

Factors Affecting the NQR Line Width in Nitramine Explosives

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Abstract. A number of factors associated with crystal quality contribute to the nuclear quadrupole resonance (NQR) line width. Imperfections such as dislocations, voids, strain and impurities can be electrical sources that distort the electric field gradient at nearby quadrupolar nuclei and broaden the observed NQR line. We measured the ¹⁴N NQR line widths in powdered samples of the nitramine explosives hexahydro-1,3,5-trinitro-s-triazine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) and 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane and show correlations with sample purity, particle size distribution and density. Cast plastic-bonded explosives containing either RDX or HMX were also studied and their line widths compared with those of the powdered samples.

1 Introduction

Nuclear quadrupole resonance (NQR) is a sensitive tool for probing the electronic environment of a quadrupolar nucleus. Crystal imperfections such as dislocations, voids, stresses and impurities may affect the electric field gradient at enough quadrupolar nuclei to broaden the NQR line in comparison to its width in a more perfect crystal. The various types and amounts of defects found in crystals are a direct result of the manufacturing process used to synthesize and recrystallize the material. High-performance liquid chromatography (HPLC) can identify impurities but cannot distinguish impurities that are embedded in the lattice from those that are not. Only cocrystallized impurities will affect the NQR line width. Optical microscopy can be used to identify and characterize crystalline defects on the microscopic scale. The density of a crystalline material is generally lower when it contains defects and is often used as a measure of the relative defect concentration. But optical microscopy, HPLC and density measurements are performed on milligram sample amounts and several samples must be examined to obtain an accurate representation of the bulk material. Crystal imperfections also affect thermal and mechanical properties and are of great interest to those who manufac-

ture and use energetic materials. The NQR line width is inherently a bulk property and has been used to explain the thermal decomposition of RDX [1]. We are exploring the use of NQR to predict a material's sensitivity to shock and strain [2].

This article focuses on the ^{14}N NQR line widths of energetic nitramines and how they are affected by impurities, particle size and density. We obtained hexahydro-1,3,5-trinitro-*s*-triazine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) and 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20) samples from several foreign and domestic explosives manufacturers and found correlations between their NQR line widths and their densities and/or purities. The ^{14}N NQR line widths in cast plastic-bonded explosives containing the RDX or HMX material were also measured and are compared with those in the powdered samples. ^{14}N NQR data for the amine nitrogens in the cyclic nitramine CL-20 are also reported for the first time.

2 Experimental

Three NQR lines are associated with each crystallographic ^{14}N site and the resonance frequencies are conventionally labeled ν_+ , ν_- and $\nu_0 = \nu_+ - \nu_-$. Nitro nitrogen lines have been observed in RDX at 502, 501, 401, 396 and 381 kHz at room temperature [3]. The nitro nitrogen NQR frequencies of HMX and CL-20 have not been reported but are also expected to lie below 1000 kHz. The tuning range of our NQR probe was 1000 to 6000 kHz and this precluded a study of the nitro nitrogen NQR line widths. The amine nitrogen frequencies of RDX, HMX and CL-20 are in the regions of 5000–5500 kHz (ν_+), 3300–4000 kHz (ν_-) and 1400–1800 kHz (ν_0). The signal-to-noise ratio is roughly proportional to $\nu^{3/2}$ and this favors the ν_+ amine lines for highest sensitivity. However, the NQR frequency varies with temperature and our NQR probe was not temperature-controlled. We measured the widths of the amine nitrogen NQR lines with the smallest temperature coefficients when those coefficients were known.

All NQR measurements were performed at room temperature at the Naval Surface Warfare Center Indian Head Division (NSWC-IH) with a pulse spectrometer that was designed and constructed at the Naval Research Laboratory (NRL). The radio-frequency field in the 20 ml sample coil was such that the free induction decay (FID) signal from a single pulse applied at thermal equilibrium was largest when the pulse width was 70 μs . The amine nitrogen NQR lines in CL-20 were located with a spin-locked spin-echo (SLSE) pulse sequence [4] in which the pulse interval in the pulse train was 1.0 ms. Scans were repeated 64–512 times at intervals of 1 or 2 s, which proved adequate for detecting the CL-20 lines. (The spin-lattice relaxation times for the ν_+ and ν_- lines of CL-20 were measured and range from 2 to 8 s.) The decay times of the SLSE echo envelope under these conditions are longer than 1 s in CL-20 and coherent echo addition is quite effective at improving the detectability of the CL-20 NQR lines.

The spin-lattice relaxation times for RDX are less than 20 ms and RDX line widths could be determined by 1-pulse (FID) or 2-pulse (spin-echo) pulse sequence experiments. Spin-lattice relaxation times for HMX and CL-20 range from

2 to 12 s and the SLSE pulse sequence was used to measure their line widths. Fortunately, the decay times of the SLSE echo envelopes of HMX and CL-20 are approximately 1 s even when the pulse separation within the pulse train is as large as 4 ms. Acquisition began at the midpoint of each 4 ms pulse interval and the 1.95 ms acquisition window provided a resolution which was sufficient for determining the HMX and CL-20 line widths (typically 1 kHz or greater). The SLSE pulse train consisted of 256 pulses and all echoes were coherently summed to improve the signal-to-noise ratio and reduce the signal averaging time.

Sample amounts ranged from 1 to 10 g and the samples were stored in the laboratory for several hours prior to the NQR measurements to ensure thermal equilibration. Each line width measurement lasted from 1 to 10 min and the temperature indicated by a digital thermometer placed near the probe was generally stable to within less than $\pm 0.2^\circ\text{C}$ during each measurement. On the basis of the reproducibility of measurements for selected RDX, HMX and CL-20 samples, we assign an uncertainty of $\pm 10\%$ to all of our line width values.

A Millennium base Waters HPLC system coupled with a Waters 490E programmable multiwavelength UV detector was used for the chemical analysis of the nitramine compounds. 4.6 by 250 mm Waters Symmetry C-18 (5 μm) and Phenomenon Luna C-18 (5 μm) analytical columns were used for those measurements. Densities were obtained with a Micrometrics AccuPyc 1330 helium gas displacement pycnometer.

3 Results and Discussion

3.1 RDX

Karpowicz and Brill [5] reported the ^{14}N NQR frequencies of the amine nitrogens of RDX over the temperature range from 77 to 338 K. The ν_+ line at 3410 kHz has the smallest temperature coefficient ($-75\text{ Hz}/^\circ\text{C}$) between 0 and 40°C . Table 1 shows the width of that line along with the median particle size and HMX impurity concentration for RDX powders manufactured by the Holston Army Ammunition Depot (US), DuPont (US) and SNPE (France). The data for samples nrs. 1–4 suggest that the NQR line width is inversely proportional to the par-

Table 1. ^{14}N NQR line widths at 3410 kHz for RDX from different manufacturers.

Sample nr.	RDX source	Median particle size (μm)	HMX content (%)	Line width (kHz)
1	SNPE	171	<0.1	0.11
2	Holston	155	10–15	0.35
3	DuPont	125	10–15	0.48
4	Holston (re-crys.)	136	<2	0.28
5	SNPE (ground)	5	<0.1	0.15

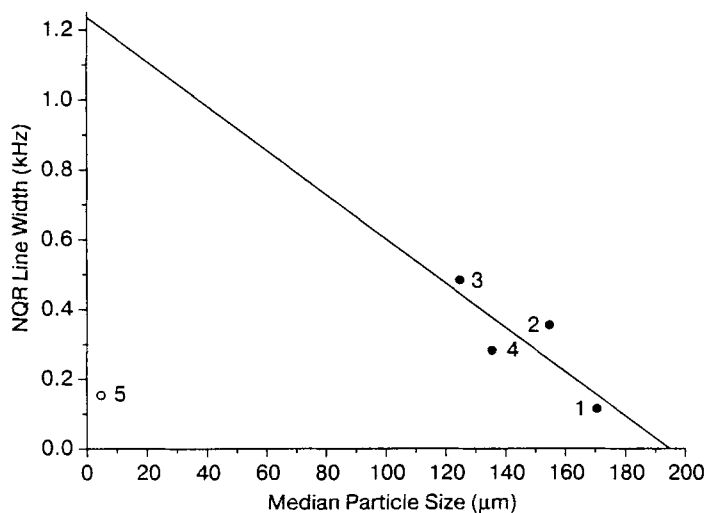


Fig. 1. NQR line width versus median RDX particle size for the samples in Table 1. Solid line is the linear least-squares fit of the solid data points.

ticle size, but the line for sample nr. 5 is much narrower than is predicted by that trend (Fig. 1). Sample nr. 5 (SNPE) was ground in a fluid energy mill process that reduced its median particle size from 171 to 5 μm and its line was probably broadened by stresses produced by milling. The manufacturing and recrystallization techniques used by Holston and DuPont result in much higher HMX concentrations than are present in the SNPE RDX. But recrystallization of Holston RDX by the proprietary SNPE process to produce sample nr. 4 reduced its HMX content from 10–15% to less than 2%, while only reducing the line width from 0.35 to 0.28 kHz. That indicates that most of the HMX in the original Holston material is not inside the RDX lattice and therefore has no effect on the RDX line width. Neither particle size nor purity alone can explain the differences in the NQR line widths in Table 1. A controlled study in which RDX purity and crystal size are independently varied is needed to determine which one is the dominant line broadening mechanism.

Erofeev and co-workers [1] observed a reduction in the RDX line width after recrystallizing samples from a Russian RDX production lot. The NQR line width in the starting material was 0.75 kHz for the same ν_1 line used in our studies and was reduced to 0.45 and 0.30 kHz by rapid and slow recrystallization, respectively. The authors attributed this line narrowing to a loss of impurities. Although they did not determine the impurity types or concentrations, their conclusion is consistent with the dependence of the line width on the HMX concentration that we find in Table 1. The size of the RDX crystals produced by slow recrystallization was 3–5 mm, and by grinding them to approximately 100 μm those authors reduced the line width further to 0.20 kHz. That reduction was attributed to cleavage along dislocations to form smaller crystals. Note that all

Table 2. ^{14}N NQR line widths at 3410 kHz for cast PBXW-108M RDX-based explosives.

Lot no.	RDX source	Line width (kHz)
PBXN1080265	SNPE	0.14
PBXN1080267	Holston (re-crys.)	0.30
PBXN1080268	Holston (re-crys.)	0.26
PBXN1080269	Holston	0.38
PBXN1080270	Holston	0.36

crystal sizes in Table 1 are less than 200 μm and the SNPE RDX line width actually increases slightly when ground. Apparently dislocations are not an important NQR line broadening mechanism for RDX crystals smaller than 200 μm .

NQR line widths for formulated PBXW-108M cast explosives are shown in Table 2. The PBXW-108M formulations contain 82% RDX with 1:1 mixtures of coarse and fine RDX powders to provide good processing characteristics. The quality of an RDX crystal should not change when it is physically mixed with binder material and RDX crystals of different sizes, and a comparison of the NQR line widths in Tables 1 and 2 shows that this is indeed the case. Samples nrs. 1, 2 and 4 of Table 1 are the coarse components of the PBXW-108M formulations in Table 2 and sample nr. 5 is the fine component of the formulation containing SNPE RDX. (Fine-powder samples of Holston and recrystallized Holston RDX were not available for NQR line width measurement.) As would be expected for a 1:1 mixture of coarse and fine powder, the NQR line width of the SNPE RDX formulation (0.14 kHz) lies between those of its coarse (0.11 kHz) and fine (0.15 kHz) powder components. The line widths of the formulations made with Holston and recrystallized Holston RDX are the same as those of their coarse-powder components within the 10% uncertainty range of our measurements. Therefore, the line widths for the fine-powder Holston and recrystallized Holston RDX must be close to those of the corresponding coarse powders.

Table 3 shows line widths in other RDX formulations. C-4 and Semtex-H are plastic military explosives, XM39 and XM43 are low-vulnerability gun propellants and China Type 72 is a landmine. C-4, XM39 and XM43 are US formulations containing RDX and binder. Those formulations probably contain Holston RDX, although the XM43 line width is somewhat larger than those of the other Holston

Table 3. ^{14}N NQR line widths at 3410 kHz for various RDX formulations.

Composition	Origin	Line width (kHz)
C-4	US	0.38
Semtex-H	Czechoslovakia	0.60
China Type 72	China	0.44
XM39	US	0.40
XM43	US	0.60

Table 4. ^{14}N NQR line widths for HMX from different manufacturers.

Source	Med. particle size (μm)	HMX deriv. (%)	Other impur. (%)	Line width (kHz)	
				3623 kHz	3737 kHz
Royal Ordnance	218	0.10	0.77	1.00	0.66
DYNO	339	0.16	0.18	1.25	0.73
Holston	345	0.16	0.08	1.38	0.77
Bofors	323	0.11	0.18	1.51	1.02
Bofors	45	0.09	0.78	1.44	1.14
DYNO	50	0.21	0.22	2.19	1.35
Holston	51	0.44	0.14	3.25	2.13

materials. Semtex-H is a Czechoslovakian composition containing RDX, PETN and binder. The China Type 72 landmine is a mixture of RDX and TNT. The NQR line widths for RDX in the U.S. and foreign compositions all lie within the same range (0.38–0.60 kHz).

3.2 HMX

Landers et al. [6] reported the ^{14}N NQR frequencies of the amine nitrogens of HMX over the temperature range from 77 to 426 K. The ν_- lines at 3623 and 3737 kHz have the smallest temperature coefficients (-48 and -24 Hz/ $^{\circ}\text{C}$, respectively) between 0 and 42°C . Table 4 lists the ν_- line widths, median par-

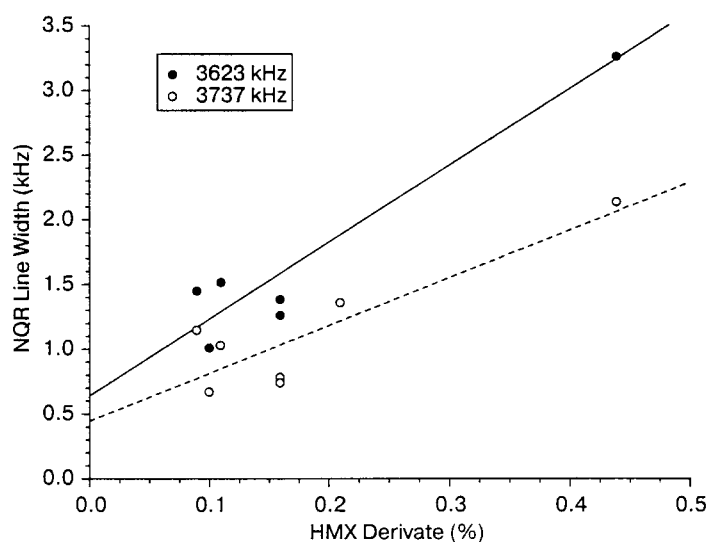


Fig. 2. Dependence of NQR ν_- line widths on HMX lattice impurities. Solid and dashed lines are linear least-squares fits of the solid and open data points, respectively.

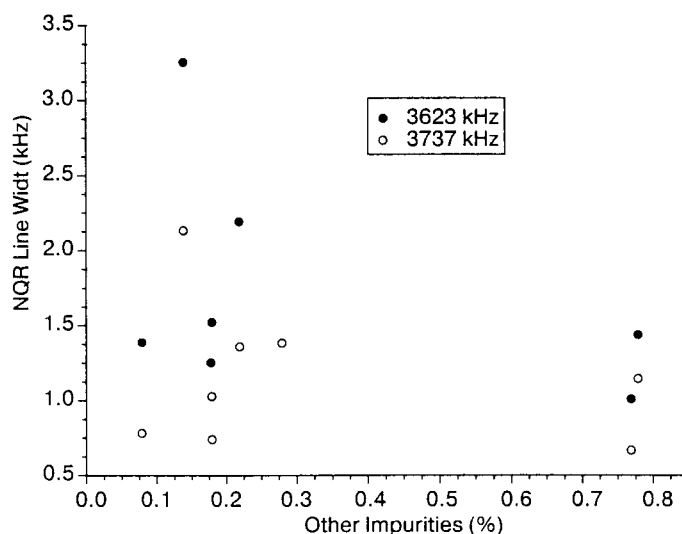


Fig. 3. NQR ν -line widths over impurities that are not embedded in the HMX lattice.

particle sizes and impurity levels for HMX from one U.S. (Holston) and three foreign manufacturers. When samples from the same manufacturer are compared, the sample with the smaller particle size always has the larger NQR line width. However, the correlation between line width and particle size among the different manufacturers is rather poor. An acetyl derivative of HMX was found in all samples and is listed in a separate column in Table 4. The rough correlations between the amount of that derivative and the HMX line widths shown in Fig. 2 indicate that a substantial amount of that derivative is in the HMX lattice. The remaining impurities appear to have no effect on the NQR line widths (Fig. 3) and are probably not cocrystallized with HMX.

The PBXN-110 cast explosives listed in Table 5 contain 88% HMX with a coarse-to-fine ratio of 3:1. All of these explosives were made with Holston HMX and the same binder material but were produced at different times and possibly by different manufacturers. The simulated line width at 3623 kHz for a 3:1

Table 5. ^{14}N NQR line widths at 3623 kHz for PBXN-110 cast explosives containing HMX manufactured by Holston.

Lot no.	Line width (kHz)
PBXN1101117	1.48
PBXN1101205	1.57
PBXN1101264	1.45
PBXN1101637	1.47
PBXN11020095	1.49
PBXN11030201	1.50

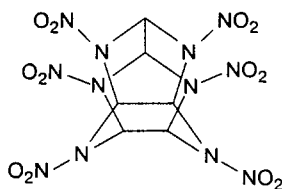


Fig. 4. Chemical structure of CL-20.

mixture of the large- and small-particle Holston powders in Table 4 is 1.57 kHz, which is within 10% of the mean line width of 1.49 kHz for the PBXN-110 formulations. The standard deviation of the PBXN-110 NQR line widths is only 2.8% of their mean, which indicates that there is very little lot-to-lot variation in the HMX crystal quality of these formulations.

3.3 CL-20

CL-20 (Fig. 4), which is also known as HNIW, was first synthesized at China Lake in 1987 and is of great interest to the energetic-materials community because of its high chemical energy and low shock sensitivity, both of which are superior to those of RDX and HMX. It has four polymorphs (α , β , γ and ϵ) that are stable at room temperature and the structures and densities of each have been established by X-ray crystallography [7]. The ϵ polymorph has the highest density and thermal stability.

The ϵ CL-20 crystal is monoclinic with a $P2_1/n$ space group and has four crystallographically equivalent molecules per unit cell. All amine nitrogen sites in the molecule are crystallographically unique, resulting in six sets of NQR frequencies. ^{14}N NQR data for the amine nitrogens of ϵ CL-20 are given in Table 6. All ν_+ and ν_- pairings used to obtain the nuclear quadrupole coupling constants, $e^2qQ/h = 2(\nu_+ + \nu_-)/3$, and asymmetry parameters, $\eta = 3(\nu_+ - \nu_-)/(\nu_+ + \nu_-)$, were confirmed by direct observation of the lines at the corresponding difference frequencies, $\nu_0 = \nu_+ - \nu_-$. We have not assigned the nuclear quadrupole parameters to amine nitrogen positions in the ϵ CL-20 lattice. Nitrogen data in Table 6

Table 6. Room temperature (24°C) ^{14}N NQR data for the amine nitrogens of ϵ CL-20. NQR lines were observed at all difference frequencies $\nu_0 = \nu_+ - \nu_-$.

Nitrogen site nr.	ν_+ (kHz)	ν_- (kHz)	e^2qQ/h (kHz)	η
1	5470	4051	6347	0.4474
2	5410	3960	6247	0.4642
3	5242	3831	6045	0.4689
4	5208	3825	6026	0.4571
5	5207	3746	5969	0.4896
6	5121	3654	5850	0.5016

Table 7. ^{14}N NQR line widths at 5242 kHz for CL-20 from different sources.

Sample nr.	Density (g/cc)	Impurities (%)	Line width (kHz)
1 (production lot)	2.0355	3	2.21
2	2.0226	4	1.95
3	2.0280	2.4	1.71
4	2.0359	0.5	0.82
5	2.0191	5	2.45
6	2.0394	3	3.5
7	2.0430	1	1.18
8 (production lot)	2.0356	0.5	0.69
9	2.0310	1	1.21
10	2.0364	1	0.97

are listed in descending order of the size of the nuclear quadrupole coupling constant.

Ten CL-20 samples were obtained from five domestic sources and one foreign source and data for those samples are given in Table 7. The major difference between each of the samples was in the method of synthesis and recrystallization of CL-20. Samples nrs. 1 and 8 were manufactured on a production scale, while the other eight were made in small-scale pilot plants. The crystal quality of the second (more recent) production lot is superior to that of the first as shown by their NQR spectra at 5207.5 kHz in Fig. 5. The doublet at that frequency is barely resolvable in sample nr. 1. Samples nrs. 6 and 7 have a median particle size of 25–30 μm . The remaining eight samples have a median particle size of

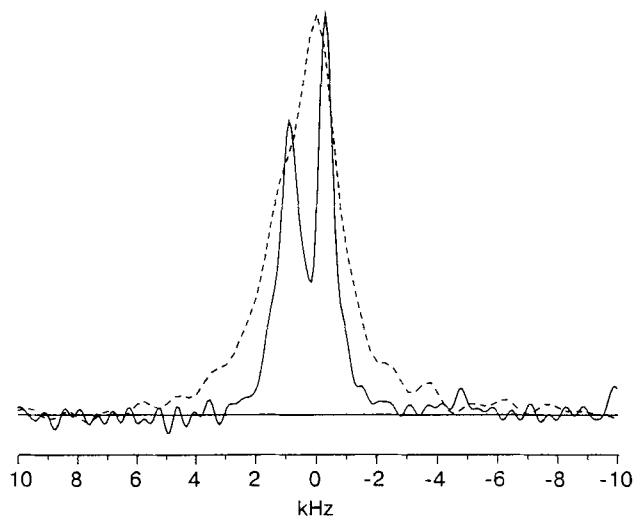


Fig. 5. Room temperature NQR doublet at 5207.5 kHz for two production lots of CL-20. Dashed and solid curves are for samples nrs. 1 and 8, respectively, of Table 7.

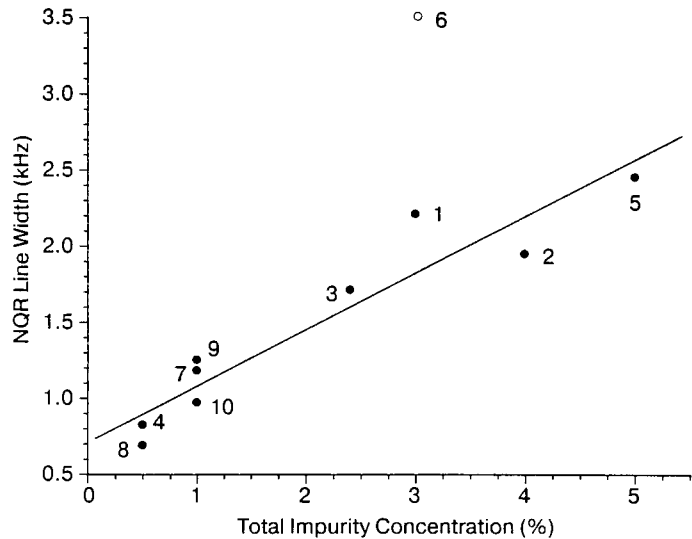


Fig. 6. CL-20 NQR line width at 5242 kHz over impurity concentration from Table 7. Solid line is the linear least-squares fit of the solid data points.

approximately 150 μm . The NQR line at 5242 kHz was chosen for line width comparisons because it was the narrowest ν_+ line that was not part of a doublet and was also free from radio-frequency interference. No explosive compositions were available for NQR measurement.

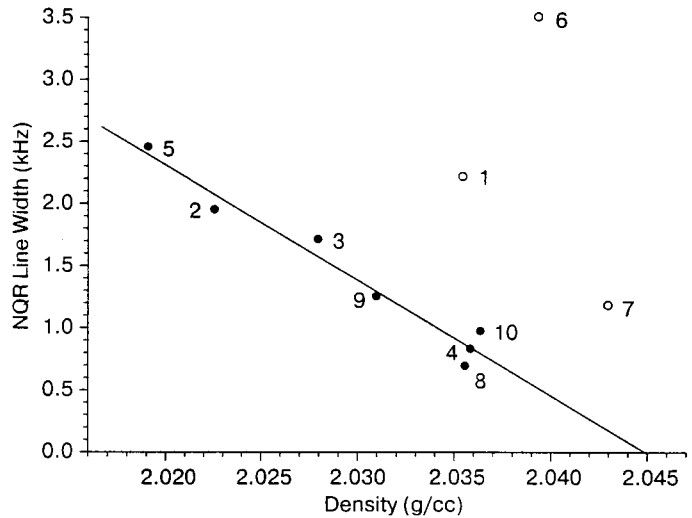


Fig. 7. CL-20 NQR line width at 5242 kHz over density from Table 7. Solid line is the linear least-squares fit of the solid data points.

Figure 6 shows the dependence of the NQR line width at 5242 kHz on the total impurity level. The rather good linear fit indicates that most of the (unidentified) impurities are in the CL-20 lattice. The deviation of the line width for sample nr. 6 from the fit is probably due to its small particle size. Figure 7 shows that there is also a correlation between sample density and NQR line width and it should be noted that extrapolation of the linear least-square fit leads to the CL-20 theoretical density (2.045 g/cm³) for a line width of 0 Hz. The deviations of samples nrs. 6 and 7 from that fit are also most likely due to their small particle sizes. The early production lot sample nr. 1 is also an outlier and that could be due to its poor crystal quality.

4 Conclusions

Many factors influence the NQR line width and even knowing the manufacturing process used to synthesize a product it may be difficult to predict which factor will dominate. Impurities, particle size and density have been shown to affect the NQR line widths of RDX, HMX and CL-20. NQR line widths are probably better indicators of overall crystal quality than any of those properties alone. Finally, our observations confirm that mixing RDX or HMX with binder material to create cast explosive formulation does not change the NQR line widths of the RDX or HMX components.

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