

SNO-STR-95-018

Secondary Concentration of Lead and Thorium from the SUF Eluate Using Solvent-Solvent Extraction

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March 16, 1995

Abstract

This report investigates the use of solvent-solvent extraction for the secondary concentration of lead and thorium.

The extraction reagents investigated in this report are:

For the lead extraction:

- diethylammonium diethyldithiocarbamate (DDDC)

For the thorium extraction:

- trioctylphosphine oxide (TOPO) and
- di-(2-ethylhexyl)phosphoric acid (HDEHP).

For all of the extractions 2-octanone was used as the organic solvent.

By scaling the results of the experiments described in this report it is expected that 70-80% of the lead and thorium in the 8 litres of SUF eluate, could be extracted sequentially into two 400ml samples of organic solvent, one containing the extracted lead and one containing the extracted thorium.

To assay the extracted lead and thorium it is proposed that a larger version of the existing $\beta - \alpha$ delayed coincidence scintillation counters be developed.

With this larger counter operational it is anticipated that the secondary concentration and assay of lead from the SUF eluate can be achieved. Although the secondary concentration is as good for thorium, further work is needed to enable its assay since a back-extraction technique for thorium has not yet been found.

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1 The Possibility of using Solvent-Solvent Extraction

1.1 Introduction

A method has been outlined for the purification and assay of the heavy water and magnesium chloride to be used in the SNO detector. This method uses a hydrous titanium oxide (HTiO) seeded ultra-filtration (SUF) system [1].

This method extracts the radium, lead and thorium isotopes onto a porous membrane which can then be eluted with acid into a volume of about 8 litres.

To elute the radium off the SUF membranes 8 litres of 0.03M nitric acid will be used. This 8 litres of SUF eluate can then undergo a known secondary concentration procedure which obtains volumes that are small enough to be assayed by some specially developed $\beta - \alpha$ delayed coincidence scintillation counters.

However, to elute the lead and thorium a stronger molarity acid is required. Using 8 litres of 0.5M hydrochloric acid gives an elution efficiency of 90% for the lead and thorium but unfortunately it also elutes about 25% of the titanium that was originally deposited on the membranes. Since there will be in total about 4 grams deposited, that means about 1 gram in the 8 litres (a solution that is 125ppm in titanium).

This large amount of titanium interferes with secondary concentration procedure which is used for radium, so an alternative procedure is needed for lead and thorium.

Solvent-solvent extraction is known to be very selective in extracting different metals, so it will be investigated to determine its suitability to be a secondary concentration procedure for lead and thorium from the SUF eluate.

1.2 Theory For Batch Extraction Techniques

In solvent-solvent extraction the process of extraction is through the formation of uncharged chemical species via chelation and ion association. The extraction efficiency of a reagent in a solvent depends primarily on the relative volumes of the aqueous and organic phases. It is also dependent on the concentrations of both the element to be extracted and the reagent used to do the extraction.

The efficiency of extraction of an element can be expressed by the distribution ratio, that is the ratio of the element in the organic phase compared to that in the aqueous phase at equilibrium.

For batch extraction the percentage extraction, $E(\%)$ at equilibrium, in terms of this distribution factor, D for an extraction using v ml of organic phase and V ml of aqueous phase is:

$$E(\%) = \left(1 + \frac{1}{D} \frac{V}{v} \right)$$

For the batch extraction experiments carried out in this report the extraction efficiency, E was measured and the distribution ratio, D calculated.

1.3 Possible Reagents

A study was made into previous literature in this area of solvent-solvent extraction for traces of lead and thorium in acidic solutions. Also, a study was made of any techniques of back-extracting the lead or thorium into an aqueous layer since an aqueous sample may be easier to assay.

- For lead the only useful extraction technique that was reported involved the extraction of lead dithiocarbamate. There are a few compounds that extract using this method:

1. sodium dithiocarbamate

This compound does extract lead but not from mineral acid solutions because the diethyldithiocarbamic acid decomposes rapidly in aqueous solution. This means it would not be suitable in 0.5M hydrochloric acid.

2. diethylammonium diethyldithiocarbamate (DDDC)

This decomposes more slowly than the sodium dithiocarbamate because the diethyldithiocarbamic acid favours staying in the organic phase. This means that lead extraction can be achieved, but the time taken for each extraction should not last longer than a few minutes. DDDC also has a known back-extraction technique [2].

3. ammonium pyrrolidinedithiocarbamate (APDC)

The literature suggested that this compound was even more stable, than the DDDC, in acidic conditions [2]. However it was also known that it was less soluble, than the DDDC, in organic solvents. (This was found to be true with 2-octanone where it was impossible to produce a solution of only a few % w/v.)

Due to this preliminary investigation the compound chosen for further study into lead solvent-solvent extraction was DDDC.

- It was found that there was a wide range of compounds used to extract thorium. Four of these compounds were examined more closely:

1. tributyl phosphate (TBP)

This is a commonly used extractant suitable for many elements, however it extracts via nitrate formation and so would require an aqueous phase of about 4M in nitrate concentration for good extraction efficiencies. Even with this presence of nitrate ions the extraction for thorium is known to be slow, so it is not a suitable extractant for the required conditions.

2. thenoyltrifluoroacetone (HTTA)

This compound extracts thorium only at pH 1. This means that it is not suitable in extracting from an aqueous phase 0.5M in hydrochloric acid.

3. trioctylphosphine oxide (TOPO)

Like TBP this compound extracts thorium via nitrate formation but according to the literature it requires the aqueous phase to be only 1M in nitric acid to achieve very large extraction efficiencies. It also has a known back-extraction technique [5]. Making the SUF eluate 1M in nitric acid is not highly desirable but it could be achieved.

4. di-(2-ethylhexyl)phosphoric acid (HDEHP)

According to an initial study this seems the most promising of the extractants since it is known to extract thorium in hydrochloric acid solutions and there are a few recorded back-extraction techniques [3], [4].

Due to this preliminary investigation the two compounds chosen for further study into solvent-solvent thorium extraction were TOPO and HDEHP.

1.4 Possible Solvents

A suitable solvent was needed which would have a low solubility in the aqueous layer and one that would separate rapidly from it to enable the speedy completion of the lead extraction compared to the half-life of ^{212}Pb which is 10.6 hours. Furthermore, it was preferred that the all of the chosen reagents be soluble or miscible with the chosen solvent so that only one would need be used for the whole solvent-solvent extraction procedure.

The normal solvents used in solvent-solvent extraction are toluene, carbon tetrachloride, chloroform and other such liquids. Both toluene and chloroform were found to be very good in many ways but their destructive qualities with plastics, their toxicities and flammability inhibits their use in laboratory experiments and more importantly at the SNO detector itself. (Carbon tetrachloride was not tested due to unavailability.)

It was found that ketones had many desirable properties except that the initially tested 2-pentanone was too soluble in water, so a higher organic chain was investigated and 2-octanone found to be a suitable solvent. For the rest of this report 2-octanone was used as the organic solvent.

2 Solvent-Solvent Batch Extraction Experiments

2.1 General Procedure

It was decided primarily for practical reasons to use about a volume of about 0.5 litres for the aqueous phase. These experiments were therefore carried out at about a 1/16th scale of the volumes needed for the secondary concentration from the SUF eluate. To make the aqueous phase have the same behaviour as the SUF eluate it was made to be 0.5M in hydrochloric acid and to have 125ppm of titanium.

In order to determine the extraction efficiencies a ^{228}Th radioactive spike of a few kBq was added to the stock. This relatively high amount of activity was used so that backgrounds due to contamination would be minimal and so that assay could be achieved using gamma counting on a GeLi detector. Measurements of the lead (^{212}Pb) and thorium (^{228}Th) concentrations were thus achieved by counting the 860keV ^{208}Tl line using the GeLi counter at different times elapsed after the experiment. That is counting about 2 hours after the experiment to assay ^{212}Pb to ensure that the ^{212}Bi has had time to grow in and that there is no ^{224}Ra contamination, and counting about 2 weeks after the experiment to assay ^{228}Th to ensure that the ^{224}Ra has grown in. ($t_{1/2}(^{212}\text{Bi}) = 60.6$ minutes, $t_{1/2}(^{212}\text{Pb}) = 10.6$ hours, $t_{1/2}(^{224}\text{Ra}) = 3.66$ days, $t_{1/2}(^{228}\text{Th}) = 1.91$ years.)

The extractions were carried out in a 1 litre separating funnel by allowing the phases to mix for a certain amount of time. This was achieved either by tilting the separating funnel by hand a number of times, or by mechanically shaking the funnel for a number of minutes. The phases were then allowed to separate which took only a few minutes, before running out the aqueous layer and collecting the less dense organic layer.

To determine the initial quantities of lead and thorium that were present a solution larger than 500ml was produced and the extra amount taken to be assayed. This made an aqueous phase volume of 500ml for the first extraction.

After each extraction 60ml of the aqueous phase was collected for counting and the rest returned to the separating funnel for any further extractions. Hence, the volume for a second extraction would be 440ml and for the third, 380ml. When back extractions were made all of the organic phases from each extraction were added together into the separating funnel, diluted with more 2-octanone and the necessary back-extraction procedure carried out. In these cases the individual extraction efficiencies had to be determined by the disappearance of activity from the aqueous phase. Detailed procedures are explained in each section.

2.2 Solvent-Solvent Batch Extraction of Lead using DDDC in 2-Octanone

2.2.1 Experiment Details

Clearly when the volume and concentration of the aqueous phases remain constant, extraction efficiencies are determined by the concentration of the reagent and the volume

of the organic phase. Another parameter is the time of contact since equilibrium may not be achieved. (This is because it is necessary to keep the contact time fairly short because of DDDC decomposition and the short ^{212}Pb half-life.)

The following table shows the experiments that were conducted in order to maximise the extraction efficiencies whilst minimising the organic phase volume:

EXP NO	EXTRACTIONS				BACK-EXTRACTION			
	Conc.(w/v) of DDDC	Vol.(v) of org	Time of Ext	No.of Ext	Total Org Vol	Vol of HNO_3	Time of Dec	Vol of H_2O
CEL5	sat sol	10ml	20 tilts	2	-	-	-	-
CEL6	2.5%	5ml	20 tilts	2	30ml	0.2ml	10mins	10ml
CEL7	2.5%	15ml	20 tilts	2	60ml	0.6ml	20mins	10ml
CEL9	sat sol	8ml	20 tilts	3	60ml	0.6ml	20mins	6ml
CEL10	sat sol	8ml	20 tilts	3	60ml	0.6ml	20mins	10ml

Here the concentration of DDDC is expressed as a weight to volume percentage of DDDC in the 2-octanone solvent, it was known [2] that this should be of the order of a few percent. The saturated solution which was used was estimated to be about 3% w/v.

The back extraction technique was to add an amount of concentrated nitric acid to the combined organic phases of each extraction in a separating funnel, and then to shake for a period of time on a mechanical shaker. This decomposes the DDDC which can then be washed into an aqueous phase using an amount of water, agitating for a short time and finally separating the phases.

2.2.2 Results

For experiment CEL10 any radium or thorium extraction was also studied but no extraction for these isotopes was observed.

The following extraction results for lead were obtained:

Exp. No.	Ext.1		Ext.2		Ext.3		Total Ext.(%)	Back-Ext. Eff.(%)	Total Back-Ext.(%)
	E%	D	E%	D	E%	D			
CEL5	51	52	65	82	-	-	79	-	-
CEL6	42	72	49	85	-	-	63	65	41
CEL7	62	54	55	36	-	-	70	81	57
CEL9	45	51	50	55	46	40	72	64	46
CEL 10	36	35	54	65	44	37	77	83	64

Since the disappearance of lead was being used to calculate efficiencies on all the experiments apart from CEL5 it was necessary to check for any sources of contamination.

The following table shows how the calculated disappearance of activity from the aqueous phase and the recorded appearance in any organic or back-extracted phases compare. The overall effect is also shown. The activity is measured in counts per second that the GeLi detector recorded and the error on all the measurements was about 5%.

Exp.No.	Disappearance from Aqueous	Appearance in Organic+Back Ext	Overall Effect
CEL5	10.7	11.2	+0.5
CEL6	8.7	8.8	+0.1
CEL7	11.5	10.0	-1.5
CEL9	5.6	4.8	-0.8
CEL10	5.2	5.4	+0.2

It can be seen that most of these results are within the errors, although there is some loss on CEL7. This could be due to losses of lead on surfaces.

2.2.3 Conclusions

The results clearly show that distribution ratios for the extraction of lead of about 50 can be readily obtained for a very short amount of contact time (typically in these experiments it was of the order of a minute or two). The preferred method being to use three sequential extractions with a saturated solution of DDDC in 2-octanone. Using 8ml of this solution for each extraction from an aqueous volume of 500ml gives 24ml of organic phase containing 70-80% of the lead that was initially in the aqueous phase. Also, it is clear that the back-extraction technique works well, being about 80% efficient at stripping the lead from the DDDC into a small aqueous volume.

2.3 Solvent-Solvent Batch Extraction of Thorium using TOPO in 2-Octanone

2.3.1 Experiment Details

As explained above the compound TOPO extracts thorium only from solutions greater than 1M in nitric acid and so all the experiments started by adding an appropriate amount of concentrated nitric acid to the aqueous phase to make it 1M in nitric acid.

The following table shows the experiments that were conducted in order to maximise the extraction efficiencies whilst minimising the organic phase volume:

EXP NO	EXTRACTIONS				BACK-EXTRACTION			
	Conc.(M) of TOPO	Vol.(v) of org	Time of Ext	No.of Ext	Total Org Vol	M of H ₂ SO ₄	Vol of BExt	Time of BExt
TEL1	0.1M	10ml	10mins	2	40ml	0.25M	10ml	10mins
TEL2	0.1M	10ml	10mins	2	40ml	0.25M	2×10ml	30mins
TEL3	0.1M	25ml	10mins	1	25ml	0.3M	2×20ml	10mins
CTEL1	0.1M	15ml	5mins	3	60ml	0.3M	20ml	10mins
TEL4	0.5M	8ml	10mins	3	60ml	9M	2×20ml	5mins

Further experimental details:

- TEL2 was carried out in a solution not only 1M in HNO₃ but also 1M in NaNO₃ since the literature suggested that this enhanced extraction efficiencies [5]
- TEL3 was using the procedure specifically outlined in [5].
- TEL2,3,4 both used two back-extractions which were of the same volume.
- CTEL1 was an attempt to combine the lead extraction and the thorium extraction. This means the extractant was also saturated with DDDC, and that the back-extraction procedure included a first step of adding 0.6ml of concentrated HNO₃ and shaking for 20mins before the H₂SO₄ was added.

2.3.2 Results

For experiment CTEL1 no lead extraction was observed. It is presumed that this is due to the DDDC decomposing in the acidic conditions.

It was also noted that during the extractions the aqueous phase gradually accumulated a yellow colouring. At the moment the source of this is unknown but it may be interference from the titanium.

The following extraction results for thorium were obtained:

Exp. No.	Ext.1		Ext.2		Ext.3		Total Ext.(%)	Back-Ext. Eff.(%)	Total Back-Ext.(%)
	E%	D	E%	D	E%	D			
TEL1	61	78	53	50	-	-	104??	0	0
TEL2	68	106	50	44	-	-	89?	0	0
TEL3	40	13	-	-	-	-	40	0	0
CTEL1	12	9	27	20	35	26	44	0	0
TEL4	30	27	42	40	42	34	78	29	23

The back-extraction efficiency for TEL4 is the combined effect of two extractions giving 10% and 19% efficiencies each.

Since the disappearance of thorium was being used to calculate efficiencies on some of the experiments it was necessary to check for any sources of contamination, as in the case for lead extraction. The activity is measured in counts per second that the GeLi detector recorded and the error on all the measurements was about 7%.

Exp.No.	Disappearance from Aqueous	Appearance in Organic+Back Ext	Overall Effect
TEL1	9.1	12.2	+3.1!!
TEL2	8.7	9.7	+1.0!
TEL3	0.8	1.2	+0.4
CTEL1	2.5	1.5	-1.0
TEL4	2.8	3.1	+0.3

This clearly shows the concerns over the reliability of the results of experiments TEL1 and TEL2 since there is a large contamination. This was believed to be coming from the bottles used for measuring the count rates. The bottles had been used in previous experiments and although thoroughly washed in 0.1M nitric acid it is possible that the 2-octanone was damaging the sides of the polypropylene bottles and depositing activity which could then not be washed away. Certainly some washed bottles gave significant count rates when measured. In all later experiments new, clean bottles were used and in these experiments the results show no signs of contamination.

2.3.3 Conclusions

The results for thorium extraction using TOPO are not as good as was expected from the literature. It is still unknown why the back-extraction technique failed to work at all until very high molarity sulphuric acid was used, when the literature suggested that 0.3M sulphuric acid would be very efficient [5]. However, the results of experiment TEL4 suggests that large extraction efficiencies for thorium can be achieved (around 80%) when the TOPO is at a high molarity and when the aqueous phase is 1M in nitric acid. Also, experiment TEL4 suggests that some back-extraction can be achieved using strong sulphuric acid. It may be possible to produce higher back extraction efficiencies by using concentrated sulphuric acid.

The preferred method for thorium extraction using TOPO is to make three sequential extractions with a contact time of 10 minutes each using 0.5M TOPO in 2-octanone. Using 8ml for each extraction from an aqueous volume of 500ml gives 24ml of organic phase containing about 80% of the thorium that was initially in the aqueous phase. It must be remembered that this technique requires the aqueous phase to be 1M in nitric acid.

2.4 Solvent-Solvent Batch Extraction of Thorium using HDEHP in 2-Octanone

2.4.1 Experiment Details

The following table shows the experiments that were conducted in order to maximise the extraction efficiencies, whilst minimising the organic phase volume:

EXP NO	EXTRACTIONS				BACK-EXTRACTION	
	v/v in% HDEHP	Vol.(v) of org	Time of Ext	No.of Ext	Total Org Vol	Method
PEL1	50	10ml	20 tilts	2	-	none
PEL2	50	10ml	20 tilts	2	-	none
PEL3	50	10ml	20 tilts	3	60ml	+3ml conc HNO ₃ for 20mins then H ₂ O rinse
CPEL1	50	10ml	20 tilts	2	-	none
CPEL2	50	20ml	20 tilts	2	-	none
CPEL3	50	10ml	2mins	3	60ml	+3ml conc HNO ₃ for 20mins then H ₂ O rinse
PEL4	50	8ml	10mins	3	60ml	2×(20ml 2M (NH ₄) ₂ CO ₃ shaken for 2mins)
PEL5	50	8ml	5mins	3	60ml	2×(20ml 6M HCl shaken for 5mins)

Further experimental details:

- PEL2 was carried out in a solution 0.1M in NaNO₃ since the literature suggested this enhanced extraction efficiencies.
- CPEL1,2,3 were attempting to combine the lead extraction and thorium extraction. This means the extractant was also saturated with DDDC.
- PEL4,5 were using back-extraction techniques as described in the literature. [3] [4]

2.4.2 Results

For experiments CPEL1,2,3 no lead extraction was observed. It is unclear exactly why this was true but it could again be due to the decomposition of the DDDC in the acidic HDEHP itself.

The following extraction results for thorium were obtained:

Exp. No.	Ext.1		Ext.2		Ext.3		Total Ext.(%)	Back-Ext. Eff.(%)	Total Back-Ext.(%)
	E%	D	E%	D	E%	D			
PEL1	44	39	32	21	-	-	57	-	-
PEL2	51	52	20	11	-	-	62	-	-
PEL3	29	20	21	17	31	17	58	0	0
CPEL1	26	18	18	10	-	-	38	-	-
CPEL2	37	15	14	36	-	-	46	-	-
CPEL3	39	32	47	39	13	6	64	0	0
PEL4	68	133	10	6	13	7	85	0	0
PEL5	50	63	29	22	10	5	58	0	0

A very small amount of activity was found in some second back-extractions with no activity in the first back-extraction. This is presumed to be due to rinsing the apparatus rather than any back-extraction efficiency, hence it was ignored.

Since the disappearance of thorium was being used to calculate efficiencies on some of the experiments it was necessary to check for any sources of contamination, as done previously. The activity is measured in counts per second that the GeLi detector recorded and the error on all the measurements was about 10%.

Exp.No.	Disappearance from Aqueous	Appearance in Organic+Back Ext	Overall Effect
PEL1	8.0	7.5	-1.5!
PEL2	5.1	6.6	+1.5!
PEL3	1.7	1.8	+0.1
CPEL1	4.8	4.7	-0.1
CPEL2	4.6	5.3	+0.7
CPEL3	2.5	2.3	-0.2
PEL4	2.5	2.9	+0.4
PEL5	2.5	2.2	-0.3

This shows that there may be some problems with the results of experiments PEL1 and PEL2, however the extraction efficiencies from these experiments were not determined by the disappearance of ^{228}Th and so the results probably do not have very large errors due to contamination. All the other experiments show no signs of contamination.

2.4.3 Conclusions

Similarly to the failure of back-extraction techniques from TOPO there is as yet no explanation as to why methods outlined in literature [3] [4] had no effect on back-extracting from the HDEHP in these experiments. It can also be seen from the results that the

distribution ratios for HDEHP extraction of thorium vary considerably and sometimes with no obvious cause. This does give some concern for repeatability. However experiment PEL4 shows that when a long contact time is used (about 10 minutes) efficiencies of about 80% can be achieved for the extraction of thorium using HDEHP.

The preferred method for thorium extraction using HDEHP is to make three sequential extractions with a contact time of more than 10 minutes each, using a solution 50% v/v in 2-octanone. Using 8ml for each extraction from an aqueous volume of 500ml gives 24ml of organic phase containing about 80% of the thorium that was initially in the aqueous phase.

3 General Conclusions on Solvent-Solvent Extraction

3.1 Extrapolating to Lower Concentrations of Lead and Thorium

To evaluate the actual concentrations of ^{228}Th that were used in the experiment, the GeLi counter was calibrated with a known ^{228}Th source ¹. It was found that in counting the 860keV ^{208}Tl line the GeLi was about 0.8% efficient. Hence 1 count/second at this peak, as measured by the GeLi, is actually equivalent to about 125 Bq.

Using:

$$\frac{dN}{dt} = -N \frac{\ln 2}{t_{1/2}}$$

And knowing that $t_{1/2}(^{228}\text{Th}) = 1.91$ years, or 6×10^7 seconds, the amount of ^{228}Th in any sample giving a measured decay rate can be calculated.

The experiments were all carried out with roughly 1kBq of ^{228}Th in 500ml, this makes it a solution about 10^{-7} ppm (1ppm= 10^{-6} g/g) in ^{228}Th .

It is estimated that the SUF eluate will be about 10^{-14} ppm in ^{228}Th . This means that we will be working with amounts of ^{228}Th and ^{212}Pb in the SUF eluate that are seven orders of magnitude lower than the amounts used in the experiments investigated for this report. It should be noted however that the SUF eluate is expected to be about 10^{-4} ppm in ^{232}Th .

There must be concerns in general as to whether these techniques will perform as well at these much lower concentrations, but there are at the moment no real reasons to expect that they would fail. It may simply prove necessary to ensure better mixing, or to use a larger relative volume of organic phase.

One particular worry is whether or not the extraction of thorium and lead could be swamped by the much greater abundance of titanium (at 125ppm). The first thing was to determine whether or not the extraction procedure ignored the titanium. For the lead extraction there was found to be no titanium extraction, this was as expected since the DDDC is known to be a very specific lead extractant.

Experiments PEL4 and PEL5 (HDEHP extraction of thorium) were also examined for titanium extraction and in this case some titanium extraction was observed at an efficiency of about 40%. Unfortunately, no such analysis could be made for a TOPO extraction of thorium due to interference of the titanium analysis method by the yellow colouring that is produced in the aqueous layer during the extraction. The literature suggests that both HDEHP and TOPO do extract titanium but with decontamination factors four orders of magnitude lower than the decontamination factors for thorium. So, even though TOPO and HDEHP extract titanium this does not necessarily become a concern when lower concentrations of thorium are present since the extractants preferentially extract thorium.

¹The source used was CRPP2 which was prepared 30.9.93 by M. Shatkay to be 2kBq of ^{228}Th in 100ml of 1M nitric acid.

If the extractants still give good decontamination factors for thorium despite extracting titanium when thorium is at 10^{-7} ppm and titanium 125 ppm, they can be expected to do the same when the thorium is at 10^{-14} ppm for the same titanium concentration.

It is anticipated that the technique outlined in this report will still be effective at extracting lead and thorium from a liquid which has much lower concentrations of these isotopes.

3.2 Solvent-Solvent Batch Extraction of Lead and Thorium from the SUF Eluate

If we assume that the results of the experiments outlined in this report can be scaled to the larger volumes and the smaller concentrations that will be the case when extracting from the SUF eluate, we have the following suggested methods for the batch solvent-solvent extraction of lead and thorium from the SUF eluate:

Isotope Extracted	No x Vol of Ext	Extraction Reagent	Contact Time	Total Org Volume	Efficiency	Comments
Lead	3 x 130ml	2-octanone saturated in DDDC	a few minutes	400ml	70-80%	Back-Ext efficiency is about 80%
Thorium	3 x 130ml	0.5M TOPO in 2-octanone	at least 10 minutes	400ml	about 80%	SUF eluate must be > 1M in HNO ₃
	3 x 130ml	50% v/v HDEHP in 2-octanone	at least 10 minutes	400ml	about 80%	-

The results of the experiments have also shown that the method for the extraction of lead is not compatible with the method for the extraction of thorium. However, it is expected that it will be possible to carry out the extractions in sequence since it has been found that the DDDC does not extract thorium and that TOPO and HDEHP both extract thorium even when DDDC is present.

Hence, it looks as though it will be possible to extract the lead and thorium sequentially from the SUF eluate, each into 400ml of organic phase.

3.3 The Continuous Solvent-Solvent Extraction of Lead and Thorium

The solvent-solvent batch extraction techniques have proved to be very efficient, however when the volumes are increased to the 8 litre scale it may become unwieldy to be using batch contact extraction. It is also difficult to see how to standardise the mixing procedure for such a large volume.

It is therefore proposed that a more appropriate method would be to use a continuous method of extraction. This involves pumping the aqueous volume through a layer of organic phase held stationary in some appropriate piece of apparatus and then separating the two phases. Since the 2-octanone is less dense than water it would be desirable to spray the aqueous phase onto the top of a layer of the organic phase and allow the aqueous phase to pass through the organic layer under the action of gravity. This would hopefully allow enough time of contact between the volumes of the two phases to extract the required isotope. Care needs to be taken not to spray too quickly or finely as then an emulsion may form and the two phases would then be very hard to separate. A preliminary experiment was performed to test the feasibility of such a system.

3.3.1 Experimental Procedure

The experiment used an aqueous volume of 2 litres that was 0.5M in hydrochloric acid, 125ppm in titanium and about 10^{-8} ppm in ^{228}Th . So this experiment is at a 1/4 scale of the volumes that will be needed for the secondary concentration from the SUF eluate. An organic phase of 50ml containing the appropriate extractant was kept as a layer in a 1 litre separating funnel by ensuring the funnel was kept half full of the more dense aqueous phase. The aqueous phase was then pumped through it at a rate of about 1 litre per minute. This was done by taking the aqueous phase from the bottom of the separating funnel and spraying it on to the organic phase at the top of the separating funnel.

Samples of the aqueous phase were taken after a period of time to evaluate the disappearance of any lead or thorium from the aqueous phase, the same volume that was taken was then replaced with a solution the same as the original aqueous phase but with no activity added, ensuring that the volume of the aqueous phase remained constant at about 2 litres.

After each extraction the majority of the aqueous phase was pumped to a holding vessel and then the organic phase was totally separated by using the separating funnel to drain off any remaining aqueous phase. All the samples were then assayed for lead and thorium content using a GeLi detector in the same way as it was done for the batch extraction experiments.

3.3.2 Results

Some practical problems were found. These included the problem of separating the two phases whilst ensuring the organic phase remained in the separating funnel. This was a technical problem but on the lead extraction some 2-octanone escaped into the rest of the pumping system (it was later recovered). The more serious problem was that many flexible plastics are not stable in 2-octanone and since a peristaltic pump was being used to pump the aqueous phase onto the organic layer, and because some 2-octanone was found to dissolve in the aqueous phase, this caused a failing of the tubing in the lead extraction. A

brief investigation into the suitability of different tubing was carried out and it was found that PharMed² and Norprene³ show no signs of deterioration after a few days of being immersed in 2-octanone. So, Norprene was used in the subsequent thorium extraction.

It must be noted that the separation technique when using this continuous extraction procedure needs to be improved as it was very difficult to carry out quickly. Also, the results showed that the activity was not all accounted for in individual extractions. It may be that it was collecting somewhere in the apparatus and when the aqueous phase was pumped away to the holding vessel it returned to circulation. At the end of the experiment the amount of activity that had disappeared from the aqueous phase was in agreement with the amount which appeared in the organic phase so there were no overall losses.

The individual extraction efficiencies, which were measured by the disappearance of activity from the aqueous phase, were therefore felt to be unreliable. The overall extraction results, which were measured by the appearance of activity in the organic phase are shown below:

Ext of:	Extraction Procedure	Total Efficiency
lead	2×(50ml of DDDC sat 2-oct for 10mins)	59%
thorium	2×(50ml of 50% v/v HDEHP in 2-oct for 30mins)	79%

The total organic volume produced by this extraction experiment is two samples of 100ml, one containing the lead and one containing the thorium. This would then be two samples of 400ml if this experiment were scaled in volume to the volumes that will be needed in the secondary concentration from the SUF eluate.

3.3.3 Conclusions

The results confirm that an HDEHP extraction of thorium can be carried out after a DDDC extraction of lead. Also, it was found that there was no noticeable decrease of extraction efficiencies for the DDDC over the 10 minutes contact time. This implies that there was no decomposition of DDDC in the acid during the extraction.

The results show that the process of continuous solvent-solvent extraction gives good extraction efficiencies and with a better experimental procedure it is anticipated that these figures could be increased. Continuous solvent-solvent extraction could provide a suitable method for the extraction and concentration of lead and thorium from the 8 litres of SUF eluate.

²PharMed is a Registered Trademark of Norton

³Norprene is a Registered Trademark of Norton

3.4 Methods to Assay the Lead and Thorium Extracted into the Organic Phase from the SUF Eluate

Once the lead and thorium is extracted into the organic phase it is necessary to develop a way to assay the amount recovered. In these experiments the concentrations of lead and thorium were chosen to be sufficient to ensure that gamma counting would be sensitive enough. However at the levels that will be present in the SUF a more sensitive low level counting technique is needed.

The method for low level counting used at present is $\beta - \alpha$ delayed coincidence and the counters used for the assay of radium are scintillation counters using 2 inch photo-multiplier tubes which can count up to 12ml of aqueous liquid provided it is less than 1M in acidity or salt content.

The methods outlined above produce about 400ml of organic liquid so further steps are needed to enable the assay of the thorium and lead content.

There are two suggested methods of performing this assay:

1. The back-extraction of lead and thorium into an aqueous phase:

The method of back-extracting has been shown to be successful in the case of lead extraction using DDDC but no method has as yet been found to work well for either technique for the extraction of thorium. The back-extraction procedure for lead extracted using DDDC is:

- Add to the organic phase 1/100th its volume in 16M nitric acid (concentrated nitric acid).
- Allow a contact time of 20 minutes.
- Wash out the lead with a small amount of water.

This back-extraction method means that 4ml of 16M nitric acid would be needed to extract the lead from the 400ml of organic phase. This could then be washed out with the lead into 12ml of aqueous solution which would be a volume small enough to be counted by the presently operational counters, unfortunately it would also be about 6M in nitric acid and this is too acidic for the scintillator. However, if this were diluted to a volume greater than about 100ml the acidity would be less and it would be possible to count it by a scintillation method.

The development of a larger $\beta - \alpha$ delayed coincidence scintillation counter is therefore desired to enable the assay of any extracted lead. This larger counter could be developed using a 5 inch photo-multiplier tube and a larger scintillation vessel. It is estimated that about 400ml of aqueous liquid could be counted on such a larger version.

Without the larger $\beta - \alpha$ delayed coincidence scintillation counter it will be necessary to use a further concentration step. This could be achieved by using a miniature SUF

system (as in the radium assay procedure) since the large titanium interference will have been removed. But this does seem to be a rather complicated overall procedure.

2. The counting of the organic phase:

If a larger counter were developed then it may be possible to assay the whole of the organic volume with no need for an extra method of concentration. The problem with this is that it is as yet unknown whether or not the 2-octanone and the extractants would quench the scintillator. One particular concern is due to the fact that the extractants in the 2-octanone produce a slight yellow colour and this may indicate that they will absorb the wavelengths of light that photo-multipliers are most sensitive to. However, if no back-extraction method for either TOPO or HDEHP is forthcoming then this will need to be examined more carefully as it may be the best way to assay the extracted thorium.

These methods are both pointing to the need for a larger $\beta - \alpha$ delayed coincidence scintillation counter. With such a counter operational then the proposed methods would enable the secondary concentration and assay of lead in the SUF eluate and it is expected also for thorium although at the moment this is less certain.

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