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THE APPLICATION OF TRACER TECHNIQUES TO THE

DETERMINATION OF URANIUM EXTRACTION COEFFICIENTS

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1D³⁴

ABSTRACT

Results of several extraction series are presented in which aluminum nitrate is used as the salting agent and dibutyl carbitol the organic extractant.

2D³⁴

INTRODUCTION

The primary purpose of this investigation was the development of a method for determining extraction coefficients of solutions of low uranium concentration. A method which appeared to have possibilities of satisfying conditions of accuracy and rapidity within limits was the use of a Geiger-Mieller counter as the analytical tool.

Because the success of this type of determination is greatly dependent upon the technique involved in various operations, a description of some of the techniques is presented before dealing with specific extraction data.

EXPERIMENTAL

The measurement of small volumes of liquid required the use of micro-pipettes. These pipettes are capable of accurately measuring as low as five microliters (5 μ). To reduce to a minimum the possibility of contamination of these pipettes a means of cleaning them was devised.

The cleaning apparatus consisted of a filtering flask fitted with a one-hole rubber stopper. The hole in the stopper was of such a size that the tip of the pipette easily passed through but the shoulder could not penetrate. With this assembly connected to an aspirator, cleaning solution, water, and acetone were rapidly drawn through the pipette producing a thorough job of cleansing and drying.

Plating the active solutions on platinum discs is the next consideration. The discs used in these experiments measured one and one-

half inches in diameter and were two and one-half mils in thickness. Three general methods of plating were tested; first, evaporation under "Infra-Radiator" lamps, second, evaporation on hotplate, and third, electrodeposition.

Evaporation under an "Infra-Radiator" lamp produces very good results when plating aqueous solutions. The sample is stippled on to the disc and evaporates quite rapidly with no tendency toward spattering. As large a sample as desired may be plated by allowing time for evaporation between additions of the active solution.

While this type of plating lends itself very well to an aqueous sample it is not applicable in the case of a liquid having a low surface tension.

Liquids such as dibutyl carbitol when placed on a disc under a heat lamp quickly spread over the entire surface of the disc and lose activity by "creeping" over the edge. The first attempt to counteract this difficulty was the scribing of a circle of slightly smaller radius than that of the disc on the surface. This did not produce completely satisfactory results as the solution often overran this "border".

These difficulties lead to the design of a disc holder which can be readily understood upon consulting the drawing in the appendix. Its purpose is as follows:

When the platinum disc is clamped in place the contact occurs between the holder and the periphery of the disc. This has the effect, when placed on the hot plate, of creating a thermal barrier to the liquid which has been pipetted onto the center of the disk. When held at the

proper temperature, evaporation proceeds very smoothly and the deposit is well centered on the disc, an advantage in counting a small quantity of material.

This method of plating was used in this work for all dibutyl carbitol solutions.

The third mentioned method, that of electrodeposition, failed in our short trial period to give quantitative results. The procedure followed for electroplating was that described in several reports on the subject.^{1,2,3,4}

Although this method produced very good looking deposits trial runs using known weights of uranium failed to plate out quantitatively. More work on exact conditions may produce better results.

Due to the fact that the α -activity of normal (700) uranium is not great enough to warrant its use as a tracer 1500 and 1900 material were employed in this capacity. These materials have α -activities of ~ 50 and 250 times respectively that of 700 uranium.

Solutions of the above (1500 and 1900 uranium) were prepared by dissolving their oxides in sufficient nitric acid and diluting to a known volume. Activity determinations were then made by plating out aliquots on platinum discs and evaporating under a heat lamp. From the counting rate of a sample having a known weight of uranium the counts per minute per microgram was determined. Data covering these runs are found in tables I and II of the appendix.

Extractions were carried out by putting the salting agent, uranium solution and carbitol in a sixty milliliter separatory funnel which was supported in a thermostatically controlled water bath (27°C). The rapid rota-

tion of stirring rods which had short "fingers" joined to them produced a good dispersion of the organic and aqueous phases. Extractions were carried out for three quarters of an hour. At the end of this time the stirring was stopped and the phases allowed to separate for about fifteen minutes while still in the bath.

By draining off the aqueous phase the organic phase was recovered and its uranium concentration determined by one of two methods. Before the development of the disc holder mentioned above it was found best to perform a water wash out on an aliquot of the organic liquid; the washout was in turn aliquoted and evaporated on the disc under the lamp. With the advent of the disc holder the organic layer could be plated directly thus eliminating the time consuming intermediate wash out step.

After plating, the disc was ignited at 700°C for five minutes and then counted. Because the counting rate for samples rarely exceeded 500 c/m no correction other than background was made.

From the counting rate of a sample the total uranium in the organic layer was computed and that of the aqueous arrived at by difference. Substitution in the following formula gave the extraction coefficient.

$$\text{Ext. Coef.} = \frac{\frac{\text{wt. U in org. phase}}{\text{volume organic phase}}}{\frac{\text{Wt. U in aqueous phase}}{\text{volume aqueous phase}}}$$

Results from runs for various concentrations of aluminum nitrate are presented in tables III and IV of the appendix. Extractions were carried out on solutions containing as low as one part per million uranium by using the 1900 material (table IV).

With the exception of a few cases dibutyl carbitol was used as the extraction agent and aluminum nitrate as the salting agent. A comparison of

the results of extractions obtained by this tracer method with those carried out on a macro basis is of interest. Comparison is made with results of studies at Brown University⁽⁵⁾ covering the same concentrations of aluminum nitrate. The macro determinations have a reported accuracy of 1 to 2 percent.

<u>Al(NO₃)₃ per 100 cc H₂O gm.</u>	<u>Coef. of Ext. from Report</u>	<u>Ave. Coef. Determined by Tracer Technique Using 1300 Material</u>	<u>Ave. Coef. Determined Using 1900 Material (one part per million)</u>
30	5.1	5.5	4.3
40	22.3	21.4	21.6
50	96.1	114.5	77.5
55	167	159	146
58	240	224	257
62	340	256	354

It will be noted in tables III and IV that the volume of the organic phase has been made small in comparison with that of the aqueous phase, especially for the determination of the higher coefficients. The question will immediately arise whether this is a justifiable procedure.

To determine this point a series of runs, table V of the appendix, was made. It is seen upon analysing this table that the accuracy of the coefficient determination is increased by decreasing the ratio of the volume of dibutyl carbitol to the aqueous volume. The reason for this is that the error introduced by probable deviation in the counting rate of a sample is reflected in the coefficient of extraction to a much greater magnitude in the case where equal or nearly equal volumes of aqueous and carbitol phases are used. It is obvious that variation of the volume ratio could not be tolerated in the case of more soluble ethers without applying a correction

for solubility.

The tracer method gives an accuracy dependent principally on the accuracy of the counting rate determination. In our experiments deviations can be attributed largely to errors in the counting rate because of the short time each sample was counted (8 minutes). This source of error becomes more and more serious as the extraction coefficient increases.

CONCLUSIONS

Several general conclusions may be drawn from the experiments of the investigation:

- (1) The tracer method works satisfactorily for a fast and reasonably accurate means of determining extraction coefficients.
- (2) Extraction coefficients remain essentially constant for all concentrations of uranium in any given system.
- (3) The degree of accuracy and range may be increased by using "hotter" tracers--such as higher U_{234} content material or better yet U_{233} .
- (4) Assuming the extraction and plating steps have been carried out satisfactorily the accuracy may be increased by longer counting of the plated sample.

REFERENCES

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TABLE I

OC-Activity of 1500 Cycle U

(Uniform arbitrary geometry in counting)

λ 1500 Solution	γ U	c/m	c/m/ γ
100	50	1848	36.9
100	50	1899	38.0
50	25	988	39.5
50	25	966	38.6
25	12.5	802	40.2
25	12.5	464	36.7
10	5	187	37.4
10	5	192	38.4
Ave. c/m/ γ			38.5

TABLE II
 α -Activity of 1900 Cycle U

Microliters of Solution	Micrograms of H ₁ N U	Counts/min.	c/m/g
5	.5	97	194
5	.5	100	200
5	.5	98	196
10	1.0	192	192
10	1.0	206	206
10	1.0	194	194
25	2.5	492	196
25	2.5	493	197
25	2.5	481	192
50	5.0	1011	202
50	5.0	976	195
50	5.0	964	193
50	5.0	930	186
50	5.0	946	189
Ave. c/m/g			195

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TABLE III

Effect of $\text{Al}(\text{NO}_3)_3$ Concentration on U Coefficient

Run No.	Volume Aqueous ml.	Volume Organic ml.	$\text{Al}(\text{NO}_3)_3$ grams	U(1500) Added (%)	Organic Aliquot	g/m of Aliquot	Total U in Organic Phase	Ext. Coef.	Remarks
a	20	20	6	1000	200	334	868	6.5	
b	20	20	6	1000	200	325	844	5.4	
c	20	20	6	1000	200	327	849	5.6	
d	20	20	6	1000	200	316	821	4.6	
e	20	10	8	1000	100	347	901	18.2	
f	20	10	8	1000	200	712	925	24.6	
g	40	2	10	1000	25	408	848	112	
h	40	2	10	1000	25	409	850	113	
i	40	2	10	1000	25	412	856	119	
j	40	1	22	1000	100*	155	806	166	0.50 ml. org. shaken into 10 ml. H_2O and 100 λ counted.
k	40	1	22	1000	200*	305	792	152	0.50 ml. org. shaken into 10 ml. H_2O and 200 λ counted.
l	42	1	23.2	2000	200*	622	1615	176	0.50 ml. org. shaken into 10 ml. H_2O and 200 λ counted.
m	80	1	46.4	1000	25	704	732	219	
n	80	1	46.4	1000	25	715	741	229	
o	80	1	49.6	1000	10	295	766	262	
p	80	1	49.6	1000	10	294	764	258	
q	80	1	49.6	1000	10*	291	756	248	200 λ org. shaken into 10 ml. H_2O and 500 λ counted.

* These are actually "wash out" aliquots - see remarks.

TABLE IV

Effect of $\text{Al}(\text{NO}_3)_3$ Concentration on U Coefficients

Grams $\text{Al}(\text{NO}_3)_3$ per 100 ml.	U Added	Aliquot		U in Aliquot micrograms	U in Org. Phase (%)	Extraction Coefficient
		Volume (ml)	Counts/min. background			
30	40	200	161	0.774	3.87	4.3
30	"	200	145	0.744	3.72	4.1
30	"	25	17	0.087	3.60	4.0
30	"	25	20	0.103	4.12	4.6
40	"	50	166	0.85	17.0	20.6
40	"	100	341	1.75	17.5	21.6
40	"	50	161	0.83	16.7	19.7
40	"	100	370	1.90	19.0	24.5
50	"	50	253	1.30	26.0	74.0
50	"	50	262	1.34	26.8	81.0
55	"	100	615	3.15	31.5	149.0
55	"	200	1181	6.06	30.3	125.0
55	"	200	1255	6.44	32.2	165.0
58	"	50	343	1.76	35.2	293.0
58	"	50	339	1.74	34.8	268.0
58	"	50	327	1.68	33.6	210.0
62	"	50	350	1.79	35.8	340.0
62	"	50	352	1.805	36.1	368.0

*Vol. Aqueous = 40 ml; Vol. Organic = 1 ml. in all runs.

TABLE V

Effect of Relative Volumes of Organic and
Aqueous on U Distribution Coefficient

Run No.	Volume Aqueous ml.	Volume Organic ml.	Grams $\text{Al}(\text{NO}_3)_3$ per 100 ml.	Total U Added (δ)	Aliquots of Org. Phase	c/m of Aliquot	Total U in org. phase	Ext. Coef.	% Error*
a	20	20	40.0	50.0	2 ml.	942	48.3	24.1	+7.6
b	20	20	40.0	50.0	2 ml.	950	48.7	37.0	+66.
c	20	20	40.0	50.0	500 λ	224	46.0	11.5	-48.
d	30	10	40.0	50.0	500 λ	401	41.1	14.0	-37.
e	30	10	40.0	50.0	500 λ	433	44.4	23.7	+6.2
f	30	10	40.0	50.0	500 λ	448	45.9	34.0	+52.5
g	40	5	40.0	50.0	200 λ	288	36.9	22.5	+ .9
h	40	5	40.0	50.0	200 λ	289	37.1	22.8	+2.2
i	40	5	40.0	50.0	100 λ	147	37.7	24.5	+10.0
j	40	1.0	40.0	50.0	50 λ	166	17.0	20.6	-7.6
k	40	1.0	40.0	50.0	100 λ	341	17.5	21.6	-3.1
l	40	1.0	40.0	50.0	50 λ	161	16.7	19.7	-11.6
m	40	1.0	40.0	50.0	100 λ	370	19.0	24.5	+10.

* The correct extraction coefficient for these runs was taken as 22.3 which has a reported accuracy of 1 to 2 percent. (5)

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