

Alternative method for degradation studies by alpha radiolysis

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Abstract

Partitioning and transmutation of components in spent nuclear fuel in order to reduce radiotoxicity and storage time require advanced separation methods and target preparation. Chemical separation methods for spent nuclear fuel are currently dominated by aqueous separation techniques, i.e. liquid-liquid extraction. The complex nature of the spent fuel matrix has resulted in many different separation processes, both implemented and under development. The extraction reagents, or active ingredients, in these systems are all prone to radiolytic degradation that may severely decrease the efficiency of the process. Many studies have been carried out utilising gamma radiation to degrade these chemicals. The reality is that the waste will contain a large number of alpha emitters, which may result in different radiolysis products composition due to the short range, but high energy, of the alpha particles. Investigation of radiolytic degradation by alpha emitters is not as widely investigated as that by gamma emitters, due to the inability to utilise outside sources. We present in this work a method to produce alpha particles in situ in samples containing standard extraction reagents. The nature of the method is based on the widely studied $^{10}\text{B}(n,\alpha)^7\text{Li}$ reaction. Dose estimations and discussions of degradation products analysis will be presented.

Introduction

Increasing global energy demand and a concern about CO₂ emissions have increased the interest in nuclear power production. The major concern with nuclear power is the used nuclear fuel which contains radiotoxic material and will need to be safely stored for millions of years, effectively indefinitely. Much of the material in the used fuel may still be useful for recycling and used as fuel in thermal reactors or in advanced reactors operating with a harder (faster) neutron spectrum. Recycling of some of the elements is currently carried out in a few countries across the globe, e.g. France, UK, Japan and a few other nations are building up momentum and infrastructure to recycle their nuclear material. The current benchmark process is based on liquid-liquid, or solvent extraction that have been found to be both efficient when operated under counter current conditions and feasible to scale up from pilot scale to full scale operations. Novel extraction systems are continually investigated to reduce the radiotoxicity of the used fuel even further and a majority of these processes are also based on solvent extraction, utilising a variety of novel as well as proven extraction reagents.

Due to the radioactive isotopes in the used nuclear fuel the solvents used for the extraction processes will come under radiolytic attack and degrade. This degradation has been shown to have detrimental effects on the process for a number of reasons. The effective extracting reagent may become inert which will result in a decrease in the extraction efficiency, the degradation product itself may extract unwanted metal ions, causing separation factors to decrease, or the radiolysis may cause larger aggregates of material to form possibly resulting in increased viscosity or third phase formation. At this date the only extraction process for used nuclear fuel used on a commercial scale is the PUREX process [1] where tributyl phosphate (TBP) is diluted in a kerosene-like solvent and used to extract mainly uranium and plutonium from the other elements in the nuclear material. TBP is known to degrade and several studies have been carried out in the past and were recently compiled and discussed in a review by Mincher, *et al.* [2]. The degradation products of TBP is predominantly the phosphoric acid form of TBP, dibutyl phosphoric acid (DBP), which is an effective extraction reagent for several metal ions causing separation factors to decrease and may reduce the recovery of uranium in the strip stage.

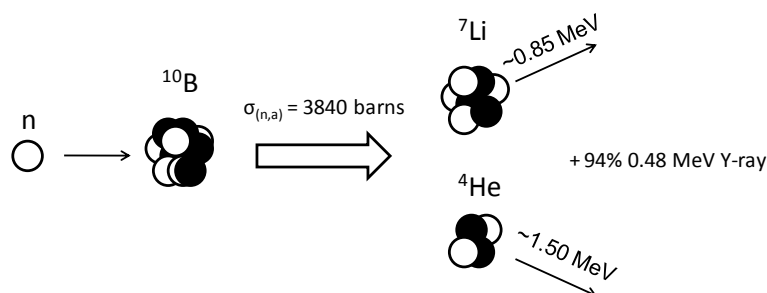
Most radiolysis studies, of both TBP and other extraction reagents, in the past have focused on the degradation due to gamma radiation. Experimentally this is much more readily achieved since the gamma radiation can be radiating from an outside source and the sample need never come into direct contact with the radioactive material. Gamma radiation deposit only small amounts of its energy as it passes through matter and radiolysis product formed may not recombine resulting, in water, in smaller radicals of hydroxide and protons. The used nuclear fuel contains a large number of heavier elements that decay mostly by alpha radiolysis. Compared to gamma radiation the alpha particles deposit all their energy in a very short distance, said to have a large Linear Energy Transfer (LET) value. This cause a much greater degree of recombination of the degradation products formed in the track of the alpha particle and degradation products from alpha radiation may differ slightly from those formed by gamma radiation.

However, due to the short range of alpha particles, radiolysis studies are much more complicated to carry out since no outside source may be used and alpha decaying material must be introduced into the sample studied. This causes problems since most alpha decaying materials are actinides and to achieve high doses isotopes having relatively high specific activity, such as ²³⁸Pu and ²⁴²Cm or ²⁴⁴Cm, must be used. Introducing this material in a sample makes post-irradiation analysis very challenging since few labs have the capability to analyse samples containing large amounts of alpha emitting actinides and the presence of the metal ions themselves may complicate the analysis. Addition of alpha emitting isotopes with very short half-life which would result in a non-radioactive sample within ~10 half-lives of the isotope is one way to get around this problem. Recent work carried out by Ekberg, *et al.* [3] utilised ²¹¹At with a 7.2 h half-life as the source of alpha particles. This method has a lot of benefits since the samples can be analysed as non-radioactive samples once the material has decayed to low levels. Indirect methods to cause alpha radiolysis in samples can be used by accelerating helium and expose the sample to a beam of high-energy helium ions. This method is useful in that the

sample can be analysed immediately after it has been exposed and has great benefit for kinetics studies. The downside of the method is that the distribution of alpha radiation in a sample may be localised to the surface of the sample being irradiated.

In this work we present a method for indirect alpha radiolysis by inducing nuclear reactions in a sample containing boron, using the same principle as in Boron Neutron Capture Therapy, (BNCT) [4]. By introducing ^{10}B in a sample and placing the sample in a neutron field the boron would capture neutrons and undergo a nuclear reaction producing α particles and lithium-7; $^{10}\text{B}(\text{n},\alpha)^7\text{Li}$ (see Figure 1).

Figure 1: Summary of the neutron-induced alpha radiolysis reaction utilised in this study



This method have been used in the past [5-7] to estimate the dose rate to water and the G-values of iron(II) oxidation (number of atoms oxidised per 100 eV energy deposited) by Fricke dosimetry [8-9]. Utilising this nuclear reaction to induce radiolytic degradation on solvents used for solvent extraction has, to the best of our knowledge, not been reported previously. The studies carried out in the 1950s by different research groups indicated that the three products from the reaction shared the total energy of 2.8 MeV. The gamma ray emitted in 94% of the reactions has an energy of $\sim 0.48 \text{ MeV}$ and will contribute to less than 1% of the total energy absorbed in the sample, i.e. dose. The alpha particle and the lithium ion have energies of $\sim 1.50 \text{ MeV}$ and $\sim 0.85 \text{ MeV}$, respectively [10]. The energy of these particles are lower than the energies of the alpha emitters normally encountered in used nuclear fuel, however the important parameter for radiolysis studies is the LET-value which, although somewhat higher at lower energies [11], is in the same order of magnitude for the fragments from the above nuclear reaction compared to alpha particles of $\sim 5 \text{ MeV}$. The lithium ion produced in the reaction would result in an ionisation density of the solution comparable, or somewhat higher, to the alpha particles. The effective G-value for iron(II) oxidation for the $^{10}\text{B}(\text{n},\alpha)^7\text{Li}$ reaction is 4.2 ferrous ions oxidised per 100 eV of energy deposited. Because all of the 2.35 MeV energy is deposited within a small volume one may assume that close to 100% is deposited in the sample and the total dose and dose rates are easily calculated.

This method has several variables, that are more or less easily controlled, which will affect the total dose to a sample. The concentration of boron, and especially the ^{10}B isotope which has a cross-section for the n,α reaction of 3840 barns ($3.84 \times 10^{-21} \text{ cm}^2$), in the sample will have a direct effect on the amount of nuclear reactions. ^{10}B in natural boron has an abundance of 19.9% but is it possible to enrich to much higher values. The most abundant boron isotope, ^{11}B , constitutes the rest of the natural boron and has a very small neutron capture cross-section of 0.005 barns. By introducing the boron containing samples to a reactor we can control the neutron flux which is directly proportional to the power under which the reactor operates. For a given boron-10 concentration the neutron flux will govern how many n,α reaction take place per second. Finally the time the samples spend in the neutron flux will yield different total doses. These studies require careful calibration of the dose rates and correlations need to be made to account for effects from neutron radiation, which should be minimal with boron present to absorb most neutrons, and gamma doses due to the vicinity of the reactor core. The presence of a gamma ray is not seen as a major problem as these effects will be accounted for by separate γ -ray experiments and the net effect may be subtracted by irradiating samples containing no boron.

Solvent radiolysis studies also require investigation of what products were produced during irradiation. As mentioned previously TBP degrades predominantly to DBP by gamma radiation and it has been indicated that this degradation product also dominates for alpha radiolysis [1]. Standard methods to investigate degradation products include mass spectrometry, often coupled to a chromatography stage to distinguish between the by-products by mass or charge. Some of the methods used may themselves induce degradation of the chemicals studied and sometimes several measurements need to be coupled to increase the certainty of the analysis. One analytical method that has not seen much use in the field of nuclear and radiochemistry is Nuclear Magnetic Resonance (NMR). This method has the benefits of being a non-destructive and quantitative technique and can if carefully operated yield very high resolution measurements. The downside of this technique is the sensitivity so that small amounts of degradation products may be challenging to distinguish from the original extraction reagent. In this work we investigate possibilities to utilise NMR to reliably distinguish between tributyl phosphate and its major degradation product, dibutyl phosphoric acid. By correlating different NMR measurements we may improve the sensitivity and lower the limit of detection of these degradation products.

Experimental

Fricke solutions containing 1 mM Fe(II), 1 mM NaCl and 0.4 M H₂SO₄ with varying concentration of boric acid (0-0.9 M) were prepared. All Fricke solutions were aerated by bubbling air through them for a minimum of 30 minutes. Calibration standards of varying concentrations of Fe(III) in 1 mM NaCl and 0.4 M H₂SO₄ were prepared. The boric acid, iron(II) sulphate heptahydrate and ferric ammonium sulphate dodecahydrate [Fe(III)] were all of ACS certified grade and obtained from Fisher Scientific. The sodium chloride was from standardised stock solutions in our laboratory made from filtered and re-crystallised NaCl. The sulphuric acid was prepared from concentrated H₂SO₄ (17.8 M) and was obtained from EMD Chemicals.

Fricke solutions without boron were placed in a caesium-137 gamma cell and exposed to gamma radiation from different periods of time and at different distance from the centre source to prepare calibration curves of the dose rates inside the cell. A set of samples were left outside the gamma cell for blanks. The solutions were analysed on a UV-VIS spectrometer (Ocean Optics JAZ) using 1 cm quartz cuvettes for their Fe(III) content observing the peak at 304 nm. The solutions of varying concentrations of Fe(III) were analysed prior to the unknown samples for calibration by Beer-Lamberts law.

Once the gamma source was calibrated samples of TBP (purity 99+%, Acros Organics) were irradiated for certain times using the ¹³⁷Cs gamma cell. Non-irradiated samples were left outside the cell as blanks during the irradiations. After irradiation the samples were placed in 7" Wilmad 535 NMR tubes, benzene-*d*₆ was added as lock solvent, and the samples were analysed at 600 MHz using a Bruker AVANCE NMR spectrometer equipped with a standard broadband probe. Solutions of different ratios of TBP and DBP (purity >97%, Aldrich) were prepared as standards and analysed by NMR as described above.

Fricke solutions with varying concentrations of boric acid were put in double-sealed containers and placed in a sample carousel (lazy Susan) next to the core of the UC Irvine 250 kW TRIGA reactor. Different sample series were irradiated at 500, 1 000, 2 000 and 3 000 W, respectively for 7 minutes. Fricke solutions with no boric acid were irradiated as blanks for correction of the gamma dose to the samples from fission and decay products, and from n,γ reactions, in the core. A set of samples were left outside the core during the irradiations to serve as blanks. After the irradiation the samples were recovered from the lazy Susan and analysed for their Fe(III) content by UV-VIS spectrometry as described above. Fricke solutions containing boric acid were also irradiated in the ¹³⁷Cs cell to observe if the G-value of Fe(III) would be effected by the boric acid present in the sample.

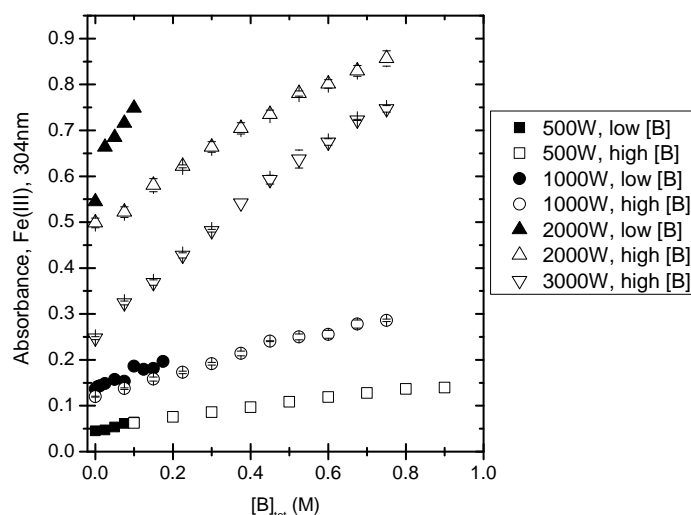
Three sample series were carried out within the same month using low concentrations of boric acid (up to 0.2 M). Later, four sample series were carried out within the same month using higher concentrations of boric acid (up to 0.9 M). The later series were made in triplicates while the early series were made as single samples.

Results

The results showed that the Fricke solutions prepared in our laboratory gave values of dose rates comparable to previous calibrations of the ^{137}Cs irradiator. The analysis of the samples from the gamma irradiation using the ^{137}Cs cell showed that addition of boric acid does not interfere with the G-values of Fe(II)-Fe(III) oxidation from gamma radiation. This is in line with previous investigations of a similar system [5,7]. Furthermore the boric acid does not interfere with the UV-VIS analysis of the Fe(III) at 304 nm, which was also in line with previous work. The samples containing boron irradiated in the reactor clearly showed that an increase in boric acid concentration resulted in an increased amount of Fe(III) produced during the irradiation, see Figure 2.

Figure 2: Fe(III) absorption in irradiated Fricke solutions as a function of total boron concentration and at various reactor powers

Closed symbols represent the early series with low [B] and the open symbols the later series with high [B]; error bars represent one standard deviation calculated from the triplicate



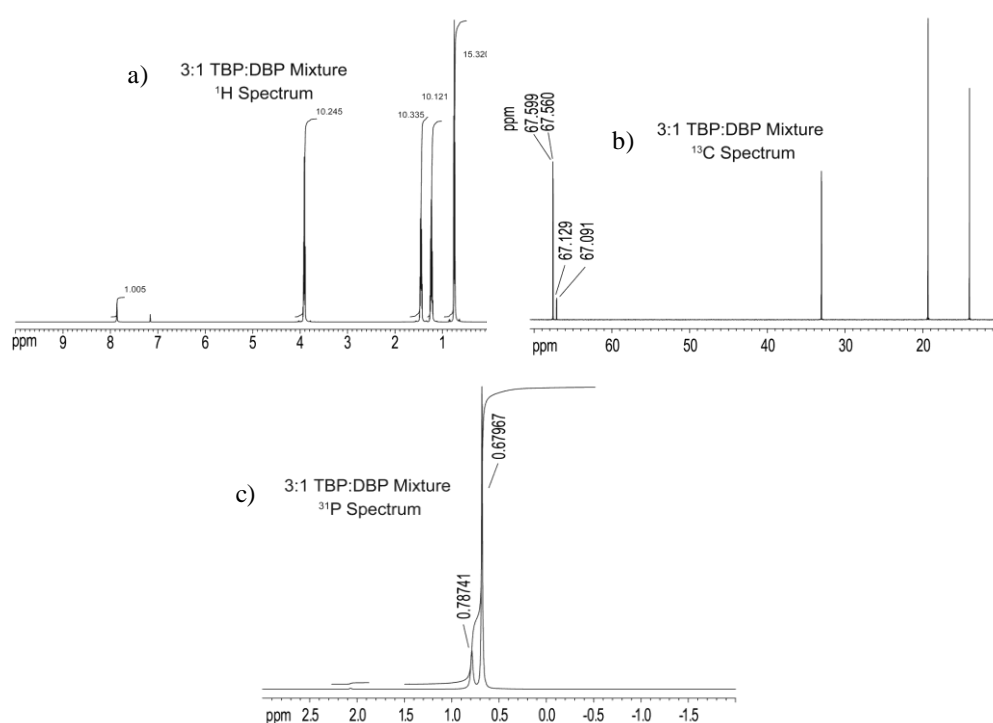
In general, an increased power would also result in higher yields of Fe(III) due to the higher neutron flux and thus higher rate of n, α reactions. However some inconsistencies were observed, e.g. the Fe(III) concentration for samples irradiated at 2 000 W with low [B] displayed a large deviation compared to lower power. The samples with high [B] irradiated at 2 000 W showed an overall higher Fe(III) concentration than corresponding sample series at 3 000 W although the net amount produced (by subtracting the [Fe(III)] at 0 M [B]) was lower for 2 000 W than 3 000 W. The inconsistency was easily explained by referring to the logbook for the UCI TRIGA reactor where all daily activities are recorded. This showed that the irradiation at 2 000 W for low [B] took place during a day of high use of the reactor and was performed immediately after an extended irradiation (~3 h at full power, 250 kW) which would result in a large build-up of fission products that will elevate the background dose. Furthermore, this background dose will not be constant but will decrease over time as the reactor is operated at lower power requiring additional correction procedures. The graph also shows that the increase in Fe(III) concentration with increasing boron concentration is not quite linear but seem to curve to lower values at high [B]. This was also observed in previous work and can be corrected for [5,7] as discussed and shown below.

Three sets of NMR spectra for TBP/DBP mixture collected in 1-D for ^1H , ^{13}C and ^{31}P -NMR are shown in Figure 3. The scale of Figure 3(a) is such that details are difficult to discern but the analysis showed that for ^1H -NMR the TBP and DBP result in significant overlap of the spin multiplets making detailed analysis challenging but perhaps not impossible. The phosphorous acid group of DBP is clearly visible in the ^1H -NMR at ~8 ppm but the nature of the hydrogen bonded proton is too volatile for quantitative analysis, i.e. the hydrogen may exchange freely between different DBP molecules. The ^{13}C -NMR can resolve TBP and DBP at the highest shifts (~67 ppm) in Figure 3(b). The ^{31}P -NMR, Figure 3(c), shows DBP and TBP as the two main peaks and a small impurity at ~2.1 ppm (~0.5% relative to total TBP/DBP) which may be monobutyl phosphoric acid or some other phosphor containing impurity. The spectrum integrals shown in Figure 3(c) indicate that the method is accurate in quantitatively determining the concentration ratio between TBP and DBP.

Figure 3: Three 1-D NMR spectra of a 3:1 (vol:vol) mix of TBP:DBP

(a) ^1H -NMR, (b) ^{13}C -NMR, (c) ^{31}P -NMR

The phosphorus NMR also shows the spectrum integrals



Discussion

The experimental results in this work shows very good consistency with the early work by Sealand and Ehrenberg, MacDonell and Hart, and Schuler and Barr [5-7]. The early studies showed that a G-value of 4.2 for the $\text{Fe(II)}\text{-Fe(III)}$ oxidation would represent the total dose due to the $^{10}\text{B(n},\alpha)^7\text{Li}$ reaction. Their work also showed that high boric acid concentration would result in self shielding and the G-value must be corrected by 0.5% for each 0.01 M of boric acid present. Furthermore, the gamma radiation accompanying the n,α reaction can be accounted for by multiplying the G-value with a factor 1.007 assuming a 1% absorption of the 0.48 MeV gamma-ray [7]. The correction for the gamma-ray to the G-value is quite minimal compared to the decrease in G due to the correction for boric acid concentration, especially at high [B].

The assumption was made that the Fe(III) concentration observed at 0 M boric acid is only due to gamma radiolysis from decay products in the reactor core and is constant at a given power level. This assumption requires that the reactor have not been run recently and any decay products in the core from previous operation have decayed to levels that can be assumed constant during the 7 min. irradiation in our experiments. Based on these assumptions and using the corrections discussed above the dose rates due to high LET radiolysis was calculated and shown in Figure 4. All dose rates could be normalised to 0 kGy/h at 0 M [B] except for the series run at 2 000 W at low [B] concentration. Figure 4 shows that after corrections the trends of dose rate versus boric acid concentration are well represented as linear plots. The slope of each plot is the dose rate per concentration of boric acid and if plotted for each series, i.e. for each reactor power used, Figure 5 is obtained.

Figure 4: Dose rates in kGy/h for high LET radiolysis as a function of boric acid concentration at various reactor powers

This data displayed is from experiments carried out with high [B] and error bars are from standard deviations calculated from triplicate samples; a linear fit for each series is also shown in the figure

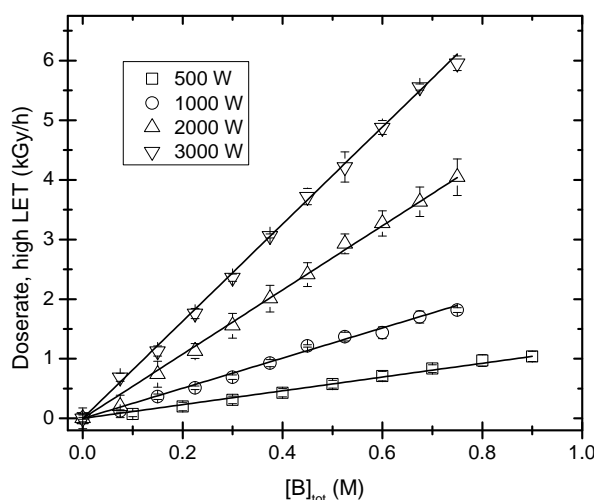
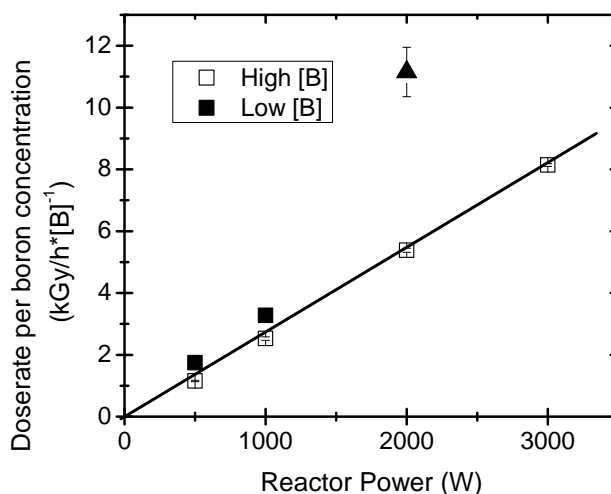


Figure 5: Dose rates per concentration of boron (kGy/h/[B]) plotted as a function of reactor power

Open symbols represent the samples series at high [B] and the closed symbols represent low [B], respectively. The closed triangle represents the series run at 2 000 W and low [B]. The line is added to the graph to guide the eye and does not represent a best fit.

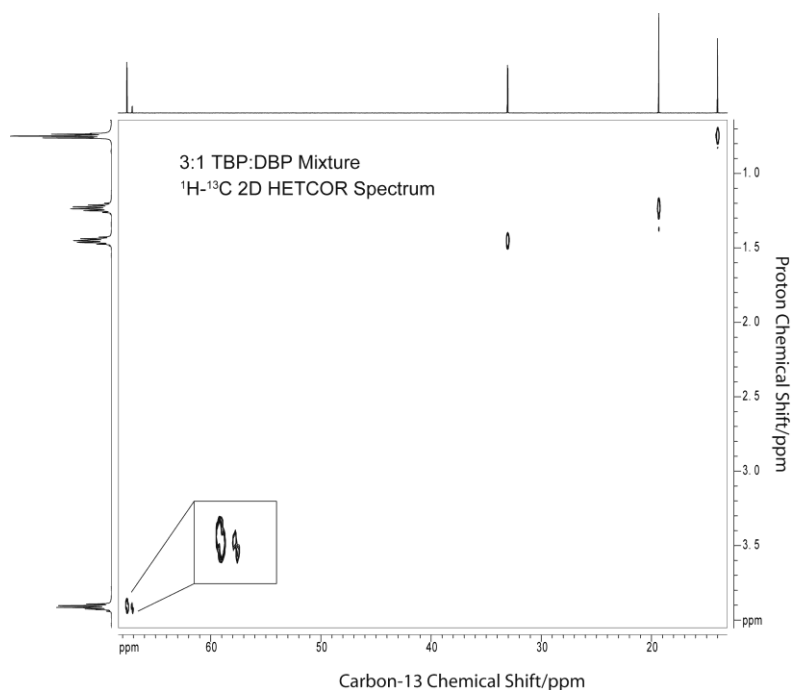


From Figure 5 it is possible to assume that the relationship between dose rate per concentration of boron and the reactor power is a simple linear function. The points at low [B] seem both somewhat elevated compared to high [B] although based on only two reliable points it is difficult to draw any conclusions. The point for 2 000 W reactor power at low [B] is offset in Figure 5 most likely due to elevated gamma dose as discussed above.

Although the 1-D ^1H -NMR spectra indicated that there was a similar molecule to TBP present in the TBP/DBP mixture it was not possible to directly observe the separate proton NMR signal from each molecule because the proton spin multiplets showed extensive overlap. A series of 1-D ^1H and ^{13}C NMR spectra were collected as a heteronuclear correlation spectrum and plotted as a 2-D NMR spectrum (Figure 6). Although the proton NMR spectra did not directly allow to separate TBP and DBP, when correlated with the ^{13}C -NMR spectra the two peaks ~67 ppm chemical shift now separate and allow us to see the separate ^1H -NMR spectra of each molecule, see small insert in Figure 6.

Figure 6: Heteronuclear correlation spectrum of a mixture 3:1 of TBP:DBP

The small square in the bottom left corner shows that the signals from TBP and DBP may be fully resolved



Conclusions

Our results show great reproducibility compared to experiments carried out in the 1950s. Also, experiments carried out at different times and at different reactor power show consistency with the exception of one sample series carried out in close proximity in time with the reactor being operated at high power. It may be possible to account for this elevated dose rate by carrying out careful calibration of the dose rate from the core using Fricke solutions without boron. However, it may be more effective and accurate to carry out irradiations when the reactor has not operated for a number of hours. This may cause limitations to the usefulness of this technique for reactors with a busy schedule, however using beam-ports, samples may be irradiated by neutrons at a distance from the core and the gamma dose may be minimised. The relationship between high LET dose rate, boron concentration and reactor power seem linear but more experimental data is needed until an accurate model can be presented. Experiments using boron compounds more compatible with an organic phase are under way to investigate the degradation

due to the $^{10}\text{B}(\text{n},\alpha)^7\text{Li}$ reaction in organic solvents. The NMR analysis of TBP/DBP mixtures indicates that it is possible to separate the signal from each molecule and quantitatively calculate the concentration of each. The sensibility on the instrument and the detection limit will be investigated but preliminary results show that relative concentrations of less than 0.5% of by-products may be detected.

Acknowledgements

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