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Drainage Ditch Soil at Sump Effluent Outlets



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by

John F. Baytos

ANALYSES FOR RESIDUAL EXPLOSIVES IN DRAINAGE  
DITCH SOIL AT SUMP EFFLUENT OUTLETS

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ABSTRACT

Determination of residual explosives in soil samples taken from drainage ditches at operating buildings is reported. Three annual inspections were made to show the effectiveness of the sump collection system at Group GMX-3 of the Los Alamos Scientific Laboratory. Only minor changes were noted in the second and third inspections after the first inspection reference bases were established. The analyses were performed by the Soxhlet extraction of the explosives with acetone, the separation of TNT and RDX/HMX by  $\text{CCl}_4$ , and a final quantitative estimation by ultraviolet absorbance techniques.

I. INTRODUCTION

The explosives processing facilities at Group GMX-3, Los Alamos Scientific Laboratory, are constructed so that scrap dust and excessive explosives particles from processing operations are washed with water into an independent sump system for the collection and settling of these explosives particles to prevent their migration into the drainage streams. After the water passes through the baffles of the sumps and is supposedly free of suspended explosives particles, it is allowed to run into drainage ditches alongside the buildings and then into the natural drainage system of the area.

We assumed that the large amount of water used during processing and cleaning inside the building at a warm temperature would dissolve some RDX and HMX, even though they are almost insoluble in water at room temperature. The

water is cooled by evaporation when it reaches open air and some of the relatively small amounts of dissolved explosives crystallize out and are deposited in the soil. In time, this dissolved explosive will build up in the soil and act as a filter matrix.

To see how well the sump system is preventing an increase in residual explosives from being carried into the drainage ditches, the safety committee has scheduled annual inspections of the outfall ditches and an analysis for residual explosives of the ditch soil where residual explosives might tend to concentrate. The first inspection established a reference base.

This report gives the results of tests for explosives in soil taken at three inspections of the drainage ditches and a historical report of an inspection made over 10 years ago in the same general area. A procedure developed for analyses of HMX/RDX ratios is reported in the Appendix.

## II. DISCUSSION OF RESULTS

The data from the first inspection are given in Table I and indicate that the soil in the drainage ditch at the sump effluent outlet from Building TA-16-260 (explosives machining building) has a high concentration of residual explosives, mostly HMX and RDX, and a low proportion of TNT. These values are believed to be representative of the soil in the drainage ditch.

The data from the second inspection from the Building-260 drainage ditch do not show startling changes (Table II). There would not necessarily be agreement with the previous report

because the sampling method is very dependent on where in the ditch samples were taken, how deep the shovel was thrust, and how much erosion and alluvion has taken place in the ditch since the previous inspection. Table III presents data collected from the third inspection, and the data are about the same as reported previously. To compare the data for Building 260, Table IV (taken from a 10-yr-old report dated March 11, 1960) shows that the present overall residual explosives content is greater. This probably should be expected because of the lapse of time. This increase is especially true of the pond center.

TABLE I  
ANALYSES OF SOIL SAMPLES FOR RESIDUAL EXPLOSIVES FROM SUMP  
EFFLUENT OUTLET DRAINAGE DITCHES AT GROUP GMX-3 OPERATING BUILDINGS

Building No. and Sample Description	Acetone <sup>a</sup> Solubles (wt%)	CCl <sub>4</sub> <sup>b</sup> Insolubles (wt%)	CCl <sub>4</sub> <sup>c</sup> Solubles (wt%)	HMX/ <sup>d</sup> RDX (wt%)	TNT <sup>e</sup> (wt%)	Total Explosives (wt%)
260-1 under concrete effluent outlet	7.7	7.1	0.4	7.0	0.00	7.0
260-2 at pond center	33.2	25.9	6.8	20.5 <sup>f</sup>	3.7	24.2
260-3 lip below dam	6.7	5.5	1.2	4.8 <sup>g</sup>	0.07	4.9
260-4 halfway between dam lip and canyon	14.5	13.4	1.0	12.9	0.12	13.0
260-5 canyon lip	4.6	4.1	0.5	3.9 <sup>h</sup>	0.10	4.0
301-6 at effluent outlet	1.7	1.1	0.6	0.8 <sup>i</sup>	0.25	1.1
303-7 at effluent outlet	0.5	0.03	0.5	0.02	0.00	0.0
305-8 at effluent outlet	0.6	0.02	0.6	0.00	0.00	0.0
307-9 at effluent outlet	1.0	0.7	0.3	0.7	0.13	0.8
300-10 at common effluent outlet	4.8	0.3	4.3	0.2	0.86	1.1
340-11 at effluent outlet	1.0	0.2	0.8	0.1	0.5	0.6
380-12 at effluent outlet	0.5	0.1	0.4	0.04	0.01	0.0
400-13 at effluent outlet	0.9	0.04	0.9	0.01	0.08	0.1
430-14 Bay I effluent outlet	13.6	1.9	11.7	1.5 <sup>j</sup>	0.12	1.6
478-15 P-Site effluent outlet	6.0	5.7	0.3	3.8 <sup>k</sup>	0.02	3.8
460-16 uncontaminated soil	0.07	0.03	0.02	0.00	0.00	0.0

<sup>a</sup>The filtrate comes from acetone Soxhlet extract on a dried, crushed, 14-mesh sieved, rolled, and quartered sample. This filtrate includes explosives, decomposition products, plastic, and other natural acetone soluble materials.

<sup>b</sup>The residue from the CCl<sub>4</sub> treatment includes the RDX and HMX fractions and other decomposition products from the acetone extract.

<sup>c</sup>The filtrate from the CCl<sub>4</sub> wash includes the TNT fraction and other unknown decomposition products.

<sup>d</sup>These values were determined on the PE 350 ultraviolet spectrophotometer. The shape of the curves indicate that most of the residue is HMX rather than RDX. In cases of doubt the IR-12 spectrophotometer was used to verify HMX/RDX ratios.

<sup>e</sup>These values were determined on the PE 350 ultraviolet spectrophotometer.

<sup>f</sup>Ratio HMX/RDX by IR-12 spectrophotometer 50/50.

<sup>g</sup>50/50, <sup>h</sup>80/20, <sup>i</sup>10/90, <sup>j</sup>95/5, <sup>k</sup>10/90, trace PETN.

TABLE II

ANALYSES OF SOIL SAMPLES FOR RESIDUAL EXPLOSIVES FROM SUMP EFFLUENT  
OUTLET DRAINAGE DITCHES AT GROUP GMX-3 OPERATING BUILDINGS

Building No. and Sample Description	Acetone <sup>a</sup> Solubles (wt%)	CCl <sub>4</sub> <sup>b</sup> Insolubles (wt%)	CCl <sub>4</sub> <sup>c</sup> Solubles (wt%)	HMX/ <sup>d</sup> RDX (wt%)	TNT <sup>d</sup> (wt%)	Explosives (wt%)
260-1 ten feet from concrete effluent outlet	3.6	3.3	0.3	3.2 <sup>e</sup>	0.0	3.2
260-2 inlet to pond	15.5	14.6	0.8	14.1 <sup>f</sup>	0.1	14.5
260-3 ten feet above dam in pond	26.3	23.3	2.9	22.1 <sup>g</sup>	0.5	22.6
260-4 five feet below dam	16.0	14.5	1.4	14.5 <sup>h</sup>	0.2	14.7
301-5 at effluent outlet	0.3	0.1	0.2	0.1	0.0	0.1
307-6 at effluent outlet	2.8	2.0	0.7	1.8 <sup>h</sup>	0.3	2.1
300-7 at common effluent outlet	19.7 <sup>j</sup>	1.0	17.9	0.6	1.1 <sup>k</sup>	1.7
340-8 at common outfall-concrete trough	2.3	0.4	1.0	0.3	0.3	0.6
345-9 at effluent outlet	0.1	0.0	0.0	0.0	0.0	0.0
380-10 at effluent outlet	0.3	0.0	0.2	0.0	0.0	0.0
400-11 at effluent outlet	0.2	0.1	0.1	0.0	0.0	0.0
430-12 Bay 1 effluent outlet	5.3	1.4	3.6	1.1 <sup>i</sup>	0.1	1.2
478-13 P-Site effluent outlet	0.6	0.3	0.3	0.2	0.0	0.2
460-14 uncontaminated soil	0.1	0.0	0.0	0.0	0.0	0.0

<sup>a</sup> The filtrate comes from the acetone Soxhlet extract on a dried, crushed, 14-mesh sieved, rolled, and quartered sample. This filtrate includes explosives, decomposition products, plastic, lubrication oils, and other natural acetone soluble materials.

<sup>b</sup> The residue from the CCl<sub>4</sub> treatment includes the RDX and HMX fractions and other decomposition products from the acetone extract.

<sup>c</sup> The filtrate from the CCl<sub>4</sub> wash includes the TNT fraction and other unknown soluble products.

<sup>d</sup> These values were determined on the PE 350 ultraviolet spectrophotometer.

<sup>e</sup> The shape of the HMX/RDX curves shows that the ratio of HMX/RDX is 99/1, <sup>f</sup> 95/5, <sup>g</sup> 90/10, <sup>h</sup> 85/15, and <sup>i</sup> 80/20.

<sup>j</sup> This soil sample was contaminated with oils and smelled of road oil and creosote. This accounts for the high acetone soluble content and the masking of clean separations of the explosives.

<sup>k</sup> This value was determined by gas-liquid chromatography to get around the masking of oil contaminants.

Data in Table I for the 300 line (explosives casting buildings) show a very low residual explosives content, even though the TA-16-300-10 common outlet has a high acetone-soluble value. The plastics and solvents used in Buildings TA-16-306 and 304 would account for the high acetone-solubles and CCl<sub>4</sub> solubles.

In Table II, data for Building TA-16-300 (common effluent outlet from the plastics processing buildings) reflect the contamination of other oils, plastics, and solvents that mask the separation of the explosives in the analyses. The soil sample at this location was coated with a road oil and creosote-smelling substance. The amount of explosives shown was not changed substantially,

and the differences shown may be due to sampling techniques.

The data in Table I for the other buildings show a low concentration of residual explosives with the exception of Buildings TA-16-430 and 478. Building TA-16-430 (pressing) has a high acetone and CCl<sub>4</sub> solubles content, but this is not reflected in the TNT content. The CCl<sub>4</sub> insoluble content shows 1.5% HMX/RDX, which is not unexpected. Subsequent inspections show very little change. The same could be said for Building TA-16-478 (high-speed machining tests). Again the residual explosives show about 3.8% HMX/RDX.

TABLE III

ANALYSES OF SOIL SAMPLES FOR RESIDUAL EXPLOSIVES FROM SUMP EFFLUENT  
OUTLET DRAINAGE DITCHES AT GROUP GMX-3 OPERATING BUILDINGS

Building No. and Sample Description	Acetone <sup>a</sup> Solubles (wt%)	CCl <sub>4</sub> <sup>b</sup> Insolubles (wt%)	CCl <sub>4</sub> <sup>c</sup> Solubles (wt%)	HMX/ <sup>d</sup> RDX (wt%)	TNT <sup>e</sup> (wt%)	Total Explosives (wt%)
260-1 ten feet from concrete effluent outlet	3.4	3.0	0.4	2.9 <sup>f</sup>	0.0	2.9
260-2 inlet to pond (50 ft from outfall)	12.4	11.6	0.7	10.8 <sup>g</sup>	0.0	10.8
260-3 ten feet above dam in pond (about 70 ft from outfall)	29.1	26.3	2.1	25.7 <sup>h</sup>	0.0	25.7
260-4 ten feet below dam	25.8	23.6	2.0	22.5 <sup>g</sup>	0.0	22.5
301-5 at effluent outlet	0.7	0.2	0.2	0.1 <sup>i</sup>	0.04	0.1
307-6 at effluent outlet	0.9	0.8	0.1	0.4 <sup>g</sup>	0.0	0.4
342-7 at effluent outlet	1.9	0.2	1.7	0.1 <sup>g</sup>	0.0	0.1

<sup>a</sup>The filtrate comes from the acetone Soxhlet extract on a dried, crushed, 14-mesh sieved, rolled, and quartered sample. This filtrate includes explosives, decomposition products, plastic, lubrication oils, and other natural acetone-soluble materials.

<sup>b</sup>The residue from the CCl<sub>4</sub> wash includes the RDX and HMX fractions and other decomposition products from the acetone extract.

<sup>c</sup>The filtrate from the CCl<sub>4</sub> wash includes the TNT fraction and other soluble products.

<sup>d</sup>These values were determined on the PE 350 ultraviolet spectrophotometer.

<sup>e</sup>These values were determined by gas-liquid chromatography to get around the masking of oil contaminants.

<sup>f</sup>The shape of the HMX/RDX curve shows that the ratio of HMX/RDX is 97/3.

<sup>g</sup>The shape of the HMX/RDX curve shows that the ratio of HMX/RDX is 95/5.

<sup>h</sup>The shape of the HMX/RDX curve shows that the ratio of HMX/RDX is 92/8.

<sup>i</sup>The shape of the HMX/RDX curve shows that the ratio of HMX/RDX is 20/80.

Comparing the data in Tables I, II, and III shows that there is very little explosives contamination of the soil in the drainage ditches of other than Building TA-16-260. If anything, the contamination is confined to the TA-16 restricted technical areas on the mesa. A report\* detailing the search for the extent of contamination of the drainage system in the canyons below the TA-16 area showed very little of these explosives contaminants found in the soil below the lips of the canyon and in the soil downstream.

### III. SAMPLING AND INSPECTION PROCEDURE

The inspection committee examined all the sump outlet drainage ditches at the first inspection. With a record of past and previous processing

techniques and magnitudes of these operations in the buildings, we decided that samples should be taken selectively where the probability of contamination and settling would be detectable and at points where the drainage water would tend to stand and allow any residual explosives to settle out. Many samples, including those from doubtful areas, were collected for the first inspection. A control sample from one uncontaminated area was also recovered. The results of these soil analyses are given in Table I.

The number of samples taken on subsequent inspections, based on the information given in Table I, was reduced because of the redundancy in taking samples where no explosive was detected on the original sample, unless there was an increase in use of explosives in the building between inspections. The results of these subsequent tests are given in Tables II and III.

\*A. Turner, "Environmental Studies at S-Site," LASL internal document (August 20, 1971).

TABLE IV  
ANALYSES OF EARTH FROM THE EFFLUENT STREAM  
FROM THE BUILDING TA-16-260 SUMP SYSTEM

Sample Description	Sample Test Number	Toluene/Acetone Extract (%)	Residue from Carbon Tetrachloride Extract (%)	Filtrate from Carbon Tetrachloride Extract (%)	RDX (%)	TNT (%)	Explosives (%)
Pond Center	7	18.9	14.2	4.5	8.5	1.3	9.8
Pond Center	8	8.8	4.8	4.0	3.5	1.3	4.8
20 feet below dam crossbar	1	9.0	6.0	2.8	4.3	1.7	6.0
30 feet below dam crossbar	2	7.5	4.3	2.8	3.3	0.7	4.0
50 feet below dam crossbar. All samples 2 to 3 in. from surface.	3	4.9	— <sup>a</sup>	1.1	— <sup>a</sup>	0.2	— <sup>a</sup>
100 feet below dam crossbar	4	4.3	3.0	1.3	2.4	0.2	2.6
150 feet below dam crossbar	5	1.0	0.7	0.3	0.5	0.02	0.5
100 feet. Same as No. 4	6	4.4	3.4	0.8	2.7	0.04	2.7

<sup>a</sup>Sample lost in analysis, data not available.

The soil in the drainage ditch was sampled by thrusting a shovel into the soil about 3 to 6 in. deep where a pool had formed. The weight of the sample was between 500 to 1000 g. This shovelful of soil was put into a jar, labeled, identified, and taken to the laboratory for testing.

#### IV. ANALYTICAL PROCEDURE

The wet samples were dried, crushed, and passed through a 14-mesh sieve. Each sample was then rolled and quartered. Ten grams were weighed and extracted with acetone in a Soxhlet apparatus for 3 h. This extraction removed all the explosives, some soluble plastics, decomposition products, and other organic acetone-soluble materials. The acetone was evaporated and weighed to get an acetone solubles content. The remaining filtrate was then treated with carbon tetrachloride (CCl<sub>4</sub>) to dissolve the TNT and leave

the HMX/RDX insoluble materials as a residue. Only part of these residues is explosives. Weighed samples were dissolved in acetonitrile (CH<sub>3</sub>CN), and scans were run on the Perkin-Elmer 350 ultra-violet spectrophotometer (PE 350) to determine the quantity of each explosive present. The shape and peak heights of the HMX/RDX curves showed that the explosives present were mostly HMX. In cases of doubt, the ratio of the HMX/RDX was determined on the Beckman IR-12 infrared spectrophotometer, where weighed samples are pressed into a potassium bromide matrix into a disk that is scanned. Results of this test are tabulated as footnotes to the HMX/RDX column in Table I. A method of determining the ratio of HMX/RDX from the UV scan was developed at this time and was verified by the IR-12 method. The procedure is reported in the Appendix. The filtrate from the CCl<sub>4</sub> was evaporated, weighed, and dissolved in



CH<sub>3</sub>CN and run similarly on the PE 350. TNT was calculated from its respective curves and peak heights.

APPENDIX  
ANALYSES OF HMX and RDX RATIOS BY  
ULTRAVIOLET (UV) SPECTROPHOTOMETER

An interesting analytical method for determining RDX and HMX in a mixture of the two explosives evolved while the above problem was being investigated on the Perkin-Elmer 350 UV spectrophotometer. Both RDX and HMX absorb monochromatic light at 227 and 195 nm (Fig. A-1), but the shape of the curves is distinctive. The pure HMX gives a saddle-shaped curve, whereas the pure RDX gives a step curve. The 50/50 mixture gives an intermediate curve. From these observations, it was then possible to determine the percentage of HMX and/or RDX in a mixture by applying Beer's law, which states absorbance is proportional to concentration. A series of calibration curves is then made on various mixtures of RDX and HMX to verify that the law holds.

To use the phenomena presented by the absorbance curves at 227 and 195 nm for determining

the percentage of each component, the ratio of peak height at 195 nm to peak height at 227 nm was determined for a series of known mixtures. This curve, peak height ratios vs concentration of HMX, is plotted in Fig. A-2.

With an unknown, a UV scan is made, the ratio of peak heights at 195 and 227 nm is taken; and the concentration of HMX is determined from Fig. A-2. The RDX percentage is determined by the difference from 100%.

An additional factoring calculation needs to be made for samples that contain impurities other than HMX or RDX. From the ratios of concentrations to peak heights at 227 nm for the pure and impure samples, the following calculations were derived.

$$C_u = \frac{(C_p)(H_u)}{(R_1 H_1 + R_2 H_2)}$$

where

C<sub>u</sub> = concentration of RDX/HMX found in an impure sample (x mg/ml),

R<sub>1</sub> = ratio percent of HMX found from Fig. A-2,

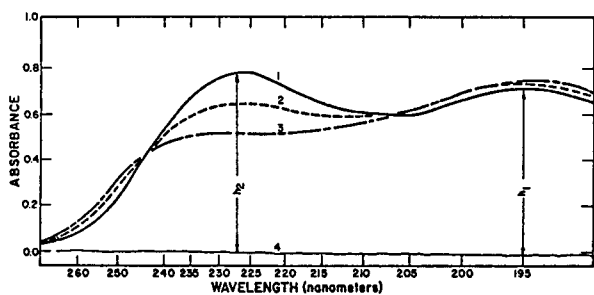


Fig. A-1. Typical UV absorbance curves on the Perkin-Elmer 350 spectrophotometer for pure HMX and pure RDX samples and mixtures in acetonitrile. Ratio is determined by measuring peak heights at 195 and 227 nm. Example in this figure is for 100% HMX: Ratio -  $h_1/h_2$ . Curves 1, 100/0, 0.2 mg/ml solution; 2, 50/50, 0.1 mg/ml solution each; 3, 0/100, 0.2 mg/ml solution; 4, Acetonitrile, base line.

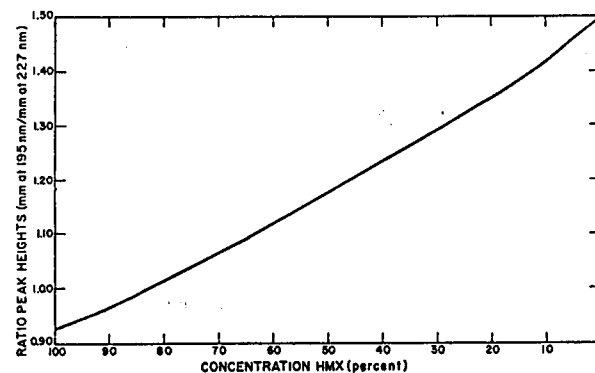


Fig. A-2. Concentration HMX vs ratio of peak heights 195:227 nm.

$H_1$  = standard peak height for pure HMX standard concentration at 227 nm,

$R_2$  = ratio percent of RDX =  $(100 - R_1)$ ,

$H_2$  = standard peak height for pure RDX standard concentration at 227 nm,

$C_s$  = concentration of standard solution (0.2 mg/ml),

$H_u$  = measured peak height of unknown at 227 nm,

$D_u$  = concentration of prepared impure sample in solution (0.2 mg/ml),

and

$$\% \text{ HMX in impure sample} = \frac{(R_1)(C_u)}{(D_u)}$$

$$\% \text{ RDX in impure sample} = \frac{(R_2)(C_u)}{(D_u)} .$$

If the original sample was aliquoted, appropriate proportioning calculations need to be made.

When determinations were made for different concentrations of samples in acetonitrile, the ratios and percentages held true.

As the peak heights are divided into only 100 to 200 parts, the precision is probably not better than 1%, but for estimation of HMX and RDX in samples like that described in the preceding section, this is sufficiently accurate.

Experimental Procedure. This experiment has been worked out on the Perkin-Elmer 350 UV spectrophotometer, which was set for zero and maximum absorbance according to manufacturer's specification.

The standardizing solutions for application of Beer's law were prepared in acetonitrile ( $\text{CH}_3\text{CN}$ ) spectrophotometric grade. Samples of pure HMX and pure RDX were weighed, respectively, into volumetric flasks to give a concentration of 0.20 mg/ml solution. HMX and RDX in various proportions were weighed separately so that their total weight equaled 0.20 mg/ml. These solutions were run on the PE 350 using acetonitrile as reference and as a base line solvent. Enough combinations were run until enough data were obtained to verify Beer's law and to develop the graph from ratios of peak heights at 195 and 227 nm vs HMX concentrations shown in Fig. A-2. A quadratic least-squares fit may be made for this graph also.

Samples of unknowns were weighed to give a solution total concentration of 0.20 mg/ml and run exactly as in the calibration run. The peak heights at 195 and 227 nm were measured and the ratio was calculated. The HMX concentration percentage was determined from Fig. A-2. If the peak heights were not maximum for that HMX concentration (Fig. A-1) because of an impure sample, then the sample needs to be factored by the equations stated above.