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Nuclear Magnetic Resonance Analysis of Total TNT Concentration in NESST Formulations

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The method is presented for the accurate determination of trinitrotoluene (TNT) concentration in NESST (nonhazardous explosive for security training and testing) samples. The technique involves chloroform solvent extraction of sand-adsorbed TNT, followed by quantitative analysis using liquid state carbon-13 nuclear magnetic resonance (NMR). The concentration of TNT is determined by comparison of integrated peak intensities using an appropriate reference compound. Samples # KTN-01-AA and # N-01-AA were found to contain 7.1 ± 0.2% TNT and 5.3 ± 0.2% TNT, respectively.

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NUCLEAR MAGNETIC RESONANCE ANALYSIS OF TOTAL TNT CONCENTRATION IN NESST FORMULATIONS

Abstract:

We are currently developing nuclear quadrupole resonance (NQR) methods for the detection of trinitrotoluene (TNT) in anti-personnel land mines. Much of this effort focusses on understanding and improving the limits of TNT detectability, and requires extensive use of NESST (Nonhazardous Explosive for Security Training and Testing) formulations. The concentration of TNT present in the NESST material must be accurately known in order to make these assessments. We have developed a method for determining the total TNT concentration in NESST formulations to within ± 0.2 weight percent. This technique involves solvent extraction of adsorbed TNT from the sand substrate of the formulation, followed by quantitative analysis using liquid state carbon-13 nuclear magnetic resonance (NMR) analysis. The two NESST formulations which were analyzed contained nominal TNT concentrations of 5-6% (sample # N-01-AA) and 7-8% (sample # KTN-01-AA); they were found, respectively, to contain 5.3 ± 0.2% TNT and 7.1 ± 0.2% TNT by weight.

Procedure:

1. 200 ml of chloroform (Fisher Brand HPLC Grade) was added to 100.0 g of NESST TNT sample # KTN-01-AA in a 1 liter beaker. The mixture was stirred vigorously at room temperature for 10 min, then allowed to settle for several additional minutes. The chloroform was decanted and gravity filtered (15 cm. Fisher Brand quantitative ashless filter paper) into a separate 2 liter Erlenmeyer flask, yielding a clear, light yellow solution. Six additional 200 ml chloroform extractions were performed on the sample, and combined in the Erlenmeyer flask.

2. The filter paper and filtrate were extracted (3 x 100 ml) by slowly pouring fresh chloroform around the top edges of the filter paper. These extracts were combined with the previous chloroform extracts.

3. The extracted sand and filter paper were allowed to air dry overnight at room temperature, then placed under vacuum for 16 h to remove traces of chloroform. The residual insoluble material remaining on the filter paper surface was carefully scraped, and combined with the extracted solid material. The weight of the remaining dried solid was found to be 92.8 g. A second series of chloroform extractions (7 x 200 ml) and a third series of acetone extractions (7 x 200 ml) on the remaining 92.8 g of sand yielded no additional weight loss.

4. The combined chloroform extracts were stripped using a water-aspirated rotary evaporator and 250 ml round bottomed flask. The chloroform was distilled until a total volume of approximately 15 ml remained; the concentrated chloroform / TNT solution was then transferred to a 25 ml volumetric flask. The 250 ml round bottomed flask

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was rinsed (4 x 2 ml) with fresh chloroform, and combined with the contents in the volumetric flask.

5. The 7.2 g of crude extract was analyzed to determine the quantity of pure TNT in the original 100.0 g of NESST sample. This was accomplished using quantitative liquid state carbon-13 nuclear magnetic resonance analysis. In this method, a known amount of an appropriate reference compound is added to the crude TNT / chloroform solution, and the quantity of TNT present is determined by comparison of integrated peak intensities with the reference compound.

6. The reference compound selected for quantitative carbon-13 NMR analysis of TNT was acetonitrile, CH_3CN. Acetonitrile contains one methyl and one nitrile carbon, and therefore yields a simplified carbon-13 NMR spectrum. The methyl carbon of acetonitrile is scalar coupled to three directly bonded hydrogen nuclei, and therefore yields a quartet in the proton-coupled carbon-13 spectrum. The methyl scalar couplings of acetonitrile are J_{CH} = 133 Hz, and the quartet is centered at a chemical shift of $\delta = 1.7$ ppm ($CDCl_3$). In particular, there is no overlap of the acetonitrile methyl quartet with the methyl quartet of TNT at $\delta = 13.8$ ppm (J_{CH} = 134 Hz). This is desirable because the relative quantities of acetonitrile and TNT can be simply determined from the integrated intensities of the respective methyl quartets if quantitative conditions of the NMR experiment are maintained. In addition, the methyl carbons of both acetonitrile and TNT are characterized by relatively short T_1 spin-lattice relaxation times (which ultimately govern the time necessary for quantitative NMR analysis). Based upon peak intensity vs. relaxation time measurements, the acetonitrile and TNT methyl carbon T_1's are estimated to be 17s and 23 s, respectively; the aromatic and nitrile carbon T_1's of TNT were not measured, but chemically similar carbon nuclei typically have T_1's in the range of 50-200 s.

The nitrile carbon of acetonitrile does not contain directly bonded hydrogen, and therefore yields a single peak in the proton-coupled carbon-13 NMR spectrum. The chemical shift of the nitrile resonance occurs at $\delta = 117.4$ ppm in deuterated chloroform, which is more than 3 ppm from the nearest (aromatic) carbon resonance of TNT. Because neither carbon resonance of acetonitrile overlaps with any of the TNT resonances, either could be used for quantitative NMR analysis. We have chosen to utilize the methyl resonances of acetonitrile and TNT because of their shorter T_1 relaxation times.

7. 1.417 g (0.0345 mol) of acetonitrile (Sigma-Aldrich, HPLC grade, 99.9+%) was added to the 25 ml volumetric flask containing the concentrated chloroform / TNT solution. Assuming the extracted TNT is reasonably pure, this quantity of acetonitrile will yield a reference methyl carbon peak intensity approximately equal to that of the TNT methyl carbon. Additional fresh chloroform was added to the volumetric flask in order to bring the volume to the 25 ml mark.

8. A 10.0 ml aliquot of the TNT/acetonitrile/chloroform solution was removed from the 25 ml volumetric flask (via syringe) and placed in a 20 mm O.D. NMR tube.

A carbon-13 NMR spectrum (Larmor frequency = 75.5 MHz) was obtained at room temperature on the TNT/acetonitrile/chloroform solution using a Bruker MSL 300 NMR spectrometer equipped with a 20 mm broadband double resonance liquid state probe. A single π/2 radiofrequency pulse (10 μs) was used for each data acquisition, followed by a relaxation delay of 180 s. The 20 mm NMR tube was not spun in the static magnetic field in order to avoid vortexing of the solution.

9. Figure 1 shows the carbon-13 NMR spectrum obtained from the TNT/acetonitrile/chloroform solution after 868 scans. The integrated intensities of each of the chemically distinct carbon nuclei of TNT and acetonitrile are listed below the peaks. In particular, the intensities for the methyl quartet of TNT ($\delta = 13.8$ ppm) and acetonitrile ($\delta = 1.7$ ppm) are 1.56 and 1.72, respectively. This yields a molar ratio of TNT:acetonitrile equal to 0.91.

10. The quantity of acetonitrile in the NMR tube from which the spectrum of Figure 1 was taken is equal to $10/25 \times 1.417$ g = .567 g (0.0138 mol). The mass of TNT in the NMR tube is thus $0.91 \times 0.0138 \times 227.13$ g TNT/mol = 2.85 g TNT/10 ml solution. The total mass of TNT extracted from the original 100.0 g of material is therefore $2.85 \times 25/10 = 7.1$ g TNT. This is only 0.1 g less than the total mass extracted from the original 100.0 g of NESST material, suggesting that the purity of extracted TNT in this sample is relatively high. The absence of *any* peaks in the carbon-13 spectrum which are not attributable to either TNT or acetonitrile is consistent with this observation.

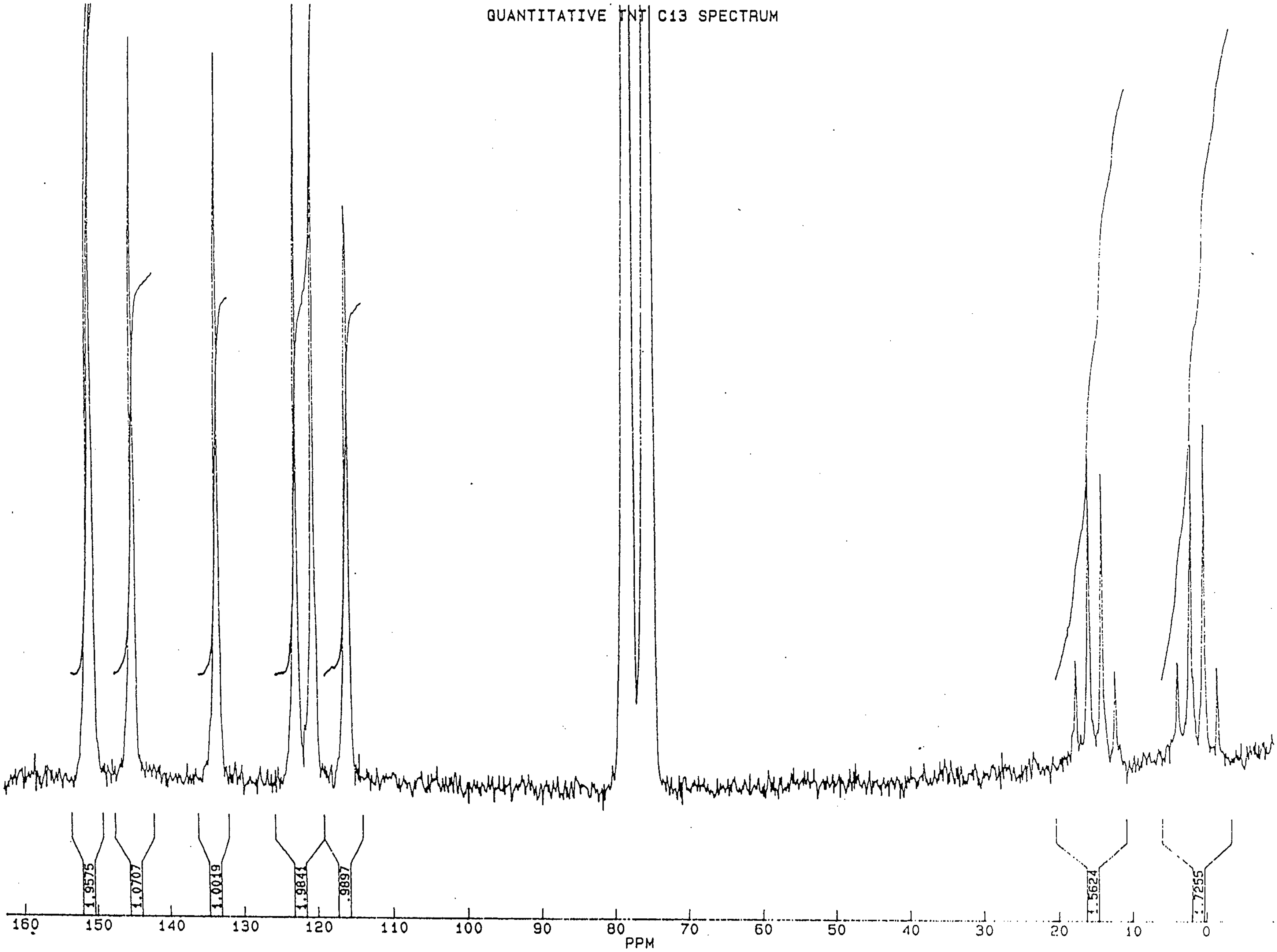
11. We estimate that the errors associated with sample weighing, volume measurement, and NMR peak integration yield an uncertainty of no more than ± 0.2g in the measured mass of extracted TNT in this sample.

12. We conclude that NESST sample # KTN-01-AA contains 7.1 ± 0.2% TNT by weight.

13. An identical analysis of NESST sample # N-01-AA (nominal TNT concentration of 5-6%) resulted in a measured TNT concentration of 5.3 ± 0.2% by weight. In this case, the mass of crude chloroform extract was identical (within experimental limits of error) to the mass of TNT as determined by carbon-13 NMR analysis, and no carbon peaks attributable to impurities were observed. These results evidence the high purity of the adsorbed TNT in this sample.

14. We acknowledge Dr. John Kury of Lawrence Livermore Laboratory for providing specimens of the NESST materials.

Figure 1


QUANTITATIVE TNT C13 SPECTRUM