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(Progress Report)

Technical Division

Chemical Process Development Section

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THE APPLICATION OF COUNTER-CURRENT BATCH EXTRACTION PRINCIPLES TO PROBLEMS OF INORGANIC CHEMISTRY

By

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Introduction

Studies on the synthesis, the isolation from complex mixtures and the purification of organic compounds, particularly those with biological activity, have stimulated the development of counter-current batch extraction techniques (1), (2). This process has been used as an analytical tool to study complex mixtures. Certain similarities exist between the conditions of application of the method to biochemical problems and the conditions of the solvent extraction purification of uranium. Therefore, the counter-current batch extraction principle has been applied to the "25" recovery process and to other problems in the separation of radioactive isotopes.

Summary

Counter-current batch extraction techniques that were successful in the separation of many similar organic compounds have proven useful in the study of inorganic compounds. Some slight variations in the distribution curves found for uranium may have been due to analytical difficulties or may have been real. This should be checked further.

Dichromate was extracted in only small amounts and apparently reacted with the hexone since none was found in any of the organic phases but a small amount (5.5%) was found in the aqueous of number 7 tube.

The analysis for the estimation of HNO_3 in the solutions used was difficult (150% material balance) therefore, the data are unreliable but probably indicate reaction between nitrates and hexone.

Ru and mixed Zr-Cb activities followed the distribution pattern for gross gamma. It is to be noted that these specific activities were influenced by the pre-treatment given them. Oxidation conditions similar to those that were anticipated for the 1200 area process cause Ru and the mixed Zr-Cb activities to be more soluble in the hexone.

Iron that had been irradiated at Hanford was found, in the extraction treatment with isopropyl ether and 5.5M HCl, to contain another gamma emitter that was less soluble in the organic phase than was the iron (perhaps cobalt). Further extraction of some of the purer iron samples gave a distribution curve that was slightly different from the theoretical. The cause of this effect should be investigated further since it has been proposed that isotopic separation might be possible in this manner.

Experimental

The Method -

Eight stage extraction, using nine separatory funnels, has been used in all the tests reported here. The nine separatory funnels hereinafter referred to as tubes, were number 0, 1, to 8 and contained 50 ml of organic phase that previously had been equilibrated with the aqueous phase. The equilibrated aqueous phase, that had originally contained 1M $Al(NO_3)_3$ and 0.1M HNO_3, was used in 50 ml portions. Into tube 0, containing 50 ml of each phase, was introduced the material that was being tested. In those cases where it was felt that the introduction of the test material would

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significantly change the existing concentrations, a synthetic aqueous solution was made to contain 1M $Al(NO_3)_3$, 0.05M HNO_3 and the desired concentration of test material.

The two phases in tube 0 were equilibrated by agitation. After separation the aqueous phase was transferred to tube 1 where it was equilibrated and the aqueous moved to tube 2. Meanwhile, fresh aqueous phase was introduced into tube 0 and after equilibration this aqueous was moved to tube 1. This process of equilibration and movement of the aqueous phase was continued until 8 aqueous portions had been used and had been equilibrated in tubes 1 to 8 inclusive. Samples of each phase from the 9 tubes were analyzed. It was possible in this way to obtain distribution coefficient in 8 of the 9 tubes and an estimate of the total amount of the test substance in each tube. The total amount of test material in each tube was plotted against the tube number.

Distribution of Uranium

Synthetic aqueous test solution (50 ml for the first portion to be introduced into tube 0) was made to contain 1M $Al(NO_3)_3$, 0.05M HNO_3 and 0.5 to 10 g U as UNH per 50 ml. Uranium was determined by the analytical group in the Chemistry Division (see tests 1 and 2 table 1).

In tests 3 and 4, however, sufficient dichromate was introduced to make the aqueous solution 0.1M. Simultaneously with the distribution of U in test 3 the distribution of dichromate was followed by titration with Fe(II), test 9. Dichromate was found only in the aqueous phases while none could be detected in the organic phases probably because of the reduction of dichromate by the hexone used.

Distribution of HNO_3

In this test (6, table 1) the bulk of the aqueous phase contained only 1M $Al(NO_3)_3$ before the preliminary equilibration with the entire volume of the hexone phase. The synthetic aqueous portion for introduction into tube 0 was made to contain 1M $Al(NO_3)_3$ and 0.3M HNO_3. The organic phase was analyzed by titration with standard alkali to a phenolphthalein end point. The HNO_3 in the aqueous phase containing 1M $Al(NO_3)_3$ was estimated by pH measurement. The amount of HNO_3 recovered was about 50% greater than that put onto the test portion. This apparent increase may have resulted from the oxidation of hexone to organic acids with HNO_3.

Distribution of Gross Gamma Activity

The distribution of the gross gamma activity was followed by introducing into the aqueous phase in tube 0 a portion of some semi-works dissolver solution made by dissolving an irradiated uranium slug in nitric acid. The metal had cooled for a period of 6 months. After the 8 extraction stages had been completed aliquots from each phase were counted for gamma in the ionization chamber (test 14, table 1).

Distribution of Ruthenium Activity

Distribution without Oxidation - Ruthenium tracer was introduced into the aqueous portion of tube 0 and the counter-current extraction made for 8

stages. Aliquots from each phase were counted in the ionization chamber within 4 hours after the tracer was introduced into tube 0. (Test 7, Table 1)

Aliquots were removed from the organic layers of tubes 4 and 8, evaporated and absorption curves measured. The fact that these two absorption curves were identical up to 1700 mg Al/sq. cm. indicated the identity of the radioactive material extracted at different periods in the process.

With dichromate oxidation - The first test with ruthenium tracer was repeated with the exception that tube 0 was also made 0.1M in sodium dichromate and the mixture allowed to stand at room temperature for 16 hours before use. In this case the entire phase (50 ml) was counted. (Test 8, Table 1)

Distribution of Mixed Zirconium-Columbium Activity

Tracer as received - The mixed Zr-Cb tracer as received from the Isotope Production Department was stabilized with oxalic acid. In this test no attempt was made to destroy the complexing agent. The tracer was added to the aqueous feed, containing no dichromate, and the equilibrations undertaken without an aging period beforehand. (Test 13, Table 1)

Tracer treated with permanganate - Sufficient permanganate was added to the tracer solution to oxidize the calculated quantity of oxalic acid present. The tracer solution was then added to the aqueous feed containing no dichromate and the equilibrations made as before. (Test 10, Table 1)

The tracer containing an oxalate stabilized solution of mixed Zr and Cb tracer was added to the aqueous feed solution (with 0.1M dichromate) and allowed to stand at room temperature. One portion was submitted to the counter-current batch process after 20 hours standing and a second sample stood for 120 hours before use. Gross gamma activity was measured in each solution without attempting to distinguish between zirconium and columbium. (Test 11 and 12, Table 1).

Extraction of Irradiated Iron

A sample of iron (shown by the spectrograph to contain only traces of contaminating copper and chromium) that had been irradiated at Hanford and allowed to cool for about six months was subjected to counter-current batch extraction between diisopropyl ether and 5.5M HCl (previously equilibrated). Here as before the layers were examined separately in the gamma ionization chamber.

A second extraction through 8 plates was made using the material from tubes 1, 2 and 3 in 2.5M HCl.

Discussion of Results:

The distribution of uranium through an eight plate counter-current batch process under conditions calculated to give a distribution coefficient of 1 showed a difference between those tests made with 0.1M $Na_2Cr_2O_7$ in the aqueous and those tests with no dichromate present. Distribution coefficients observed in tubes 3, 4 and 5 at the end of eight equivalent stages were greater than 1 (1.03 to 1.43) for tests 1 and 2 table 1 without dichromate and less in those tests (3 and 4, table 1) where dichromate was used.

Insufficient data exist to explain this observed difference in the distribution coefficients. While it is possible that the dichromate might be involved in some reaction concerning uranyl nitrate and hexone, the fact that the difference is not an analytical interference has never been established. Less difference was found in the plotted curves than was anticipated by the observed differences in distribution coefficients.

Nitric acid was observed (C, figure 1) to be distributed under conditions that lead one to suspect the decomposition of hexone by the nitric acid. This was further supported by the high material balance.

The gross gamma activity was found distributed (D, figure 1) in a manner indicating high water solubility. Mixed zirconium and columbium, in general, followed a similar pattern (F, figure 1). Ruthenium, however, was more soluble in hexone than the other fission products studied so far. Solubility in hexone was increased by the use of dichromate. (E, figure 1)

The distribution of the mixed Zr-Cb activity (stabilized by oxalate or citrate) was affected by the oxidation procedure used on the tracer. The highest affinity for water was noted in the untreated sample. Treatment with dichromate and permanganate permitted the activity to be extracted by the hexone.

The iron that had been irradiated and allowed to cool for several weeks was found to have a gamma emitter that possessed a lower distribution coefficient than that of the iron itself(G). Further treatment of some or the purer iron samples showed little additional separation(H). It has been suggested, however, that the separation of isotopes might be accomplished in this way. Work on this separation will be started later.

Figure 1

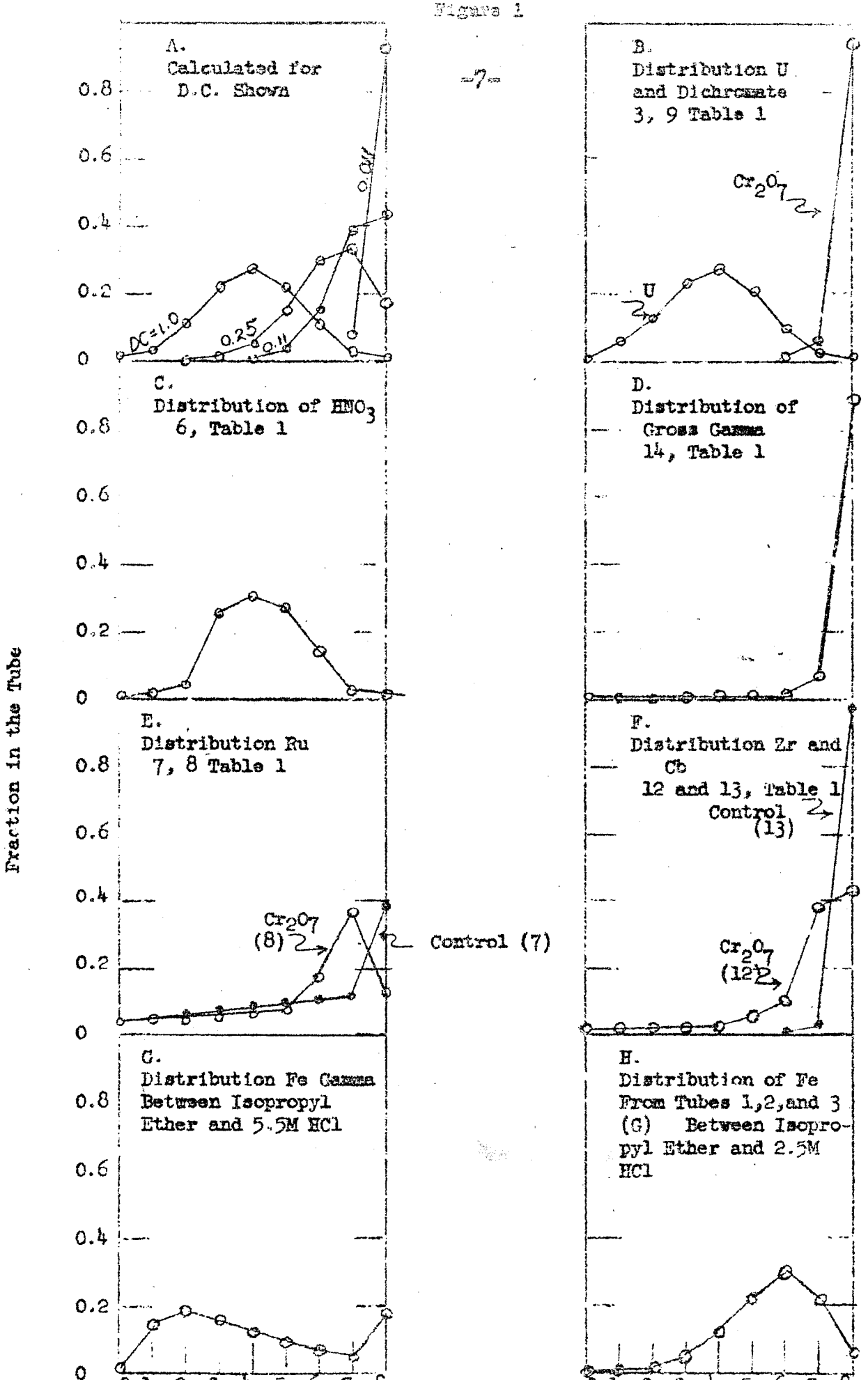
A.
Calculated for
D.C. Shown
DC=1.0
0.25
0.11
0.01
B.
Distribution U
and Dichromate
3, 9 Table 1
Cr_2O_7
U
C.
Distribution of HNO_3
6, Table 1
D.
Distribution of
Gross Gamma
14, Table 1
E.
Distribution Ru
7, 8 Table 1
Cr_2O_7
(8)
Control (7)
F.
Distribution Zr and
Cb
12 and 13, Table 1
Control
(13)
Cr_2O_7
(12)
G.
Distribution Fe Gamma
Between Isopropyl
Ether and 5.5M HCl
H.
Distribution of Fe
From Tubes 1,2,and 3
(G) Between Isopro-
pyl Ether and 2.5M
HCl
Fraction in the Tube
0.8
0.6
0.4
0.2
0

Table 1

Drawing No. 5831

Counter Current Batch Distribution

Aqueous 1M $Al(NO_3)_3$, 0.1M HNO_3

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Equal Volume of Hexone and Aqueous Equilibrated before Test Substance Added
In Test, 50 ml each Phase used

Item Number	Conditions		Tube Number 0	1	2	3	4	5	6	7	8
1.	1 g. Uranium	Fraction of Uranium	0.016	0.053	0.145	0.224	0.283	0.197	0.061	0.016	-
		D.C.	-	1.65	1.20	1.43	1.11	1.03	3.06	3.00	-
2.	1 g. Uranium	Fraction of Uranium	0.008	0.039	0.115	0.219	0.274	0.218	0.105	0.023	0.001
		D.C.	-	1.64	1.30	1.21	1.11	1.25	1.34	2.28	-
3.	10 g. Uranium $0.1M\ Na_2Cr_2O_7$	Fraction of Uranium	0.005	0.038	0.124	0.233	0.276	0.205	0.094	0.023	0.002
		D. C.	-	1.01	0.89	0.90	0.96	0.91	0.89	0.95	0.72
4.	0.5 g. Uranium $0.1M\ Na_2Cr_2O_7$	Fraction of Uranium	0.007	0.043	0.104	0.200	0.266	0.220	0.123	0.033	0.003
		D. C.	-	0.96	0.99	1.00	0.96	0.85	1.05	1.33	2.18
5.	Calculated for D.C =1	Fraction of Uranium	0.004	0.031	0.109	0.219	0.274	0.219	0.109	0.031	0.004
6.	HNO_3 (0.5M)	Fraction of HNO_3	0.009	0.019	0.041	0.255	0.301	0.272	0.145	0.031	0.010
7.	Ru* Tracer as obtained	Fraction of Ru* Activity	0.034	0.051	0.066	0.073	0.081	0.092	0.104	0.117	0.385
		D.C.	-	2.2	1.6	1.2	0.96	0.87	0.80	0.54	0.11
8.	Ru* with $0.1M\ Na_2Cr_2O_7$	Fraction of Ru* Activity	0.035	0.049	0.046	0.057	0.064	0.087	0.172	0.367	0.125
		D.C.	-	3.67	2.44	2.26	1.66	1.01	0.38	0.15	0.13
9.	$0.1M\ Na_2Cr_2O_7$ test number 3.	Observed Fraction of $Cr_2O_7^=$	-	-	-	-	-	-	0.005	0.055	0.940
		calculated for a D.C.= 0.008	-	-	-	-	-	-	0.001	0.061	0.938
10.	Zr-Cb ($KMnO_4$ equivalent to oxalic acid	Fraction of Zr-Cb	0.0003	0.023	0.026	0.036	0.048	0.046	0.058	0.130	0.633
		D.C.	-	0.004	0.04	0.02	0.04	0.02	0.01	0.004	0.005
11.	Zr-Cb tracer, $0.1M\ Na_2Cr_2O_7$ 120 hours at r.t.	Fraction of Zr-Cb.	0.011	0.010	0.011	0.013	0.017	0.025	0.046	0.100	0.736
		D.C.	-	2.36	1.22	0.47	0.28	0.15	0.08	0.06	0.008
12.	Aliquot of 11 20 hours at r.t.	Fraction of Zr-Cb.	0.018	0.018	0.015	0.017	0.028	0.049	0.100	0.381	0.436
		D.C.	-	2.50	1.10	0.53	0.42	0.23	0.13	0.05	0.009
13.	Zr-Cb tracer, as is	Fraction of Zr-Cb	-	-	-	-	-	-	0.001	0.025	0.974
		D.C.	-	-	-	-	-	-	0.04	0.01	0.005
14.	Gross Gamma (no dichromate)	Fraction	0.001	0.002	0.003	0.005	0.007	0.010	0.017	0.069	0.882
		D.C.		0.9	0.6	0.5	0.4	0.4	0.2	0.06	0.003

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Literature Cited

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   - Analytical Chemistry 20, 134 (1948)

2. Bush et al - Analytical Chemistry 20, 121 (1948)
   J. Pharmacol. 85, 244 (1945)

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