BOUND AND FREE MOISTURE IN EXPLOSIVES AND PLASTICS*

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ABSTRACT

Proton NMR of Triaminotrinitrobenzene (TATB) and its plastic bonded derivatives reveals a Pake doublet spectrum with a superimposed mobile water peak. Mobile water concentrations as low as 0.25% can be readily measured whereas lower concentrations become more difficult because of integration and signal to noise problems. We have not been able to sort out rigidly bound water from TATB protons. Care must be taken to eliminate materials from the NMR probe that could contribute to the water resonance. In particular teflon tape has been found to contribute a strong mobile water resonance which overlaps that measured for TATB.

INTRODUCTION

We are interested in measuring the total water contained in organic solid materials and the distribution of this water between mobile and tightly bound species. Presumably this distribution will allow predictions of the availability or potential release of water to the surroundings.

Proton NMR not only has the potential for quantitatively measuring the total water content via a measurement of the water protons, it also has the potential to distinquish, by means of line widths, the type of water, i.e., bound or mobile, being measured.

Proton NMR spectra of solids are usually interpreted in terms of Pake's work on gypsum[1], $CaSO_4 \cdot 2H_2O$. His studies revealed that for single crystals with fixed waters of crystallization the proton spectrum can be explained in terms of a classical magnetic dipole interaction between the two protons. The quantum mechanical interpretation of the dipolar interaction of two protons results in a doublet spectrum, the Pake doublet, which extends over 40KHz. The separation of the Pake doublet for a single crystal exhibits a dependence on the orientation of the crystal with respect to the magnetic field. For a powder sample, the resonance is broader and the angular

dependence lost. For water molecules with free rotational movement, however, the resonance does not exhibit the doublet structure and the line width is an order of magnitude narrower.

There are two relaxation times, the spin-lattice relaxation time, T_1, and the transverse relaxation time, T_2, which must be mentioned. The spin lattice relaxation time determines how often the total magnetization can be faithfully measured by a $\pi/2$ radiofrequency pulse. It will take $\sim 5T_1$, for the magnetization to reestablish itself completely after a $\pi/2$ pulse. Each proton species will have its own T_1 and the longest T_1 determines how often the $\pi/2$ pulse can be repeated. For solids T_1 can be minutes or even hours and is usually determined by paramagnetic impurities. The transverse relaxation time, T_2, is a measure of the line width in the frequency domain and determines the rate at which the NMR signal decays after a $\pi/2$ pulse. T_2 thus determines how rapidly the NMR signal must be sampled in order to faithfully reproduce the signal. For solids T_2 is of the order of microseconds and for liquids milliseconds.

A solid of particular interest to us is triaminotrinitrobenzene (TATB) and its plastic bonded (with Kel-F) derivatives. TATB exhibits limited solubility in even the best of solvents, presumably due to its high order of internal hydrogen bonding and therefore methods capable of examining the solid are desired. At present, water content of TATB is measured by a Karl Fischer titration after an exhaustive water extraction by methanol using a blender. Although this method is the method of choice for the absolute determination of water[2], it requires a typical sample/analysis sequence which takes time, it does not distinquish between bound and free moisture, and one must assume that all water present in TATB is extracted without creating water from the decomposition of the explosive during the blending cycle.

METHOD
Experimental NMR Requirements for Accurate Area Measurements

We have been able to measure the proton spectrum of solid TATB Fig. 1 with a spectrometer built for solids work by Sandia National Laboratory, Livermore. In contrast to a high resolution proton spectrometer, which cannot be used for these measurements, the Sandia instrument has the necessary rf power and response time to observe spectra with widths of 40KHz or more. Because of the wide NMR line widths, the free induction decay (FID) observed after a $\pi/2$ rf pulse decays very rapidly with a time constant of T_2. In order to obtain a faithful reproduction of the absorption it is necessary to obtain as many digitized points as possible during the initial decay. The Sandia instrument was set to digitize the signal at a rate of 1 or 2μs/point.
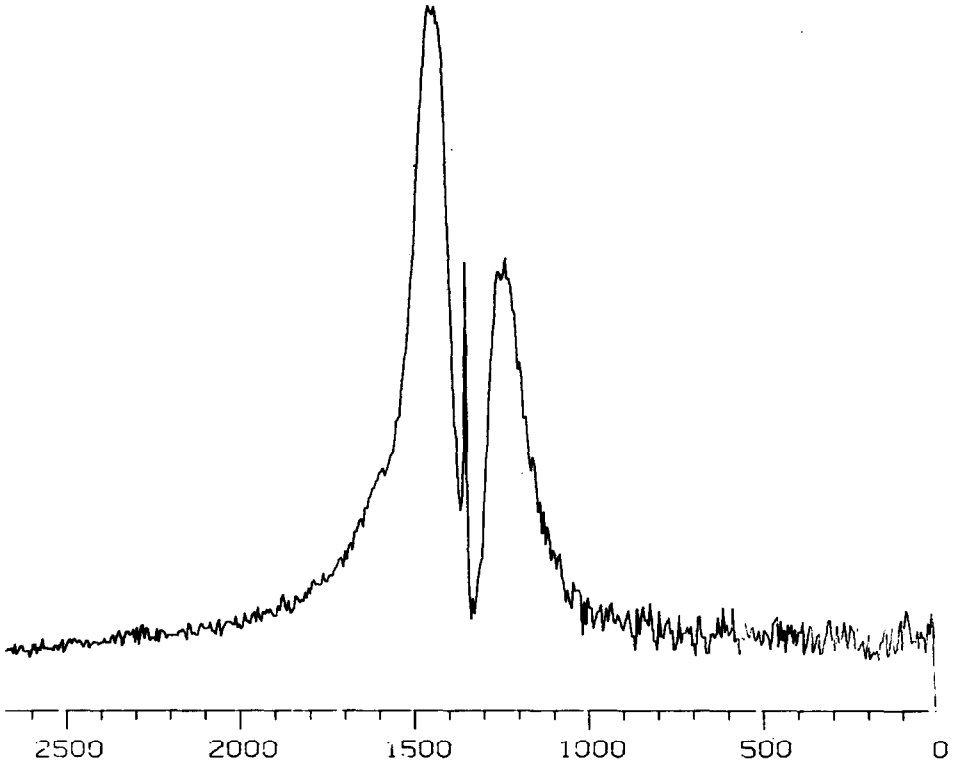
Fig. 1. Proton spectrum in PPM of PBX 9502 (TATB with 5% Kel-F) obtain with a sweep width of 500 KHz, a recycle time of 100 sec, at a frequency of 186.5 MHz, and 100 scans.

For our experiments, the data for one FID was gathered in a storage oscilloscope and then transferred to a computer for signal averaging and subsequent processing.

We have found it necessary to sweep either 250 or 500 KHz in order to obtain a flat base line on either side of the absorption peaks-the Pake doublet plus superimposed mobile water peak. The flat base line is required for proper integration of the total signal.

Spin lattice relaxation times of protons in solids, which determines how fast signal enhancement can be performed, are appreciably longer than those of liquids. In addition, different sample preparations can vary appreciably from one another depending on their paramagnetic impurity content. Usually the higher the purity of the sample, the greater the T_1 value. Figure 2 illustrates the proton spectrum acquired with a very short recycle time of 75 msec. The sharp peak is mobile water whereas the TATB protons have
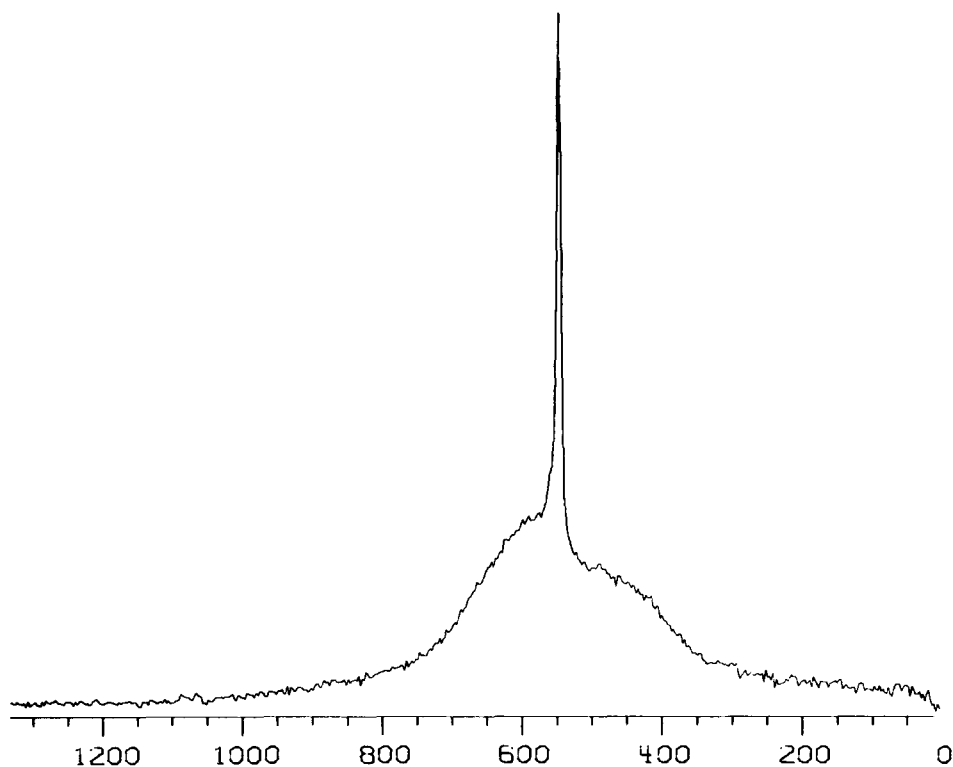
Fig. 2. Proton spectrum in PPM of PBX 9502 obtained with a sweep width of 250 KHz, a recycle time of 75 msec, and 1000 scans.

"disappeared" into the broad lump. A spectrum obtained with a more "normal" liquid recycle time appears in Fig. 3. This spectrum can be compared with that of Fig. 1. Note that the intensity of the Pake doublet is less for the 10 sec recycle delay spectrum than the same spectrum with the longer recycle delay, 100 sec. Fig. 1. This indicates that this spectrum, Fig. 3, has been accumulated faster than at least 5 T_1 and will yield incorrect area ratios. Either T_1, can be determined by conventional means or the recycle delay time increased until the spectral area is constant.

Once spectra are obtained which accurately reflect proton concentrations, i.e., with a recycle delay of at least $5T_1$, it is necessary to obtain integrals of the total proton area and the mobile proton (water) area. The fact that the mobile proton peak resides on a sharply, sloped region of the Pake doublet, Fig. 1, presents some difficulties in accurately measuring its area. We have tried three different integration methods: intergration with
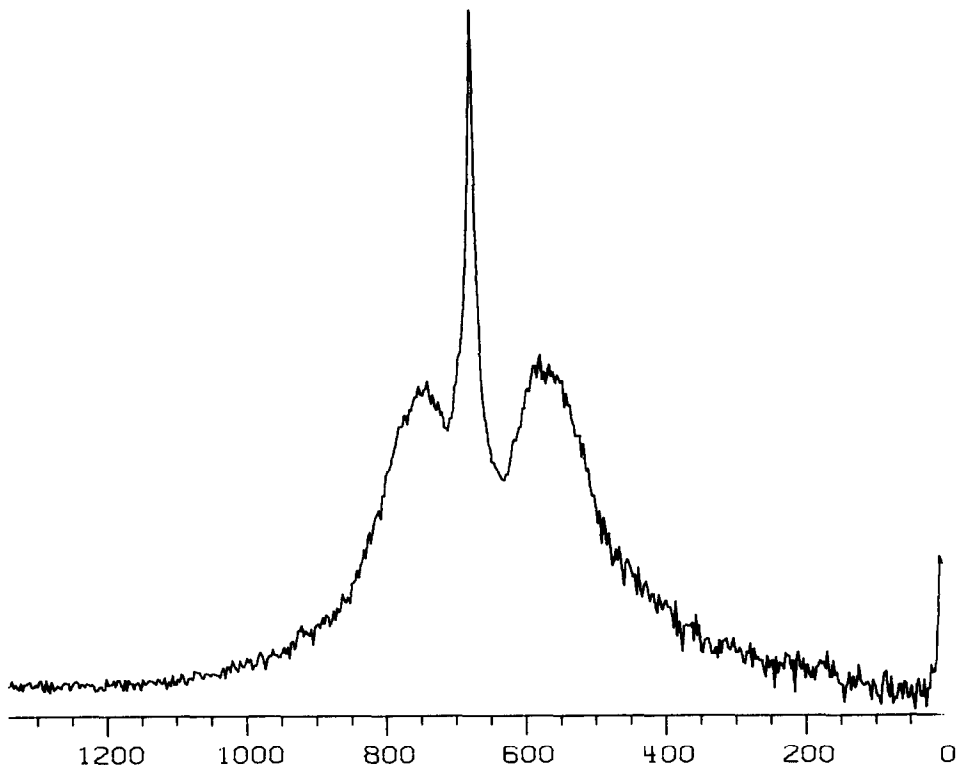
Fig. 3. Proton spectrum in PPM of PBX 9502 obtained with a sweep width of 250 KHz, a recycle time of 10 sec and 100 scans.

normal computer software (Nicolet Magnetics Corp.), cut and weigh techniques, and an interaction method[3] which calculates the correction required to straighten the base line on either side of a narrow region of the mobile water peak. The latter method has been found to be more accurate and/or less tedious than the other two.

Artifacts

    In addition to obtaining an accurate proton counting by proper choice of recycle delay times, sufficient rf power to span the spectral width, use of a fast digitizer etc., it is necessary to avoid probe contaminants which can contribute to the mobile water. For instance, our probe design uses a Helmholz coil which requires that the sample lie on its side. We initially used glass tubes closed with teflon tape and detected in the tape a mobile water signal larger than that exhibited by our TATB samples. We subsequently stoppered the glass tubes with a glass plug. In addition, it was necessary to

flow nitrogen at a rate of 55 SCFH (1560 SLH) to removed moisture from the
probe which also contributes to the mobile water peak. Probe contaminants
could contribute to the broad TATB protons. A blank spectrum obtained without
TATB indicated no appreciable signal.

Water Measurements in Solid TATB

With the NMR solids instrument designed and built by Sandia we can set the
following limits for detection of mobile water in solids

$\qquad$ 1% or higher : relatively easy

$\qquad$ 0.25 to 1.0% : without too much difficulty, requires 2-3 hours of
$\qquad\qquad\qquad\qquad$ averaging

$\qquad\qquad$ <0.25% : difficult - overnight averaging.

It appears the principle problem is that for very low water content, the
mobile water peak becomes lost in the strong Pake doublet signal Fig. 4. A
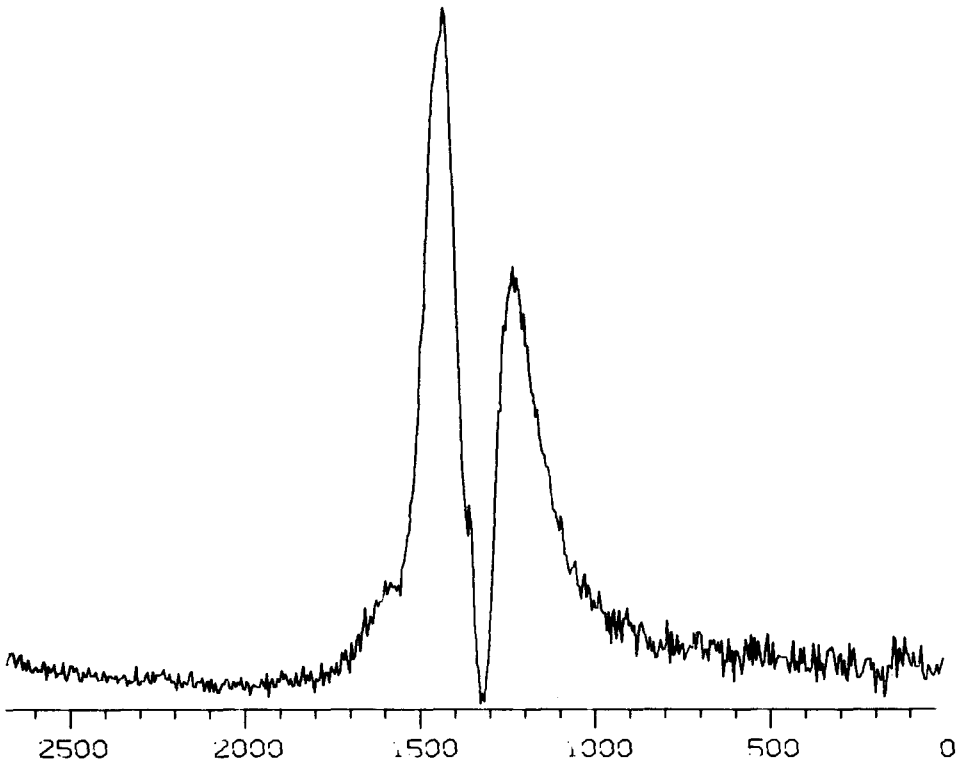

Fig. 4. Proton spectrum in PPM of chips of a tablet of PBX 9502 obtained
with a sweep width of 500 KHz, a recycle time of 100 sec and 100 scans.

possible approach to this problem would be to do peak subtraction of a standard water-free TATB spectrum from a low water content spectrum. The accuracy of this method would have obvious limitations, i.e., subtraction of two large peaks to yield a small peak.

We have made (mobile) water determinations on a number of plastic bonded TATB samples which have previously been analyzed by a Karl Fischer procedure at Pantex[4] and one TATB preparation that had been analyzed for water by a thermogravimetric technique. In all cases our values are higher than those reported by Pantex, Table 1. One possible reason for this bias could be too short a recycle time which would tend to increase the water content.

TABLE 1

Water Content of TATB type Explosives Measured by NMR, Karl Fischer Titration, and Weight Loss on Heating.

	NMR	KF	WT. LOSS
PBX 9502-006	0.27 0.48	0.11	---
PBX 9502-012	0.34 0.28	0.18	---
PBX 9502-Tablet	0.04	0.32	---
PBX 9502-Tablet 1 week at 70 C	0.19	0.02	---
TATB B630	0.37	---	0.30

Our initial object was to find a method that would allow us to measure the water content in solids in the 0.2% or less range without standards and be able to distinquish between free and bound water. This preliminary report indicates that NMR can measure free water in solids at the 0.25% level, but in the chosen case, TATB, cannot distinquish bound water from amine protons. We have not, as of yet, been able to verify how accurate our measurements are. In particular, our results do not yet agree with the Karl Fischer titration values. Further data gathering, experience with integrating the small water peak in the presence of the large Pake doublet, and more information about the relaxation properties of these compounds will hopefully resolve any discrepancies.

The moisture content of TATB below 0.25% should be readily measureable by NMR with the use of standards. Figure 2 illustrates how the mobile water can

be separated from the Pake Doublet if short recycle times are used. Accurate standards should allow a lower limit of perhaps 0.02%.

Appendix

Method of Calculating Weight Percent Water in Plastic Bonded TATB.

$$\text{Wt\% } H_2O = \frac{\text{wt. water} \times 100}{\text{wt. } H_2O + \text{wt TATB} + \text{wt. Kel-F}} \tag{1}$$

We measure (1) Area of water protons
(2) Total proton area

$$\text{Wt. of water} = \frac{k \ (\text{Area of water}) \times (\text{mol. wt } H_2O)}{2} \tag{2}$$

$$\text{Wt. of TATB} = \frac{k \ (\text{Area of TATB protons}) \times (\text{mol. wt. TATB})}{6} \tag{3}$$

where k is an instrumental constant of proportionality. We have assumed that the tightly bonded water contribution to the TATB protons is negligible. Since the fraction of Kel-F used in the various plastic bonded derivatives of TATB is known:

$$\frac{\text{wt. Kel-F}}{\text{wt. Kel-F} + \text{wt TATB}} = \text{Fraction Kel-F} = f \tag{4}$$

$$\text{wt Kel-F} = \frac{(\text{Wt TATB}) \ f}{(1-f)} = \frac{f}{1-f} \ k \ (\text{Area TATB}) \times (\text{mol. wt TATB}) \tag{5}$$

Finally,

$$\text{wt \% } H_2O = \frac{(\text{Area water}) \times 100}{(\text{Area water}) + 258(0.0185 + f/1-f)(\text{Area TATB})} \tag{6}$$

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