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WHITE OAK LABORATORY

A STUDY OF THE ORGANIC COMPONENTS OF RED WATER

BY
Thomas N. Hall
G. William Lawrence

26 OCTOBER 1976

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The red water produced by the Sellite purification of crude TNT has been analyzed for potentially useful organic compounds. The results can be summarized as follows:

(1) Only two potentially useful organic substances are present in red water in concentrations sufficiently high to justify their recovery: 2,4-dinitrotoluene-5-sulfonic acid

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(2.7 weight % determined in this study, compared to 6-8 weight % reported by Radford Army Ammunition Plant), and 2,4-dinitrotoluene-3-sulfonic acid (1.2 weight % determined in this study, compared to 2-4 weight % reported by Radford).

(2) A small amount of α-TNT (0.6 weight %) can be easily recovered from red water by filtration.

alpha

(3) Eight weight percent of red water is a complex mixture of unidentified, red, water-soluble organic compounds resulting from the degradation of α-TNT by the Sellite. This mixture has no obvious commercial value, but, unfortunately, accompanies the dinitrotoluene sulfonic acids when they are extracted from freeze-dried red water. A separation has been accomplished by research techniques (gel filtration); the large scale practicality of this separation has not been demonstrated.

Finally, it was concluded, on the basis of analyses of crude TNT, that red water cannot be considered a practical source of 1,3,5-trinitrobenzene or 2,4,6-trinitrobenzaldehyde.

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A STUDY OF THE ORGANIC COMPONENTS OF RED WATER

The sellite process for the purification of crude TNT produces a dark red liquid called "red water". The only environmentally safe method for disposing of the red water is an expensive incineration process.

The purpose of this study was to determine whether significant amounts of commercially valuable organic compounds are present in red water. The recovery and sale of such compounds would reduce the cost of subsequent incineration. It was confirmed that red water contains two potentially useful organic compounds: 2,4-dinitrotoluene-5-sulfonic acid and 2,4-dinitrotoluene-3-sulfonic acid. Red water was shown to contain four percent of these acids.

This work was funded by Picatinny Arsenal (SARPA-M1C-F). Our task WR-5203-B was sponsored by MIPR 6311-0011. The report which follows should be considered a status report, and not a final report, because funding was terminated before the task was completed.

Julius W. Enig
JULIUS W. ENIG
By direction

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INTRODUCTION

The nitration of toluene to 2,4,6-trinitrotoluene (α-TNT) by the Canadian Industries, Limited process (reference 1 (a)) and other processes produces a crude product contaminated by the following types of organic impurities*: (i) "unsymmetrical" isomers of α-TNT resulting from the dinitration of m-nitrotoluene (see Figure 1 and reference 1 (b)); (ii) oxidation products, such as 2,4,6-trinitrobenzyl alcohol, 2,4,6-trinitrobenzaldehyde, and 2,4,6-trinitrobenzoic acid (references 3, 1(c)), sym-trinitrobenzene (reference 1(d)), di- and tri-nitrocresols (references 5, 1(c)), and tetranitromethane (references 5, 1(e)). The major impurities are 2,4,5-trinitrotoluene (up to 2.0%) (reference 1(d)) and 2,3,4,-trinitrotoluene (up to 1.2%) (reference 1 (d)).

The crude α-TNT cannot be used directly in ordnance items because the impurities cause exudation which results in increased sensitivity, poorer performance, and possible premature detonation (reference 6). The current method for purifying the crude TNT produced by the Canadian Industries, Ltd. continuous process used by both the Joliet and Radford Army Ammunition Plants (JAAP and RAAP) is called the Sellite process. This process involves the reaction of the crude molten TNT with 16% aqueous sodium sulfite at a pH between 8.3 and 8.5 in a counter-current flow system (see Appendix A for details). The "unsymmetrical" isomers are removed from the crude TNT by conversion to water soluble, colorless sulfonic acid salts by reactions such as (1) and (2) (reference 7). Other reactions must proceed during the selliting operation, because the spent Sellite solution is a dark red-brown color, and is in fact called "red water".

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*For a discussion of the impurities in crude TNT and typical thin layer chromatograms of crude TNT, see references 1(b) and 1(c).

(1) J. A. Kohlbeck, C. D. Chandler, Jr., and R. L. Dickenson, "Continuous TNT Process Characterization Study", May 1973; available from Chief Engineer, Radford Army Ammunition Plant, Radford, VA 24141. (a) pp 7-12; (b) p. 21; (c) p. 22; (d) p. 40; (e) p. 16; (f) p. 161 (g) p. 46.

(2) E. de Beule, Bull. soc. chim. Belge, 42, 27 (1933).

(3) J. A. Kohlbeck, C. D. Chandler, and W. T. Bolleter, J. Chromatog. 46, 173 (1970).

(4) V. Dala'k, E. Hromadkova and K. Svmejkal, Chem. Prumysl., 13, 629 (1963). See also references cited therein.

(5) C. D. Chandler, J. A. Kohlbeck. W. T. Bolleter, J. Chromatog., 64, 123 (1972).

(6) T. Urbanski, "Chemistry and Technology of Explosives," Vol. I, The Macmillan Co., New York, N. Y., 1964, p. 376.

(7) O. L. Brady, S. W. Hewetson and L. Kelin, J. Chem. Soc., 125, 2400 (1924).

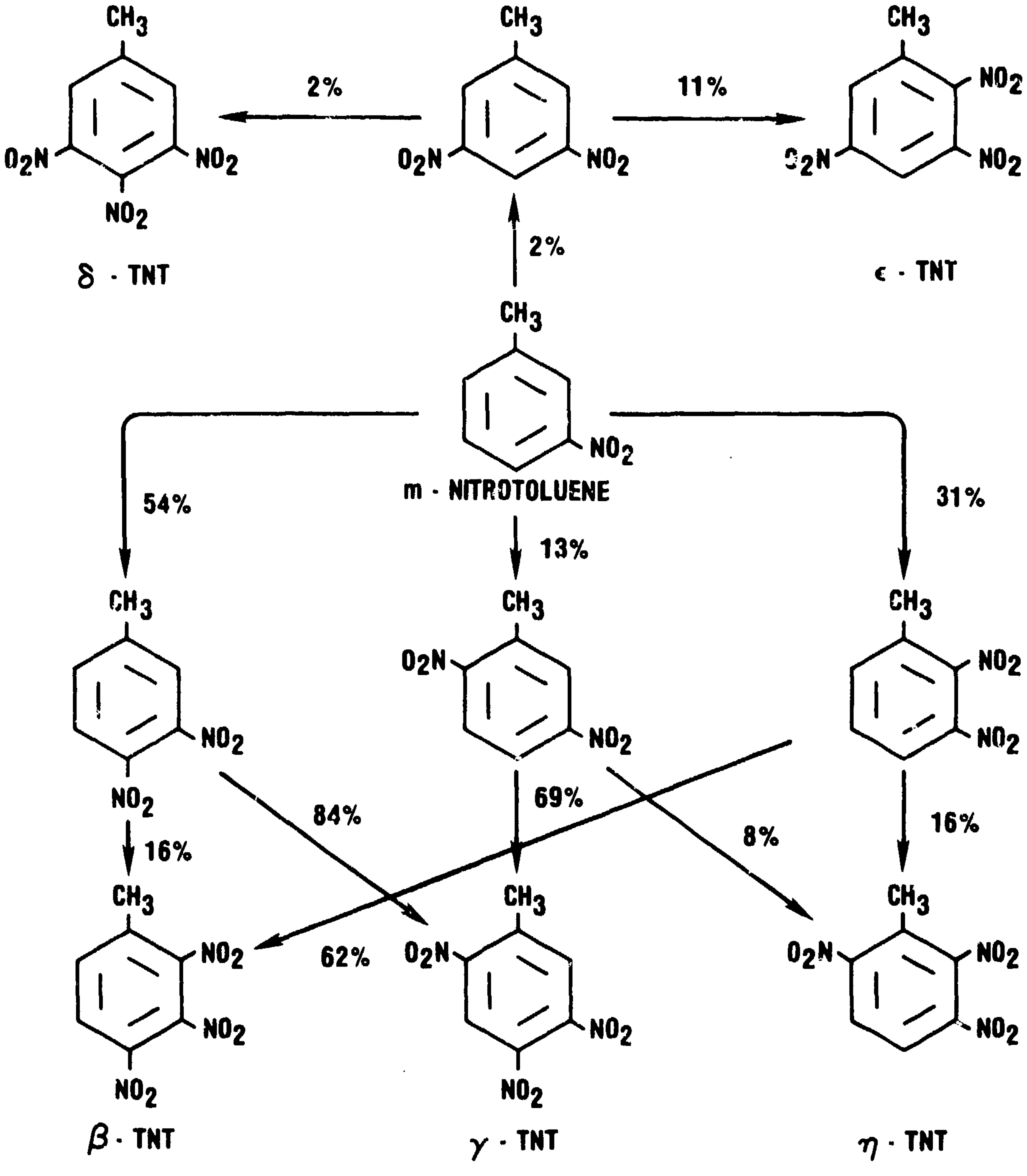
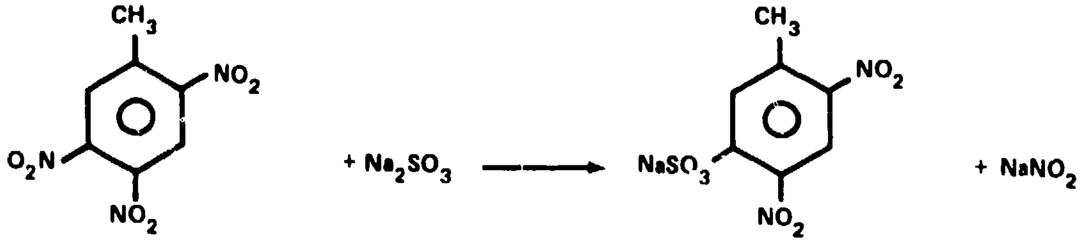


FIG. 1 PRODUCTS OF THE NITRATION OF m–NITROTOLUENE (TAKEN FROM REF 2:
E de Beule, Bull. soc. chim Belge, 42, 27 (1933)

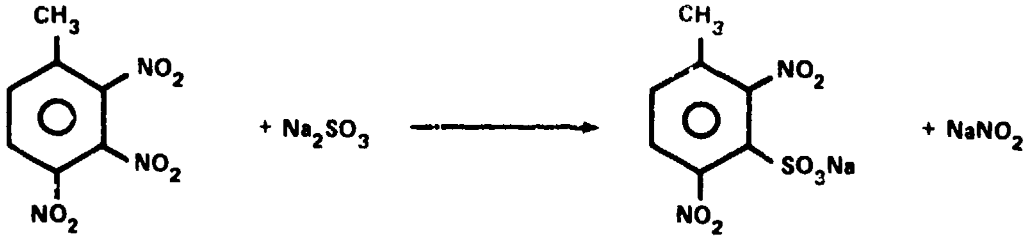
(1)



2,4,5-TNT

SODIUM 2,4-DINITROTOLUENE-5-SULFONATE

(2)



2,3,4-TNT

SODIUM 2,4-DINITROTOLUENE-3-SULFONATE

The safe disposal of "red water" is not a simple problem to solve, for it cannot be dumped into the sewer system without prior processing. In the past, the red water disposal problem was solved by selling it, after concentration at the TNT plant, to paper mills which incinerated it to sodium sulfate for use in pulping. Unfortunately, the paper mills are not interested in purchasing red water now, because the incineration costs more than the market value of the sodium sulfate.

Thus, the TNT plants are faced with three alternatives: (1) increase the cost of the TNT to pay for the incineration; (2) separate marketable substance(s)* from the red water to pay for the incineration; (3) use a completely different purification process whose effluents either could be processed economically prior to disposal, or had a market value without processing. This project is concerned mainly with the second alternative listed above; emphasis is to be placed on the organic content of the red water.

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*An example is TNB, which has been suggested as a safe high explosive fill for ordnance items subject to "cook-off" conditions because it is thermally stable well above its melting point (121°C). The high cost of synthesizing TNB has undoubtedly prevented its serious consideration for this and other applications. If red water proved to be relatively rich in TNB, or compounds convertible to TNB, such as TNBAL or TNBOH, recovery of these compounds might well defray the cost of incinerating the red water. Bolleter's estimates of the composition of red water indicate that red water should indeed be a good source of TNB and TNB precursors (reference 8).

(8) W. T. Bolleter, paper given at the Environmental Quality Standards Research Conference, 13 October 1972, Edgewood Arsenal.

The Non-Polar Organic Content Of Red Water

We sampled red water at JAAP in May, 1975, and analyzed it at the plant to minimize compositional variation due to decomposition. The red water was found to consist of two phases: a dark red-brown aqueous solution (pH 8.6) and a tan organic solid. Acidification* of the aqueous phase produced additional non-polar organic solid matter. After separation of these two solid fractions, the last traces of non-polar organic substances were removed by extraction of the aqueous phase with benzene and then with ether. Concentration of these extracts yielded black oils.

The non-polar organic fractions were subjected to thin layer chromatography, and the α-TNT content determined (see Table 1). The chromatograms of the oils and the solid precipitated by acidification showed at least four additional non-polar organic components, none of which were 1,3,5-trinitrobenzene (TNB), 2,4,6-trinitrobenzaldehyde (TNBAL), or 2,4,6-trinitrobenzyl alcohol (TNBOH). If these substances were present in any of the fractions, their content must have been at least one order of magnitude less than the α-TNT content of red water ($< 0.05\%$).

In summary, the largest single non-polar organic component of red water was found to be α-TNT, 94% of which is in the solid suspended in the red water. The total amount of α-TNT recoverable from red water is 0.6% by weight. Unfortunately, the α-TNT is unstable in contact with acidified red water, the loss after a week being between 10% (pH 4.0) and 13% (pH 1.9).

A final note should be added concerning the reproducibility of the non-polar organic content of red water. For a 72 liter sample of red water acidified to pH 3.7 and then aged for a week, the suspended solid and the solid precipitated by acidification totaled only 0.27 weight %.

It is not clear why the non-polar organic content of the 72 liter red water sample was significantly less than that found for the 2.5 liter sample. It should be noted, however, that the 72 liter sample was acidified without prior removal of the solid present, that the 72 liter sample was drawn when no "re-work" TNT** was being added and

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*Acidification is necessary to stop the basic degradation of the nitroaromatics, and to decompose any Meisenheimer compounds to the parent nitroaromatics. Two acidification pH's were used in order to assess the effect of pH on the stability of the non-polar organics. The acidification pH was found to influence markedly not only the stability of the non-polar organics, but also the percentage of the non-polar organic fractions separated from red water (vide infra).

**α-TNT which fails to meet specification is "re-worked" (i.e., mixed with crude TNT and then sellited).

that the efficiency of separation at the Selliter wier would directly affect the amount of solid formed when the red water is cooled.

TABLE 1

THE COMPOSITION OF RED WATER: THE NON-POLAR ORGANIC FRACTIONS

FRACTION	ACIDIFICATION pH	WT.% OF RED WATER	α-TNT CONTENT (WT.%)
Suspended Solid	-	0.62	95.5
Solid Precipitated By Acidification	1.9	0.22	9.3
Extractable Oils	4.0	0.25	16.4

The Polar Organic Content of Red Water

The polar organic content of red water is by our analyses, 13.1 weight percent, one third of which consists of a mixture of dinitrotoluene sulfonic acids (mainly 2,4-dinitrotoluene-5-sulfonic acid and 2,4-dinitrotoluene-3-sulfonic acid, amounting to 2.7 and 2.0 weight percent of the red water). Our thin layer chromatographic analyses indicated that if 2,4,6-trinitrobenzoic acid (PiCOOH) were present in the red water, its concentration could not be more than 1/10 of the concentration of the 3- or 5-sulfonic acids. The rest of the polar organics consist of a complex mixture of red, water-soluble matter (RPOM) resulting from the degradation of α-TNT by sellite (vide infra). The sulfonic acids are stable in red water acidified to pH 1.9 or 4.0 for at least one week.

The 5- and 3-sulfonic acids are the direct result of the reaction of 2,4,5- and 2,3,4-trinitrotoluene with the $SO_3^=$ present in the sellite solution. Since crude TNT contains 2.0% of the former and 1.2% of the latter (Radford analyses, reference 1(d)), and since crude TNT and sellite are reacted on an approximate 1:1 weight basis, our analyses are reasonable, considering that variation in the process parameters affects the "meta isomer" content. Bolleter reports that red water has 6-8 weight % of the 5-sulfonic acid and 2-4 weight % of the 3-sulfonic acid. (reference 8)

Characterization of the Red Polar Organic Matter (RPOM) in Red Water

Red water was shown to contain 8.4 weight % of the RPOM by gel filtration techniques (8 weight % by TLC techniques). The gel filtration fractionated the red water (adjusted to pH 7.0) into 77 fractions. Ninety-three percent of the RPOM was contained in six of these fractions (fractions 15-19, and 24). After drying, these six fractions were analyzed for C, H, N, S, Na, and H_2O; Table 2 gives

TABLE 2

ATOMIC RATIOS FOR THE RED POLAR ORGANIC MATTER IN RED WATER

Fraction Number	C/N	C/S	C/H	Na/S	N/S	O/S	C/Na
15	3.58	3.51	2.93	1.50	0.98	5.40	2.34
16	2.32	8.08	1.27	2.95	3.48	13.50	2.74
17	1.48	5.63	4.27	3.05	3.80	12.60	1.84
18	2.37	5.30	3.84	1.62	2.23	8.55	3.13
19	2.76	6.58	1.35	1.19	2.38	6.61	5.56
24	3.09	7.77	2.11	1.01	2.51	6.96	7.70
Sodium Dinitrotoluene Sulfonate	3.50	7.00	1.40	1.00	2.00	7.00	1.00
TNT	2.33	-	1.40	-	-	-	-
Mono-sulfite Adduct of TNT	2.33	7.00	1.40	2.00	3.00	9.00	3.50
Di-sulfite Adduct of TNT	2.33	3.50	1.40	2.00	1.50	6.00	1.75

the atomic ratios (corrected for H_2O) derived from these analyses. The six fractions had the following properties: (1) infrared absorptions consistent with O-H and/or N-H stretching, N-O stretching in nitro compounds or nitronate salts (or alternatively, absorption characteristic of the carboxylate anion), C-O stretching, and S-O stretching in sulfonic acid salts; (2) a solubility in methanol and ethanol which indicated the absence of any gross contamination by inorganic salts; (3) only weak pmr absorptions in D_2O and DMSO-d_6.

Without further purification, one is not justified in assigning chemical structures to any of the six fractions of the RPOM. However, the following observations should be made:

(i) The RPOM is indeed organic, the carbon content varying from 15 to 29% for the six fractions.

(ii) The RPOM must be derived mainly from α-TNT, because the level of impurities in crude TNT is too low to account for a red polar organic content of 8%. The two major impurities in crude TNT, 2,3,4- and 2,4,5-trinitrotoluene, are converted by the sellite to dinitrotoluene sulfonic acids which have been separated from the RPOM (see experimental).

(iii) The fact that Na/S $>$ 1 for fractions 15-18 indicates that the sodium is associated with some other anionic function besides sulfonate, such as carboxylate nitronate or phenoxide. The absence of any strong pmr absorptions (specifically for CH_3) suggests, or at least is consistent with, the oxidation of the methyl group to carboxylate.

(iv) The RPOM is hygroscopic. Therefore, C/H values can be considered only approximate, and the infrared absorptions in the 3500 cm^{-1} region may be partially or completely due to water. Hammersley has found infrared absorptions in this region for carefully dried samples of Red TNT (produced by the reaction of α-TNT and KOH), even when the sample compartment of the spectrophotometer was purged with dry nitrogen (reference 9).

(v) The O/S values are estimates only, because the oxygen analysis of each fraction was calculated as 100% less the sum of the percentages for C, H, N, S, and Na.

(vi) The low value of C/N for fraction 17 (compared to the value for TNT) suggests attack of the TNT by a nitrogen-containing nucleophile, such as nitrite ion.

(vii) The red color of the RPOM is not due to Meisenheimer compounds, because red water and water solutions of the RPOM are still deep red at pH 2. Furthermore, one can infer from the elemental analyses that none of the six fractions contain, as a major component, the product of the rearrangement of a Meisenheimer compound to a stable species.

(viii) Fractions 19 and 24 "fit" the atomic ratios for a dinitrotoluene sulfonic acid. These fractions were shown to contain no significant amounts of either the 2,4-dinitrotoluene-3- or -5- sulfonic acids. Isomeric sulfonic acids would be present in red water at only the trace level.

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(9) V. L. Hammersley, "Historical and Experimental Studies of Alkali and Trinitrotoluene Reaction," WQEC/C 75-192 (Naval Weapons Support Center, Crane, IN), 6 October 1975. p. 83

(ix) Reductive sulfonation via the Piria reaction (references (10), (11)) would result in more hydrogen, and less oxygen, than found for the six fractions. Since these analyses are subject to an unassessed error, Piria products cannot be ruled out.

(x) Sulfite reduction of the nitro groups of TNT does not seem likely, because the products would contain much less oxygen than any of the six fractions.

Feasibility of Isolating 1,3,5-Trinitrobenzene (TNB) and 2,4,6-Trinitrobenzaldehyde (TNBAL) from Red Water and of Producing TNB from Yellow Water

Bolleter has estimated that red water has the following composition: 0.2-0.5 weight % TNBAL-bisulfite addition compound, 0.3-0.5 weight % TNB-sellite complex, 0.2-0.5 weight % TNBOH, and 0.1-0.5 weight % PiCOONa (ref. 3). In contrast, our thin layer chromatograms of the non-polar fractions of acidified red water failed to show visually detectable amounts of TNB, TNBAL or TNBOH; if these compounds were present in red water, we estimate that their concentrations could not exceed about 0.05% of the red water.

The maximum concentration of TNB and TNB precursors in red water cannot exceed their concentrations in the crude (unsellited) TNT, since the crude TNT and sellite are reacted on a 1:1 weight basis at JAAP. We have shown by chromatographic methods that crude TNT has 0.003 weight % TNBAL and 0.05 weight % TNB. Radford's analysis of the nitrobody from nitrator 6 at JAAP shows 0.01 weight % TNB (ref. 1(g)). In a recent private communication by C. D. Chandler of RAAP, the following analyses by RAAP of the nitrobody from nitrator 6 at JAAP were reported: 0.06 weight % TNBOH, 0.03 weight % TNBAL, 0.31 weight % PiCOONa, and a trace of TNB. Thus, we conclude that the maximum possible concentration of TNB, TNBAL and TNBOH in red water is too low to consider their isolation feasible. The amount of TNB in acidified red water should be less than the amount in crude TNT because we have shown that TNB is decomposed by aqueous sodium sulfite (both buffered and unbuffered) at 85°C.

The Purification Of Crude TNT With H_2O_2 - Borax

Since the sellite process leads to red water from which no significant amounts of useful organic compounds can be easily isolated, we decided to investigate other methods for purifying crude TNT. One attractive method is to convert the "meta" isomers to dinitrocresols, which can be extracted from water with organic solvents. The main problem with this method is that, in order to make the aqueous base sufficiently reactive, the pH must be raised to a level which causes noticeable degradation of the TNT. Therefore, we decided to investigate the use hydroperoxide anion, whose nucleophilicity toward aromatic substrates has been suggested to

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(10) R. Piria, Ann., 78, 31 (1851).
(11) H. Krauch and W. Kunz, "Organic Name Reactions," John Wiley and Sons, Inc., New York, N.Y., 1964, p. 359.

exceed that of OH^- (reference 12). If HOO^- is indeed a stronger nucleophile than OH^- in the displacement of the labile nitro group of the meta isomers, then one would be able to "clean up" the crude at a lower pH than required by OH^-, and, thus, hopefully, avoid degradation of the TNT.

We have found that stirring crude TNT with aqueous H_2O_2 - borax at 95° is indeed an efficient method of removing 2,4,5- and 2,3,4-trinitrotoluene from crude TNT. The best procedure found so far requires three 15 minute extractions, the first one with 5.0% borax and 5.9% H_2O_2, and the second and third with 10% borax and 2.0% H_2O_2. During these extractions, the pH does not exceed 8.4. The aqueous extracts are deep orange to yellow, indicating some, but not extensive, degradation. We have estimated that 100% of the 2,4,5-isomer, and 85% of the 2,3,4- isomer are removed from the crude TNT.

The use of borax as the base for generating HOO^- is particularly advantageous because the pH tends to drop during the first extraction. If the concentrations of borax and hydrogen peroxide are chosen properly, this drop can be prevented. Apparently the mechanism is that, as the hydrogen peroxide decomposes, the equilibrium between borate and the weaker base, perborate, is shifted toward borate.

EXPERIMENTAL

The Non-Polar Organic Content of Red Water

An "on-the-spot study" of the red water produced by TNT Plant #4 (CIL continuous process) at JAAP was made during the period 8-21 May 1975. The aims of this study were to determine the effect of acidification pH, and the effect of aging on the nature and amount of non-polar organic material in red water. The study was made at the plant to minimize compositional changes due to instability.

Sampling Technique

Since red water consists of two phases, we adopted the following technique to insure representative sampling: Two 6-liter Erlenmeyer flasks were placed in ice baths, and a 500 ml sample of red water was drawn for each flask directly from the trough leading to the red water concentration vat. The samples were drawn within a one minute period, and represented the total effluent. The sampling was repeated every five minutes until above five liters had been collected in each flask. The pH of both 5-liter samples of red water was found to be 8.7 at room temperature.

Isolation Procedure

The non-polar organics were separated from the two 5-liter red water samples by the scheme given in Figure 2. A 25% aqueous H_2SO_4 solution was used for acidification. Filtrate A from one of the

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(12) J. Miller, "Aromatic Nucleophilic Substitution," Elsevier Publishing Co., New York, N.Y., 1968, p. 202.

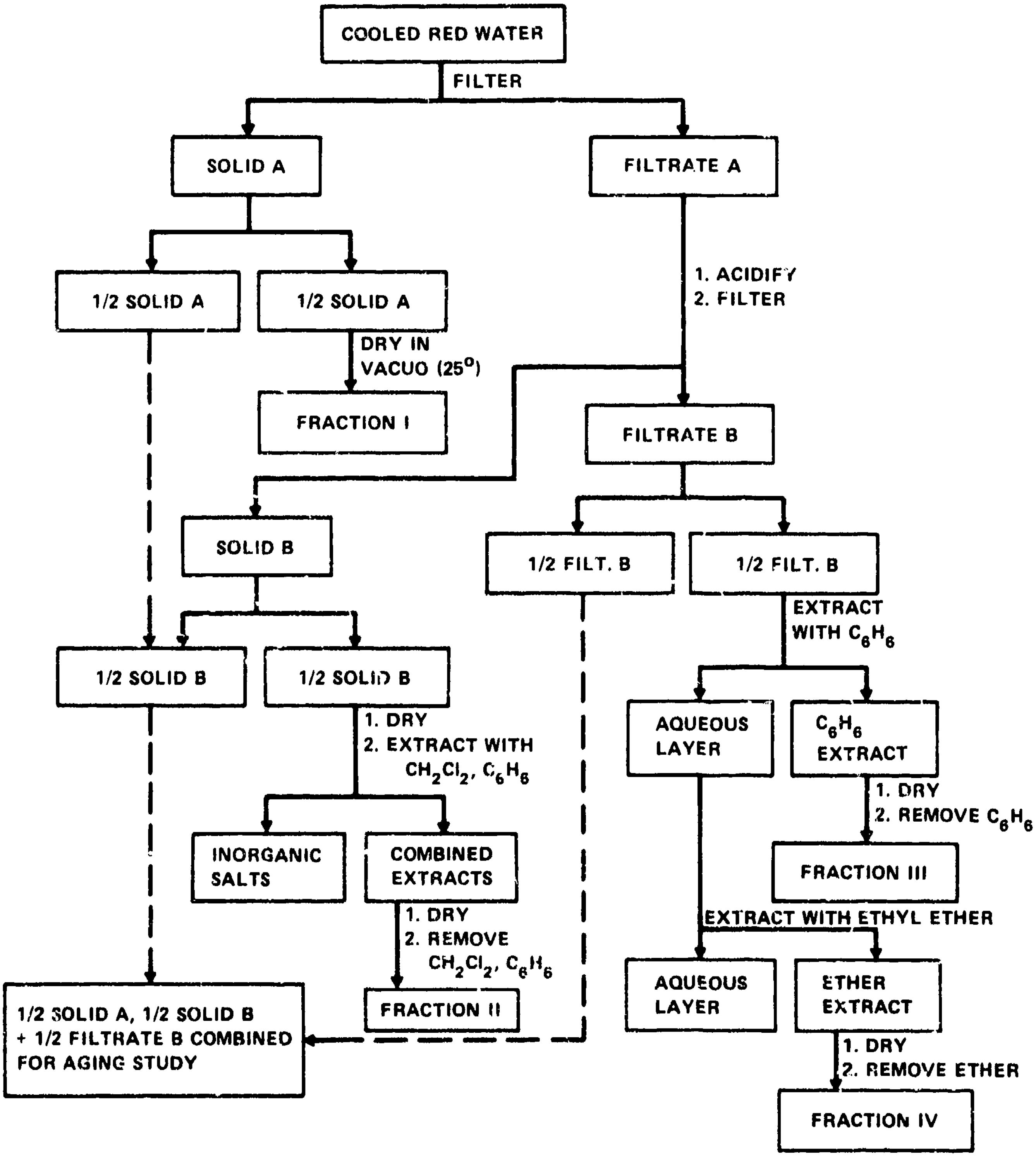

FIG. 2 SCHEME FOR THE ISOLATION OF THE NON-POLAR ORGANICS FROM RED WATER

5-liter samples was acidified to pH 4.0, and Filtrate A from the other 5 liter sample to pH 1.9. Solid A was light brown in color, and consisted of hard, well-formed crystals. For both pH's, Solid B consisted of a mixture of very hard, well-formed tan crystals and soft, dark brown crystals. For both pH's, Fractions III and IV were viscous, black oils. Table 3 gives the percentages of the four non-polar organic fractions separated from the red water according to the scheme of Figure 2, both initially and after a week's aging in the dark.

TABLE 3

PERCENTAGE OF THE FOUR NON-POLAR ORGANIC FRACTIONS IN RED WATER

	Initial Composition		Composition After 1 wk aging	
Fraction	pH 1.9	pH 4.0	pH 1.5	pH 3.7
I	0.59	0.64	*	*
II	0.22	0.02	*	*
I+II	0.81	0.66	0.85	0.72
III	0.15	0.19	0.20	0.20
IV	0.19	0.06	1.15	0.08
I+II+III+IV	1.15	0.91	1.20	1.00

*No results are given for Fractions I and II of the aged, acidified red water because the aging study was performed with combined Fractions I and II.

Analysis for α-TNT (2.5 Liter Scale)

Benzene solutions of the four non-polar organic fractions were quantitatively spotted on Mylar sheets coated with a 0.25 mm layer of silica gel mixed with a binder and a fluorescer activated by 254 nm radiation; α-TNT and other reference compounds were also spotted on the sheets. The sheets were subjected to PMD, using a developer consisting of a mixture of benzene, cyclohexane and ethyl acetate (50/45/5, v/v). The spots corresponding to α-TNT were removed and analyzed spectrophotometrically (see Appendixes B and C). The amount of α-TNT in the four non-polar fractions was calculated, assuming 100% extraction efficiency (see Appendix B). Table 4 gives the results for fresh and aged red water. Table 5 gives the amount of α-TNT in red water, by fraction.

The chromatograms of the non-polar fractions showed between two and four easily discernable spots in addition to the spot for α-TNT and a spot at the origin for more polar material. Fraction I (for both pH's) showed two minor additional spots, Fraction II (pH 2) three additional spots (two of which were yellow), Fraction III (pH 2) one additional minor spot, Fraction III (pH 4) two additional minor spots (one of which was yellow), Fraction IV (pH 2) two additional minor spots, and Fraction IV (pH 4) three additional minor spots and an unresolved yellow band. None of the additional spots had the R_f value for TNB, TNBAL or TNBOH. Thus, if the latter compounds were present in any of fractions, their concentrations could not have been more than 1/10 that of the α-TNT.

TABLE 4

PERCENTAGE OF α-TNT IN THE FOUR NON-POLAR ORGANIC FRACTIONS

	Initial Composition		Composition after 1 wk aging	
Fraction	pH 1.9	pH 4.0	pH 1.5	pH 3.7
I	95.1	95.8	*	*
II	9.3	tr	*	*
I+II	71.8	92.6	61.2	72.7
III	9.5	21.6	15.6	18.7
IV	tr	tr	tr	tr
I+II+III+IV	51.8	71.8	39.9	56.6

*See footnote for Table 3

TABLE 5

PERCENTAGE OF α-TNT IN RED WATER, BY FRACTION

	Initial Composition		Composition after 1 wk. aging	
Fraction	pH 1.9	pH 4.0	pH 1.5	pH 3.7
I	0.56	0.62	*	*
II	0.02	tr	*	*
I+II	0.58	0.62	0.52	0.54
III	0.01	0.04	0.03	0.04
IV	tr	tr	tr	tr
I+II+III+IV	0.59	0.66	0.55	0.58

*See footnote for Table 3

Analysis for α-TNT (72 Liter Scale)

On 21 May, a 72-liter sample of red water was drawn from TNT plant #4 at JAAP (running without "re-work") over a 40 minute period, using the same sampling technique described above for the 5 liter samples, but, of course, increasing the volume collected to 2.7 liters every five minute period. After cooling the 72 liter sample to about 35°C, the sample was acidified to pH 3.7 with 25% aqueous sulfuric acid, and transferred to four 5-gallon carboys. After a week, the solid was filtered off, and dried; the weight of the solid amounted to 0.27% of the red water. In contrast, the sum of Fractions I and II amounted to 0.72% of the red water analyzed on the 2.5 liter scale. The filtrate was extracted twice with benzene and twice with ether, using, for each extraction, one liter of extraction solvent for two liters of filtrate. The extracts were dried, concentrated by rotary evaporation, and the concentrates pumped at about 1 mm Hg pressure to remove traces of benzene and ether. The residues from the benzene and ether extractions (viscous, black oils) amounted to 0.16% and 0.04% of the red water, respectively. In contrast, Fraction III amounted to 0.20% and Fraction IV to 0.08% of the red water analyzed on the 2.5 liter scale.

THE POLAR ORGANIC CONTENT OF RED WATER, DETERMINED BY THIN LAYER CHROMATOGRAPHY

The Dinitrotoluene Sulfonic Acid Content

Red water (previously acidified and freed of non-polar organics by extraction with benzene and then ether) was quantitatively spotted on a glass plate coated with a 0.3 mm layer of silica gel and a fluorescer activated by 254 nm radiation. Reference samples of 2,4-dinitrotoluene-5-sulfonic acid and 2,4-dinitrotoluene-3-sulfonic acid were spotted on the same plate. The plate was subjected to PMD, using a developer consisting of a mixture of ethanol, ethyl ether, benzene and concentrated ammonium hydroxide (54/50/84/12, v/v). The spots corresponding to the two reference acids were scraped off the plate, and the silica gel extracted according to the procedure given in Appendix B. The extracts were then analyzed spectrophotometrically, using the extinction coefficients given in Appendix C. Table 6 summarizes the results.

TABLE 6

PERCENTAGE OF 2,4-DINITROTOLUENE-5-SULFONIC ACID (I) AND 2,4-DINITROTOLUENE-3-SULFONIC ACID (II) IN RED WATER

Sulfonic	Initial Composition		Composition after 1 wk aging	
Acid	pH 1.9	pH 4.0	pH 1.5	pH 3.7
I	2.6	2.7	2.4	2.8
II	1.8	2.1	1.8	2.0

The Red Polar Organic Content

A 2.00 g sample of red water (previously acidified to pH 4.0 and then freed of non-polar organics by extraction with benzene and then with ether) was neutralized to pH 7.0 with aqueous sodium hydroxide. Removal of the water from the sample under reduced pressure left 0.38 g of a red-brown solid. The latter was extracted with 20 ml of methanol, leaving 0.14 g of a nearly white (presumably inorganic) solid. Evaporation of the methanol left 0.24 g of a red-brown solid, which was re-dissolved in 4 ml of methanol. This solution was streaked onto a 20 x 20 cm glass plate having a 0.6 mm coating of mixture of silica gel, a binder and a fluorescer activated by 254 nm radiation. The plate was subjected to PMD, using a developer consisting of a mixture of ethanol, ethyl ether, benzene and concentrated ammonium hydroxide (54/50/84/12, v/v). After drying, the plate showed two fairly well separated bands: one for the dinitrotoluene sulfonic acids, and, below it, a red-brown band which started just above the origin. The red-brown band was scraped off the plate, and the silica extracted with methanol. Removal of the methanol from the extract left 0.16 g of a red-brown solid (amounting to 8% of the red water sample. By difference, the dinitrotoluene sulfonic acid content amounted to 4%.

FRACTIONATION OF THE POLAR ORGANIC MATTER IN RED WATER BY GEL FILTRATION

A 30.0 g portion of red water* was allowed to concentrate to a thick solution by evaporation in air. This solution was poured into a 2.5 x 50 cm glass column containing 150 g of 120-230 mesh filtration gel (EM-GEL PGM 2000, E. Merck, Darmstadt, W. Germany).

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*Prior treatment: acidified to pH 3.7 with sulfuric acid, filtered, extracted twice with benzene and twice with ether, neutralized to pH 7.0 with aqueous sodium hydroxide.

The column was eluted with water. After 33 10-ml fractions had been collected, the eluant was changed to 50% methanol-50% water (v/v), and, after 21 10-ml fractions had been collected, the eluant was changed to pure methanol. Each fraction was poured onto a tared watch glass; after the liquid had evaporated, each watch glass was weighed again to obtain the weight of material eluted. Table 7 gives the weights of these residues.

The residues could be divided into five groups on the basis of their appearance: Group I (fractions 1-14) - hard, well-formed inorganic crystals, white to tan in color; Group II (fractions 15-19) - dark red, "varnish-like" solids; Group III (fractions 20-23) - well-formed crystals, medium-red in color* ; Group IV (fractions 24-37) - dark-red, "varnish-like" solids; and Group V (fractions 38-77) - solid films, changing from red to yellow as fraction number increased.

CHARACTERIZATION OF THE RED POLAR ORGANIC MATTER IN RED WATER

The gel filtration of 30.0 g of red water resulted in 77 solid fractions, divided into five groups (see p. 19). The material responsible for the color of red water was clearly in Groups II (fractions 15-19) and IV (fractions 24-37). Since fractions 15-19 and fraction 24 accounted for more than 93% of Groups II and IV, these six fractions were studied in some detail. Since Group I was shown to be inorganic, and Group III to be mainly a mixture of 2,4-dinitrotoluene-3-sulfonic acid and 2,4-dinitrotoluene-5-sulfonic acid, no further characterization of these groups was attempted.

Water and Elemental Analyses

The solid residues from fractions 15-19 and 24 were homogenized by grinding, dried for 16 hours at room temperature in a vacuum desiccator, and single determinations of carbon, hydrogen, nitrogen, sulfur and sodium made (all weighings were made under low humidity conditions). Table 8 gives the results. Since the dried residues were hygroscopic, and since there was no assurance that the drying procedure removed all of the water, the residues were re-dried for 16 hours at room temperature in a vacuum desiccator, and then analyzed for water by the Karl-Fisher method. Table 8 also gives these results.

Infrared Absorption Spectra

Infrared absorption spectra of the dried residues from fractions 15, 16 and 17 were measured using the KBr pellet method and a Beckman IR-4 Infrared Spectrophotometer set for a 15 minute scan time and the standard program for this scan time. Table 9 gives the results,

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*Shown by TLC to be mainly 2,4-dinitrotoluene-3-sulfonic acid and 2,4-dinitrotoluene-5-sulfonic acid.

TABLE 7

GEL FILTRATION OF RED WATER: SOLID CONTENT OF THE ELUANT, BY FRACTION[a]

Fraction Number	Weight Solid, mg	Fraction Number	Weight Solid, mg.
1	12.2	40	0.3
2	12.5	41	2.1
3	11.2	42	2.9
4	12.7	43	2.8
5	12.0	44	2.9
6	13.0	45	2.2
7	10.6	46	2.6
8	8.4	47	2.3
9	12.0	48	2.2
10	37.0	49	1.9
11	64.8	50	2.0
12	136.2	51	11.3
13	605.6	52	3.0
14	172.0	53	3.7
15	554.2	54	3.9
16	345.1	55	2.9
17	506.2	56	1.8
18	443.2	57	1.7
19	298.1	58	1.9
20	180.7	59	2.4
21	456.7	60	2.1
22	597.5	61	2.0
23	428.8	62	2.0
24	210.4	63	2.1
25	74.0	64	2.1
26	29.5	65	2.0
27	14.7	66	1.5
28	8.8	67	1.4
29	6.8	68	1.9
30	7.5	69	2.0
31	5.0	70	1.5
32	5.0	71	1.7
33	4.0	72	2.3
34	3.0	73	3.6
35	3.1	74	3.3
36	3.6	75	5.7
37	3.0	76	6.0
38	2.6	77	4.0
39	2.4		

a. See p. 18 for experimental details.

TABLE 8

ELEMENTAL AND WATER ANALYSES OF THE RED POLAR ORGANIC MATTER IN RED WATER.

Fraction Number	%C	%H	%N	%Na	%S	$\%H_2O$
15	18.48	1.41	6.02	15.15	14.05	7.86
16	18.98	2.20	9.54	13.30	6.27	8.50
17	14.92	0.97	11.77	15.50	7.08	6.08
18	19.38	1.33	9.53	11.35	9.76	7.91
19	25.70	2.50	10.85	8.90	10.43	8.04
24	29.26	1.87	11.04	7.29	10.06	6.30

TABLE 9

FREQUENCIES OF THE INFRARED ABSORPTION PEAKS OF THE RED POLAR ORGANIC MATTER IN RED WATER.

Material Studied	Spectral Region*								
	O-H Stretch.	C=N Stretch.	NO_2 Asy. Stretch.	NO_2 Sym. Stretch.	$-SO_3^-$ Asy. Stretch.	C-O Stretch.	$-SO_3^-$ Sym. Stretch.	Z-N Stretch. in $Z-NO_2$	S-O Deform. in $-SO_3^-$
Fract.15	3560(s)	1640(s)	1560(s)	1370(m)	1220(s)	1125(s)	1040(s)	-	700(m)
Fract.16	3510(s)	1640(s)	1550(s)	1380(s)	1220(s)	1120(w)	1050(s)	840(w)	660(m)
Fract.17	3560(s)	1640(m)	1550(m)	1380(s)	1220(m)	1130(w)	1050(s)	840(w)	700(m)
2,4-Dinitro-toluene-5-sulfonic acid	3550(w)	1620(w)	1540(s)	1360(m)	1230(s)	1120(w)	1050(s)	840(m)	660(m)
Red TNT	3430(m)	1620(s)	1550(s)	1370(s)	1270(s)	1130(s)	-	830(w)	730(m)

* Frequencies are in cm^{-1}. The letters in parentheses indicate the strength of the absorption: s = strong, m = medium, and w = weak.

and also a comparison with the absorption spectra for 2,4-dinitrotoluene-5-sulfonate and "Red TNT" produced by the reaction of equimolar amounts of α-TNT and KOH (ref. 9). Note the following: (1) the "assignments" should be considered tentative; (2) a variety of absorptions occur in the 840 cm^{-1} region (C-N stretching in aromatic nitro compounds, O-N stretching in nitrate esters, and C-H deformation in tetrasubstituted benzene drivatives); (3) Hammersley has attributed the 1550 and 1370 cm^{-1} absorptions of "Red TNT" to a nitronate salt; (4) the absorption spectra of Fractions 15, 16 and 17 have essentially the same absorption peaks, all of which are much broader and stronger than the corresponding peaks of 2,4-dinitrotoluene-5-sulfonic acid; (5) the C-O stretching peak for Fraction 15 is much stronger than the corresponding peak for Fractions 16 and 17.

Proton Magnetic Resonance Spectra

These spectra were run on a Varian HA-100 Spectrometer, using frequency sweep and solutions containing 6-8 weight percent of the red polar organic matter in D_2O or dimethylsulfoxide-d_6. No peaks could be found with the instrument settings normally used for this concentration range. However, if the recorded gain was attenuated 7-10 times, weak absorptions with the following chemical shifts (in ppm relative to TMS) were found for the D_2O solutions: Fraction 15 - 2.91, 2.30, 3.10, 4.08, and 8.86; Fraction 16 - 8.55 and 9.0; Fraction 19 - 2.5, 2.6 and 9.4; Fractions 17 and 18 failed to show any peaks, even with the increased gain. The dimethylsulfoxide-d_6 solution of Fraction 15 showed only a slight rise and fall of the base line between 6.5 and 7.5 ppm (relative to TMS) when the recorder gain was attenuated 7 x the normal setting. Without attenuating the recorder, 2,4-dinitrotoluene-5-sulfonic acid in dimethylsulfoxide-d_6 gave the following chemical shifts (in ppm relative to TMS): 2.54, 7.91, and 8.30.

Solubility in Methanol and Ethanol

The residues from fractions 15-19 and 24 were completely soluble in methanol at room temperature, suggesting that the residues were not grossly contaminated by inorganic salts. Weighed amounts of the residues from fractions 15-18 were stirred at room temperature with 10 ml of ethanol in tared centrifuge tubes. The tubes were then centrifuged, the ethanol solutions drawn off, and the tubes weighed after pumping in a vacuum desiccator. Table 10 summarizes the results.

TABLE 10

ETHANOL SOLUBILITY OF THE RED POLAR ORGANIC MATTER IN RED WATER

Fraction Number	Initial Weight,g.	Weight Insoluble,g.	% Dissolved	Color of Extract	Nature of Matter Extracted
15	0.294	0.258	12	tan	brown oil
16	0.063	0.050	20	yellow	yellow crystals + brown oil
17	0.196	0.139	29	yellow	yellow crystals + brown oil
18	0.116	0.024	79	red	red, amorphous matter

ANALYSIS OF CRUDE (UNSELLITED) TNT FOR 1,3,5-TRINITROBENZENE (TNB) AND 2,4,6-TRINITROBENZALDEHYDE (TNBAL)

The following scheme was used for the analysis of crude TNT:

(a) Ten grams of crude TNT was crystallized from benzene-hexane, and then from CCl_4.

(b) The crystallization filtrates were combined and diluted quantitatively. Measured volumes of the latter were streaked onto 20 x 20 cm glass plates having a 2 mm coating of silica gel 60 (Brinkmann Instruments, Inc.). The plates were then subjected to programmed multiple development (PMD).

(c) The bands on these plates having R_f values corresponding to TNB and TNBAL were removed and extracted with benzene. The extract was then spotted on 20 x 20 cm Mylar sheets having a 0.25 mm coating of silica gel.

(d) After PMD of the Mylar sheets, discrete spots having the R_f for TNBAL were easily detected; the total quantity of TNBAL, estimated by the spot-area method, amounted to 0.003% of the crude TNT.

(e) Since the Mylar sheets failed to show spots having the R_f for TNB, bands which generously straddled the R_f for TNB were removed from the sheets and extracted with benzene. The extract was spotted on fresh 20 x 20 cm Mylar sheets coated with 0.25 mm of silica gel. These sheets, after PMD, also failed to show discrete spots for TNB. Bands straddling the R_f for TNB were removed, and extracted with benzene. This extract was analyzed for TNB, using a Hewlett-Packard Research Chromatograph (Model 5750), fitted with a 12 foot x 1/8 inch Hewlett-Packard stainless steel column packed with 10% UC-W98 silicone gum rubber on 80-100 mesh Diaport-S. A peak with the exact retention time of TNB was found; the quantity of TNB found amounted to 0.05% of the crude TNT.

REMOVAL OF 2,3,4- AND 2,4,5-TRINITROTOLUENE FROM CRUDE TNT BY REACTION WITH AQUEOUS H_2O_2-BORAX

A 5.0 g portion of crude TNT (taken from a 50 g sample which had been homogenized by grinding) was transferred to 25 ml Erlenmeyer flask. Five ml of an aqueous H_2O_2-borax solution (stabilized with 0.08% pentasodium diethylene triamine pentaacetate) was pipetted into the flask. The flask was placed in a steam bath, and stirred magnetically for a measured time after the TNT had melted. The flask was then cooled in an ice bath to solidify the TNT, and the aqueous solution poured off. The procedure was repeated 2 or 3 times with fresh H_2O_2 solutions, the last solution containing acid in place of borax. Table 11 summarizes the data.

TABLE 11

EFFICIENCY OF REMOVAL OF "META ISOMERS" FROM CRUDE TNT BY AQUEOUS BORAX-H_2O_2 SOLUTIONS

Experiment No.	Extraction No.	Composition of Aq. Soln.		Extraction Time, Min.	pH of Aq. Soln.		% $CH_3C_6H_2(NO_2)_3$ Removed	
		% H_2O_2	% Borax		Initial	Final	2,4,5-	2,3,4-
A	1	5.9	5	15	6.84	6.92		
	2	2.0	10	15	8.43	7.75		
	3	2.0	10	15	8.43	8.00		
	4	2.0	0	15	4.61	6.80	100	85
B	1	5.9	5	15	6.84	6.87		
	2	2.0	5	15	8.07	7.08		
	3	2.0	5	15	8.07	7.55		
	4	2.0	0	15	4.61	5.46	90	75
C	1	5.9	10	15	6.91	8.96		
	2	2.0	10	15	8.43	8.42		
	3	2.0	0	15	4.61	6.24	75	65
D	1	6.9	10	10	6.69	9.00		
	2	2.0	10	10	8.38	8.21		
	3	2.0	10	10	8.38	8.02		
	4	2.0	0	10	4.61	6.48	90	75
E	1	5.9	7.5	10	6.87	8.90		
	2	3.0	10	20	7.89	8.58		
	3	2.0	0	10	4.61	6.18	75	65

After the TNT samples had been washed with the acid-H_2O_2, they were analyzed for 2,3,4- and 2,4,5-trinitrotoluene as follows: solutions containing the same weight of the TNT sample, crude TNT, and the 2,3,4- and 2,4,5-trinitrotoluenes were quantitatively spotted on a Mylar sheet coated with a 0.25 mm layer of silica gel and a fluorescer activated by 254 nm radiation. The sheet was developed twice in a mixture of benzene-cyclohexane-ethyl acetate (50/45/5, v/v). The efficiency of removal of the contaminating trinitrotoluenes was estimated visually: Table 11 gives these estimates. It was noted that crude TNT contains some minor impurities which are not affected by H_2O_2-borax, but are removed effectively by selliting.

SUMMARY AND CONCLUSIONS

Analysis of red water from JAAP has shown the following:

(1) Only two potentially useful organic substances are present in red water in concentrations sufficiently high to justify their recovery: 2,4-dinitrotoluene -5- sulfonic acid (2.7 weight % by our analysis, compared, to 6-8 weight % reported by Radford) and 2,4-dinitrotoluene-3-sulfonic acid (1.2 weight % by our analysis, compared to 2-4 weight % reported by Radford).

(2) A small amount of α-TNT (0.6 weight %) can be easily recovered from red water by filtration.

(3) Red water cannot be considered a practical source of TNB or TNBAL.

(4) Eight weight percent of red water is a complex mixture of unidentified, red, water-soluble organic compounds resulting from the degradation of α-TNT by sellite. This mixture has no obvious commercial value, but, unfortunately, accompanies the dinitrotoluene sulfonic acids when they are extracted from freeze-dried red water. A separation has been accomplished by research techniques (gel filtration); the large scale practicality of this separation has not been demonstrated.

SUGGESTIONS FOR FUTURE WORK

1. Optimize the H_2O_2 method for the purification of crude TNT, and determine whether the resulting TNT meets the required specification.

2. Investigate the reaction of pure TNT with sodium sulfite, with emphasis on product characterization and methods of minimizing degradation.

3. Assess the practicality of producing 2,4-dinitrotoluene-5- and -3- sulfonic acids from red water by gel fitration.

4. The feasibility of producing TNB from yellow water should be assessed*.

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*The significant amount of PiCOONa reported by RAAP to be present in crude TNT (see p. 11) suggests that the yellow water produced by washing crude TNT prior to selliting should be analyzed for PiCOOH. Yellow water could be considered a good source of TNB if it proved to have a reasonable high concentration of PiCOOH, because the latter is readily converted to TNB by heating a neutralized solution.

GLOSSARY

CIL - Canadian Industries, Ltd.

DMSO - Dimethyl Sulfoxide

EDA - Ethylene Diamine

JAAP - Joliet Army Ammunition Plant

PiCOOH - 2,4,6-Trinitrobenzoic Acid

PMD - Programmed Multiple Development

pmr - proton magnetic resonance

RAAP - Radford Army Ammunition Plant

RPOM - Red Polar Organic Matter

TLC - Thin Layer Chromatography

TNB - 1,3,5-Trinitrobenzene

TNBAL - 2,4,6,-Trinitrobenzaldehyde

TNBOH - 2,4,6-Trinitrobenzyl Alcohol

APPENDIX A

DESCRIPTION OF THE RADFORD (CIL) SELLITING PROCESS (Ref. 1(f))

1. GENERAL. A two-phase counter-current system consisting of a molten nitro-body phase and an aqueous phase.

2. ACID WASHER. A 5-stage mixer-settler unit, each stage using cleaner water than the previous stage. The waste water is called YELLOW WATER; it is 15-25% in total acidity and 0.5% in α-TNT.

3. FIRST SELLITER. The selliting solution is a mixture of fresh Sellite solution (16% Na_2SO_3), taken from the SELLITE DISSOLVER, and Sellite solution from the SECOND SELLITER. pH_o = 8.3-8.5. Waste is RED WATER.

4. SECOND SELLITER. Fresh Sellite solution from the SELLITE DISSOLVER + SO_2. Waste returned to FIRST SELLITER.

5. POST-SELLITE WASHER. A 5-stage mixer-settler unit. Waste returned to SELLITE DISSOLVER.

6. FINISHING BUILDING. TNT sent to FINISHING BUILDING as a slurry of process water and transfer water. In the FINISHING BUILDING, the TNT is separated from the water, dried, flaked and boxed.

APPENDIX B

RECOVERY OF NITROAROMATICS FROM THIN LAYER CHROMATOGRAPHY PLATES

Aliquots of stock solutions of all the compounds in Table XII were spotted on thin layer chromatography plates coated with 0.25 mm silica gel. The spot for each compound was scraped off and stirred with a measured volume of DMSO to extract the nitroaromatic compound. After removal of the silica gel by centrifugation the DMSO solution was analyzed for the nitroaromatic using the conditions and an aliquot of the values given in Table 12 of Appendix C. We found that at least 95% of the nitroaromatic was recovered by this technique, with the exception of sodium 2,4-dinitrotoluene-3-sulfonate. For the latter compound, we found that stirring the silica gel with water at 50° for 30 minutes gave 75% recovery (compared to essentially nil for the DMSO extraction). It was also found that, for α-TNT, and 2,4-dinitrotoluene-3- and 5-sulfonic acids, essentially the same recovery efficiency was obtained after the plates had been subjected to development.

APPENDIX C

DETERMINATION OF THE MOLAR EXTINCTION COEFFICIENTS OF SOME DI- AND TRI-NITROBENZENE DERIVATIVES IN EDA-DMSO

The molar extinction coefficients of some of the nitroaromatics expected to be present in red water were determined in mixtures of ethylenediamine (EDA) and dimethyl sulfoxide (DMSO), following the method of Glover and Kayser (reference 13). Table 12 summarizes the results.

Stock solutions of TNBAL in benzene, α-TNT in benzene, and TNBOH in dichloromethane were made up, and 5-10 Ml aliquots diluted with the specified EDA-DMSO mixture. For the other compounds in Table XII, weighed samples were dissolved in DMSO, and then diluted with DMSO and EDA to the specified composition.

The spectral envelopes of TNBAL and sodium 2,4-dinitrotoluene-3-sulfonate in the specified EDA-DMSO solutions were found to change with time, the strongest absorption peak for the former changing from 453 nm to 512 nm, and for the latter from 530 nm to 438 nm. Reproducible values of ε for the 438 nm peak of the sulfonic acid were obtained if the optical density was measured after 16 hours (at room temperature). However, for TNBAL, the 512 nm absorption was found to reach a maximum value, and then to drift down with time, as expected, reproducible values of ε at 512 nm could not be obtained using the maximum optical density values. Therefore, we adopted the unusual technique of measuring ε when the optical densities at 512 nm and 453 nm were equal, hoping thereby to minimize the effects of degradation. This technique succeeded reasonably well, the average deviation in ε being only twice that obtained for stable solutions.

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(13) D. J. Glover and E. G. Kayser, "Quantitative Spectrophotometric Analysis of Polynitroaromatic Compounds by Reaction with Ethylene Diamine, NOLTR 67-175, 15 Dec 1967.

TABLE 12

MOLAR EXTINCTION COEFFICIENTS OF SOME DI- AND TRI-NITROBENZENE DRIVATIVES IN EDA-DMSO

COMPOUND	VOL. % EDA	No. Determinations	No. of Weights	Conc. Range[a]	Max. λ, nm	$10^{-4}\varepsilon$[b]	Av. Dev., %
2,4-Dinitrotoluene-5-sulfonic acid	7.5-30	4	3	12.5-2.5	362	1.24_8	1.4
Sodium 2,4-Dinitrotoluene-3-sulfonate · 2.5 H_2O	40	5	5	6.0-8.8	438	1.81_4	1.1
	40	6	6	5.5-9.5	-	-	-
2,4,6-Trinitrobenzaldehyde	15	14	4	1.8-0.8	(512)[c]	(2.14)	1.9
2,4,6-Trinitrobenzoic Acid	15	3	3	4.0-6.5	453	2.13_8	0.8
2,4,6-Trinitrobenzyl Alcohol	15	6	2	5.2-1.9	465	2.81	1.1
2,4,6-Trinitrotoluene	80	4	2	6.5-1.3	464	2.32	0.4

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a. 10^5 x molarity

b. ε= molar extinction coefficient, in liter-mol^{-1}-cm^{-1}

c. Spectral envelope changes rapidly; O. D. @ 512 nm increases, and O.D. @ 453 nm decreases, with increasing time. The value of ε refers to an iso-density value, i.e., when O. D. @ 453 nm equals O. D. @ 512 nm.

TABLE 12
(continued)

MOLAR EXTINCTION COEFFICIENTS OF SOME DI- AND TRI-NITROBENZENE DERIVATIVES IN EDA-DMSO

COMPOUND	Max. λ, nm	$10^{-3}\varepsilon^{b}$	Av. Dev., %	Conditions
2,4-Dinitrotoluene-5-sulfonic acid	410	5.91	0.7	rapid equilibration at room temp.; envelope and max. O.D. constant for at least 30 min.
Sodium 2,4-Dinitrotoluene-3-sulfonate - 2.5 H_2O	530	(0.9)	10	Read after 16 hrs. at room temp.
2,4,6-Trinitrobenzaldehyde	530	4.35	3.0	Read after 2 hrs.
	(453)^{c}	2.14	1.9	Read after ca. 20 min, when O.D. @ 512 nm equals O.D. @ 453 nm
2,4,6-Trinitrobenzoic Acid	505	12.4_2	0.3	Heat 20 min. @ 50°, cool to room temp, read
2,4,6-Trinitrobenzyl Alcohol	555	14.5	2.0	rapid equilibration at room temp.;envelope and max. O.D. constant for at least 30 min
2,4,6-Trinitrotoluene	540	15.1_5	1.3	requires about 10 min. equilibration at room temp.; max. O.D. drifts down after this time

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