Supporting information for "Solvent Extraction of Gold with Biomass Chemicals".

Contents

Materials

The HVO100 biodiesel was produced by Neste and purchased from the Tanka filling station which is at the Lidbil garage at Torggatan 54 in Vara. The fuel was purchased on the 10th of May 2022. To safely transport the HVO100 away from the filling station and to comply with the regulations associated with the sale of motor fuel to the general public a painted (purple) 5 L steel motor fuel can was purchased from Bildelen Nordstrom in Vara (A town of *circa* 4200 people in Västra Götaland County in Sweden close to the E20 road and the railway track between Borås and Uddevalla). The HVO100 was dispensed on a fine day without rain from a pumping machine designed for fueling cars at 13:27 Paris time into the steel fuel can. The pumping machine has a hose and nozzle which is dedicated for the dispensing of the Neste biodiesel. The HVO100 fuel was transferred to borosilicate bottles before being used in the experimental work.

The medical grade paraffin sample (300 ml) was produced by APL (Prismavägan 2, 141 75, Kungens Kurva, Sweden) and was purchased via the web sites of Apotea AB. The full name of APL is Apotek Produktion & Laboriatorier, which is a state owned company. Their telephone number is +46(0)10 447 9600 and their website is at www.apl.se.

The lamp oil was purchased from the museum shop at Cesarstugan (Falköping 521 94, Sweden).

The malonamide extractant was prepared during the PhD studies of Mikhail. by the reaction of diethyl malonate and *bis*-(2-ethylhexyl) amine. It had been vacuum distilled before bottling. Note that the malonamide is very viscous and difficult to pipette. Cyanex 923 was supplied by Cytec some years ago before in 2015 it was acquired by Solvay. Note Cytec was a spin off company from the American Cyanamid Company. Cyanex 923 is a mixture of long chain trialkyl phosphine oxides which is a liquid at room temperature.

Scrap gold in the form of damaged jewellery was purchased from a pawnbroker (Pantbanken Sverige) which is at Norra Hamngatan 36, 411 06 Gothenburg (Göteborg) in Sweden. The gold was 18 Karot gold (810 mg) which is believed to have been an earing. The jewellery was flattened by hammering it against a steel surface while it was wrapped in paper to increase its surface area. The gold was combined with 16 M nitric acid (5.595 grams) and 12 M hydrochloric acid (4.47 grams). After allowing this to stand (90 minutes) it was diluted with water to a volume of 60 ml. The slurry of silver chloride and the gold solution was transferred to polyethene centrifuge tubes. After centrifugation (3000 rpm five minutes) the supernatant was transferred to a polyethene tube. It was then transferred in small amounts into a borosilicate beaker (20 ml) in which it was reduced down by evaporation by heating on a hot plate in a fumehood to a volume of *crica* 3 ml. The deep green liquid was transferred to a 15 ml polyethene tube before the beaker was rinsed with water (2 ml). The rinse water was combined with the gold stock in the polyethene tube. Examination with ICPOES indicated that this gold stock contained 19581 ppm of copper (2 %) and 102531 ppm gold (10.3 %)

Alumina (particle size 0.063 to 0.200 mm, 70 to 230 mesh) was supplied by Merck. The product was aluminiumoxide 90 which is article number 1097 and was Brockman grade with an activity between II and III. The specification for this grade of alumina is that a 10 % slurry in water will have a pH between nine and ten.

Argon gas for the ICPOES and ICPMS machines was supplied by AirLiquid in 50 L cylinders.

All other chemicals unless otherwise stated were supplied by Aldrich.

Instrumentation

For the experiments with lower metal concentrations an iCAP Q Inductively Coupled Plasma Mass Spectrometer (ICPMS) supplied by Thermoscientific was used. The machine is equipped with a ASX520 sample changer

For the experiments with higher metal concentrations an iCAP Pro Inductively Coupled Plasma Optical Emission Spectrometer (ICPOES) supplied by Thermoscientific was used. The machine is equipped with a ASX560 sample changer.

Gas chromatography mass spectroscopy experiments were conducted with a 7820A gas chromatography machine supplied by Agilent (A company formed when HP {Hewlett-Packard split off the medical products, chemical analysis and other instrumentation section into a new company}). The machine was fitted with a HP-5MS column. Coupled to the 7820A is a 5977E MSD mass spectroscopy detector. The column length is 30 meters, the bore of the column is 0.25 mm. The thickness of the coating is 0.25 micron. The inlet temperature is 250 °C, aux1 (transfer line) is 280 °C, the MS source is at 230 °C and the MS quadrapole is at 150 °C. The injection volume is 1 microlitre, injected at a rate of 3 ml min-1. The column starts at 60 \degree C, is held for 1 minute after injection before being heated at 20 \degree C min⁻¹ to 300 \degree C. After a dwell time of 2 minutes the acquisition is halted and the column oven allowed to cool.

Alpha counting was done using an ORTEC semiconductor detector using samples dispersed on stainless steel planchets. It is important to obtain a thin film of the active material on the planchet, the samples were heated first with an infra red lamp and then with a butane / air flame. After cooling the samples were transferred into the counter. The gap between the sample and the detector was a vacuum (oil filled rotary roughing pump)

Liquid scintillation counting was performed using a Wallac Guardian 1414 liquid scintillation counter supplied by PerkinElmer life sciences. Glass scintillation counting vials (7 ml) were used. Diluent samples were examined using Emulsifier Safe cocktail while for urine samples Hionic Fluor was used.

Grinding of printed circuit boards was done using a Retsch SM300 mill operated at 3000 rpm. For the first grinding campaign a fine sieve was used in the mill to prevent oversized particles entering the product hopper. For the second campaign a coarse sieve (4 x 4 mm holes) was used. The solid product from the second campaign was sieved using a series of stainless steel sieves. The hole sizes on these sieves were 4, 2, 1.4, 1, 0.71, 0.18 and 0.09 mm. The stacks of sieves were shaken using a Retsch AS200 shaking machine. Samples of the different size fractions were digested with *aqua regia* before the solutions were examined with ICPOES. External calibration was used for these experiments.

Methods

Distribution ratios

Distribution ratios were determined by shaking the denser phase with the light (organic) phase in a glass vial which is equipped with a polyethene lid. After shaking the lower layer was sampled using an air displacement pipette (1000 μ l) equipped with a polyethene tip. The general method is the same as was used before in Foreman's group at Chalmers. If needed for a stripping experiment the organic layer was transferred from the vial using the same equipment.

A typical experiment was conducted in the following manner, a glass vial was labelled with a serial number and fitted with a push on cap. The mass of the vial was recorded, to the vial was added between 500 and 700 µl of the denser phase. The vial was recapped and the gross mass determined again. Then the lighter (organic) phase was added, we aimed to keep the volumes of the two phases equal. The vial was recapped and the mass determined again. Then parafilm (a blend of polyolefins and paraffin wax) was wrapped around the union between the glass vial and the polyethene cap. Note with some plastic caps a failure to do this step will result in the lid coming off the tube during shaking. The tube was placed inside a thermostated shaking machine where it was shaken (60 minutes). After shaking the tube was centrifuged before being opened.

The shaking tubes were examined after the centrifugation, shaking tubes which had solid particles in either liquid layer or at the interface were rejected.

Additionally if the organic phase split from one phase into three phases then the tube was rejected. In one case the organic phase split into two layers one was presumed to be diesel fuel rich and the other contained mainly extracted metal complexes with the extractant. For information below is shown a photograph of three tubes where the organic phase has split into two layers thus giving three layers in the tubes.

The air displacement pipette has a button on the top, we use adjustable pipettes which are purely mechanical they contain no electrical parts. We start by fixing a tip to the pipette, next using a thumb we press down to the first stop. Then we insert the tip of the pipette into the lower phase in the vial, with a little additional force on the button we blow out a bubble from the tip to clean any organic phase out of the tip. Then we slowly relax the force on the button to allow it to rise to the top of its travel while keeping the pointed end of the pipette in the lower phase. When no force is on the control button on the top the pipette is raised thus taking the tip out of the vial. The outside of the tip is wiped with paper towel before the liquid in the tip is dispensed (by pushing down on the button) into a preweighed 15 ml plastic (polystyrene, polyethene or polypropylene) vial. The new mass of the vial is recorded and then to the vial is added dilute mineral acid (9.5 ml of matrix acid) to dilute the sample for either the ICPOES or ICPMS machine. The vials were then capped, weighed and then shaken before use.

While in the past in the Foreman group it has been common to use ruthenium as an internal standard for ICPOES, it was found while working on the TARANTULA project that when oxalic acid was added to the matrix acid that the ruthenium disappeared from solution. As a result we changed to using rhodium (1 ppm) for ICPOES work when we had oxalic acid present in the acid. The oxalic acid was used to modify the behaviour of niobium and tantalum. As the 2 litre polyethene bottle used to hold high purity hydrochloric acid was contaminated with oxalic acid from recent TARATNULA project experiments on niobium / tantalum we choose to continue to use rhodium as the internal standard.

For ICPMS work we used hydrochloric acid diluted in MQ water with a lower concentration of rhodium as the internal standard. For gold work in the ICPMS it is important to add a sulfur containing matrix modifier, we use the amino acid methionine at 10 grams per litre (1 %).

Chloride concentration of choline chloride stock

The chloride concentration of choline chloride stock solution was determined by titration with silver nitrate solution (0.10011 M) using potassium chromate as an indicator. The titration used a manual burette (50 ml) which is held using a burette clamp which is attached to a clampstand. As the majority of the clamp stands in the Foreman lab have had their bases painted with red hammerite to reduce the formation of rust and other corrosion products, a sheet of white paper (paper hand towel) was placed under the conical flask which holds the chloride solution being titrated. The clamp stands were treated first by brushing with a steel brush and soaking in oxalic acid to remove rust deposits before being dried. Then they were painted using red hammerite.

Average value 4.914 moles per litre.

Average density 1.097 grams per ml

Acid Base Titration method

A dilute sodium hydroxide solution was made by dissolving sodium hydroxide pellets (8.0741 g) in a glass volumetric flask (2 L). After the dissolution of the pellets the volume was increased to 2 L. A dilute nitric acid solution was made by diluting concentrated nitric acid (6.25 ml) to 2 L in a volumetric flask.

To obtain the ratio of volume between the sodium hydroxide and the dilute nitric acid four separate portions (10 ml) of the sodium hydroxide solution were spiked with bromothymol blue solution and were titrated with the nitric acid. The volumes used were 18.2, 18.0, 17.8 and 17.9 ml. It was calculated that the volume ratio between the nitric acid and the sodium hydroxide was 1.7975 : 1.0000

To standardize the solutions a known volume (0.5 ml) of a 1 M sulfuric acid volumetric standard (Purchased from Aldrich) was combined with our dilute sodium hydroxide solution (20 ml), this mixture was spiked with bromothymol blue and then titrated with the dilute nitric acid. In three experiments 17.55, 17.55 and 17.50 ml of nitric acid were used. It was calculated that the dilute nitric acid was 0.0543 moles per litre.

Thus the dilute sodium hydroxide is 0.0976 moles per litre.

Liquid scintillation counting method for the determining of the solubility of water in a diluent

WARNING: In the same way as it would be the height of folly to attempt to do lion taming, ride a motorcycle, handle highly venomous snakes (such as cobras), fly an aircraft, prepare puffer fish for human consumption, do high voltage electronics and perform dentistry without being properly taught how to perform these actions. It is equally inadvisable to for the ordinary chemist to perform radiochemistry without specialist training.

Equally even while one of the authors (MF) has training both in radiochemistry and high voltage electronics it would be inadvisable to perform such work without the correct plant and equipment present. For example one should not perform radiochemistry either on the kitchen table or in a normal chemical laboratory where the room is not designed / built / operated in such a way to prevent the spread of radioactivity and facilitate decontamination. Equally I would not attempt to work on a 4 x 3CX800A7 amplifier (One was marketed by Linear Amp UK with the poetic name "Invader") in a place where children have access to the equipment if I was the only person present with experience of high voltage electronics (My reasoning is if I have to leave the room then I have the potential to leave a child with access to a high power high voltage rig). To get the full 3 kW output from the amplifier I would need a 2200 volt DC supply for the anodes which is able to deliver 1 A to each valve.

Also however well equipped and well trained you might be, there will be times when you are unfit to perform some types of work. Ignoring workers impaired by medication, alcohol or other street drugs it is important to note that even a common cold can render you unfit to perform some types of work. If you think you might be ill you should strongly consider if you are fit to perform work with either radioactive or nonradioactive chemicals in a chemical laboratory.

Tritium (³H) is radioactive, open sources of tritium should only be used by a trained radiochemist working at a site suitably equipped for such work. Note that it is impossible to measure tritium with a Geiger-Muller tube detector as the low energy of the beta particles make them unable to pass through the mica window of a GM tube used for beta emitters.

Now after being suitably warned here is the experimental method. As you will later discover the world's worst radiochemist is able to do themselves less harm with the tritium stock needed for the experiment than it is possible to do to one's self in a traditional organic, inorganic or organometallic chemistry laboratory.

Scintillation cocktail was dispensed into glass scintillation vials. It is important for reasons of radiological safety to place the cocktail in the vial before a radioactive solution. A general rule in radiochemistry is to always where possible add the radioactive solution last to a vial, this reduces the number of operations where open containers of radioactivity have to be manipulated.

Before performing the radioactivity work a layer of clean paper towels were laid on the floor of the fumehood. Their purpose is to both provide a means of soaking up a spill and to also provide a clean (uncontaminated) surface inside the hood. At Chalmers in nuclear chemistry unless a radiochemical hood has been completely emptied, thoroughly cleaned and verified by the radiation protection officer to be free of contamination it is treated as if it is contaminated. Objects may be passed freely into the hood but the vast majority of objects are only allowed out of the hood if they are sealed inside plastic bags.

It is normal to wear a disposable gloves if one needs to touch an object or surface inside the hood. For most of the work MF worn one glove, one hand is considered to be the "dirty hand". The dirty hand manipulates radioactive objects while the clean hand (ungloved) holds the pipette handle, when more than 1 kBq of activity is being pipetted then a filter pipette is used to prevent the transfer of droplets into the pipette. As the 200 microlitre pipette had to reach deep inside the polyethene tube holding the diluted tritium stock solution, the majority of the shaft of the pipette was wrapped with parafilm from the bottom up in a spiral manner. Outside the hood glass vials had the diluents added to them and were placed inside small plastic pots to prevent them falling over or touching the paper. The tritium solution was added to the glass vials, these were capped. A loose tag was left on the parafilm which allows a gloved hand to hold the parafilm before the clean hand rotates the pipette thus unwinding the protective parafilm layer from the pipette shaft. Then the tip was ejected from the pipette into a rigid waste container to which was added the parafilm.

The capping and decapping process processes required both hands, for these operations gloves were worn on both hands. After capping the vials they were shaken by hand before being allowed to settle (90 minutes). The tubes were opened before samples (500 microlitres) were withdrawn from them using a 1000 microlitre pipette. Before sucking up the sample into the pipette a liquid scintillation vial was prepared and placed in clean plastic beaker, the sample of the diluent was dispensed into the liquid scintillation vial with great care to avoid contamination of the outer surfaces of the counting vial. Then the cap was screwed onto the vial with an ungloved hand before the vial was lifted out of the hood using an ungloved hand. It is important to shake the vial until the contents of the vial is homogeneous. If the contents after shaking is cloudy or otherwise not homogeneous then the sample volume is excessive.

The labels for the tubes were written on the lids, the tubes were then placed in the liquid scintillation counter for measurement.

Note that these instructions are provided for information alone, merely reading them will not enable a person without experience / training of working with open radioactive sources to perform the work without the supervision of a radiochemist. Also note that the methods and systems of work used at different radioactivity sites vary, so a trained nuclear / radioactivity worker will always need site specific training.

For example consider shoes for use in radioactivity areas. While visiting the waste vitrification site at Sellafield I was issued with black steel toe capped shoes for use in the radioactive area (C2 level), while at nuclear chemistry in Chalmers black clogs are used in rooms where no or a little radioactivity is handled. For a higher contamination level at Chalmers we use a white clog, in the event that we have to walk on an exceptionally contaminated floor we tend to put overshoes onto white clogs.

At Chalmers we work in such a way that we confine the radioactive contamination to the inside of our fumehoods and gloveboxes. An event which causes radioactivity to appear on a surface outside the fumehood such as on the floor is regarded as a radioactivity spill and is promptly dealt with. We use white clogs in areas where greater amounts of radioactivity are handled as the floor has a greater potential to be contaminated (We still aim to keep the floor free of contamination).

I was informed by the late John Peckett that at Harwell in radioactivity areas which would correspond to a C2 at Sellafield or blue area at Ringhals that the shoe used was a red leather shoe. While at Ringhals(A Swedish nuclearsite) I wore blue push on shoesin areas which have the potential forslight contamination on the floor (Blue areas). It should be clear that as the nuclear / radioactivity sector does not have a uniform policy on the colour of the shoes one wears in a room where the floor is likely to be uncontaminated but has the potential to be contaminated, it should be obvious that even an experienced radioactivity worker will need some site specific training if they need to perform work at a new site.

Experiments

Experiment 1

A solution of the malonamide in untreated HVO100 was made by dissolving *circa* 0.5 ml (0.4206 g) of the malonamide in the diluent (4.5 ml of HVO100, 3.4284 g).

A solution of gold and copper in a mixture of sodium and hydrogen chlorides was made up according to the following table.

The solution of gold and copper chlorides from the gold scrap was combined with water, dilute hydrochloric acid and saturated sodium chloride solution. This was pipetted into a series of nine shaking vials (970 to 978). To three of the vials was added the HVO100, to three the solution of the malonamide in HVO100 and to three was added a hydrocracked HDO fuel from skyNRG. The vials were shaken by hand for one minute before being centrifuged (4000 rpm for ten minutes).

In the tubes (970, 971 and 972) which contained HVO100 and the copper / gold solution a solid was observed at the interface between the two liquids. This formation of crud makes it impossible to measure the distribution ratio and thus these tubes were not sampled. The tubes were then subject a second centrifugation at 5300 rpm for 10 minutes, this failed to resolve the third phase problem.

Tubes (973, 974 and 975) which contained the malonamide solution in HVO100 had two homogeneous layers in them, so they were then sampled. Tubes (976, 977 and 978) contained the skyNRG fuel, these in common with tubes 973 to 975 had two clear layers in them. Thus they were sampled. For the tubes using skyNRG only 400 microlitres was used of each phase

A stripping experiment was performed using 400 ul of each phase

Mean disitribution ratios obtained with the malonamide in HVO100

The experiment was also conducted using Aliquat 336 (5 % v/v) in 3,7-dimethyloctanol. Due to the low copper concentration in the loaded organic phase it was not possible to determine the copper distribution ratio in the stripping stage of the experiment.

Distribution ratios

Experiment 2 (Extraction of Au, Cu, Pb and Pd) with different concentrations of the malonamide.

A solution of metals in a mixture of sodium chloride and hydrochloric acid was made in the following way.

The dilute hydrochloric acid used was 1.57 moles per litre and was determined by back titration using our standardized sodium hydroxide and dilute nitric acid.

The copper, lead, palladium and zinc stock was made in the following way. To an empty 15 ml polyethene ICP vial was added anhydrous copper(II) chloride (10 mg), anhydrous zinc(II) chloride (10 mg), a saturated solution of lead(II) chloride in water (1 ml), Palladium stock in dilute sodium chloride (291 mg) and water (4 ml).

A series of solutions of the malonamide in HVO100 were made. Firstly a 30 % (v/v) stock of the malonamide in HVO100 was made by combining the two liquids.

The 30 % (v/v) malonamide stock was further diluted to form 5, 10 and 20 % (v/v) solutions of the malonamide in HVO100.

A series of shaking vials were set up

Experiment 3 (Extraction of Au, Bi, Cr, Ni, Pb, Pd and Zn)

A mixed bismuth, chromium and lead stock solution was made by combining lead(II) chloride (0.6903 g), bismuth(III) oxide (0.7414 g), concentrated hydrochloric acid (66.8723 g) and water (55.0943 g). To this stock was added chromium(III) chloride hexahydrate (2.135 g).

A solution of lead, bismuth and chromium(III) in different choline chloride concentrations was made for another project by adding water, choline chloride stock and the mixed bismuth, lead and chromium stock into polyethene vials (15 ml). After an initial solvent extraction experiment in 2021 the solutions were spiked with small amounts of the gold stock from the earing, a palladium stock and a mixed nickel / zinc stock before being used for the solvent extraction experiments in this paper.

The experiment can be summed up with four graphs.

30 % MA in HVO

Cyanex 923 in HVO100

None of the four extraction systems were able to extract any of the nickel or chromium present in the solutions shaken with the organic layers.

Distribution ratios obtained with 30 % (v/v) aliquat 336 in 3,7-dimethyloctanol

Distribution ratios obtained with 30 % (v/v) cyanex 923 in HVO100

Experiment 4 (Effect of acid concentration on the extraction)

Sodium chloride was dissolved in water, samples of the resulting solution were titrated using silver nitrate (0.1 M) using chromate as the indicator. The end point was judged by eye as when a stable red colouration was seen in the flask into which silver nitrate (0.10011 moles per litre) was added. The same general method was used as was used to determine the concentration of the choline chloride solution.

Average of the three concentrations is 3.37 moles per litre. Standard deviation 0.029 moles per litre.

Due to the high acidity of the hydrochloric acid stock (*crica* 3 M) it was impossible to use chromate as the indicator. To determine the concentration of the hydrochloric acid a sample was placed in a conical flask to which a known excess of sodium hydroxide solution was added. The resulting alkaline mixture was spiked with bromothymol blue solution before being titrated to a yellow end point with dilute nitric acid.

Average of the three determinations is 2.96 moles per litre. Standard deviation is 0.0109 moles per litre.

Experiment 5 (Metal contamination of HVO100)

Superpure nitric acid was added to MQ grade water in a polyethene bottle (2 L) which had been rinsed many times with super pure nitric acid and had been used exclusively by Mark Foreman for the preparation and storage of super pure nitric acid for 15 years. The concentration of the nitric acid was 1 mole per litre.

Small aliquats of this super pure nitric acid (800 µl) were placed in glass shaking vials, to these vials was added HVO100 fuel (1.6 ml) either before or after standing over alumina. The vials were capped with polyethene caps before being shaken by hand (two minutes). After centrifugation (4000 rpm for 10 minutes) the lower layers were sampled by removing 500 µl by pipette. There were then diluted in 15 ml polyethene vials with 1 M hydrochloric acid containing 0.5 % oxalic acid made by dissolving the acids in MQ water.

The diluted samples of acid shaken with HVO100 were examined with a ICPOES machine. The machine was set up to record the intensities of ultraviolet light associated with many elements.^A These elements included all the non radioactive alkaline earth metals, lithium, sodium, potassium, first row transition metals, boron, aluminium, silicon, phosphorus, lead, cadmium, zinc, mercury, lanthanum, yttrium and neodymium.

Element	Untreated HVO100	HVO treated with alumina
Scandium		
Titanium	No	No
Vanadium	No	No

^A Aluminim, phosphorus, boron, lead, calcium, mercury, silicon, tin, cobalt, zinc, magnesium, copper, cadmium, strontium, nickel, bismuth, barium, lanthanum, scandium, iron, beryllium, ruthenium, rhodium, manganese, chromium, vanadium, titanium, lithium, yttrium, sodium, neodymium, potassium,

Experiment 6 (Solubility of water in HVO100)

Diluents (2 ml) were shaken with a solution of tritium as tritiated water combined with normal water (0.2 ml) in shaking tubes. The samples were allowed to stand (90 minutes) to allow the two liquid layers to separate. The upper layer was sampled and then examined with liquid scintillation counting. For comparison the tritiated water mixed with normal water was examined with liquid scintillation counting.

The counting time was set to 3600 seconds (one hour) per tube, but the machine was set up so that if a tube reached 10000 counts that the counting time would be terminated early to save time.

Initial gold extraction experiment using pure diluents (RJ)

Gold extraction by dilute solutions of aliquat 336 in dimethyl octanol from sodium chloride solutions.

Distribution ratios obtained with a 1 % solution of aliquat 336 in dimethyloctanol when the main electrolyte was choline chloride.

Kinetics of the extraction of gold

The organic phase was a 10 % (v/v) solution of the *N,N,N',N'*-*tetrakis* (2-ethylhexyl) malonamide in HVO100. This was shaken with a solution of gold(III) and copper(II) in a mixture of hydrochloric acid and sodium chloride solution. The mass of the 50 ml polyethene vial used to make up the starting solutions for the extraction experiments is summarised in the following table.

Experimental results

Effect of acid concentration on the gold extraction

Sodium chloride and hydrochloric acid were dissolved in water to form the stock solutions. These were titrated with silver chloride (using a chromate indicator) and in an acid / base titration using dilute sodium hydroxide (back titration with dilute nitric acid).

The sodium chloride concentration was 3.37 moles per litre while the hydrochloric acid stock was 2.96 moles per litre. Using these stock solutions a series of aqueous starting solutions were made. In the following table the amounts of the liquids required are displayed.

The intent was to keep the total chloride concentration at 2 moles per litre. The contribution of the metal stocks to the chloride content of the final solutions was ignored.

The solvent extraction experiment was conducted with MIBK using the 2 mole per litre acid and the 0 mole per litre acid. With no acid the gold disitribution ratio was over 100 while with the 2 mole per litre acid it was greater than 1000.

Extraction of gold and other elements with other organic reagents from hydrochloric acid.

A solution of metals was formed by adding aqueous solutions to a 50 ml polyethene vial.

Equal volumes of the aqueous phase and a series of organic layers were shaken for two hours at 25 ^oC before centrifugation and sampling of the aqueous layer.

The organic phases were 10 % TEHMA (*N,N,N',N'-tetrakis*-(2-ethylhexyl) malonamide in HVO100, pure tributylphosphate, acetophenone, pure tetrabutyl malonamide (TBMA), L-menthone, 30 % DEHBA (Di-2-ethylhexyl butamide) in HVO100, 30 % tributyl phosphate in HVO100, 10 % tetrabutyl malonamide in HVO100, 30 % tetrabutyl malonamide in HVO100 and 30 % DEHPA (Di-(2-ethylhexyl) hydrogen phosphate) in HVO100.

The solutions of TBMA in HVO100 formed intractable third phases with the aqueous layer. The acetophenone was very difficult to sample (both layers have similar densities).

Prediction of the performance of a process for the decontamination of ²¹⁰Pb polluted gold.

Imagine that we were to start with gold with a level of ²¹⁰Pb which is one million times higher than the acceptable limit.

If the extraction was to occur using 30 % malonamide using HVO100 as a diluent using an aqueous phase which is operating at the chloride concentration which causes the lead distribution ratio to be 0.03, under these conditions the distribution ratio of gold will be far above 100, so we can assume that a total extraction of gold will occur. We assume that we have a later stage which recovers all the gold and lead out of the loaded organic phase at the end.

With one stage of extraction then we will have 2.9 % of the lead extracted, the gold coming out of this stage will now be 29000 times too contaminated for use. If we pass the organic phase bearing the gold into a counter current battery of mixer settlers or some other contactors then it will be possible to clean up the gold.

With three stages of counter current scrubbing (back extraction of the unwanted element) then the three scrub stages will remove 99.9976 % of the lead which enters the scrub stage. The gold is now at 66 % of the limit.

If we wanted to be very sure an additional scrub stage could be added to the process, with four scrub stages the scrub section will remove 99.9999 % of the lead which enters it. As a result the gold would be then only at 2 % of the limit.

Even if we assume that a total extraction of the ²¹⁰Bi occurs in the first section then if we make a pessimistic assumption that the bismuth disitribution ratio in the scrub section is 0.5. Then with three stages we will remove 93 % of the bismuth in the scrub section.

The main threat posed by ²¹⁰Pb contamination in jewellery is bremsstrahlung (braking radiation) generated by the interactions of the high energy beta particles from 210 Bi with the gold metal. If we assume that all the lead is removed from the gold and 7 % of the bismuth remains (three scrub stages) then the dose rate to the skin in contact with gold jewellery fabricated on the day of the separation will be equivalent to that after allowing the untreated contaminated gold to stand for 84.4 years.

If the separated gold was allowed to stand for 81 days then the bremsstrahlung emission would be one million times lower than the original gold.

If we moved to four scrub stages then 3.22 % of the bismuth would remain in the gold, this only reduces the cooling time after the separation to about 76 days.

If we change the scrub stage to use a higher concentration of chloride where the bismuth distribution ratio will now be 0.036 then with three scrub stages the ²¹⁰Bi level will only be 45 times the limit after the scrub (99.9955 % of the bismuth scrubbed out). This will require a further cooling time of 28 days.

With four scrub stages then the cooling time after the separation will be 3.5 days before the ²¹⁰Bi level in the gold is sufficiently low.

Note that as no stable isotope of polonium exists we have not measured the distribution ratios of polonium so we can not predict how this element will behave in the process. As the physical half life of $210P$ o is 140 days, then storage of the gold after removal of the lead for 7.7 years would ensure

that the polonium contamination in the gold will be one million times lower. While 439 years is a very long time for gold to be kept in a secure store it may be reasonable to store gold for eight years.

For comparison the gold which is one million times as radioactive as the limit a cooling time of 439 years would be required if no chemical separation is used.

Radiological health and safety justification of the use of tritium in the work.

The use of tritium is a single one off experiment which is not intended to be repeated by the readers if they are using HVO100 as a diluent. It is an experiment which is used at Chalmers as an alternative to the Karl Fisher titration. As the use of X-ray generators for X-ray Diffraction (XRD) and X-ray fluorescence (XRF) is considered an acceptable radiation practise in papers published in a range of RSC journals including green chemistry. It is reasonable to compare the use of tritium to XRD equipment.

Let us assume that we use a staggering 100 MBq of tritium for the work, in real life we will aim to work with much less tritium.

If we consider the worst possible accidents in a radioactivity area with tritium. The IAEA have reasoned that the smallest creditable amount of tritium which when dispersed is able to cause an injury which leads to either death or a permanent effect which lowers a person's quality of life is 2000 TBq.

They consider a series of scenarios, one or more of these is able to cause either death of a serious injury. It is not in the public interest to attempt to deduce which of the three is the one of greatest concern.

- Inhalation of one thousandth of the radioactive source, this would be inhaling 2 TBq of tritium.
- Swallowing (ingestion) of 0.001 % (20 GBq) of the tritium.
- Skin contamination with 1 % of the source (20 TBq of tritium) spread over 1 m^2 of skin

Based on these values it can be concluded that if the world's worst radiochemist was to do the experiment using 100 MBq of tritium (1 MBq of tritium per shaking tube, and to measure 100 solubilities of water) using our method while working in a poorly ventilated room on the open bench then they would not be able to have an intake which would result in death or permanent disability. This behaviour would result however in ejection from nuclear chemistry at Chalmers. We imagine that the national nuclear / radiation regulatory body would be dismayed at such conduct and would take action.

The annual limit of intake (ALI) for inhalation and swallowing tritium is 1.1 GBq. So if our hypothetical "worst radiochemist in the world" takes leave of their senses and swallows the entire 100 MBq of tritium. Then they would have an intake which is less than 10 % of the annual intake limit.

The IAEA classifies radioactive sources into five broad classes depending on their ability to cause death / injury when mishandled. Based on the advice which the IAEA give on the classification of radioactive sources, the 100 MBq of trtium is a category five source. This is a source which is unable to cause death or injury in a creditable accident.

If we compare the use of tritiated water with the use of X-ray diffraction equipment, many X-ray diffraction sets use working beams which are able to cause localised injuries which are comparable with those caused by the mishandling of high activity sources.

Table of category one to five sources as defined by the IAEA.

My assessment of a 2 kW DC input copper anode X-ray tube based on the scenario that a person accidently places their hand in a working beam is that the X-ray source could in seconds deliver a dose which causes an injury to the skin. For skin effects I would rate the XRD source as category two but for effects deep in the torso I would rate it as being below category two.

This places a typical diffraction set at about the same level as the ¹³⁷Cs source which was stolen from a radioactive waste store in Tammiku (Estonia) in 1994. This source could be safely manipulated without shielding using a 1 m long pair of tongs if the worker is able to work quickly. The Tammiku source contained between 150 GBq and 7.4 TBq of ¹³⁷Cs (IAEA D value is 100 GBq). This places the source in either in category two or three

As a result the gamma dose rate at one meter (Between 15.3 and 764 mSv hr⁻¹ at 1 m) will be such that a classified worker^B could manipulate the source with a 1 m long pair of tongs. At the upper activity limit the worker would need to complete the task in less than 90 seconds to avoid reaching their annual exposure limit (20 mSv). While at the lower activity limit for the source the worker would have more than one hour to perform the task.

The radiation field from the Tammiku source at 20 cm would be weaker than what would be expected for a unmonochromated working beam for an X-ray diffraction machine. We would expect the XRD machine's source to be able to cause a small radiation burn after less than one minute of exposure, but due to the low photon energy (less than 50 keV) we would expect that the XRD source would be able to deliver a life-threatening dose to the vital organs inside the torso.

The Annual Limit of Intake (ALI) for tritium for a classified worker (nuclear worker with the medical clearance needed for the highest radiation exposures allowed by law in either the UK or the EU) is high. In Sweden the ALI is set at 1100 MBq for both inhalation and oral exposure to tritium. The 100

B Classified worker is the UK term for a radiation worker who is allowed to be exposed up to the annual limit for workers, these are workers over the age of 18 who are subject to medical supervision (regular blood tests and medical examinations). A biological basis exists for limiting the radiation exposure of children and young people, as a result below the age of 16 radiation work is forbidden. In Sweden and other EU countries such persons are described as "Category A radiation workers". Currently the exposure limits for classified workers (Category A workers) are whole body, lens of eye, skin and hands / feet are 20, 20, 500 and 500 mSv per year (Swedish implementation of the regulations is SFS 2018:506). Category B workers (non classified radiation workers) are limited to 6, 6, 150 and 150 mSv per year of exposure to their whole body, lens of eye, skin and hands / feet.

MBq does not come near to the ALI, so even in the world's worst radiochemist was to swallow all of the 100 MBq tritium stock they would not exceed the ALI.

For workers oral exposure to tritium as tritiated water is considered by the IRCP to cause the person to have an effective dose which is proportional to the tritium intake.

42 pSv Bq⁻¹, so if a worker was to have an intake of 1 MBq of tritium then they would commit to an effective dose of 42 microSv. Thus if the intake was 100 MBq then the committed effective dose would be 4.2 mSv. This is 21 % of the yearly limit for occupational exposure of a classified worker.

For inhalation of tritium as tritiated water the dose coefficient is 18 pSv Bq $^{-1}$ so exposure via the lungs is less harmful.

Derivation of equations used to model the gold extraction.

If we assume that the only forms of gold present in the aqueous phase are the neutral complex (AuCl₃) and the anionic complex (AuCl₄⁻) then we can write this equation for the fraction of the gold which is in the form of the anionic complex.

$$
\frac{[AuCl_{4}^{-}]}{[AuCl_{3}]+[AuCl_{4}^{-}]} = \frac{\left(\frac{k_{4}[Cl^{-}]{f}_{Cl^{-}}[AuCl_{3}]f_{AuCl_{3}}}{f_{AuCl_{4}^{-}}}\right)}{[AuCl_{3}]+\left(\frac{k_{4}[Cl^{-}]{f}_{Cl^{-}}[AuCl_{3}]f_{AuCl_{3}}}{f_{AuCl_{4}^{-}}}\right)}
$$

Divide the right hand side by $[Aucl₃]$, this then gives us.

$$
\frac{[AuCl_{4}^{-}]}{[AuCl_{3}^{-}]+[AuCl_{4}^{-}]} = \frac{\frac{k_{4}[Cl^{-}]{f}_{Cl^{-}}f_{AuCl_{4}^{-}}}{f_{AuCl_{4}^{-}}}}{1+\frac{k_{4}[Cl^{-}]{f}_{Cl^{-}}f_{AuCl_{3}^{-}}}{f_{AuCl_{4}^{-}}}}
$$

If the right hand term in the denominator on the right hand side is far greater than 1, then we can write,

$$
\frac{[AuCl_{4}^{-}]}{[AuCl_{3}^{-}]+[AuCl_{4}^{-}]} = \frac{\frac{\left(\frac{k_{4}[Cl^{-}]{f_{c}}_{l} - f_{AuCl_{3}}}{f_{AuCl_{4}^{-}}}\right)}{\left(\frac{k_{4}[Cl^{-}]{f_{c}}_{l} - f_{AuCl_{3}}}{f_{AuCl_{4}^{-}}}\right)} = 1
$$

Which means that all of the gold is present in the anionic tetrachloro complex. This will make the later equations more simple. Now if we have an equation for the extraction of the anion by the aliquat 336 (liquid anion exchanger) which defines the extraction constant.

$$
F_{A u C l_4} - f_{C l} - [C l^-] [A u C l_4^-]_{org}
$$

$$
k_{ex} = \frac{f_{C l_0 - f_{A u C l_4} - [C l^-]_{org}[A u C l_4^-]}}{f_{C l_{org}} - f_{A u C l_4} - [C l^-]_{org}[A u C l_4^-]}
$$

We can rearrange the equation to give us the reciprocal of the gold disitribution ratio

$$
\frac{\begin{bmatrix} A u C l_{4}^{-} \end{bmatrix}}{\begin{bmatrix} A u C l_{4}^{-} \end{bmatrix}_{org}} = \frac{f_{A u C l_{4}^{-}}}{k_{ex} f_{C l_{org}} f_{A u C l_{4}^{-}} \begin{bmatrix} C l^{-} \end{bmatrix}_{org}}
$$

Turn everything upside down to give us

$$
D_{Au} = \frac{\left[A u C l_4^- \right]_{org}}{\left[A u C l_4^- \right]} = \frac{k_{ex} f_{Cl_{org}} - f_{AuCl_4^-} \left[C l^- \right]_{org}}{f_{AuCl_{4_{org}} - f_{Cl} - \left[C l^- \right]}}
$$

Now we introduce a new constant U which allows us to put the organic layer activity functions and the concentration of the chloride anions in the organic phase into a single constant.

$$
D_{Au} = \frac{k_{ex}Uf_{AuCl_4^-}}{f_{Cl_-}[Cl^-]}
$$

If we use a Pitzer equation with two terms in the polynomial as written below for the activity fuction

$$
\log f = \frac{-z^2 S \sqrt{l}}{1 + \left(\frac{3\sqrt{l}}{2}\right)} + A[Ch^+] + B[Ch^+]^2
$$

Now we can write

$$
f = 10 \left(A[ch^+] + B[ch^+]^2 - \frac{z^2 s \sqrt{I}}{1 + \left(\frac{3\sqrt{I}}{2}\right)} \right)
$$

Then as we are interested in one activity function divided by another we can write.

$$
\frac{f_1}{f_2} = \frac{10^{4[ch^+] + B[ch^+]^2 - \frac{z^2S\sqrt{I}}{1 + \left(\frac{3\sqrt{I}}{2}\right)}}}{\sqrt{a^2[ch^+] + B^2[ch^+]^2 - \frac{z^2S\sqrt{I}}{1 + \left(\frac{3\sqrt{I}}{2}\right)}}}
$$

If we transform back to the log form then we now get

$$
\log\left(\frac{f_1}{f_2}\right) = \left(\frac{-z^2S\sqrt{I}}{1 + \left(\frac{3\sqrt{I}}{2}\right)} + A[Ch^+] + B[Ch^+]^2\right) - \left(\frac{-z^2S\sqrt{I}}{1 + \left(\frac{3\sqrt{I}}{2}\right)} + A'[Ch^+] + B'[Ch^+]^2\right)
$$

As all the anions are monoanions, the Debye-Huckel terms cancel out thus giving us a more simple equation.

$$
\log\left(\frac{f_1}{f_2}\right) = A[Ch^+] + B[Ch^+]^2 - (A'[Ch^+] + B'[Ch^+]^2)
$$

We can change our equation to use delta A and delta B terms which represent the differences between the A / B and the A' / B' terms.

$$
\log\left(\frac{f_1}{f_2}\right) = \Delta A \left[Ch^+\right] + \Delta B \left[Ch^+\right]^2
$$

Now if we transform ourselves back to the non log form we get.

$$
\frac{f_1}{f_2} = 10^{\left(\Delta A \left[Ch^+\right] + \Delta B \left[Ch^+\right]^2\right)}
$$

We can then use this to create the equation which appeared in the paper

$$
D_{Au} = \frac{K_{ex}U 10^{\left(\Delta A \left[Ch^{+}\right] + \Delta B \left[Ch^{+}\right]^{2}\right)}}{\left[Cl^{-} \right]_{aq}}
$$

We can repeat this process for equations which a derived from activity function equations which include a $\theta\phi$ term to take account of the effect of replacing aqueous media with the ethaline. Using the same method in algebra we then end up with.

$$
D_{Au} = \frac{K_{ex}U 10^{(\theta \Delta \phi + \Delta A [Ch^+] + \Delta B [Ch^+]^2)}}{[Cl^-]_{aq}}
$$

Assessment of skin exposure to the hydrocarbon diluents

The fraction of the oral reference dose (RfD) which would be adsorbed by a 70 kilo man who immerses his hands (840 cm² skin area) in the liquid every day. Using the following equation where P is the permeability constant, A the area, C the concentration in the fuel mixture and t (exposure time) the mass of the indivicual compounds in JP8 adsorbed into a person via the hands can be calculated.

 $Mass = PACt$

Estimate of the energy consumption of a fume hood

A single fume hood which is 1 meter wide, is opened to a width of 0.1 m and has a face velocity of 0.5 ms⁻¹. Then in one hour this fume hood will remove 180 cubic meters of air. As air has a density of 1.2 kg m⁻³ and a heat capacity of *circa* 1 kJ kg⁻¹ K⁻¹ then on a Swedish winter's day (In Vara, Skara or Skövde) when the outside temperature is -20 °C and the workplace temperature is 20 °C. Then 2.4 kW will be required to heat the air delivered into the building to replace the air removed by the fume hood. While in London 540 W will be required when the outdoor temperature is the average 11 $^{\circ}$ C. If we were to assume the energy for one week of the additional heating demand created by the fume hood in the Swedish winter was in the form of diesel fuel (circa 10 kW hr L⁻¹), then this fuel would be sufficient to drive a modest car from Imperial College (London) to the outskirts of Aberdeen (Northern Scotland).

Second grinding campaign

A total of 13.637 kilos of printed circuit boards were ground and then sieved. The majority of these printed circuit boards were from computers and other similar electronic items.

Table of amounts of metal in solids which passed through sieves of a given size.

Solvent extraction of barium, calcium, lithium, magnesium and strontium from perchlorate media.

Extraction of s block metals from sodium chloride

Extraction of s block metals from sodium nitrate solution

Distribution ratios obtained with variable Cyanex 923 in solvent 70 in aqueous saturated NaClO⁴ (8.14 M)

Distribution ratios obtained with variable Cyanex 923 in solvent 70 in aqueous NaClO₄ (2.44 M)

Distribution data for the s block elements being extracted from sodium perchlorate solution by 30 % Cyanex 923 in solvent 70.

40 7,44 9,13 40 7,64 9,21 40 7,79 8,77 50 9,54 10,8 50 10,0 11,7 50 10,5 10,8 60 11,2 13,5 60 12,5 13,7 60 12.0 13,6 70 13,1 15,5 70 14,4 15,9 70 13,8 16,2 80 16,2 17,5 80 17,4 19,4 80 17,1 18,1 90 18,9 21,6 90 19,9 22,3 90 $|20,2|$ 22,0 100 21,8 21,8 100 22,5 22,5 100 $\Big|$ 25,3 25,3

Lithium distribution ratios obtained with a 8.14 M sodium perchlorate solution using Cyanex 923 in either the skyNRG biokerosene or Euculyptol. The wavelength was 670.784 nm using an axial view of Barium distribution ratios obtained with a 8.14 M sodium perchlorate solution using Cyanex 923 in skyNRG biokerosene. Using an axial view of the plasma.

Barium distribution ratios obtained with a 8.14 M sodium perchlorate solution using Cyanex 923 in Euculyptol. Using an axial view of the plasma.

Solvent extraction of the s-block metals using HVO100 as the diluent

Extraction data obtained with 5 % (v/v) cyanex 923 in HVO100

Barium, lithium, magnesium and strontium disitribution ratios obtained with 10 % (v/v) cyanex 923 in HVO100.

Distribution data for barium, lithium, magnesium and strontium obtained with 30 % cyanex 923 in HVO100

GCMS traces of kerosene grades

TIC (HVO100)

skyNRG

Total ion current for skyNRG kerosene

Total ion current for the solvent 70 kerosene