FINAL REPORT

Mixed-Radiation-Field Dosimetry Utilizing Nuclear Quadrupole Resonance

Contract DE-FG02-89ER12890

DOE/ER/12890--3
DE93 010086

Submitted to:

DOE/ER Nuclear Engineering Research Program
Applied Nuclear Sciences

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Argonne, IL 60439

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MIXED RADIATION FIELD DOSIMETRY UTILIZING NUCLEAR QUADRUPOLE RESONANCE

FINAL REPORT

Introduction

This project proposed to develop a novel dosimetry system capable of directly evaluating the chemical/biological damage caused by neutrons, photons, or both in a single measurement. The dosimeter itself was to consist of a small volume of biological equivalent material to be probed for radiation damage with Nuclear Quadrupole Resonance (NQR) techniques. NQR has previously been utilized as a sensitive probe of structural and chemical changes at the molecular level for a variety of organic compounds. The biological equivalent materials used in this study had a density similar to tissue (tissue equivalent), the same atomic components as tissue, and similar molecular configurations. These compositional and structural requirements were very important so that the neutron interactions that occur in tissue also occurred in the dosimeter materials.

The overall objective of this study was to investigate a methodology to perform accurate mixed-field (neutron and photon) dosimetry for biological systems. The specific objectives, as cited in the original proposal, were:

1. Choose a biological material that has an atomic composition suitable for applications as a mixed-field dosimeter, while also providing a simple NQR spectrum and strong signal strength.

2. Characterize the NQR spectral changes of the dosimeter material as a function of photon absorbed dose and energy.

3. Characterize the NQR spectral changes of the dosimeter material as a function of neutron absorbed dose and energy.

4. Characterize the NQR spectral changes of the dosimeter materials in mixed radiation fields delivering known absorbed doses of neutrons and photons at known energies.

5. Optimize the characteristics of this dosimetry system for routine dosimeter applications.

This document reports on work performed during the project period.

1. Dosimeter Material Selection

A number of potential dosimeter materials were examined for their NQR and radiation responses. The initial selection of candidate dosimeter materials was based on the results of a literature review of previously performed NQR spectroscopy and radiation chemistry oriented experiments. The compounds chosen for initial experiments were selected on the basis of the number and type of nitrogen sites in the compound, the resonance characteristics of the compound, and the various types of radiation damage that may be manifest in the material. Each of these materials was experimentally evaluated to determine the strength and lineshape of the ^{14}N NQR signal.

A series of samples were chosen for these studies based upon strong NQR responses, desirable compositions and structural properties. These samples are included in the family of urea derivatives, i.e. each is based on basic molecular units similar to that of urea. The specific materials chosen were:

1. Urea

2. Thiourea

3. Guanidine Carbonate

4. Guanidine Sulfate

Urea provides the simplest molecular form of these compounds and contains two equivalent nitrogen sites, resulting in a strong NQR signal and a simple spectral response. Thiourea also has a simple molecular structure very similar to that of urea except the oxygen atom in urea is replaced by a sulfur atom in thiourea. This change, however, causes the two nitrogen sites to become slightly inequivalent, so that they result in nitrogen resonances at two different frequencies. The resonant frequencies are close enough together that they may be observed simultaneously using pulsed NQR techniques, but must then be deconvoluted to quantify the contributions from each site.

Guanidine carbonate and guanidine sulfate have more complex molecular structures consisting of multiple urea-like molecular units connected by carbonate or sulfate groups, respectively. These materials contain six nitrogen sites, which are typically all inequivalent. In guanidine sulfate the resonance frequencies are in close proximity and may all be observed simultaneously using pulsed NQR techniques. This leads to the more difficult problem of deconvolving six individual signals from the NQR response in order to perform a quantitatively meaningful interpretation. Guanidine carbonate required two pulse excitation and quantification of the spin echo instead of the simpler free induction decay (FID).

This selection of compounds was made in order to take advantage of the similarities in the structural units of each of the compounds while permitting a variation in the level of complexity of the associated bonding structures for different compounds. The chemical structure of urea family compounds is given in Fig. 1. It is expected that the more complex compounds will exhibit greater sensitivity to radiation induced changes because of the greater opportunity for bonding rearrangements. To fully understand these changes, however, it was also necessary to identify the changes that can result in the fundamental molecular units of the compounds, necessitating detailed studies of simple compounds such as urea and thiourea.

Data Analysis Techniques

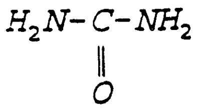
To accurately quantify the spin-spin relaxation times characterizing the FIDs of these materials, several advanced data analysis techniques had to be developed. These included Fourier transform techniques, linear algebra techniques (HSVD), and multiple site nonlinear curve fitting.

In order to quantify spin-spin relaxation times of the FID, nonlinear curve fitting programs were developed. Figure 2 illustrates how the two simple FIDs (the simple exponentially damped waveforms) from different nitrogen sites combine to produce a complex Free Induction Decay. Nonlinear curve fitting algorithms permit the accurate determination of the spin-spin relaxation times as well as the relative weighing of the individual nitrogen sites contributing to the signal for up to three separate sites. For greater than three sites it is very unlikely that a nonlinear curve fitting algorithm will converge on a unique solution. These techniques have proven to be most useful for the analysis of urea and thiourea samples, which have one and two nitrogen sites, respectively.

For sample compounds containing a greater number of sites more elaborate data analysis techniques are required. In order to separate the contributions from the individual sites, the FID is transformed from the time domain, to the frequency domain via Fourier transform techniques. This permits the separation of individual resonant frequencies and consequently the contributions from individual nitrogen sites. Because information of the phase of the signal is lost during data acquisition, it must be resupplied in order to obtain meaningful interpretations from the Fourier transformed data. This requires an additional, and time consuming, step in data analysis. Analyses requiring Fourier transforms are consequently very computational and time intensive operations, but necessary at this point of the research in order to separate contributions from physically different nitrogen sites in guanidine sulfate and guanidine carbonate samples.

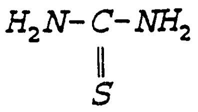
A non-iterative procedure for retrieving harmonics was developed by Kung and co-workers and published in 1983 using state

a. UREA



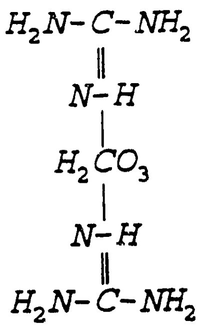
$$\begin{array}{c} H_2N-C-NH_2 \\ \| \\ O \end{array}$$

b. THIOUREA



$$\begin{array}{c} H_2N-C-NH_2 \\ \| \\ S \end{array}$$

c. GUANIDINE CARBONATE



$$\begin{array}{c} H_2N-C-NH_2 \\ \| \\ N-H \\ | \\ H_2CO_3 \\ | \\ N-H \\ \| \\ H_2N-C-NH_2 \end{array}$$

Figure 1.

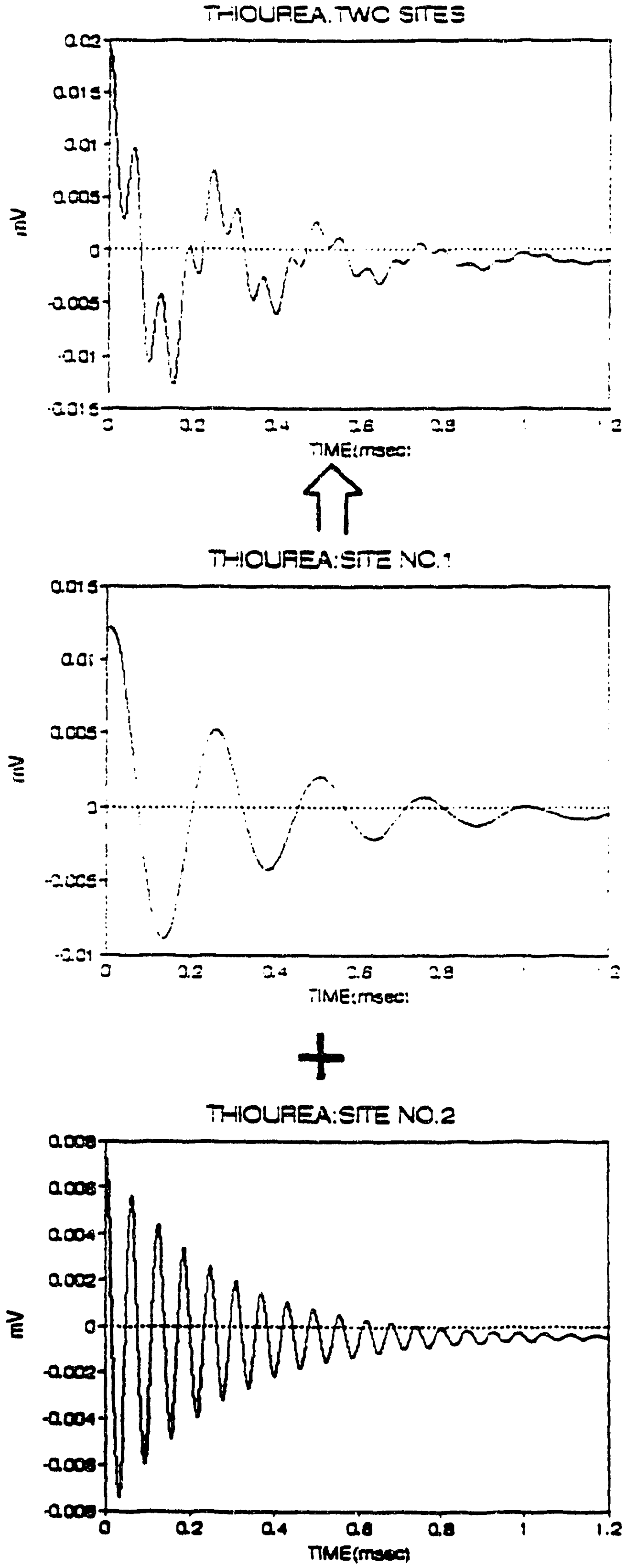

THIOUREA.TWO SITES
THIOUREA:SITE NO.1
THIOUREA:SITE NO.2
mV
TIME(msec)
0.02
0.015
0.01
0.005
0
-0.005
-0.01
-0.015
0.008
0.006
0.004
0.002
-0.002
-0.004
-0.006
-0.008
0.2
0.4
0.6
0.8
1
1.2

Figure 2.

space concepts. This method was implemented for magnetic resonance time domain spectra via linear algebra and published under the name Hankel Singular Value Decomposition (HSVD) by Barkhuijsen and others in 1987. The name Hankel is used because the HSVD method uses a data matrix with Hankel structure: all elements on a cross diagonal (running from lower left to upper right) have the same value. The standard model function

$$v(t) = \sum_{i=1}^{N} A_i \cos(2\pi f_{d_i} t + \phi_i)\, e^{-\frac{t}{T_{2_i}}} \qquad (1)$$

where A_i, f_{di}, ϕ_i ,and T_{2i} are the amplitude, resonance difference frequency, phase, and spin-spin relaxation time, for the *ith* component, respectively. The above equation is modified to

$$x_n = \sum_{k=1}^{K} c_k\, e^{[(-\frac{1}{T_2} + i\omega_k)\Delta t]^n} \qquad (2)$$

where x_n is the nth data point up to the final Nth point, K is the number of signal poles present in the signal (two poles for each exponentially damped sinusoid), c_k is the kth complex coefficient which includes the associated amplitude and phase information. A brief outline of the method is given here. Singular value decomposition of the data matrix is carried out and the resultant matrices are factored into row vectors and column vectors. The resultant matrices give back the signal poles and other magnetic resonance parameters by standard reduction techniques. More information on HSVD can be found in Iselin [1992], Hintenlang et al. [1992], and de Beer and van Ormondt [1991]. General information on SVD can be found in Press et al. [1989] and Lawson and Hanson [1974]. While techniques are available for estimating the parameter errors in SVD analysis, the most useful error analysis is of the errors in the final curve fitting using the Levenberg-Marquart method since the nonlinear least squares curve fit gives the "best" fit [de Beer and van Ormondt, 1991].

It was originally anticipated that most data analysis in this project would involve straightforward quantification of NQR parameters directly from the FID using Fourier transform techniques and nonlinear curve fitting. While this can be done for the simple spectra from urea, other candidate dosimeter materials require more sophisticated data analysis techniques. We have consequently spent a greater effort on the development of data analysis techniques than originally anticipated. Currently, the vast majority of tools required for detailed analysis of the NQR signals were developed and used in routine data analysis. An example of an experimental NQR signal with fitted curve is depicted in figure 3.

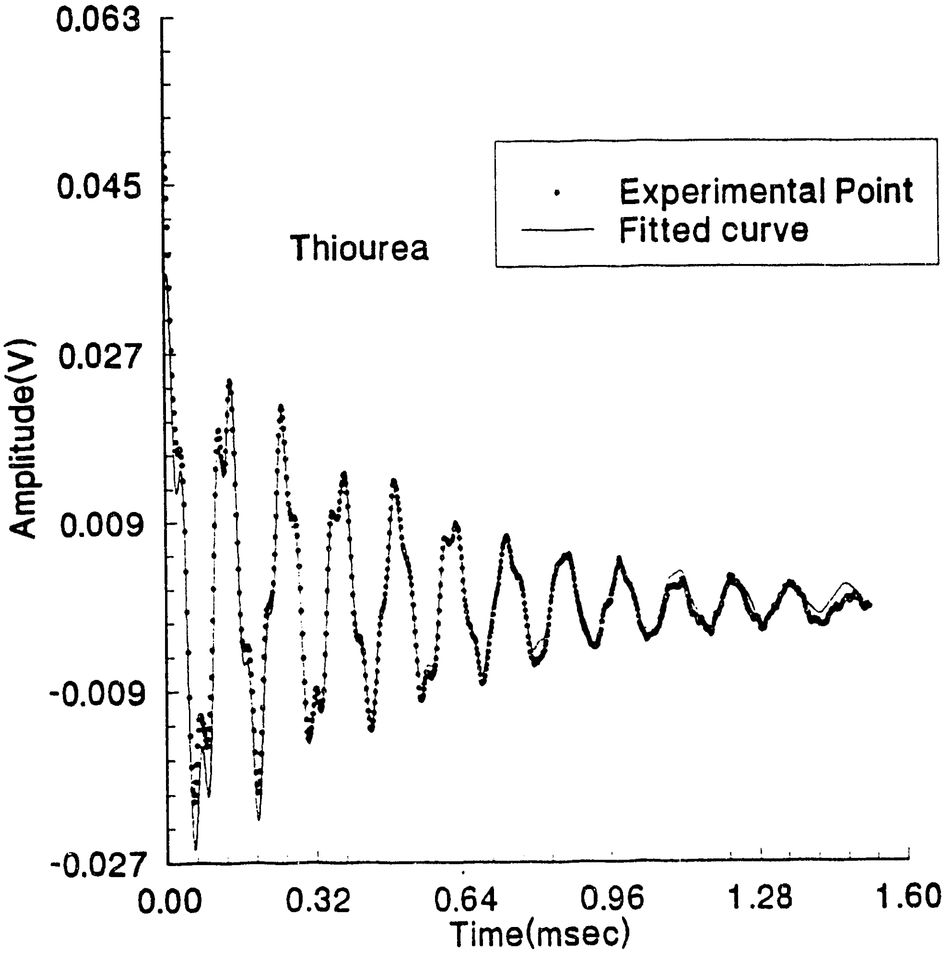

0.063
0.045
0.027
0.009
-0.009
-0.027
Amplitude(V)
0.00
0.32
0.64
0.96
1.28
1.60
Time(msec)
Thiourea
• Experimental Point
—— Fitted curve

Figure 3.0

Dosimeter Materials Radiation Response

To examine the effects of radiation that are similar to those that may be manifest in biological materials it is expected that the sample material should not only be biologically equivalent, but should have as nearly the same chemical composition as biological tissue as possible. Since a major component of all biological systems is water, it is not sufficient to have only a biological based material, such as a crystalline amino acid, present, but water molecules must also be incorporated into the material. These water molecules permit the important contributions of chemical damage that occur through the hydrolysis of water to manifest themselves in the dosimeter.

The response of hydrated samples to irradiation may therefore be expected to be very different from that of the dry, polycrystalline sample of those same materials. This has been demonstrated in all materials for which irradiation studies have been carried out. Urea, thiourea, guanidine sulfate, and guanidine carbonate exhibited very little response to photon irradiation, as expected, when irradiated and observed in a dry polycrystalline form. Hydrated urea exhibited markedly different behavior when similar studies were performed with dry samples. Water added to guanidine carbonate intensified trends identified in the radiation response of dry material. Thiourea and guanidine sulfate react with water and could not be hydrated.

2. Dosimeter Materials Gamma Response

Urea

Dry urea had no changes in NQR parameters when gamma irradiated up to 500 kGy. Hydrated urea provided a clear radiation response for this material to gamma rays. The spin-spin relaxation time (T_2) of hydrated urea exhibited a strong dependence on the delivered gamma dose in the range 0-300 Gy, as shown in Fig. 4. The spin-spin relaxation time decreases roughly exponentially with increasing radiation dose, providing a good correlation between the spin-spin relaxation time and the radiation dose. The precise mechanisms governing these changes are not yet understood and are the subject of continuing investigation.

Thiourea

Thiourea has two non-equivalent nitrogen sites resulting in a more complex FID than urea. (See Fig. 2 for an example of the FID of thiourea.) Samples of thiourea exposed up to 0.5 MGy from ^{60}Co gamma rays have not shown any effect on the NQR parameters.

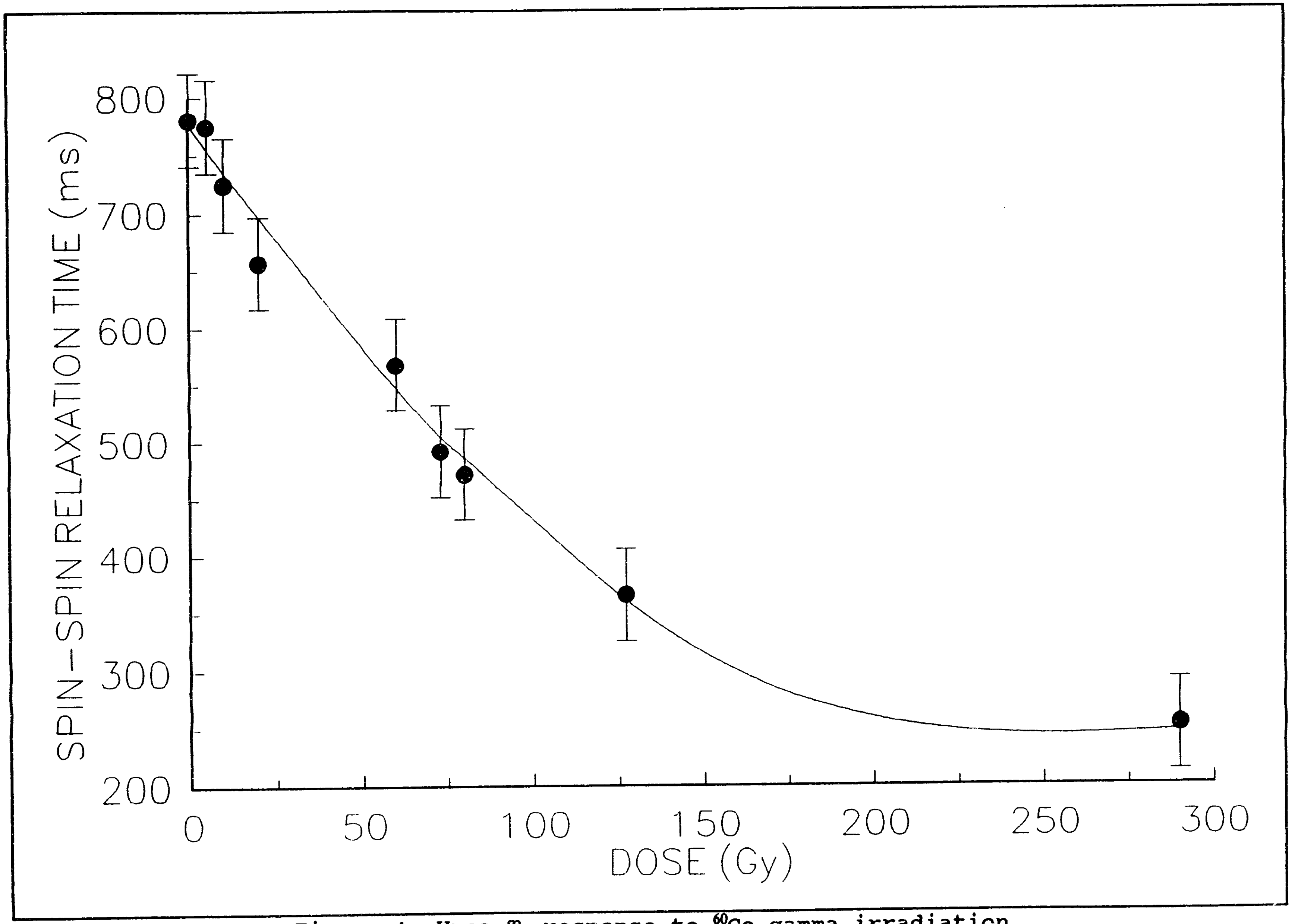


Figure 4 Urea T_2 response to ^{60}Co gamma irradiation

Guanidine Carbonate

The spin echo of guanidine carbonate was analyzed by HSVD after photon irradiation in the 0-5000 Gy range. The samples were dry, hydrated, or with added propanol or butanol. The added water (or alcohol) was to look for indirect effects on the guanidine carbonate from radicals formed, from the solvent, during irradiation. No changes in the NQR parameters were detected except for the following case. With 3 ml water added to a 15 g sample and subsequently irradiated to 5000 Gy, the resonance frequency lowered in the near term and then returned to pre-irradiation levels over the course of several months. These data are reported in Fig. 5.

Guanidine Sulfate

Guanidine sulfate has a more complex NQR spectra than the other compounds discussed thus far. Guanidine sulfate has six resonant frequencies that may all contribute to the NQR signal. The response from the respective nitrogen sites must be separated in order to evaluate the response of the samples to irradiation. The power spectral density Fourier transform (PSD FFT) in the frequency range from 5-40 kHz from the reference frequency is shown in Fig. 6. The complexity of separating these different peaks in the frequency domain led to Mr. Iselin's master's thesis [1992] (see attachments).

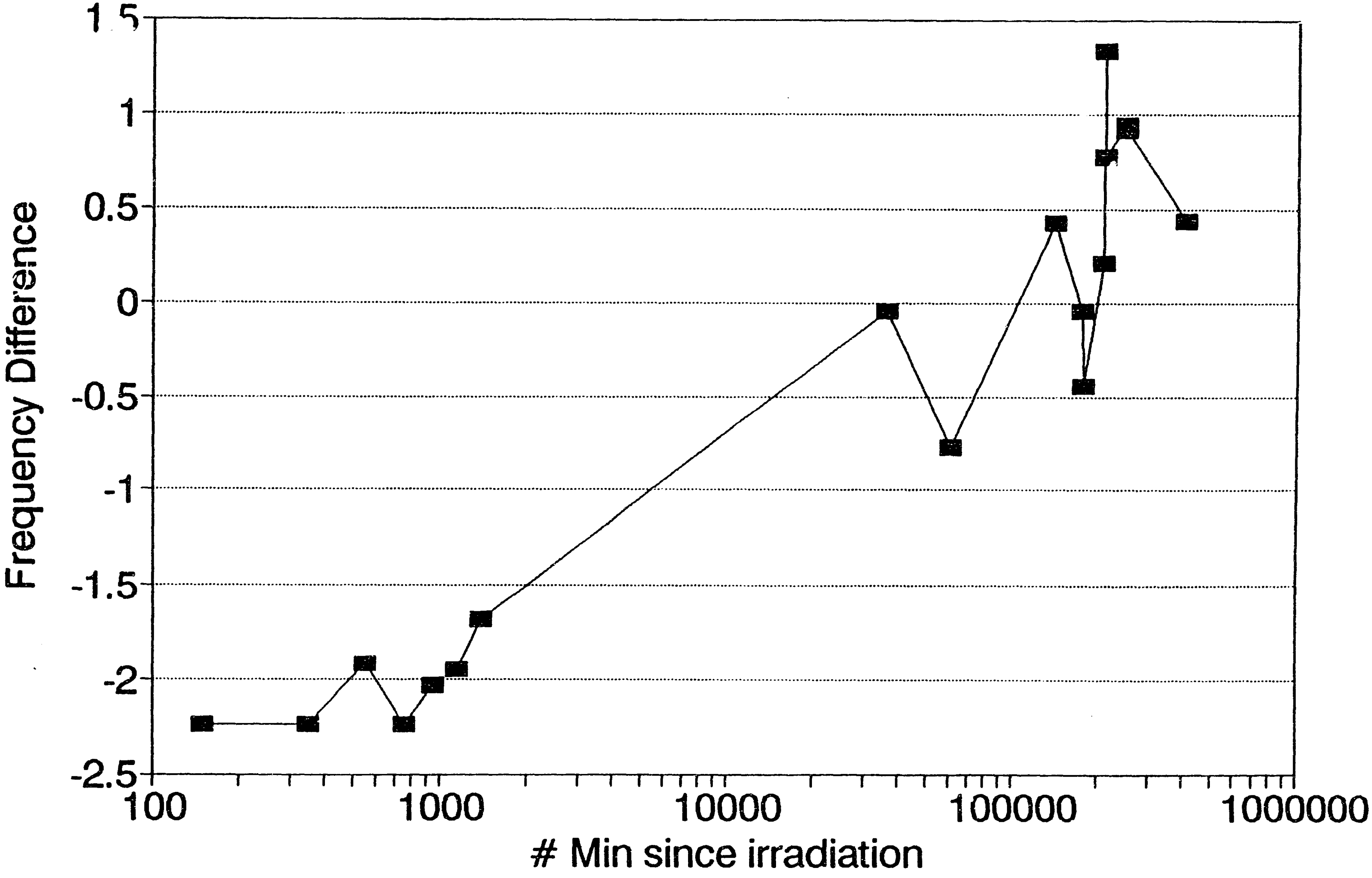
3. Dosimeter Materials Neutron Response

Urea

Hydrated urea samples showed a drastic decrease in the NQR signal amplitudes upon neutron irradiation with fluences > 1×10^{19} m^{-2} from the University of Florida Training Reactor (UFTR) and the other NQR parameters could not be extracted.

Thiourea

Neutron irradiation studies of thiourea demonstrate a decrease in the amplitude and spin-spin relaxation time of the FID with site number 1 appearing to be the more sensitive site. The neutron fluence < 1×10^{19} m^{-2} did not show effects on either amplitude or spin-spin relaxation time. Figure 7. shows the variation of NQR signal amplitude with neutron fluence from the UFTR. The number of molecules unable to contribute in the amplitude signal were estimated to be 1.2×10^{7} per fast neutron (2 MeV) impinging on the thiourea sample.



GUANIDINE CARBONATE
3 ml water added, Irradiated 0.5 MR

Figure 5.0

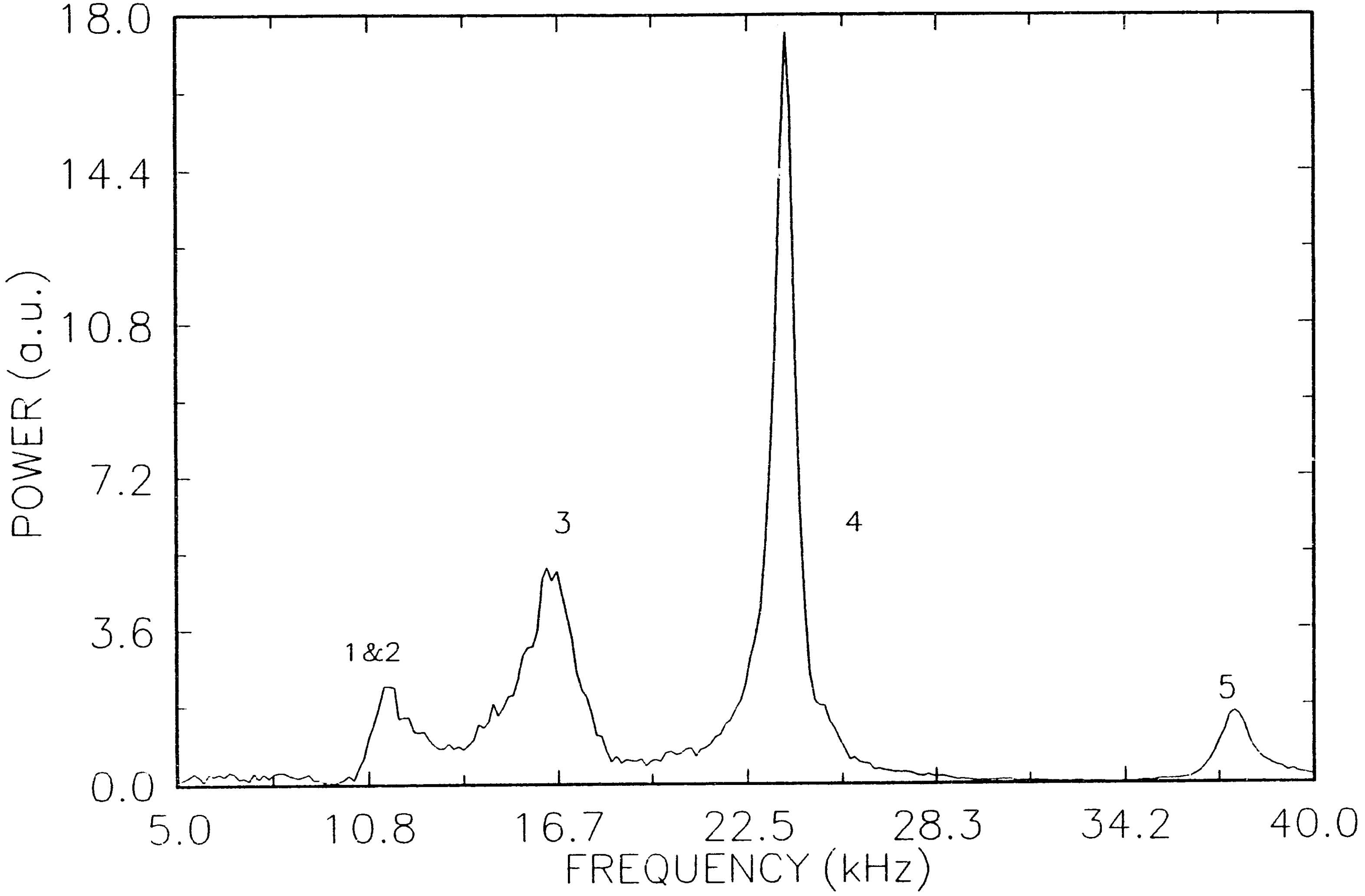


Figure 6 PSD FFT of guanidine sulfate

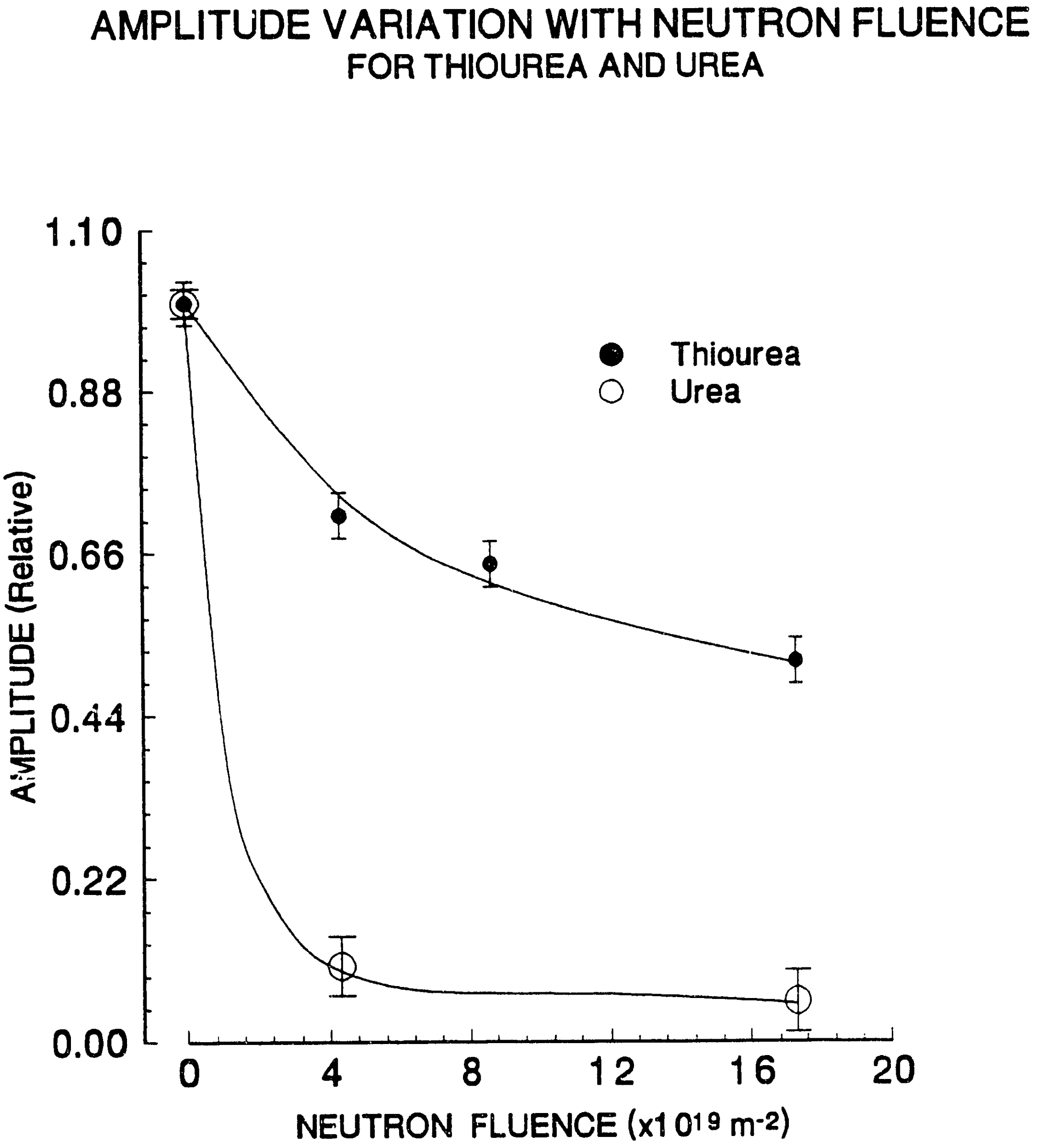

AMPLITUDE VARIATION WITH NEUTRON FLUENCE
FOR THIOUREA AND UREA
● Thiourea
○ Urea
AMPLITUDE (Relative)
1.10
0.88
0.66
0.44
0.22
0.00
0
4
8
12
16
20
NEUTRON FLUENCE (x10^19 m^-2)

Figure 7.0.

Guanidine Compounds

The neutron response of the guanidine compounds was not studied due to the difficulty in precisely quantifying the NQR parameters even in the reference standards.

4. Mixed Gamma-Neutron Exposure Response

None of the compounds studied demonstrated a response to both gammas and neutrons which could be adequately quantified for dosimetric purposes. Although hydrated urea showed a response to gamma dose, the neutrons from reactor irradiation completely eliminated the NQR signal being monitored.

5. Optimize NQR Dosimetry System for Routine Dosimetry Use

The simpler compounds, urea and thiourea, did not show a radiation response strong enough for the detection of low levels of radiation and thus are not useful for routine dosimetry. The more complex compounds may be useful, but their complex NQR spectrum did not allow for quantification of the response based on the present knowledge of how radiation interacts with organic molecules.

CONCLUSIONS

Radiation effects on several organic compounds were evaluated for both photon and neutron irradiations. Hydration of these materials typically provides a greatly increased sensitivity to both forms of radiation exposure, although not all materials lend themselves to this treatment without changing the chemical structure of the compound. Urea was found to be the most stable hydrated compound and provides the best sensitivity for quantifying radiation effects using NQR techniques.

Urea permits a straight-forward quantification of each of the important parameters of the observed NQR signal, the FID. Several advanced data analysis methods were developed to assist in quantifying NQR spectra, both from urea and materials having more complex molecular structures, such as thiourea and guanidine sulfate. Unfortunately, these analysis techniques are frequently quite time consuming for the complex NQR spectra that result from some of these materials. The simpler analysis afforded by urea has therefore made it the prime candidate for an NQR dosimetry material.

The moderate sensitivity of hydrated urea to photon irradiation does not permit this material to achieve the levels of performance required for a personnel dosimeter. It does, however, demonstrate acceptable sensitivity over dose ranges where it could provide a good biological dosimeter for several areas of radiation processing. The demonstrated photon sensitivity could permit hydrated urea to be used in applications such as food irradiation dosimetry. This material also exhibits a good sensitivity to neutron irradiation. The precise correlation between neutron exposure and the parameters of the resulting NQR spectra are currently being developed.

Although not all of the materials studied have demonstrated a strong response to irradiation, they have provided additional insight into the basic mechanisms of radiation-induced structural changes in biological materials. The basic research performed to investigate these phenomena demonstrate that radiation induces subtle bond deformations, as well as complete bond restructuring. These are evidenced by the observed increase in the distribution of the NQR parameters. The insight into basic radiation interaction mechanisms with biological systems is under further investigation and is likely to permit an experimental evaluation of a number of parameters for photon and neutron microdosimetry problems.

The results of hydrated urea can be employed for gamma dose measurements in dose range which is usually needed in radiation processing. The number of molecules affected per neutron on thiourea were estimated. Although the result was obtained using high neutron fluence in the experiment, the number of molecules damaged is independent of neutron fluence. This result could be a useful parameter in microdosimetry.

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