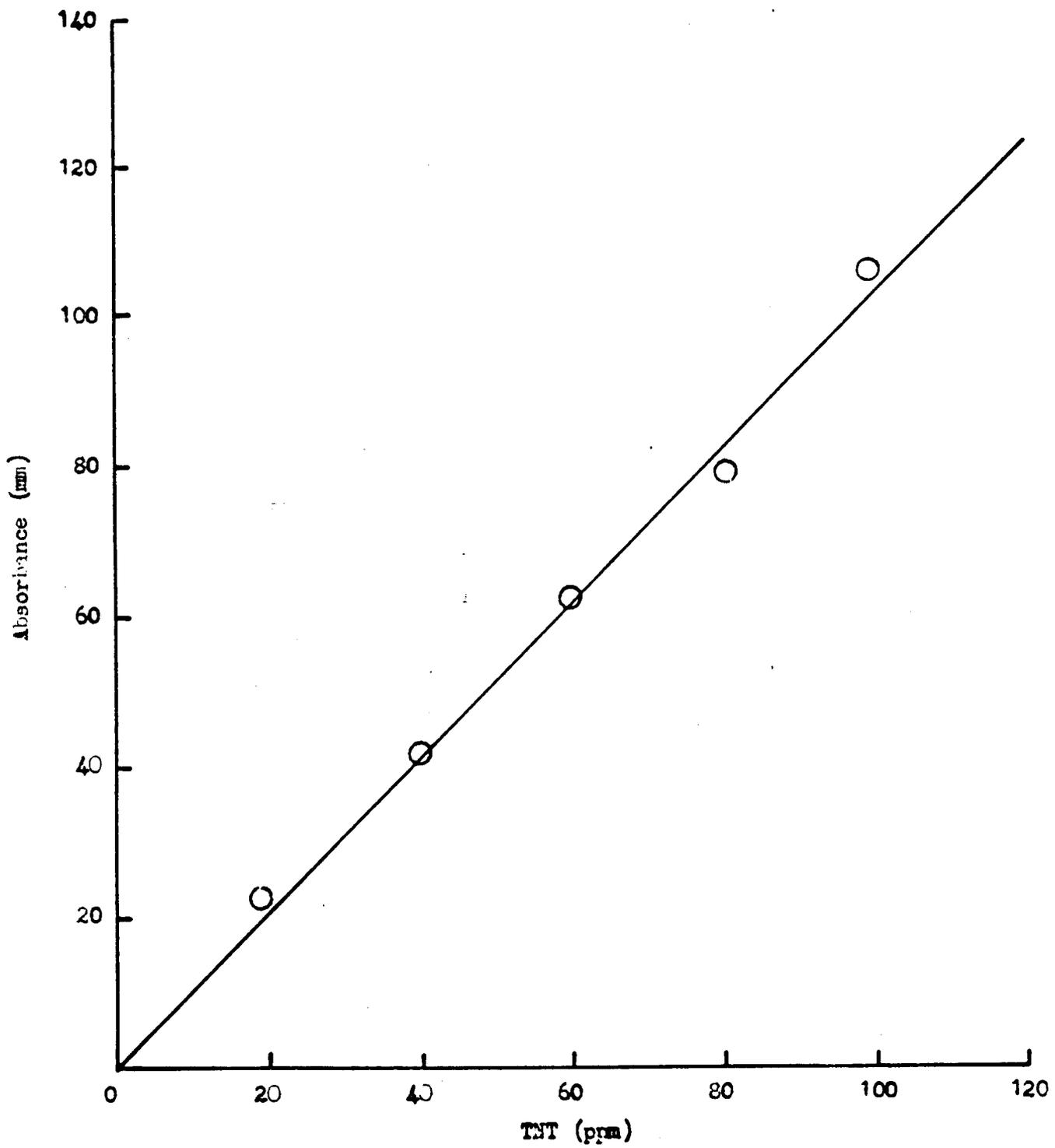
RDX (ppm) versus Absorbance (arbitrary units) at 230 mμ with a 1 cm cell

Figure 2



PMX (ppm) versus Absorbance (mm) at 230 m μ with a 1 cm cell

Figure 3



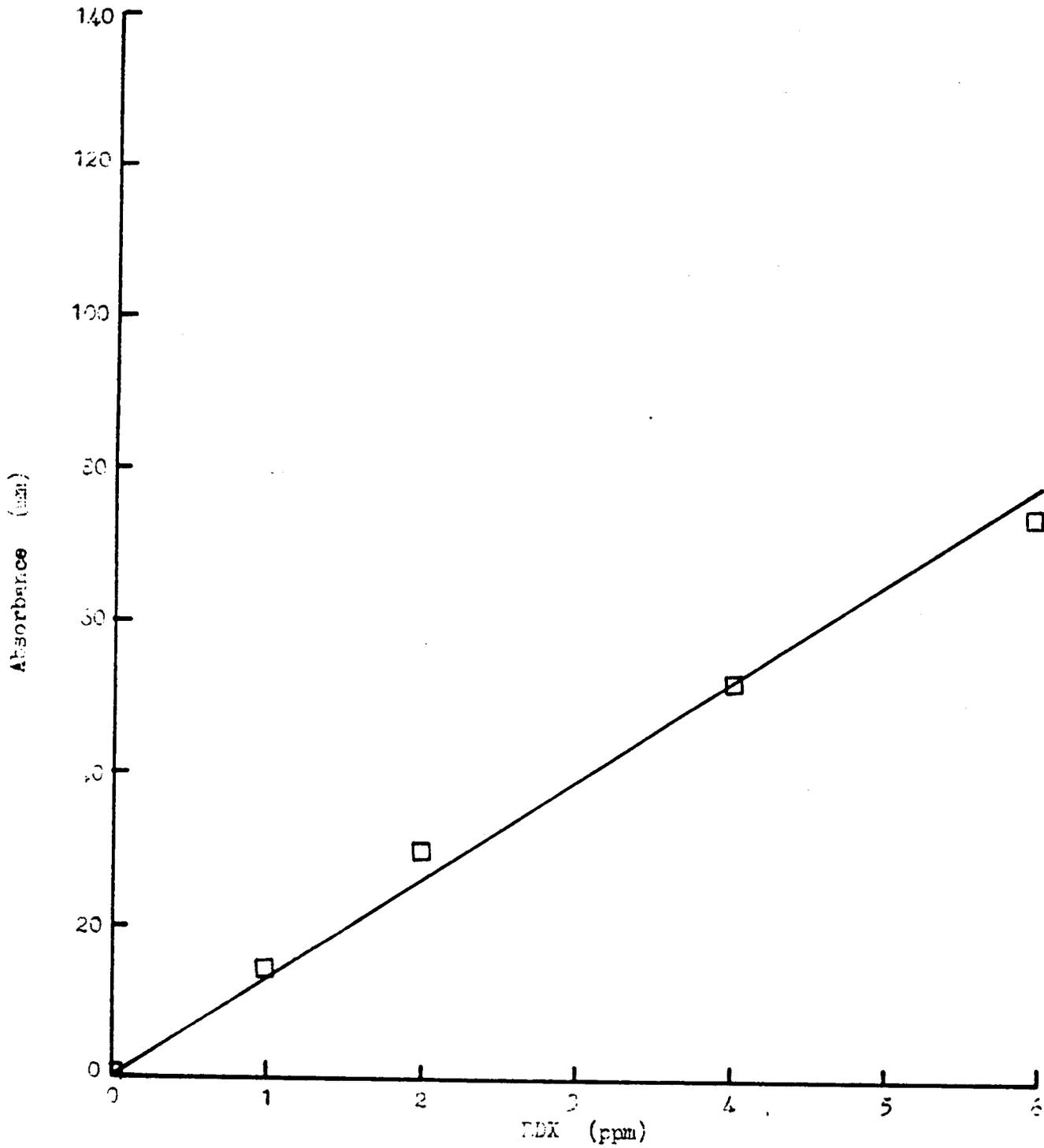
TNT (ppm) versus Absorbance (mm) at 230 m μ with a 1 cm cell

Figure 4

A gas chromatographic method was attempted, but a suitable solvent that could sufficiently extract HMX and RDX from water could not be found. Attempts to find a column that would separate HMX showed that HMX undergoes decomposition on the column. This attempt was dropped and a colorimetric method was investigated.

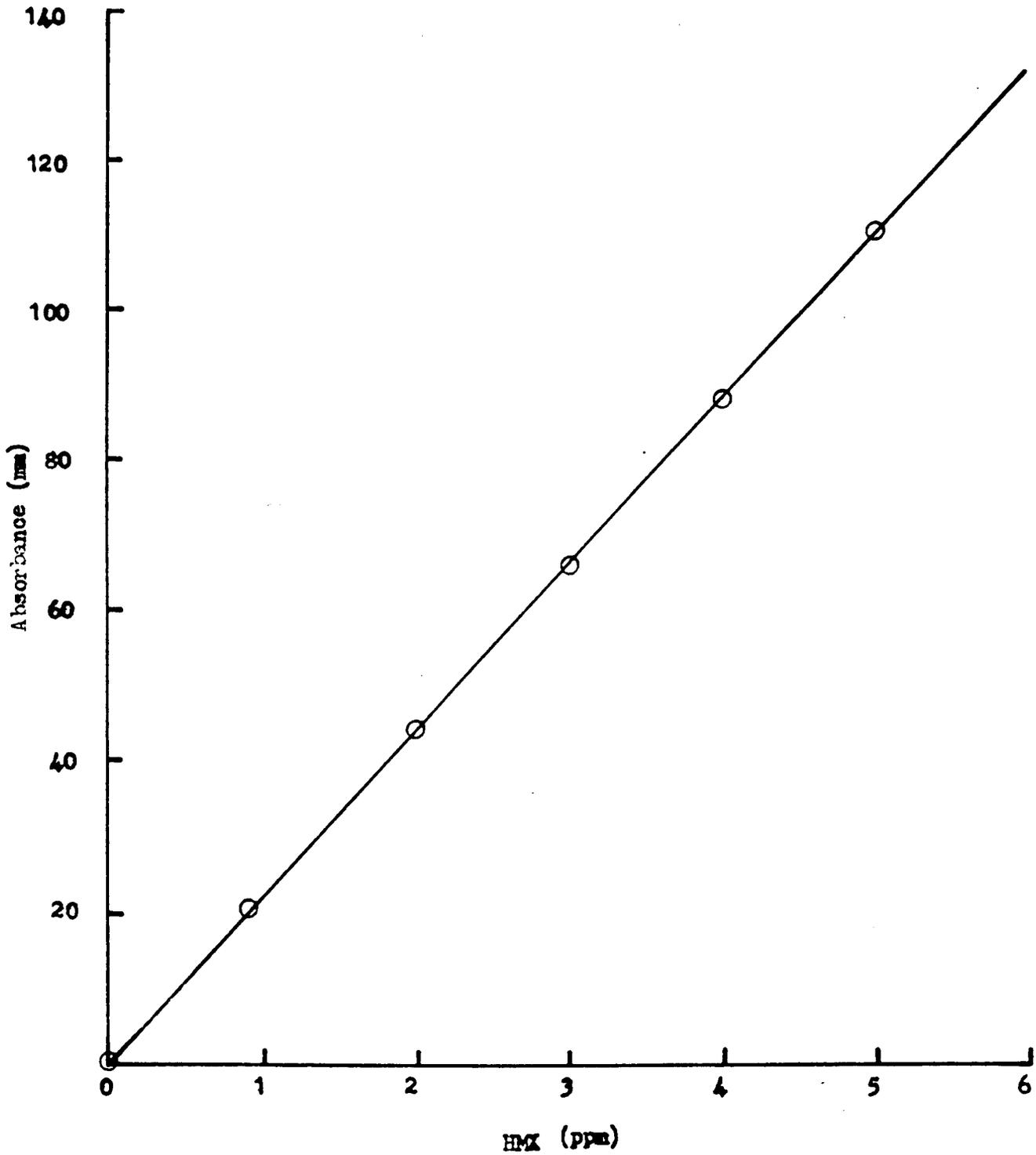
When RDX or HMX is treated with concentrated sulfuric acid in the presence of a chromotropic salt solution [sodium 1,8-dihydroxynaphthalene-3,6-disulfonate, $(HO)_2C_{10}H_4(SO_3Na)_2$] a violet to purple color is produced, depending on the concentration of RDX and HMX present. It is this color that provided the basis for the analysis of RDX and HMX in water.

The method outlined was used for the determination of HMX and RDX concentrations in water: 2 ml of water containing an unknown amount of HMX and RDX was mixed with 0.5 ml of an aqueous 2% chromotropic salt solution. This solution was diluted to 25 ml with concentrated sulfuric acid and the resulting reaction produced a color that could be analyzed in the visible region on a Perkin-Elmer 350 UV-VIS-NIR Spectrophotometer. Thirty minutes were allowed for the solution to cool and for full color development. The exact kinetics or products of the reaction are not yet known, but it is known that some sort of condensation reaction occurs and a violet to indigo color is produced in the presence of organic nitro compounds. Major absorbance occurs at 565 to 540 m μ and 475 m μ . A plot of absorbance (mm) versus concentration (ppm) prove to be linear and standard curves for HMX, (0 to 5 ppm) and RDX, (0 to 7.6 ppm) were run. A developed solution of 2 ml of distilled water was used in the reference (Figures 5 and 6).



Developed solution of RDX (ppm) versus Absorbance at 565 mμ with a 1 cm cell

Figure 5



Developed solution of HMX (ppm) versus Absorbance at 565 mμ with a 1 cm cell

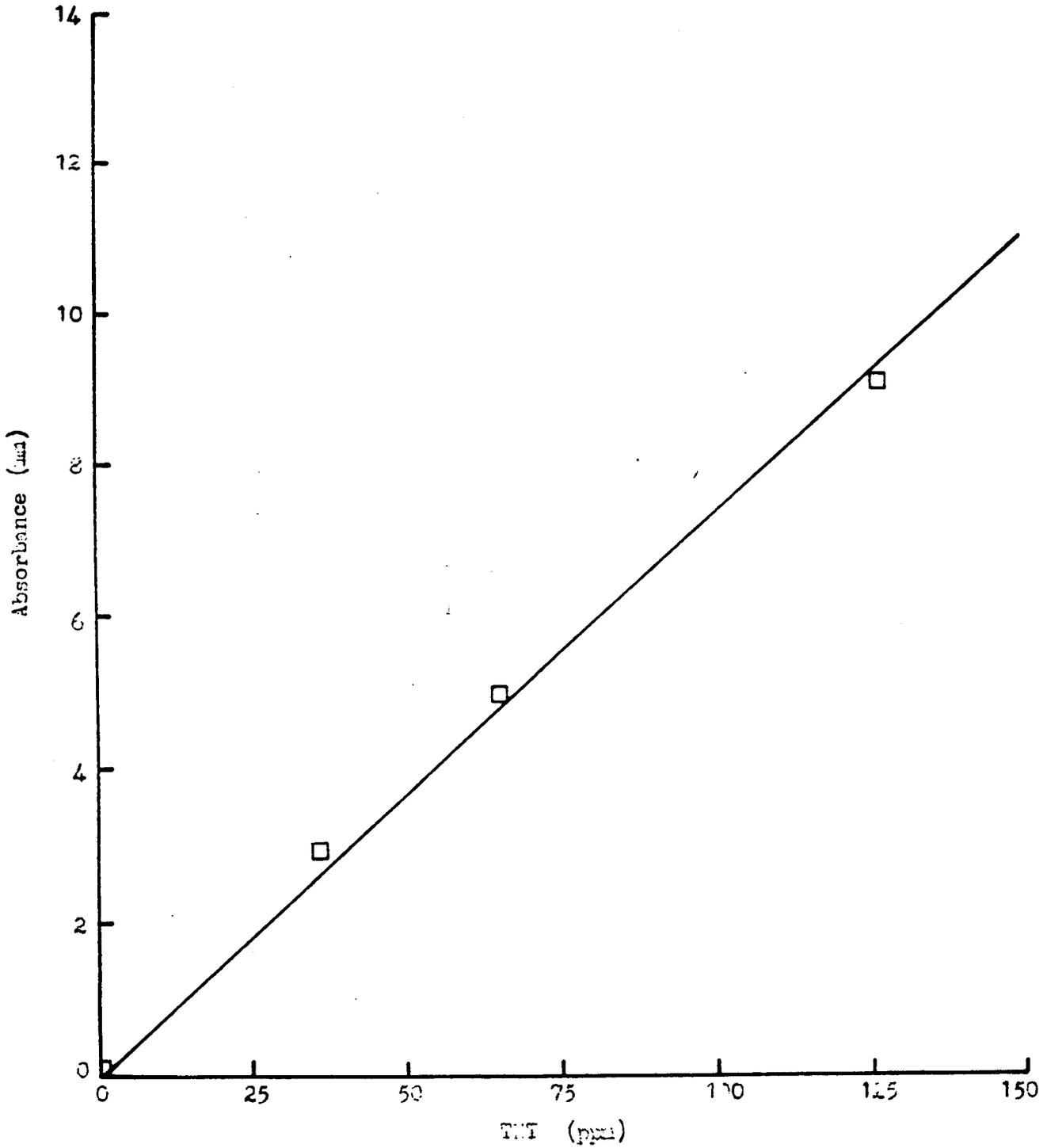
Figure 6

A brown to light yellow color was produced with TNT and inorganic nitrates. Standard curves from known concentrations of TNT and $\text{Ba}(\text{NO}_3)_2$ were run to determine their absorbance at the 565 m μ region (Figures 7 and 8).

The procedure relies on the presence of nitro compounds and nitrates. It was assumed that all nitrate and nitro compounds came from HMX, RDX, TNT, or $\text{Ba}(\text{NO}_3)_2$ because of the nature of operations at S-Site. By determining TNT and barium content first, the absorbance at 565 m μ from the developed solution due to these two could be subtracted from the total absorbance and the concentration of RDX-HMX determined. No attempt was made to break down further the RDX-HMX concentration, and all data produced were those of combined RDX-HMX concentrations. Final data were obtained by assuming HMX and RDX to be present in equal amounts and 43% of the total absorbance is due to RDX and 57% of total absorbance is due to HMX.

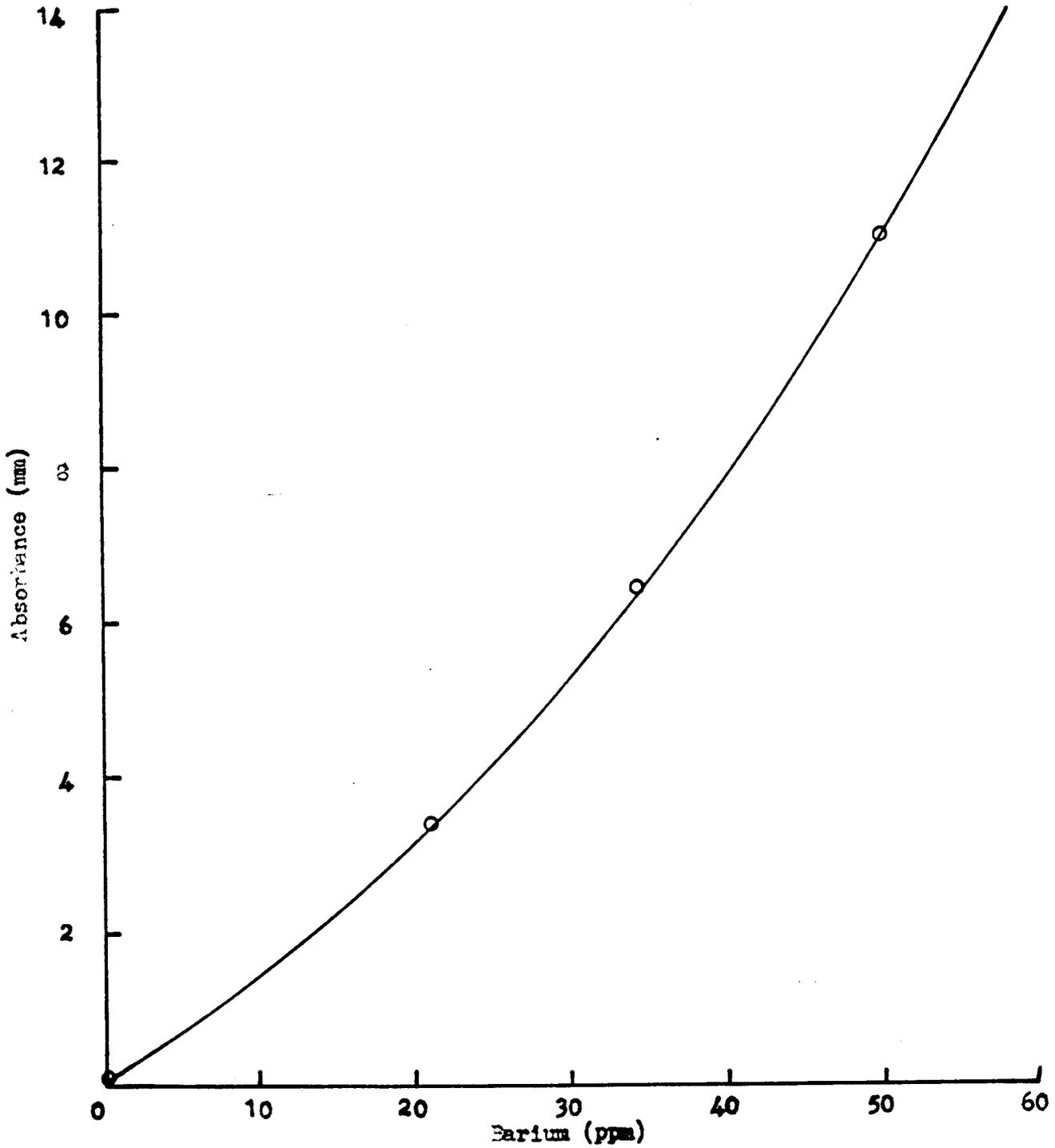
In the analysis of soil samples for HMX and RDX, 10 grams of the soil were Soxhlet extracted with 200 ml of water for four hours. The resulting water solution was analyzed by the previous outlined procedure for water samples. The limit of detection of the water samples was shown to be 0.5 ppm combined RDX and HMX, although this could be expanded by water stripping and employment of larger cells. Limit of detection of soil samples was 5 ppm.

The stability period of the chromotropic salt solution was about 4 hours. After 4 hours, the solution slowly turned to a darker brown color and its absorbance at 565 began to increase. The stability of the developed colors



Developed solution of TNT (ppm) versus Absorbance at 565 mµ with a 1 cm cell

Figure 7



Developed solution of Barium (ppm) versus Absorbance at 565 mμ with a 1 cm cell

Figure 8

was less than three hours. The original purple color began to lose intensity in the 565 to 540 m μ region after three hours. Fresh solutions of indicator had to be made up for each series of runs. 2,7-Naphthalenediol was tried as an indicator. It, too, produced a typical violet to purple color with HMX-RDX, but its use was discontinued when its stability period in water was found to be less than two hours.

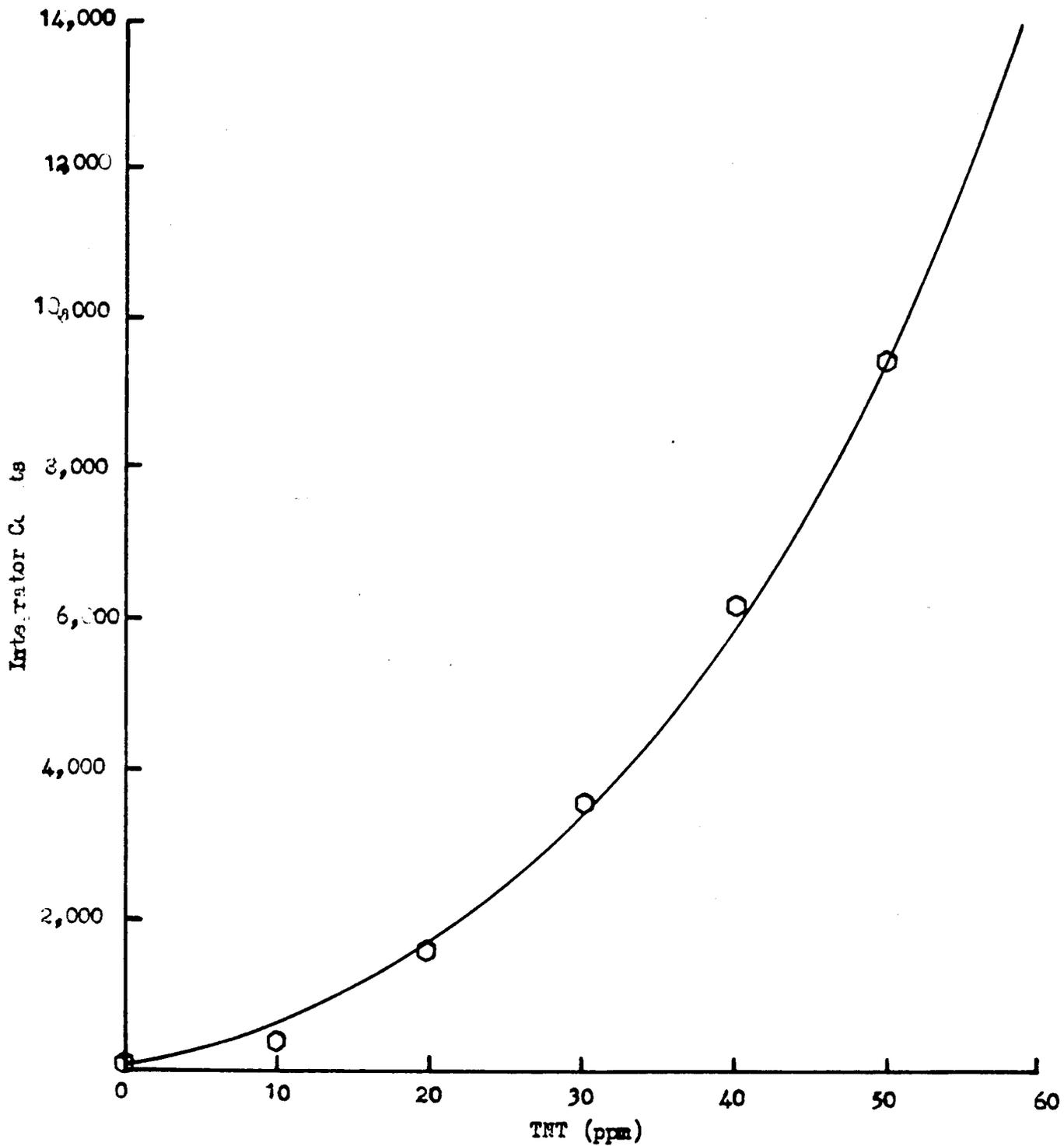
TNT was analyzed by gas chromatography. A 3' x 3/16" stainless steel column was packed with 30% high-vacuum silicone grease on 40/80 mesh firebrick. The column temperature was 200°C and the helium flow was 50 cm³ per minute. TNT was extracted from the water with CHCl₃ and from the soil samples with acetone. The acetone extract was stripped and the resultant residue dissolved in a known volume of CHCl₃. The solubility of TNT is 19 grams per 100 grams of CHCl₃ and 0.0130 grams per 100 grams of water. Retention time for the TNT was about 5 minutes and a Hewlett-Packard Electronic Integrator, Model 3370A, was used to obtain quantitative data.

The following information was gathered from a series of standard TNT samples in CHCl₃ (Table 3 and Figure 9).

TABLE 3

INTEGRATOR

<u>ppm</u>	<u>Counts</u>
5	22
10	225
20	1558
30	3678
40	6329
50	9498



TNT (ppm) versus Integrator Counts

Figure 2

Barium was analyzed by atomic absorption spectrophotometry with the Perkin-Elmer Model 303 Atomic Absorption Spectrophotometer. The wavelength of analysis was 5536 Å. Sodium chloride was added to the solutions to eliminate ionization interferences. Water samples were analyzed directly and 10 grams of the soil samples were extracted with 200 ml of water for three hours. Detection limits were 1 ppm in water and 10 ppm in the soil. Standards for barium analysis were prepared from $Ba(NO_3)_2$.

Boron was analyzed by emission spectroscopy with the ARL Spectrographic Analyzer, Model 26000-1. A set of Spex G-Standards, 0.0001, 0.001, 0.01, and 0.1%, were employed as standards. Soil samples were mixed with spectroscopic grade graphite powder in the ratio of 9 parts powder to 1 part soil whereas water samples were evaporated directly into the electrodes. The spectrographic lines for analysis appear at 2496.7 and 2497.8 Å. Detection limits were 10 ppm in soil and less than 1 ppm in water.

SAMPLES - LOCATION AND ANALYSES

Samples of soil and effluent water were obtained at various locations adjacent to operating buildings and in the canyons which make up the drainage system for S Site. The location of these samples are mapped in Figure 10. The samples obtained from the Site proper are enclosed in a square, those obtained from Water Canyon in a circle, and those obtained from Del Valle Canyon in a hexagon. The results of the analyses are listed.

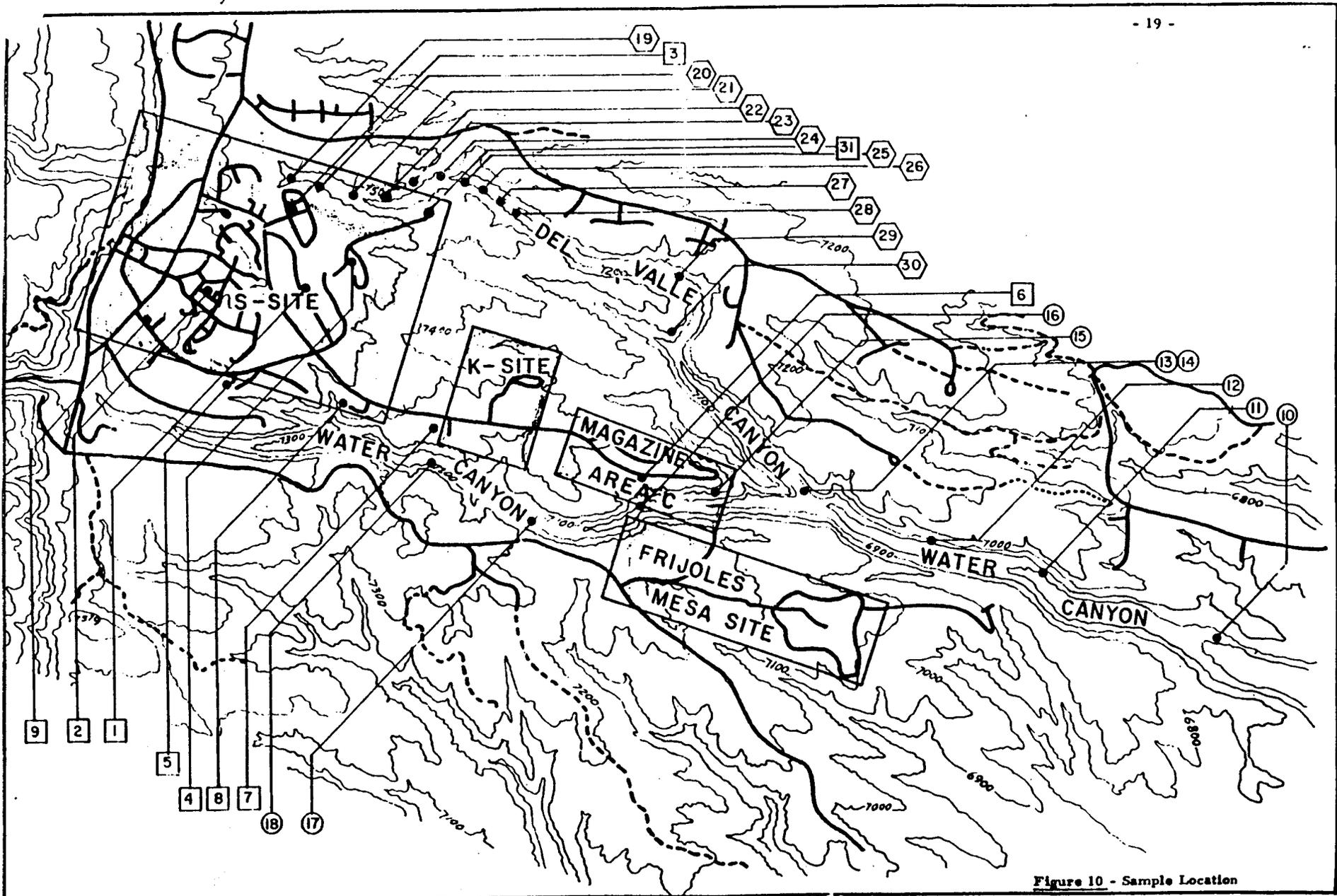


Figure 10 - Sample Location

S-Site Area Sample No.	Location and Description	Analyses and Results			
		Barium (ppm)	Boron (ppm)	TNT (ppm)	RDX-HMX (ppm)
1	Samples taken from settling tank exit pipes of Buildings 301 and 302 following kettle washing operations. The kettles had been used to prepare cyclotol and baratol melts.	22		72	1
2	Sample removed from final tank of sewage disposal system, Building 532. Sample taken at 1410 hours and flow was estimated to be 100 gpm.	None		None	None
3	Sample taken from settling tank exit pipe of Building 260. Building activity consisted of cleanup following varying operations that included machining of PBX 9404, 9011, 9407, X-0223, miscellaneous inert compositions, and cast explosives.	4		33	~0.3
4	Water sample removed from exit drain of settling tank of Building 340, Bay 104. Seven hundred gallons of water had been flushed through the system before the sample was removed.	None		None	None
5	Water sample removed from exit drain of Building 430, Bay 1, settling tank after 800 gallons of water had been used during operations.	None		None	None
6	Soil sample taken 200 yards south of Magazine TA-37-17	None		None	None
7	Soil sample taken 200 yards south of Building 380. This is the open drain for the building.	<10		11	<1

<u>S-Site Area</u> <u>Sample No.</u>	<u>Location and Description</u>	<u>Analyses and Results</u>			
		<u>Barium</u> <u>(ppm)</u>	<u>Boron</u> <u>(ppm)</u>	<u>TNT</u> <u>(ppm)</u>	<u>RDX-HMX</u> <u>(ppm)</u>
8	Soil sample taken 50 yards south of Building 370. This is the open drain for the building.	19		None	None
9	Soil sample removed from open drainage 50 yards west of Building 460. This sample was removed for control purpose and should show no trace of contamination.	None		None	None
31	Soil sample removed from open drain area 10 yards due west of Building 389 on the canyon edge. This is the natural drainage area for the burning pit.	14		None	None
Water Canyon					
<u>Sample No.</u>					
10	Soil sample removed from surface of canyon bed approximately three miles east of confluence of Del Valle Canyon.	None	None	None	None
11	Soil sample removed from surface of canyon bed approximately two miles east of confluence of Del Valle Canyon.	None	None	None	None
12	Soil sample removed from surface of canyon bed approximately one mile east of confluence of Del Valle Canyon.	None	None	None	None
13	Soil sample removed from canyon bed 25 yards east of confluence of Del Valle Canyon. One half of the sample was removed from the surface, one half was removed six inches below the surface	None	None	None	None

Water Canyon
Sample No.

Location and Description

Analyses and Results

<u>Barium</u> <u>(ppm)</u>	<u>Boron</u> <u>(ppm)</u>	<u>TNT</u> <u>(ppm)</u>	<u>RDX-HMX</u> <u>(ppm)</u>
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0.8	None	None	None
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14 A water sample was removed from the same location after a heavy rain on August 19, 1971. Flow was estimated at 50 gpm past this point.

None	None	None	None
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15 Soil sample taken from the same location as 13 except it was removed from the bank for a control.

None	None	None	None
------	------	------	------

16 Soil sample removed 200 yards west of the Del Valle Canyon confluence. Sample was removed from the surface.

None	None	None	None
------	------	------	------

17 Soil sample removed 400 yards west of the Del Valle Canyon confluence. This location forms the canyon drainage bed due south of Magazine TA-37-17.

None	None	None	None
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18 Soil sample removed 600 yards west of the Del Valle Canyon confluence. This area is due south of K-Site.

Del Valle Canyon
Sample No.

19 Water sample of surface drainage from Building 260. This area is about 300 yards from the building at the bottom of the canyon. Water goes underground and the flow is approximately 10 gpm.

30		3	1.5
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20 Soil sample removed 400 yards from Building 260. Sample was removed from the surface.

9		1	0.6
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Del Valle Canyon**Sample No.****Location and Description****Analyses and Results****Barium Boron TNT RDX-HMX
(ppm) (ppm) (ppm) (ppm)**

21	Soil sample removed 100 yards downstream from Sample 20. Sample was removed from soil surface.	3	< 1	None
22	Water sample from spring downstream 100 yards from Sample 21.	1	None	None
23	Water sample taken at a point where drainage from burning ground hits canyon floor.	27	None	None
24	Water sample removed from canyon floor approximately 100 yards from Building 389. Flow was estimated to be 15 gpm.	15	None	None
25	Water sample removed approximately 100 yards downstream from Sample 24 location. Flow was estimated to be 10 gpm.	8	None	None
26	Water sample removed approximately 100 yards downstream from Sample 25 location. Water lay in pools and was not flowing.	11	None	None
27	Soil sample removed from surface approximately 100 yards downstream from Sample 26 location.	<10	None	None
28	Soil sample removed from surface approximately 100 yards downstream from Sample 27 location.	<10	None	None
29	Soil sample removed from surface in area serving as R-Site drainage.	Positive	None	None
30	Soil sample removed from surface approximately 100 yards downstream from Sample 29 location.	Positive	None	None

SUMMARY AND ACKNOWLEDGMENTS

This series of environmental studies revealed that very little, if any, barium, TNT, HMX, or RDX is getting to the Del Valle-Water Canyon confluence. Within our limits of detection, Water Canyon seems relatively free of any of the analyzed species. Because of the low solubility of HMX, RDX, and TNT in water, one would not expect to find these in a great quantity of any reasonable distance from their operational point. Del Valle Canyon appears to be the only area where some species may travel any distance. The waste material from Building 260 travels a short distance down Del Valle Canyon. This could be because there is a constant flow of water in Del Valle Canyon between Buildings 260 and 389. An underground spring 400 yards from Building 260 enters the canyon drainage bed and serves to carry waste water from Building 260 down Del Valle Canyon. The water at several places goes underground. These underground ventures could serve as a natural filter in removing RDX, HMX, TNT, barium, or boron from the water.

Barium traveled further down Del Valle Canyon than any other species. The concentration of barium decreased steadily from Buildings 260 to 389. At a point behind the burning ground, the barium concentration began to increase again and continued to increase up until 500 yards past the burning ground. Soil samples taken 600 and 700 yards past the burning ground showed barium still present but less than 10 ppm. A sample was taken behind Group GMX-11, Building 209, and it showed barium still present on Del Valle Canyon drainage bed.

There is a large amount of barium nitrate exposed to the environment near Building 389. The stockpile is on the canyon edge and rain constantly washes a steady supply of barium down into Del Valle Canyon. For this reason, barium was detected in larger concentrations behind the burning ground and further down the canyon. How much barium is present in the canyon and how far it will travel will surely depend on how much rainfall is received in the area.

In the analysis of the soil samples, all samples were taken from the topsoil no more than six inches deep. It is possible that, over a period of time, some species have seeped below the topsoil and into the subsoil. No studies were made on the subsoil.

No previous data are available for comparison and, therefore, no evaluation can be made regarding how long it may take for certain species to build up in the soil and water or how fast they move down the canyon. More studies will undoubtedly have to be carried out at a later time for comparison to this data.

I extend special thanks to Gene F. Mortensen, Mortimer Schwartz, Stanley K. Yasuda, John F. Baytos, and Herbert L. Keller for assistance and guidance rendered.