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Impacts on process safety of gas generation

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Summary

GH2 values have been measured for deaerated i-SANEX and GANEX solvent systems under irradiation by 5.5 MeV He2+ ions. Despite the difference in compositions between the two solvent systems, very similar GH2 values (3.41-3.51 molecules/100eV) were measured. This value is greater than that measured under ? irradiation (2.0-2.5 molecules/100eV). These values of GH2 are likely to represent the bounding case for H2 production in a process due to the idealised conditions; a lack of oxygen and nitrate in the organic phase are anticipated to increase GH2 values. Key recommendations for further work include: repeating the experiment in more process like conditions ? inclusion of nitrate, dissolved oxygen and water; a fundamental study of the mechanistic pathways to H2 formation, in order to elucidate the cause of the similarity in GH2 for the two very different systems; and to perform a full analysis of the expected doses that a solvent might receive during use in next generation reprocessing.

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EXECUTIVE SUMMARY

G_{H_2} values have been measured for deaerated *i*-SANEX and GANEX solvent systems under irradiation by 5.5 MeV He^{2+} ions. Despite the difference in compositions between the two solvent systems, very similar G_{H_2} values (3.41-3.51 molecules/100eV) were measured. This value is greater than that measured under γ irradiation (2.0-2.5 molecules/100eV). These values of G_{H_2} are likely to represent the bounding case for H_2 production in a process due to the idealised conditions; a lack of oxygen and nitrate in the organic phase are anticipated to increase G_{H_2} values. Key recommendations for further work include: repeating the experiment in more process like conditions – inclusion of nitrate, dissolved oxygen and water; a fundamental study of the mechanistic pathways to H_2 formation, in order to elucidate the cause of the similarity in G_{H_2} for the two very different systems; and to perform a full analysis of the expected doses that a solvent might receive during use in next generation reprocessing.

INTRODUCTION

As part of the GENIORS programme NNL have been tasked with investigating the gas generation during irradiation of solvents proposed for next generation fuel cycles. The chosen solvents are relevant for the *i*-SANEX and GANEX fuel cycles, comprising of 5 v/v.% 1--octanol with 0.2 M *N*,*N*,*N*',*N*'-tetraoctyldiglycolamide (TODGA) in hydrogenated tetrapropylene (TPH, a French diluent similar to odourless kerosene (OK)) and 0.5 M *N*,*N*'-dimethyl-*N*,*N*'-dioctylhexyloxyethylmalonamide (DMDOHEMA) with 0.2 M TODGA in OK, respectively.

Many previously published studies of irradiation of solvents have primarily focussed on the effect of γ radiation, investigating how this affects the extraction capacity of the solvent [1], [2], [3], [4]. Here we aim to understand and quantify the effect of α radiation on the solvent system, both in terms of quantifying the rate of hydrogen generation, G_{H_2} and the rate of loss of extractant species. This will be achieved using a tandem linear accelerator to produce a He^{2+} beam as an artificial, non-radioactive and tuneable source of α radiation analogues. The effect of α radiation will then be compared to that of γ in an attempt to separate and quantify the effect of each radiation type.

The He^{2+} beam was setup to provide He^{2+} ions with an energy of 5.5 MeV once they had traversed the small (~3 mm) air gap between the end of the beamline and the Mica window of the irradiation cell. 5.5 MeV was chosen as this is the approximate energy of α particles produced from the spontaneous α decay of ^{241}Am, $^{238\text{-}242}$Pu. This was done following established procedures within the Dalton Cumbrian Facility (DCF).

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Initial tests of the rate of gas generation with dose were performed with pure n-dodecane using beam currents of 1, 3 and 5 nA. This demonstrated that the rate of gas generation was proportional to the current up to the maximum beam current tested, 5 nA, as previously observed in the facility. At a fixed incident particle energy, beam current is directly proportional to dose rate so it is preferable to use the maximum current possible without changing the track chemistry. However, at very high dose rates inter–track chemistry or mixing effects can influence the hydrogen yield. Therefore, it is important that the chosen current is within the region that the hydrogen yield is proportional. Where deviations occur the H_2 precursor species are consumed between different particle tracks, decreasing the amount of H_2 produced. Unfortunately, this can happen in beamline experiments where a relatively large amount of energy is deposited in a very small volume at the end of the beamline. In a real process the decaying nuclei, and therefore the energy deposited, is relatively uniformly spread throughout the volume, minimising inter-track chemistry. In order to decrease the likelihood of inter-track chemistry, rapid stirring is also applied to the system whilst under irradiation. Therefore, the samples were irradiated for a fixed time with a 5 nA beam of He^{2+} ions to achieve desired doses. After each dose interval, Ar was passed through the entire sample to degas all the generated H_2. The H_2 content was measured by Gas Chromatography with Thermal Conductivity Detection (GC-TCD) to allow calculation of G_{H_2} values for each solvent system. Additionally, after each dose interval, aliquots of the mixed organic (after Ar bubbling) were taken for subsequent Gas Chromatography with Flame Ionisation Detector (GC-FID) measurement in an attempt to obtain $G_{(TODGA/DMDOHEMA)}$ values.

EXPERIMENTAL

SETUP

BEAMLINE

Helium ions were stimulated from a helium plasma using a TORVIS ion source and accelerated in a National Electrostatics Corporation 5 MV tandem pelletron, model 15SDH-4 [5]. A 6mm diameter collimator and exit window were used to give a uniform illumination of the liquid cell [6]. Dose measurement was made by collecting the charge from the cell using a Keithley 6517B/E electrometer. The incident ion beam from the accelerator was at 10.3 MeV but undergoes energy losses in the titanium exit window (density = 3.8 mg/cm^2) to the beamline

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and the mica entrance window (density = 5.572 mg/cm^2) of the sample cell. Calculation using the SRIM code determined that the energy of the ions entering the liquid was 5.5 MeV [7].

IRRADIATION CELL

The cell utilised for the irradiations was of a proprietary design, previously used very effectively within DCF. An image of the cell can be found in Figure 1 - left. This was modified to create a sampling port on the upstream side of the Ar flow as shown in Figure 1 – right. A variety of commercially available epoxy resins were tested for material compatibility (resistance) with the chosen solvent formulations. All were found to withstand prolonged contact (>1 week) with no failures or mass changes. The resin chosen to affix the Mica window to the irradiation cell was a titanium-based epoxy (Varian Torr Seal 2 part epoxy resin) on the basis that it would be easy to visually detect ingress of the yellow-tinged solvent through the white resin.

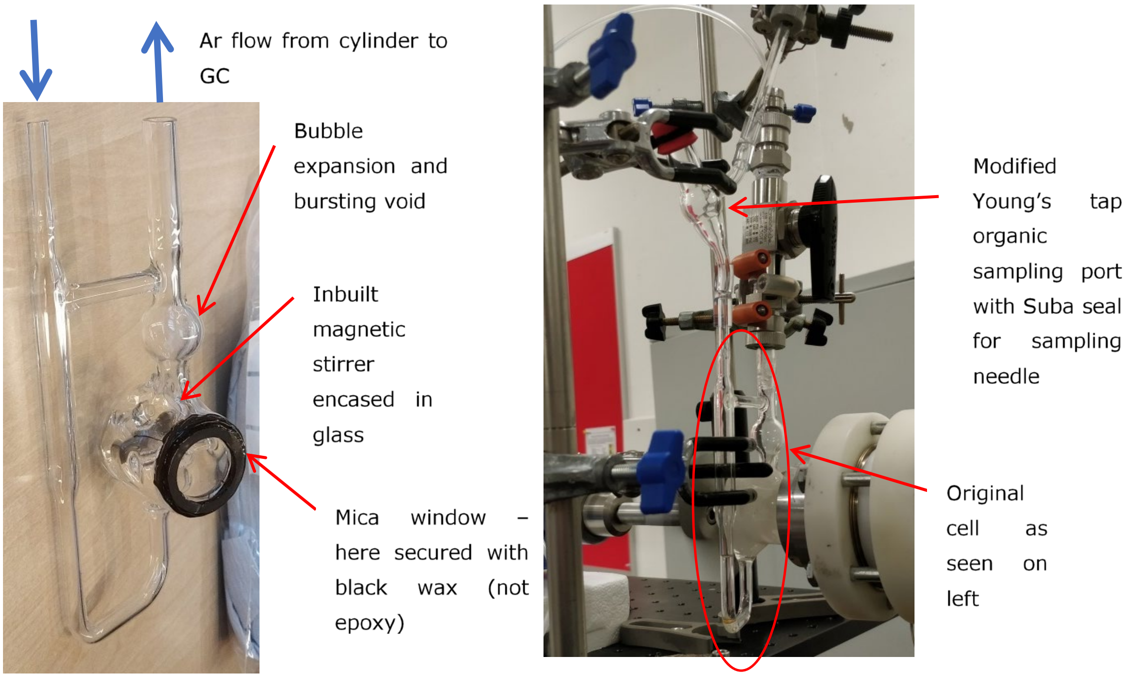
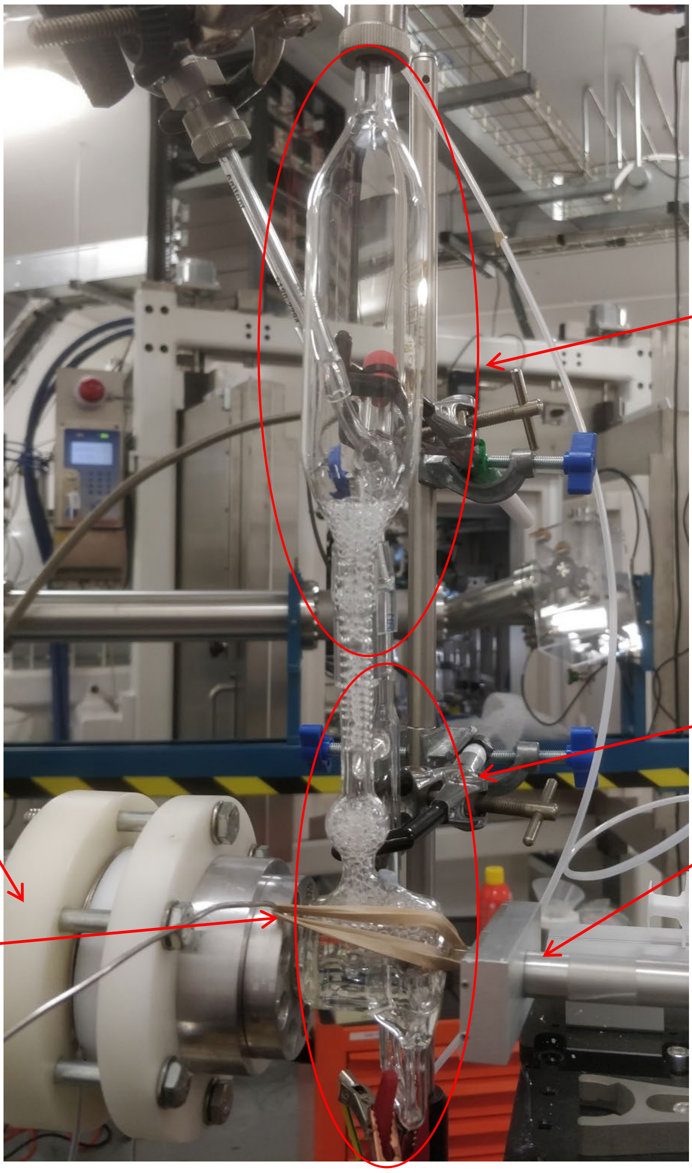


Figure 1 Picture of irradiation cell with annotation of gas flow, stirrer and Mica window (*left*) and the same cell in situ, with organic sampling port GC attachments added (*right*).

GC SETUP

An SRI 8610C GC with an SRI 2 ft, 5 Å molecular sieve column was used to quantify hydrogen production during irradiations. The oven temperature was 80 °C, with an argon carrier gas with a flowrate of 20 mL/min at 27 psi. Hydrogen measurement was performed by a Thermal Conductivity Detector (TCD). The GC carrier gas was diverted through the entire irradiation cell for each measurement. Calibration was performed by injecting known volumes of pure hydrogen into the organic sampling port (as seen in Figure 1, right). All calibrations were performed in situations representative of the experiment, i.e. the cell contained an organic phase, which the hydrogen moved through with the purge argon to ensure that the broadening caused by diffusion was similar between the samples and calibrations.

Due to the increased viscosity of the *i*-SANEX and GANEX solvents, cf. pure *n*-dodecane, it was found necessary to add in a large ‘bubble expansion void’ section to the downstream side of the Ar flow midway through the irradiation of the *i*-SANEX solvent. This was required as the small expansion void on the cell was found to be inadequate during initial degassing. As seen in Figure 2, the use of a 100 mL pipette provided a large enough void to prevent the organic phase from contaminating the GC column.



Additional bubble expansion void with GC fittings at top during measurement – bubbles can be seen in lower section. To the rear is the organic sampling port which can also be seen.

Original cell as seen in Figure 1 (left)

End of beamline

Ar purge to end of beamline to prevent O_3 build-up and subsequent corrosion. Rubber band holds cell in contact with stage end

Magnetic stirrer

Figure 2 Annotated picture of the final irradiation cell setup.

PRELIMINARY STUDIES

n-dodecane (20 mL) was irradiated for equal time periods with beam currents of 1, 3 and 5 nA with He^{2+} ion energy of 5.5 MeV in the sample (i.e. after passing through the Mica window) and the evolved H_2 measured by GC-TCD.

ORGANIC PHASE PREPARATION

TODGA (2.91 g, 5.01 mmol) and DMDOHEMA (6.04 g, 12.5 mmol) were made up to 25 mL with Odourless Kerosene (OK) allowing for overnight dilation - the GANEX solvent. TODGA (2.91 g, 5.00 mmol) and 1 octanol (1.25 mL) were made up to 25 mL in TPH again allowing for overnight dilation – the *i*-SANEX solvent.

IRRADIATIONS

The chosen solvent (21 mL) was added to the irradiation vessel and degassed with a 5 min flow of Ar. After degassing, the sample was irradiated with rapid stirring (enough to remove the sample in contact with the Mica window) with a beam current of ~5 nA and incident ion beam energy in the solvent of 5.5 MeV for a fixed time period. The total energy (J) applied to the sample was calculated through summation of charge as measured in the final Faraday cup on the beamline (see Equation 1).

ORGANIC SAMPLING

After each dose interval an ~1 mL sample of the organic was removed for GC-FID analysis. An aliquot of the sample was diluted (dilution factor 20) in HPLC grade hexane (Fisher). GC calibration was performed using standard solutions of known concentration with dilution factors from 10 to 100. The GC setup was: injection volume = 1 µL, split = 200:1, injection port temperature = 290 °C, Agilent amine inerted liner with glass wool, Column = DB-35 (30 m, 0.32 mm, 25 µm), He carrier, flow rate = 2 mL/min, oven regime = 60 °C for 2 min then ramp at 20 °C/min to 290 °C with a hold for 31 min. GC-MS analysis of a sample of each solvent was performed at The University of Manchester Chemistry Department for confirmation of analyte signal assignment.

RESULTS AND DISCUSSION

The density of the initial solutions was measured in order to calculate dose values in Gy. The results are presented in Table 1.

Table 1 Masses of 1 mL of each solvent system used to calculate the density of the fresh, unirradiated solvent.

Sample	GANEX sample mass (g)	*i*-SANEX sample mass (g)
1	0.8499	0.7815
2	0.8544	0.7776
3	0.8528	0.7756
Average	**0.852**	**0.778**

The total accumulated deposited energy can be converted in to a dose following Equation 2. The preliminary *n*-dodecane irradiation results are presented graphically in Figure 3. They show that the production of H_2 is linear with respect to the beam current (here expressed as energy deposited in eV). The G_{H2} for *n*-dodecane is proportional to the gradient of the line as discussed by LaVerne. [8] The value of 5.32 molecules/100eV is very similar to that measured by LaVerne of 5.3 molecules/100 eV. The similarity of value and linearity of response demonstrates that the chosen beam current (and therefore dose rate) does not alter the inter-track chemistry of the system and that the rate of stirring was sufficient.

Equation 1: Equation for calculating the energy deposited in the sample and subsequently G_{H2}. Where, E_{dep} is the energy deposited (eV), C is the total charge deposited in the sample (C), e is the charge on the electron, 2 accounts for He^{2+} being doubly charged and E_α is the incident energy of the He^{2+} ion (eV).

$$E_{dep} = \frac{C}{2e} * E_{\propto}$$

It is customary to discuss irradiation data in terms of dose expressed in Grays, where a Gray is the amount of energy deposited per mass of media in J/kg. Therefore, the dose can be calculated following Equation 2:

Equation 2: Equation for the calculation of dose, d (Gy), where V is the total volume the energy is deposited in to (mL), ρ is the density of the solution (g/mL) and e is the charge of the electron.

$$d = \frac{1000 * E_{dep}e}{V\rho}$$

Combining Equation 1 and Equation 2 gives the reduced form of Equation 3, below.

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Equation 3: Equation for calculating the dose received by the organic phase, definitions can be found above.

$$d = \frac{500CE_{\alpha}}{V\rho}$$

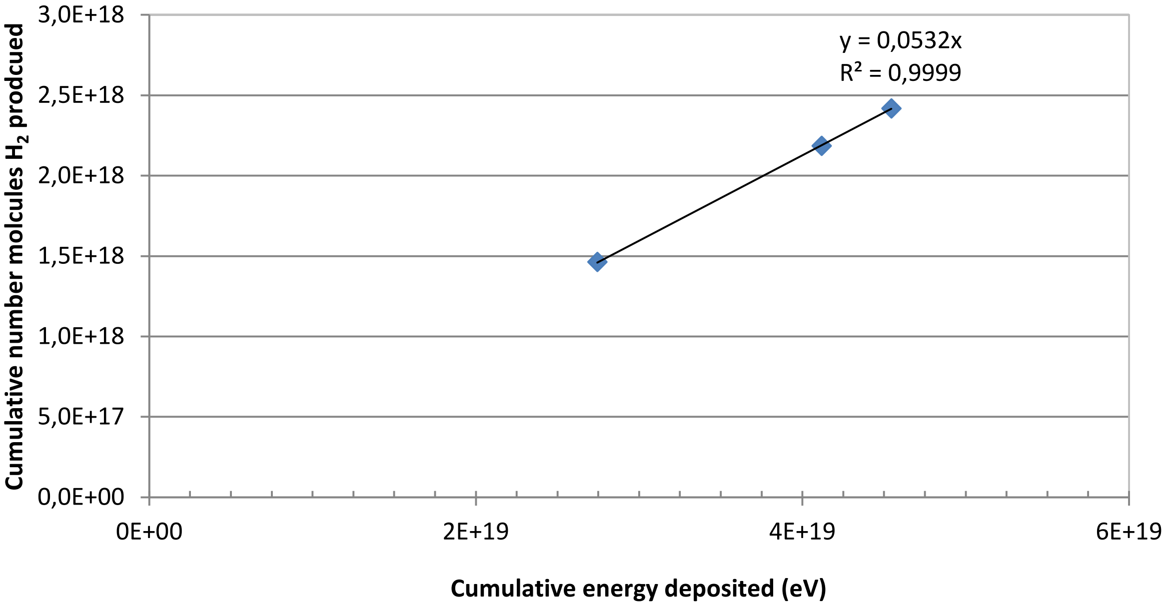

Figure 3 Graphical depiction of the H_2 peak area against the total accumulated charge in the sample for pure *n*-dodecane. The points represent beam currents of ~1, 3 and 5 nA from left to right, respectively.

Following the initial tests, 5 nA was selected as the beam current for the solvent irradiations. 21 mL of each solvent was irradiated and the amount of $H_{2(g)}$ produced measured at each dose interval. Dose intervals were selected to prevent $H_{2(g)}$ levels exceeding the calibrated range and provide organic samples for further analysis.

Partway through the experiments an expansion chamber to prevent entrainment of the solvent directly into the GC column was added. This expansion chamber was added to the set-up after the fourth *i*-SANEX measurement (*i*-SANEX irradiations were completed before the GANEX, see Figure 2). Additionally, one of the $H_{2(g)}$ samples for the GANEX solvent was lost through a failed connection. This is highlighted in Table 2 below, but for discussion around total accumulated $H_{2(g)}$ the result was inferred by averaging the regression and progression of the results before and after (highlighted yellow in Figure 4 – top). The results are presented in Table 2 where the highlighted row is the lost sample. The slopes of the lines in Figure 4 are proportional to G_{H_2}, however, the G values presented were calculated from the proportionality of the total accumulated amount of hydrogen produced by the total accumulated energy deposited (eV); the gradient of the least squares (linest) fit, forced through 0 multiplied by 100. This method removes errors associated with any density changes and masses recorded for the samples as well as the lack of Ar carrier gas pre-saturation (as discussed by LaVerne *et al.*) [8]. This calculation provides values of 3.41 and 3.51 molecules/100eV for the GANEX and *i*-SANEX solvents, respectively.

Table 2 Data from the irradiation of the *i*-SANEX (upper) and GANEX (lower) solvent systems. * denotes where an organic sample was taken after H_2 measurement.

Solvent	Total Time (min)	Accumulated charge in time period (C)	Energy deposited (eV)	Volume in cell (mL)	Dose at interval (Gy)	Accumulated dose (Gy)	H2 peak area	Accumulated peak area	Molecules H2	Accumulated molecules H2	Accumulated molecules H2 per gram (molecules/g)
i-SANEX	5	1.35E-06	2.32E+19	21.00	228	228	195	195	6.98E+17	6.98E+17	4.27E+16
	20	4.52E-06	7.76E+19	21.00	761	989	770	965	2.75E+18	3.45E+18	2.11E+17
	40	5.98E-06	1.03E+20	21.00*	1007	1996	990	1955	3.54E+18	6.99E+18	4.28E+17
	70	8.60E-06	1.48E+20	19.77	1537	3532	1384	3339	4.95E+18	1.19E+19	7.76E+17
	100	8.35E-06	1.43E+20	19.77*	1492	5025	1403	4743	5.02E+18	1.70E+19	1.10E+18
	130	9.08E-06	1.56E+20	18.86	1702	6726	1598	6340	5.71E+18	2.27E+19	1.54E+18
	160	9.50E-06	1.63E+20	18.86	1780	8506	1574	7915	5.63E+18	2.83E+19	1.93E+18
	190	9.07E-06	1.56E+20	18.86*	1699	10204	1530	9445	5.47E+18	3.38E+19	2.30E+18
	230	1.19E-05	2.04E+20	17.87	2345	12549	1968	11413	7.03E+18	4.08E+19	2.93E+18
	290	1.88E-05	3.23E+20	17.87	3715	16265	3312	14725	1.18E+19	5.26E+19	3.78E+18
	350	1.79E-05	3.08E+20	17.87*	3546	19810	3137	17862	1.12E+19	6.38E+19	4.59E+18
GANEX	20	6.1E-06	1.05E+20	21.00	938	938	914	914	3.27E+18	3.27E+18	1.83E+17
	40	5.7E-06	9.81E+19	21.00*	878	1816	839	1753	3.00E+18	6.27E+18	3.50E+17
	100	1.8E-05	3.04E+20	20.00	2861	4676	3041	4794	1.09E+19	1.71E+19	1.01E+18
	150	1.5E-05	2.50E+20	20.00	2345	7022	2412	7206	8.62E+18	2.58E+19	1.51E+18
	200	1.5E-05	2.51E+20	20.00*	2354	9376	2397	9603	8.57E+18	3.43E+19	2.01E+18
	240	1.2E-05	2.11E+20	18.90	2100	11476	2055	11658	7.35E+18	4.17E+19	2.59E+18
	270	7.9E-06	1.35E+20	18.90*	1341	12817	1247	12905	4.46E+18	4.61E+19	2.86E+18
	330	1.6E-05	2.74E+20	17.92	2878	15696	2582	15487	9.23E+18	5.54E+19	3.62E+18
	410	2.1E-05	3.60E+20	17.92*	3776	19472	3580	19067	1.28E+19	6.82E+19	4.46E+18
	470	1.9E-05	3.21E+20	16.90	3568	23040	3034	22101	1.08E+19	7.90E+19	5.48E+18
	530	1.8E-05	3.07E+20	16.90	3416	26455	2923	25025	1.04E+19	8.94E+19	6.21E+18
	555	7.2E-06	1.24E+20	16.90*	1376	27832	1090	26115	3.90E+18	9.33E+19	6.48E+18

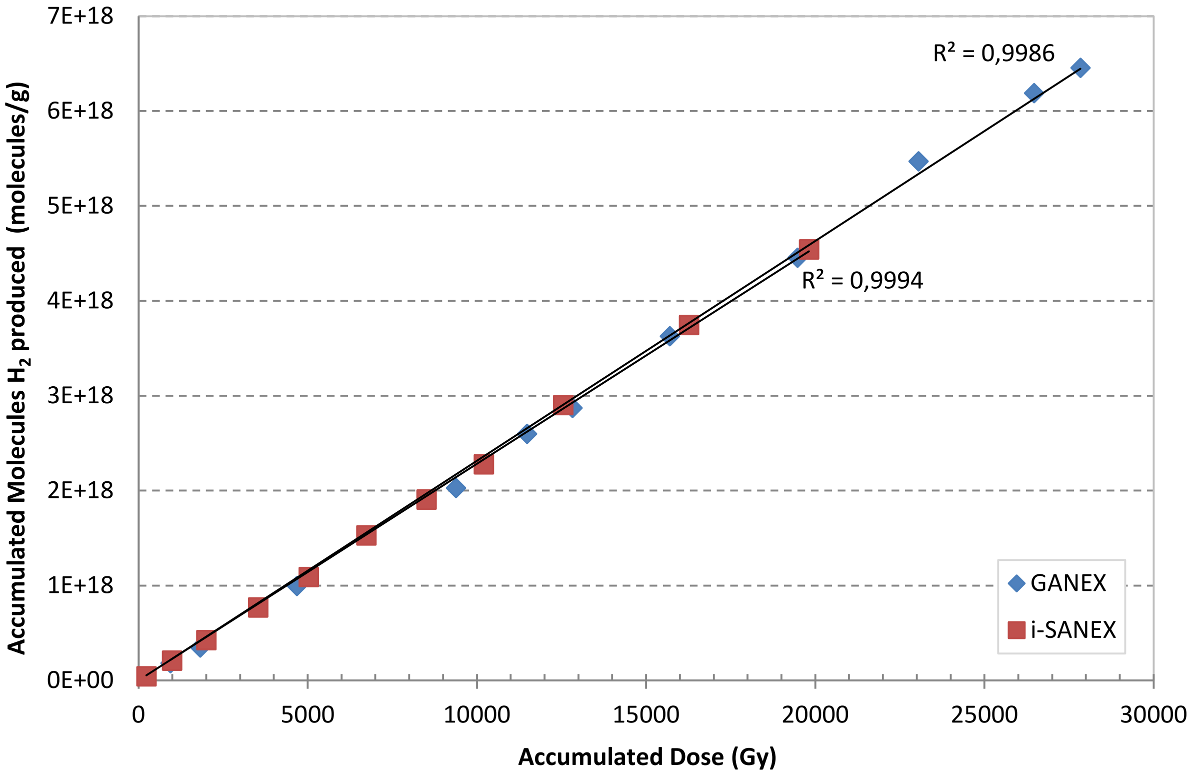

Figure 4 Graphs of the results of H_2 measurement for the irradiation of *i*-SANEX and GANEX solvents against dose. The number of molecules of H_2 produced per unit mass is plotted against the dose received (interpolated point not plotted).

From these data it is clear that these solvent systems produce a lower yield of H_2 than pure *n*-dodecane. Values for OK and TPH have not been measured here or elsewhere but for deaerated hexane and *n*-dodecane with 5 MeV He^{2+} ions, G_{H_2}=4.8 and 5.3 molecules/100eV, respectively, was reported by LaVerne[8]. This decrease cannot be simply due to a decreased volume fraction of the diluent decreasing G_{H_2} as the magnitude of the decrease is different for each solvent (remaining diluent volume fraction of ~82 % and ~61 % for the *i*-SANEX and GANEX systems, respectively). It seems likely that there are two processes occurring. One which is dependent only on alkyl chains (where the extractants still contain them) and one that is completely suppressed/quenched by DMDOHEMA/TODGA. This explains why the G_{H_2} values are similar despite the greater decrease in *n*-dodecane content in the GANEX solvent alongside an increase in the similar amide/ether functional groups of DMDOHEMA and TODGA. This can be investigated by performing irradiations with increasingly small quantities of the extractants, which should slowly decrease G_{H_2} until the levels seen here. Either way, it is clear that the solvent mixtures here suppress the formation of $H_{2(g)}$ relative to pure alkane diluents like hexane and *n*-dodecane. Interestingly, previously measured γ irradiation G_{H_2} values for the deaerated *i*-SANEX components in a *n*-dodecane diluent were 2.0-

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2.5 molecules/100eV [9]. This is in agreement with most comparisons between α and γ irradiations where γ irradiation normally yields less $H_{2(g)}$ than α, i.e. lower linear energy transfer radiation produces lower G_{H_2} [10], [11] . Although it should be noted that in some instances the reverse trend is found, for example with hexane, as reported by LaVerne [8].

The G_{H_2} values measured here represent the largest rates that are likely to be found in a process for α radiation as it has been shown in dodecane and hexane that the addition of O_2 to the system suppresses H_2 formation [8]. However, understanding the possible bounding cases for H_2 formation is important for designing a full scale, safe process. Further understanding of the effect of the radiation on the extractant itself, in terms of; $G_{\text{-extractant}}$, is also important in order to evaluate the implication of radiolytic solvent degradation upon the process performance. Radiolysis of the solvent can lead to loss of extraction efficiency (decreased distribution coefficients) or retention of extracted species in the solvent phase (decreased stripping efficiency). To that end, measurement of the extractant concentration post α irradiation was attempted by gas chromatography. Analyte identity was confirmed by GC-MS. Once the method had been developed it allowed separation of all of the major solvent components. The diluent, octanol, and small impurities eluted in <5.5 min followed by the extractants. DMDOHEMA elutes at ~17.5 min and TODGA at ~32.5 min. The molecular ion peak of DMDOHEMA can be seen in Figure 5, however, the molecular ion for TODGA is not observed in this chromatogram, likely a result of the electron ionisation 'charging' technique used – this being quite an aggressive treatment– it was however visible using electrospray ionisation (a softer technique).

Measurement of the change in TODGA and DMDOHEMA concentration during the irradiation showed that there was no change throughout the dose range used here. Given the relatively low doses (<30 kGy) in this work this is to be expected considering the $G_{\text{-TODGA}}$ values reported by Sugo *et al.* of 0.022±0.001 [12].

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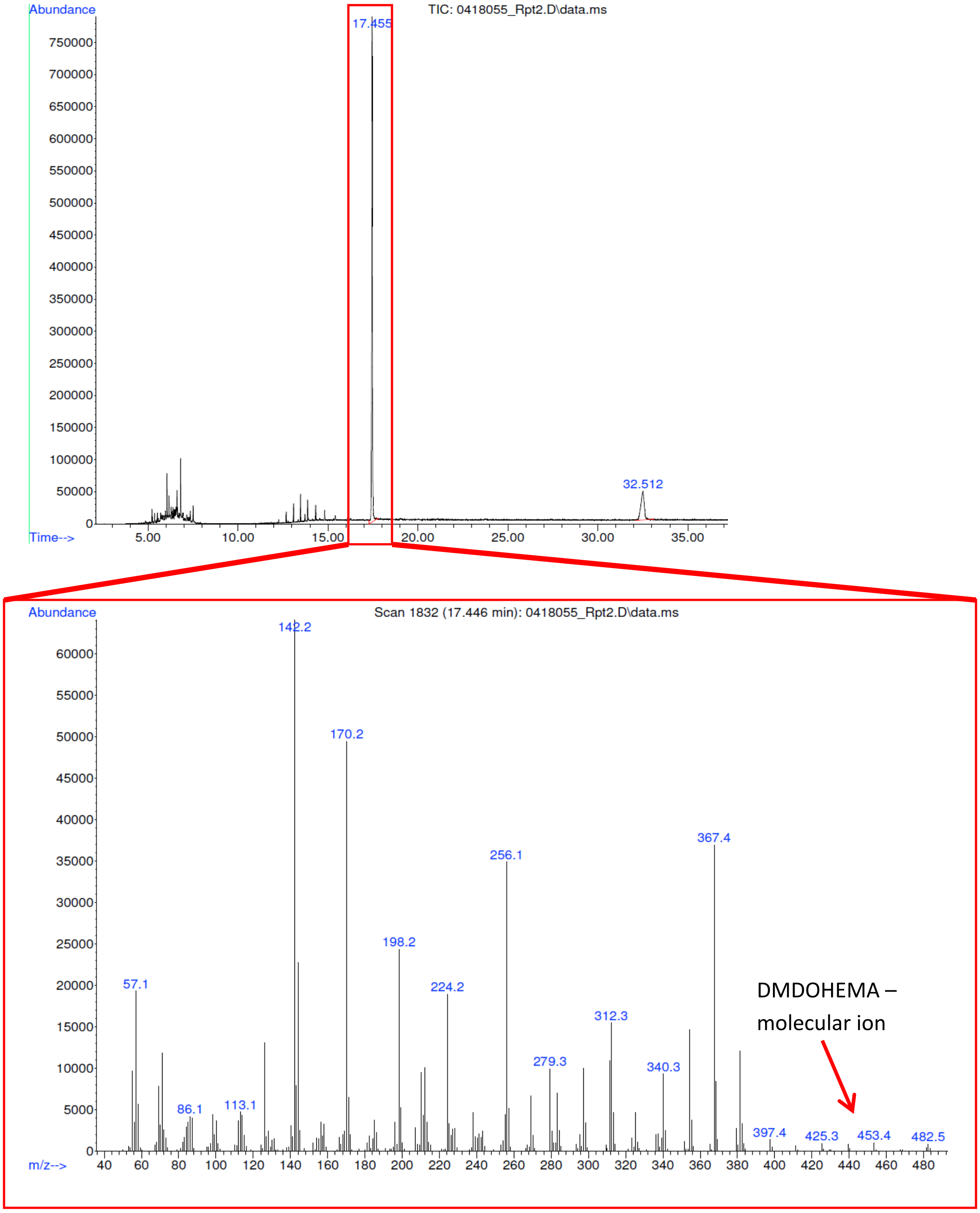

DMDOHEMA – molecular ion

Figure 5 Top: EI-MS spectrum of the sample eluted at 17.446 min from the GC analysis of the 4th GANEX organic sample with the GC chromatogram inset.

CONCLUSIONS

The measurement of G_{H_2} for *i*-SANEX and GANEX solvent systems has been achieved under de-aerated conditions with 5.5 MeV He^{2+} particles at a flux of 5 nA. Initial testing with pure *n*-dodecane demonstrated that there are no secondary dose rate effects at this beam current. Irradiation of *i*-SANEX and GANEX solvents was achieved and demonstrated linearity of H_2 production with increasing dose, despite the loss of one sample. Both organic phase compositions exhibited similar G_{H_2} values, despite the variation in composition; the EURO-GANEX solvent contained DMDOHEMA and employed OK as the diluent, compared to the *i*-SANEX solvent that included a phase modifier of 1-octanol and utilised TPH as the diluent. The measured G_{H_2} values were 3.41 and 3.51 molecules/100eV for the GANEX and *i*-SANEX solvents, respectively. These are larger than those reported for γ irradiation (~2.0-2.5 molecules/100eV). The idealised conditions that the experiments were performed in are expected to represent a maximum bounding case for H_2 production as the addition of O_2 is known to decrease H_2 production.

RECOMMENDATIONS

There are a few recommendations for further work as a result of this work.

- It is recommended that these experiments are repeated with more variables such as higher dose rates, pre-contacting with H_2O/HNO_3 and aeration.
- It is recommended that experiments are undertaken to elucidate the different pathways by which H_2 can be formed and how TODGA/DMDOHEMA limit/affect them. Undertaking experiments similar to Asmus (using small quantities of deuterated ammonia) may help in this regard [13].
- It is also recommended that a full understanding of the expected dose rates of the proposed processes be modelled to understand the maximum doses that might be expected. Higher doses may also allow the calculation of $G_{\text{-extractant}}$ where it was not possible here due to the relatively low doses.

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