

Solubility of 2,4-Dinitrotoluene and 2,4,6-Trinitrotoluene in Water

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Measurements of the aqueous solubility of 2,4-dinitrotoluene (DNT) and 2,4,6-trinitrotoluene (TNT) are reported. Previous data reported for DNT is sparse, and the values are inconsistent with those reported herein. Data for TNT compare very well with previously reported values, which provides confidence in the methods used.

Introduction

The majority of explosives found in antipersonnel and antitank landmines contain 2,4,6-trinitrotoluene (TNT). 2,4-Dinitrotoluene (DNT) is a common manufacturing byproduct in the synthesis of TNT¹ and is believed to be a principal component in the canine olfactory detection of buried landmines.² Recent efforts to develop an electronic dog's nose have prompted a careful evaluation of the transport of chemical signatures from buried landmines through the soil to the ground surface. One of the important soil transport processes affecting the movement of these nitroaromatic compounds is the upward advection in soil water induced by evaporation.³ In the near-surface soil environment of the buried landmine, the soil temperature can fluctuate by as much as (or more than) 60 °C. Because water solubility is strongly dependent on temperature, this has a significant impact on the mass transport of nitroaromatic chemicals in soils.

The water solubility of TNT has been reported by many reference handbooks^{1,4,5} based on the work of Taylor and Rinkenbach.⁶ A recent study and review⁷ has shown that the data of Taylor and Rinkenbach⁶ might be biased high by about 50%. Solubility data for DNT is very limited, with most reports^{1,8,9} referring to a summary in Army Materiel Command¹⁰ showing values of (0.027, 0.037, and 0.254) g/100 g at (22, 50, and 100) °C, respectively. The objective of this work was to complete solubility measurements of TNT and DNT at soil temperatures expected in near-surface soils.

Materials and Methods

Apparatus and Experimental Procedure. A 125-mL Erlenmeyer flask was filled with 100 mL of deionized water and placed into a constant-temperature bath. The water was stirred using a Teflon-coated magnetic stirring bar. Ten minutes prior to sampling, stirring was ceased to allow any solid phases to settle. The water temperature was controlled by a constant-temperature water bath (Neslab, model RTE-101) recirculated through a copper coil in the water bath. The temperature was measured with a mercury thermometer (± 0.1 °C). Approximately 100 mg of 2,4-dinitrotoluene (Aldrich, >99.5%) was placed into the water and allowed to mix for 1 week. Military-grade TNT (re-crystallized three times, >99.5%) was used with about the same starting conditions as the DNT.

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All volumetric measures were first determined gravimetrically (± 0.00001 g) and then converted to volumetric values with density values at 22.8 °C. Water samples (~1 mL) were collected by disposable pipet and placed into a 10-mL vial containing about 6 mL of deionized water to limit precipitation, especially from the higher-temperature conditions. To determine whether any chemical residue remained in the pipet, about 1.5 mL of acetonitrile was pulled in and then placed into a 2-mL autosampler vial for quantitation. Three water and three acetonitrile wash samples were obtained at each temperature. The temperature was started at the low end, ramped up to the top end, and then returned back to the low end. The solution remained at the desired temperature for 2–7 days before samples were taken. Each DNT sample was analyzed in duplicate, and each TNT sample was analyzed in triplicate.

The water samples were analyzed by RP-HPLC using a Waters 600E system controller, Waters 717 plus autosampler, and Waters 996 photodiode array. Samples (10 μ L) were injected into Brownlee Spheri-5 RP-18 5 μ m 4.6 \times 250 mm column and eluted with a 65:35 methanol/water run in isocratic mode. The photodiode array was run in scan mode, with accumulation of all peaks found from 230 to 400 nm for the elution time of 2,4-DNT or 2,4,6-TNT.

The acetonitrile wash sample was quantified with a 1- μ L injection into an HP 6890 gas chromatograph equipped with a micro electron capture detector and a 0.53 mm \times 6 m RTX 225 0.1- μ m film thickness column. The split/splitless injector was programmed for a 220 °C inlet temperature and a starting column temperature of 100 °C for 2 min, which was ramped to 200 °C at 10 °C/min and then held for 7 min.

Results and Discussion

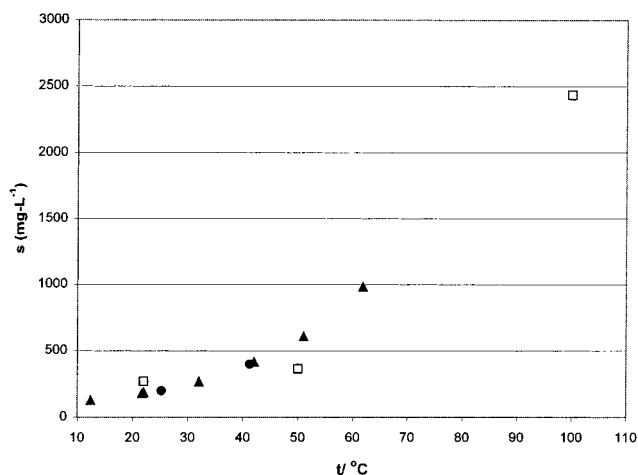
Tables 1 and 2 show the solubility summary data for DNT and TNT, respectively. Although the total (sum of water sample and acetonitrile wash) appears to be larger than the water sample only for each temperature, there is no statistically significant difference ($p < 0.05$). The small variances in both the water and the acetonitrile rinse samples give confidence that crystalline solids were not collected during sampling. Figure 1 shows the total solubility values for DNT as compared to the Army Materiel Command¹⁰ data. Data from this study show very different results from the Army data, with values 30% less at 22 °C and 65% greater at 50 °C. Figure 2 compares the TNT results from this study to those of Ro et al.,⁷ Spanggord et al.,¹¹ and Taylor and Rinkenbach.⁶ Results from this work

Table 1. Solubility of 2,4-DNT [s/(mg/L)]

T (°C)	water plus CH ₃ CN rinse		water sample only		approach
	mean	SD	mean	SD	
12.4	130	3.0	129	2.9	rising
22.0	189	6.1	188	5.3	rising
21.7	183	4.8	182	4.2	rising
32.0	270	1.3	269	1.1	rising
42.0	418	1.3	416	1.2	rising
51.0	610	1.9	608	1.8	rising
61.8	983	5.7	975	8.5	rising
41.2	400	1.7	397	0.8	falling
25.2	200	2.3	199	2.2	falling

Table 2. Solubility of 2,4,6-TNT [s/(mg/L)]

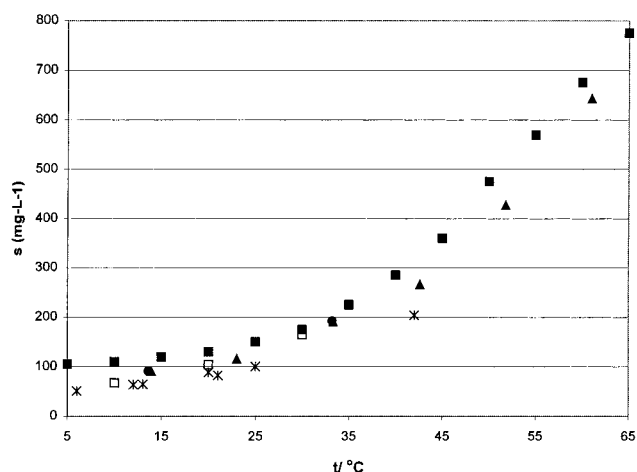
T (°C)	water plus CH ₃ CN rinse		water sample only		approach
	mean	SD	mean	SD	
13.9	91	7.9	86	1.8	rising
23.0	116	2.4	115	2.1	rising
33.3	191	0.7	191	0.5	rising
42.6	266	0.6	266	0.7	rising
51.8	428	3.7	427	3.4	rising
61.0	643	3.4	641	4.6	rising
33.2	192	8.0	191	6.8	falling
13.6	90	1.3	90	1.3	falling
13.6	92	1.0	92	1.0	falling

**Figure 1.** DNT solubility: (□) Army Materiel Command (1971); (▲) this study, rising to temperature; (●) this study, falling to temperature.

show TNT values consistently less than those of Taylor and Rinkenbach⁶ but greater than those of Ro et al.⁷ The data are very consistent with data reported by Spanggord.¹¹ For both DNT and TNT, visible precipitation occurred in the sampling pipet in the short time during transfer to the vial for only the >60 °C conditions.

Conclusions

The aqueous solubility of DNT and TNT was measured by direct sampling of a suspension of crystalline material in deionized water. Filtration of the samples was not performed because of concerns with loss of analyte on filter media. The acetonitrile rinse of the pipets shows that small residues remained in the pipets, but the loss was not statistically significant when compared to sampling and analytical errors. The solubility data for DNT reported here are very different from previously reported values. However, the values were repeatable when rising-to-temperature and falling-to-temperature conditions are compared. The TNT data are consistent with previously reported data,

**Figure 2.** TNT solubility: (■) Taylor and Rinkenbach (1923), interpolated data; (▲) this study, rising to temperature; (●) this study, falling to temperature; (*) Ro et al., 1996; (□) Spanggord, 1983.

bridging a gap between two data sets and very close to one other.

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