

TRI-*n*-BUTYL PHOSPHATE AS AN EXTRACTING SOLVENT FOR INORGANIC NITRATES—I

ZIRCONIUM NITRATE

K. ALCOCK, (the late) F. C. BEDFORD,
W. H. HARDWICK, and H. A. C. MCKAY
Atomic Energy Research Establishment, Harwell, Didcot, Berks

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Abstract—The extraction of tracer zirconium by 19% v/v (0.69 M) tri-*n*-butyl phosphate (TBP) in kerosene has been studied from aqueous solutions consisting of (i) nitric acid, (ii) nitric acid *plus* an inextractable nitrate (sodium nitrate), and (iii) nitric acid *plus* an extractable nitrate (uranyl nitrate). The partition coefficients increase steeply with rising acidity, they are little affected by substitution of sodium nitrate for nitric acid, and they fall considerably on addition of uranyl nitrate to the system.

THIS is the first of a group of papers dealing with the extraction by tri-*n*-butyl phosphate (TBP) of the nitrates of elements which are of interest to the atomic energy programme. Zirconium is of particular importance because it is one of the most readily extractable of the longer-lived fission products, and is therefore one which frequently contaminates thorium, uranium or plutonium salts prepared by solvent extraction.

This paper is based on an earlier A.E.R.E. report.⁽¹⁾ It is intended to discuss the physical chemistry fully elsewhere.

EXPERIMENTAL

Preparation of Zr⁹⁵ tracer

The tracer used was prepared from a solution of fission products in nitric acid by extraction first into 19% TBP in kerosene from 8 M HNO₃, followed by backwashing into water, and then into 0.05 M TTA (thenoyltrifluoroacetone) in benzene from 1 M HNO₃. The resulting TTA solution was left standing over 1 M HNO₃. When a specimen of Zr⁹⁵ was required, the phases were stirred for 30 min to extract the Nb⁹⁵ daughter, which is also radioactive. The Zr⁹⁵ was then extracted into 8 M HNO₃. Traces of TTA were eliminated by scrubbing with benzene followed by air-sparging. The solution was normally used the same day to avoid too much growth of Nb⁹⁵.

Purity of TBP

The TBP was generally purified by the method described by ALCOCK, GRIMLEY, HEALY, KENNEDY, and MCKAY.⁽²⁾ A few comparative experiments with material which had merely been washed with alkali and water revealed the inadequacy of this method of treatment; the aqueous phase was 5.1 M HNO₃ and the TBP was diluted to 19% in kerosene:

⁽¹⁾ H. A. C. MCKAY, W. H. HARDWICK, and F. C. BEDFORD A.E.R.E. C/R 923 (1952).

⁽²⁾ K. ALCOCK, S. S. GRIMLEY, T. V. HEALY, J. KENNEDY, and H. A. C. MCKAY *Trans. Faraday Soc.* **52**, 39 (1956).

	Tracer initially in aqueous phase				Tracer initially in organic phase		
	Partition coefficient (org/aq) after				Partition coefficient (org/aq) after		
	15 min	45 min	90 min	120 min	30 min	60 min	90 min
Pure TBP	0.41	0.46	0.46	—	0.58	0.52	0.58
Alkali-washed TBP	0.85	1.10	—	1.22	1.58	1.81	1.91

The much better agreement of the forward and backward partitions and the lack of a drift with time, demonstrate the superiority of the more highly purified solvent.

Dilution of TBP

The work reported here was nearly all carried out with 19% v/v (0.69 M) TBP in "odourless" kerosene.

Partition measurements

Partition coefficients were determined by stirring *ca.* 5 ml of each phase together in a centrifuge tube for about 30 min, centrifuging, and separating the phases for analysis. It later became apparent that 5 min stirring is usually ample and that centrifuging can be dispensed with, and in subsequent papers in this series the procedure was simplified accordingly. The solutions were not thermostated in the present work, but the ambient temperature was fairly constant at 20–23°C.

The Zr^{95} concentrations used were generally in the range 10^{-11} to 10^{-12} M. At these levels the formation of polynuclear species by hydrolysis is unlikely to be important,⁽³⁾ but radiocolloids involving trace impurities might still cause difficulties. For this reason we used a highly acid zirconium stock solution (8 or 10 M HNO_3), and only exposed the zirconium to lower acidities for the duration of the actual experiment. Furthermore in the experiments with nitric acid, the zirconium was first extracted into 19% TBP, and the partition coefficients were determined by equilibrating this TBP phase with various aqueous phases. Inextractable species in the original aqueous solution would be eliminated by this back extraction procedure. PEPPARD, MASON, and MAIER⁽⁴⁾ used a similar procedure, back-extracting twice and comparing the two results obtained.

In the experiments with added sodium or uranyl nitrate the TBP phase was conditioned to approximately the equilibrium acidity and uranyl nitrate concentration by shaking with several (e.g. four) successive volumes of the aqueous phase, with no zirconium tracer present. The tracer was then added, in 8 or 10 M HNO_3 , to further aqueous phase, and a final equilibration was carried out.

Zirconium analyses were carried out by γ -counting, nitric acid analyses by alkali titration, and uranium analyses colorimetrically by the peroxide method.

RESULTS and DISCUSSION

Extraction from nitric acid solutions

The results obtained with 19% TBP in kerosene are given in Table 1.

The extraordinary rise in the partition coefficient at high acidities was quite unexpected and it seemed advisable to test whether it could be due to trace impurities. A measurement was therefore made at an acidity of 11.4 M in the presence of 0.001 M inactive zirconium; this is still effectively a trace concentration, yet it should greatly

⁽³⁾ J. S. JOHNSON and K. A. KRAUS *J. Amer. Chem. Soc.* **78**, 3937 (1956); A. J. ZIELEN and R. E. CONNICK *ibid.*, p. 5785.

⁽⁴⁾ D. F. PEPPARD, G. W. MASON, and J. L. MAIER *J. Inorg. Nucl. Chem.* **3**, 215 (1956).

TABLE 1

HNO ₃ conc. (aq)	0.98	2.02	2.25	3.01	4.01	4.96	5.19	6.04	6.94 M
Partition coeff. (org/aq)	0.015	0.045	0.051	0.120	0.23	0.49	0.53	0.90	1.37

HNO ₃ conc. (aq)	7.98	8.03	9.1	10.2	10.5	11.2	12.2	13.1 M
Partition coeff. (org/aq)	2.37	2.02	4.4	8.2	9.8	11.4	40	134

minimize the effect of trace impurities. The figure obtained was 19.5, compared with 21 interpolated from the data at tracer levels. In a further experiment, three successive backwashes were carried out at 11.6 M HNO₃, giving partition coefficients of 43, 46, and 51 respectively; these are reasonably constant, though on the high side.

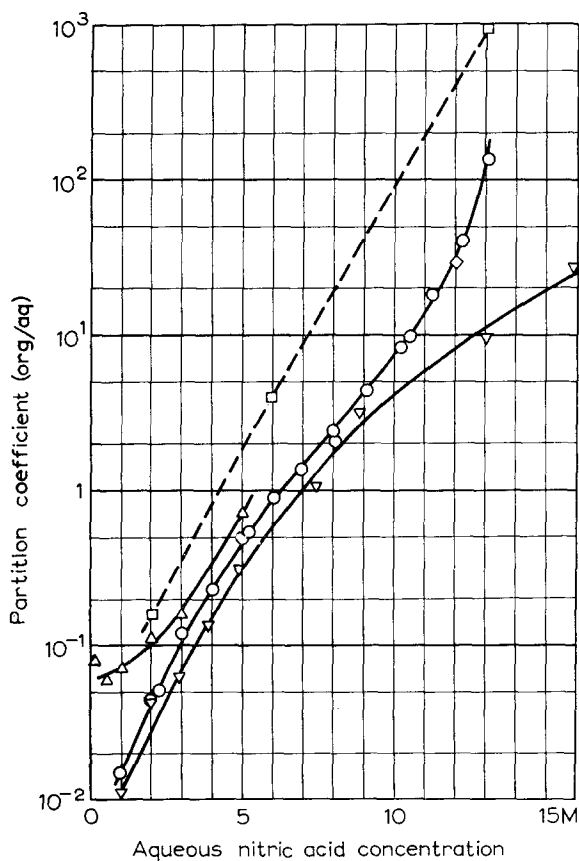


FIG. 1.

- Our data, 19% TBP in kerosene.
- ▽ MURBACH and McVEY,⁽⁶⁾ 30% TBP in CCl₄.
- △ BRUCE,⁽⁶⁾ 15% TBP in Varsol.
- PEPPARD, MASON, and MAIER,⁽⁴⁾ 100% TBP.
- ◇ Ditto, 25% TBP in benzene.

Results by other authors⁽⁴⁻⁶⁾ are compared with ours in Fig. 1. It is a little surprising that the extraction does not always increase with increasing TBP concentration; presumably this is due to the different diluents used.

The present authors also obtained some results at greater dilution of the TBP in kerosene. The partition coefficient varied approximately with the square of the TBP percentage, indicating the formation of $\text{Zr}(\text{NO}_3)_4 \cdot 2\text{TBP}$. The original experimental basis for this conclusion has, however, been criticized by MURBACH and McVEY,⁽⁵⁾ and a new series of measurements extending to lower TBP concentrations has therefore

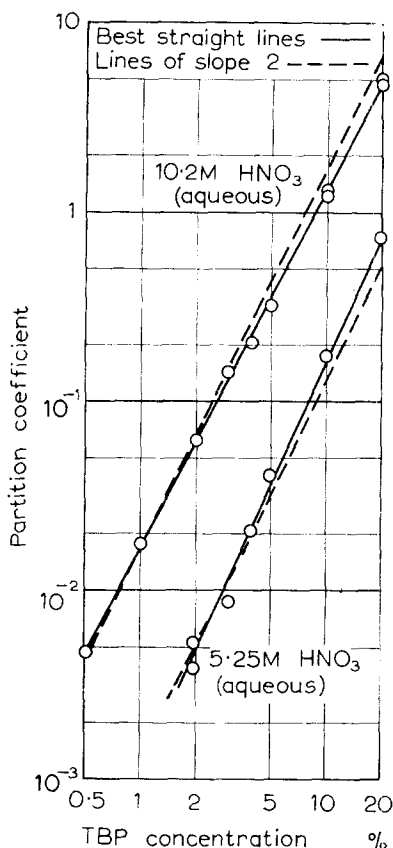


FIG. 2.

been made by HESFORD⁽⁷⁾ at 25°C, with the results shown in Fig. 2 (which are probably of rather greater accuracy than our earlier results). The best lines through all the points in Fig. 2 are of slopes 2.2 at 5.25 M HNO_3 and 1.9 at 10.2 M HNO_3 . In our view this implies, without much doubt, a square law in the limit at low TBP concentrations (say <1% in kerosene), with deviations from this law at higher TBP concentrations due to nonideality of the organic phase. It certainly seems improbable that the limiting law would be for instance a cubic.

⁽⁵⁾ E. W. MURBACH and W. H. McVEY U.S.A.E.C. LRL—115 (1954).

⁽⁶⁾ F. R. BRUCE *Peaceful Uses of Atomic Energy*, Vol. 7 (United Nations, New York, 1956) Paper P/719.

⁽⁷⁾ E. HESFORD Private communication.

It is interesting to note that LEVITT and FREUND⁽⁸⁾ found a similar square law in chloride solutions, and deduced the formation of $\text{ZrCl}_4 \cdot 2\text{TBP}$.

Extraction in presence of sodium nitrate

Our results with 19% TBP in kerosene are given in the accompanying table. The sodium nitrate itself is almost inextractable.

TABLE 2

Concentrations			Partition coefficient (org/aq)
HNO_3 (aq)	NaNO_3 (aq)	HNO_3 (org)	
1.00 M	0.0 M	0.115 M	0.015
0.99	1.0	0.205	0.05 (0.045)
0.99	2.0	0.27	0.12 (0.12)
0.99	3.0	0.33	0.25 (0.23)
0.99	4.5	0.41	0.64 (0.65)
0.99	6.0	0.48	1.41 (1.40)
2.00	0.0	0.28	0.045
2.00	1.0	0.37	0.14 (0.12)
2.00	2.0	0.42	0.26 (0.23)
2.00	3.0	0.47	0.48 (0.49)
1.98	4.0	0.51	0.66 (0.89)
1.98	4.5	0.54	0.74 (1.12)
1.98	5.0	0.56	1.06 (1.40)

The figures in brackets in the last column of Table 2 are the partition coefficients in presence of nitric acid only (taken from Fig. 1) at the same nitrate ion concentrations as in the mixtures with sodium nitrate. In most cases the two partition coefficients are very similar. This means that the controlling factor is the total nitrate ion concentration. With other elements there is always a rise in extraction when sodium nitrate replaces nitric acid; the absence of such a rise with zirconium may be due to hydrolysis, which is considerable even at acidities of 1–2 M.^(3,9)

Extraction in presence of uranyl nitrate

Uranyl nitrate differs from sodium nitrate in being itself extractable into TBP, and its presence in the organic phase reduces the amount of free solvent and hence the extraction of zirconium. Our results with 19% TBP in kerosene are given in Table 3. At *ca.* 2 M HNO_3 the ratio of the partition coefficients for zirconium and uranium is approximately constant. This arises because each nitrate forms a complex incorporating two molecules of solvent, so that both partition coefficients depend on the square of the amount of free TBP, i.e. the amount not combined with either nitric acid

⁽⁸⁾ A. E. LEVITT and H. FREUND *J. Amer. Chem. Soc.* **78**, 1545 (1956).

⁽⁹⁾ R. E. CONNICK and W. H. MCVEY *J. Amer. Chem. Soc.* **71**, 3182 (1949).

TABLE 3

Concentrations				Partition coefficient (org/aq)		
HNO ₃ (aq)	UO ₂ (NO ₃) ₂ (aq)	HNO ₃ (org)	UO ₂ (NO ₃) ₂ (org)	Zirconium	Uranium	Ratio
2.00 M	0.000 M	0.28 M	0.000 M	0.045	—	—
1.97	0.0235	0.15*	0.156	0.0185	6.6	0.0028
1.97	0.086	0.11*	0.24	0.0072	2.8	0.0026
1.98	0.21	0.07*	0.30	0.0047	1.44	0.0033
5.00	0.000	0.61*	0.000	0.55	—	—
5.02	0.0045	0.44*	0.099	0.50	22	0.023
5.12	0.087	0.15*	0.27 [†]	0.134	3.1	0.043
5.37	0.32	0.03*	0.35	0.076	1.07	0.071
4.95	1.01	0.02*	0.36 [†]	0.024	0.35	0.069

* Estimated from other data.

[†] By difference.

or uranyl nitrate. At *ca.* 5 M HNO₃ there are too many complications for this simple proportionality to hold.

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