

Further text on selected topics.

Removal of unwanted metals by solvent extraction from gold.

We further explored the solvent extraction chemistry by measuring the distribution ratios of bismuth(III), chromium(III), gold(III), lead(II), nickel(II), palladium(II) and zinc(II) using a 30 % solution of *N,N,N',N'*-tetrakis-2-ethylhexyl malonamide in HVO100 at different chloride concentrations. The gold distribution ratios were far higher than those of the other metals. While bismuth and palladium were extracted when the chloride concentration was very low, when the chloride concentration was higher they were rejected. While lead and zinc are both weakly extracted when the chloride concentration is moderate, their distribution ratios never exceeds 0.14. No chromium or nickel extraction was observed. The weak extraction of lead offers a means of its separation from the gold at an early point in a solvent extraction process.

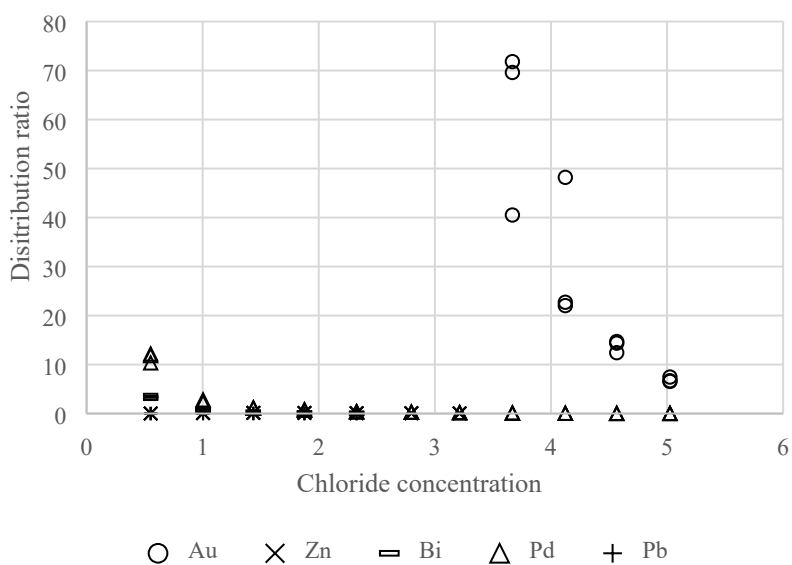


Figure 2. Distribution ratios of bismuth, gold, lead, palladium and zinc obtained with a 30 % (v/v) solution of the malonamide in HVO100 from different solutions of choline chloride with hydrochloric acid (0.55 M). When the chloride concentration was lower than 3.3 M the gold distribution ratio was greater than 100. Distribution ratios above 100 or below 0.01 are not shown.

When iron and gold in dilute hydrochloric acid was shaken with MIBK, the distribution ratios were 0.013 and over 100, but then the hydrochloric acid concentration was 2 moles per litre the iron and gold distribution ratios were 1.2 and over 1000. With a 1:1 ratio of the liquid phases the MIBK would extract 55 % of the iron in the feed solution thus giving us potential for iron contamination of the gold stream. None of the other elements were extracted by MIBK. For the malonamide solution we found that as the hydrochloric acid content of the aqueous was increased the distribution ratio increased, it is possible that two extraction mechanisms are in operation at the same time. We can reason that protonation of the malonamide can form a cationic extraction agent which extracts the tetrachloroaurate(III) anion to form an ion pair in the organic phase as an alternative to the formation of a complex of gold trichloride (AuCl_3) with the Lewis basic malonamide. With the solution of the malonamide in HVO100 the iron distribution ratio was always below 0.04, it is difficult to estimate the iron(III) distribution ratios with the malonamide solution but we estimate that the gold/iron separation factor¹ is about 1000. While the gold distribution ratios obtained with the malonamide are lower than those obtained with MIBK, we reason that the greater selectivity of the malonamide solution against iron would simplify the plant by allowing us to use fewer stages for the iron scrubbing (selective back extraction of iron). We also note that tributyl phosphate is able to extract iron(III) from hydrochloric acid.¹

¹ Separation factor is defined as one distribution ratio divided by another. $SF_{\text{Au/Fe}} = D_{\text{Au}} / D_{\text{Fe}}$

While we were pleased that in the experiments where little if any iron was extracted by our malonamide, we considered the question of why did our malonamide (*N,N,N',N'*-*tetrakis*-2-ethylhexyl malonamide) failed to extract iron while *N,N'*-dimethyl-*N,N'*-dihexyl malonamide (DMDHMA) and *N,N'*-dimethyl-*N,N'*-dicyclohexyl malonamide (DMDCMA) are very able to extract iron(III).ⁱⁱ Costa *et. al.* in 2007 reported that the slope analysis suggested that two malonamide molecules were required for the extraction of each iron atom and that no aggregation occurred in solution. When the extraction of americium(III) by *N,N'*-dimethyl-*N,N'*-dioctyl malonamide and *N,N,N',N'*-*tetra*-butyl malonamideⁱⁱⁱ along with dipropyl-*N,N'*-dioctyl malonamide^{iv} were compared and combined with slope analysis for different malonamides it was concluded by Cuillerdier *et. al.* in 1991 that steric hinderance close to the amide nitrogen suppresses the americium extraction. The *N,N,N',N'*-*tetrakis*-2-ethylhexyl malonamide had been made during Mikhail Tyumentsev's PhD work in which he sought a malonamide better able to extract lanthanides, and it had been regarded as a failed extractant due to its poor ability to extract lanthanides thus little of it was used. We considered the question of could we have accidently chosen a malonamide which is optimised for gold extraction. We used molecular mechanics to consider the difference in steric energies between the iron(III) and gold(III) trichloride *bis*-malonamide complexes where the malonamide was either *N,N,N',N'*-*tetra*-ethyl malonamide or *N,N'*-dimethyl-*N,N'*-dipropyl malonamide. It was found that the energy difference between the two complexes was smaller for gold than for iron. This can be rationalized by the fact that the gold atom has a larger radius thus increasing the distance between the ligands attached to it.

Table 3. Summary of computational results (molecular mechanics, the structures are within the ESI in the form of Brookhaven protein database files)

Metal	Energy predicted by molecular mechanics (kCal mol ⁻¹)		Difference
	<i>N,N,N',N'</i> - <i>tetra</i> -ethyl malonamide	<i>N,N'</i> -dimethyl- <i>N,N'</i> -dipropyl malonamide	
Iron	3387.0381	3383.9307	3.1074
Gold	3340.7122	3340.4616	0.2506

While we judged the malonamide to be the best extraction agent, we considered the extraction using other reagents which are commercially available. A 30 % (v/v) solution of a trialkyl phosphine oxide extractant (Cyanex 923) in HVO100 was shaken with the metal solutions, again gold extraction was seen. The ionic liquid trioctyl methyl ammonium chloride (Aliquat 336) has been extensively used as an extractant, we found that it is poorly soluble in HVO100 but we found that it could be formulated into an organic phase with either tetrahydrogeraniol (3,7-dimethyloctanol) or eucalyptol. We found that a 30 % (v/v) solution of trioctyl methyl ammonium chloride in tetrahydrogeraniol failed to extract chromium or nickel from chloride media but were able to extract the other elements when the chloride concentration was low. The bismuth, lead, palladium and zinc distribution ratios decreased as the chloride concentration increased, when the chloride concentration was greater than 2 mole dm⁻³ the distribution ratios for all four of these elements was less than one. Under these conditions the gold distribution ratio was still above 1000.

Preliminary results for the extraction of s block metals

When solutions of lithium and alkaline earth cations in weakly acidic solutions of sodium perchlorate were shaken with a 30 % solution of Cyanex 923 in our standard aliphatic kerosene (solvent 70) it was found that lithium and the alkaline earth metals (Mg, Ca, Sr and Ba) were extracted. With increasing sodium perchlorate concentration higher distribution ratios were obtained (Figure 6).

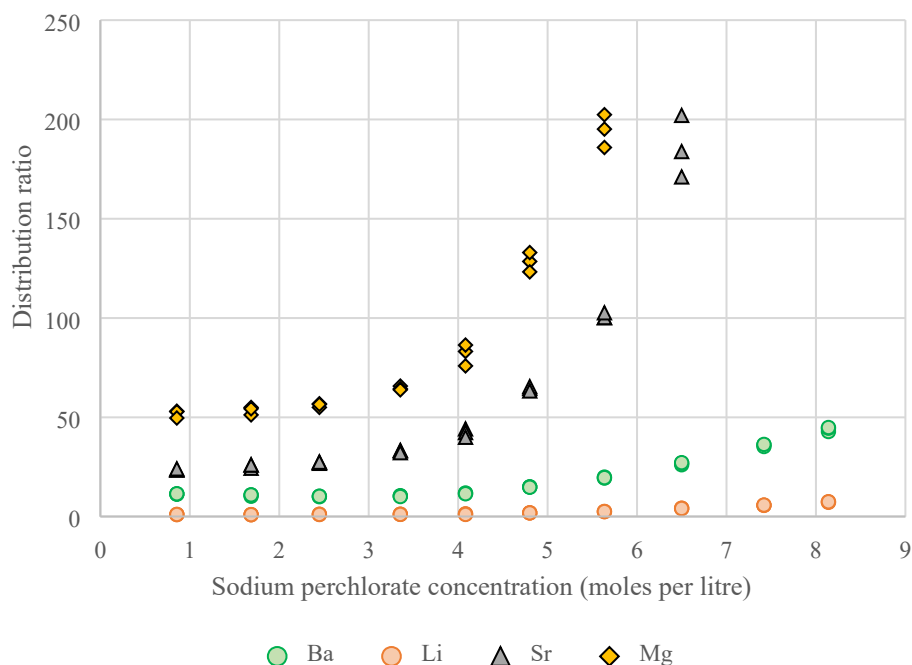


Figure 11. The variation of the distribution ratios of barium, lithium, magnesium and strontium as a function of the sodium perchlorate concentration. The organic phase was Cyanex 923 (30 % v/v) in solvent 70. The calcium distribution ratios are too high for reliable measurement.

As nitrate and chloride salts are cheaper and more environmentally sustainable the extraction experiment with 30 % cyanex 923 in solvent 70 (*circa* 0.76 moles per litre) was repeated with both strong solutions of sodium nitrate and sodium chloride which had been spiked with the metals. In the sodium chloride experiment no extraction was observed while in the sodium nitrate experiment only a moderate extraction of calcium was observed. A sample of a sustainable aviation kerosene type fuel (skyNRG fuel) were obtained. The skyNRG fuel was made by hydrocracking hydrodeoxygenated waste vegetable oil. In an experiment we obtained solvent extraction data in both the conventional petroleum kerosene and skyNRG's biokerosene. These were compared with those obtained in the ethereal terpene solvent eucalyptol. In this experiment a saturated sodium perchlorate solution which had been spiked with lithium and the alkaline earths was shaken with different concentrations of cyanex 923 in the three diluents.

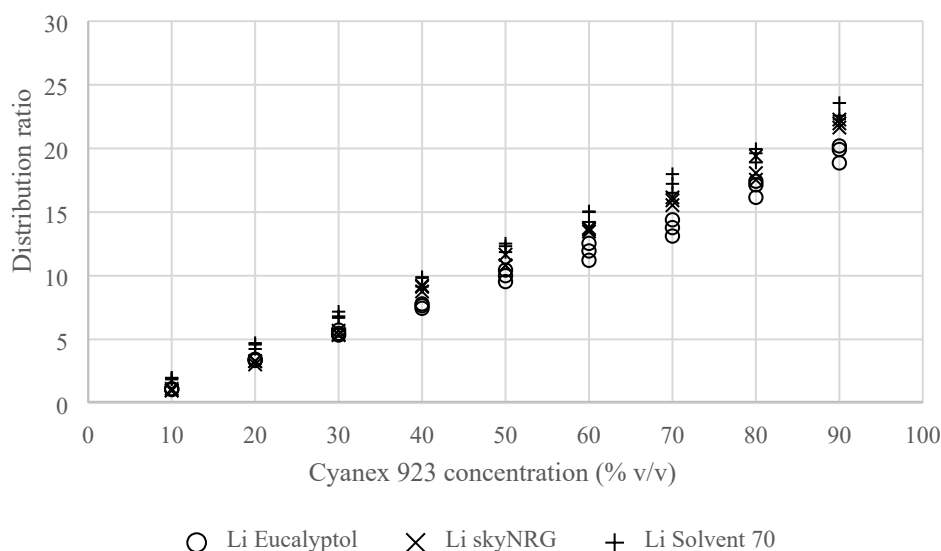


Figure 12. Lithium distribution ratios obtained by shaking saturated sodium perchlorate with different concentrations of cyanex 923 in three different diluents.

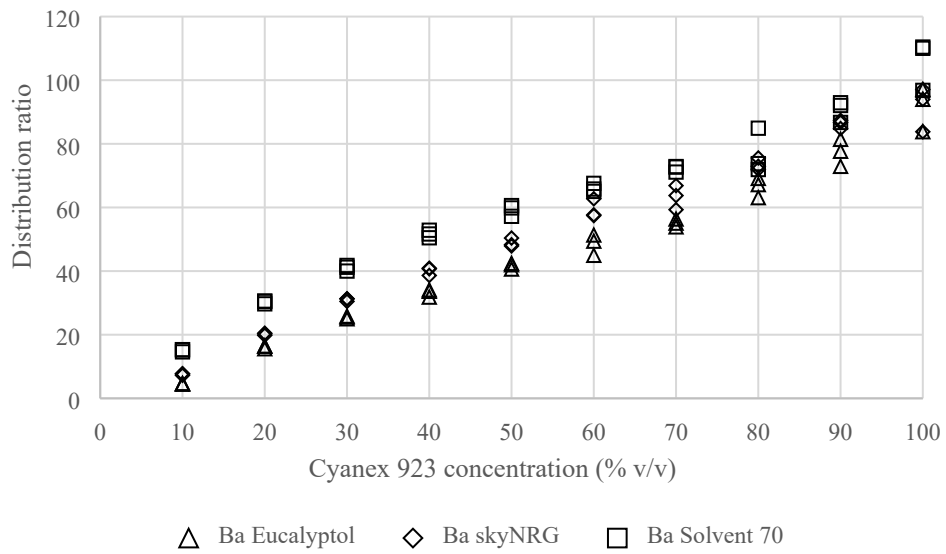


Figure 13. Barium distribution ratios obtained by shaking saturated sodium perchlorate with different concentrations of cyanex 923 in three different diluents.

With all three diluents very similar graphs were obtained for lithium (Figure seven). For the lower concentrations of cyanex 923 in the three diluents the distribution ratios decreased in the order solvent 70, skyNRG and eucalyptol. This can be reasoned to be due to some subtle changes in the activity functions of the extractant and the metal complex in the organic layer.

Distribution ratios obtained using ¹⁵²EuExtractions performed using ¹⁵²Eu in very dilute nitric acid

Tube number	DEHPA content of organic phase (% v/v)	D _{Eu}
2564	0,5	2,193E+01
2565	0,2	1,773E+00
2566	0,2	1,837E+00
2567	0,2	1,764E+00
2662	0,5	2,254E+01
2655	0,15	8,140E-01
2654	0,15	8,463E-01
2653	0,15	8,445E-01
2650	0,1	2,665E-01
2651	0,1	2,592E-01
2652	0,1	2,647E-01
2559	1	1,270E+02
2560	1	1,230E+02
2556	2	2,844E+02
2557	2	3,338E+02
2558	2	2,961E+02
2561	1	1,260E+02
2660	5	3,623E+02
2659	5	5,237E+02
2661	5	8,655E+02
2662	0,05	3,274E-02
2663	0,05	3,388E-02
2664	0,05	3,402E-02
2658	10	8,063E+02
2563	0,5	2,032E+01
2656	10	5,081E+02
2657	10	6,984E+02

Extractions performed using solutions of Cyanex 923 in HVO100

Tube number	C923 content of the organic phase (% v/v)	D _{Eu}
2538	0,191464	5,559E-01
2539	0,191464	5,613E-01
2540	0,191464	5,547E-01
2541	0,094001	6,778E-02
2542	0,094001	6,784E-02
2543	0,094001	7,123E-02
2553	0,488011	9,971E+00
2555	0,488011	9,899E+00
2554	0,488011	9,782E+00
2550	1,000935	1,117E+02
2551	1,000935	1,078E+02
2552	1,000935	1,107E+02
2545	0,045709	7,356E-03
2544	0,045709	7,819E-03
2546	0,045709	8,051E-03
2535	0,017926	1,047E-03

Solvent extraction results obtained using DEHPA using non radioactive (inactive AKA stable) lanthanum, neodymium and calcium

The organic phase was 30 % by volume DEHPA in HVO100, the aqueous phases were nitric acid which had been spiked with lanthanum, neodymium, magnesium, calcium, strontium and barium. No extraction of magnesium, strontium or barium was observed in the experiments.

Tube number	Acid	D _{La}	D _{Nd}	D _{Ca}
2406	0,518606	0,179687	0,77084	0,02089
2407	0,518608	0,180241	0,796754	0,007563
2408	0,518801	0,18118	0,795573	0,029513
2409	0,268591	1,318201	6,297416	0,104204
2410	0,268571	1,300715	6,291582	0,109016
2411	0,268543	1,30948	6,367755	0,108916
2412	0,126246	11,46484	37,34878	0,501945
2413	0,126429	13,3845	64,57962	0,513336
2414	0,126548	13,46986	66,40362	0,52883
2415	0,074992	59,51832	206,2388	1,48654
2416	0,075112	62,06289	216,2396	1,527381
2417	0,075087	62,2463	229,9009	1,530461
2418	0,051727	152,3808	-	3,028218
2419	0,051754	165,508	-	3,053947
2420	0,051722	134,8424	-	3,045628
2421	0,037792	-	-	5,1809
2422	0,037814	-	-	5,240433
2423	0,037812	-	-	5,232553
2424	0,028803	-	-	7,796465
2425	0,028831	-	-	7,892849
2426	0,028875	-	-	8,198286

Variable DEHPA experiment

The diluent was HVO100, the extraction agent was DEHPA at different concentrations in the alkane diluent.

Tube number	DEHPA content (% v/v)	D _{Ca}	D _{La}	D _{Nd}
2632	50	0,393737	11,87521	37,68747
2633	50	0,391664	11,93538	37,57487
2634	50	0,407474	12,7959	43,96704
2635	40	0,280931	8,697698	28,85743
2636	40	0,300397	8,990415	28,89695
2637	40	0,308993	9,464466	32,03214
2638	30	0,187019	5,711822	19,62917
2639	30	0,189394	6,04821	20,71105
2640	30	0,19058	5,985057	20,50456
2641	20	0,088978	2,933167	10,12697
2642	20	0,093866	3,038073	10,46205
2643	20	0,097981	3,090196	10,74412
2644	10	0,026267	0,806398	2,874211
2645	10	0,010016	0,820531	2,96883
2646	10	0,020491	0,836855	2,976282
2647	5	-	0,186194	0,698583
2648	5	-	0,200587	0,740295
2649	5	-	0,196819	0,740169

Extraction of calcium and magnesium from sodium nitrate solution by Cyanex 923

The organic phase was 30 % (v/v) cyanex 923 in HVO100

Tube number	[NaNO ₃]	D _{Mg} 383,826 nm	D _{Ca} 183,801 nm
2244	6,909	2,236	17,385
2245	6,909	2,597	19,759
2246	6,909	2,490	19,124
2247	6,032	1,536	13,911
2248	6,032	1,538	13,798
2249	6,032	1,503	13,699
2250	5,157	0,906	9,841
2251	5,157	0,897	9,573
2252	5,157	0,909	9,743
2253	4,306	0,532	6,507
2254	4,306	0,513	6,385
2255	4,306	0,544	6,583
2256	3,448	0,255	3,736
2257	3,448	0,295	4,195
2258	3,448	0,294	4,159
2259	2,589	0,148	2,556
2260	2,589	0,132	2,493
2261	2,589	0,146	2,615
2262	1,707	0,057	1,187
2263	1,707	0,061	1,271
2264	1,707	0,055	1,271
2265	0,881	0,000	0,465
2266	0,881	0,000	0,466
2267	0,881	0,000	0,469

Extraction of alkaline earth metals from acetate buffer by DEHPA in HVO100

Tube number	DEHPA % (v/v)	D _{Be}	D _{Sr}	D _{Ba}
2707	50	28,313	136,399	89,414
2708	50	26,113	133,494	89,739
2709	50	25,417	133,379	88,565
2710	40	9,842	96,046	64,894
2711	40	18,047	87,079	59,782
2712	40	17,518	56,435	44,458
2713	30	7,480	72,627	48,205
2714	30	9,300	60,297	42,686
2715	30	6,529	63,874	44,572
2716	20	1,928	91,183	52,199
2717	20	3,233	92,195	47,681
2718	20	2,778	98,941	52,465
2719	10	1,119	360,709	183,225
2720	10	1,073	451,856	197,411
2721	10	1,004	385,526	177,735
2722	5	0,905	327,558	172,171
2723	5	0,949	537,483	223,954
2724	5	0,960	287,509	163,388

ⁱ N. Eiichi, T. Hitoshi, I. Hitoshi, O. Takao and O. Taijiro, *Bulletin of the Chemical Society of Japan*, 1983, **56**, 1832.

ⁱⁱ M.C. Costa, I. Pêczek, Z. Sadowski, S. Natu and A.P. Paiva, *Solvent Extraction and Ion Exchange*, 2007, **25**, 463.

ⁱⁱⁱ C. Cuillerdier, C. Musikas, P. Hoel, L. Nigond and X. Vitart, *Separation Science and Technology*, 1991, **26**, 1229.

^{iv} C. Musikas and H. Hubert, *Solvent Extraction and Ion Exchange*, 1987, **5**, 877.