

Note

Liquid-liquid extraction of trivalent lanthanides from nitric acid by 2-mercapto-4, 4, 6-trimethyl-(1H, 4H)-pyrimidine-1-acetic acid

Ashok Kumar

Institute of Chemical Sciences, Devi Ahilya University,
Indore 452 001, India

Received 2 April 1996; accepted 2 September 1996

A new method for the extraction and spectrophotometric determination of La(III), Pr(III), Nd(III), Sm(III), Gd(III) and Tb(III) from dilute aqueous nitrate media by 2-mercapto-4, 4, 6-trimethyl-(1H, 4H)-pyrimidine-1-acetic acid (MTPAcH) has been developed. Various polar organic solvents have been examined. Maximum enhancement is observed in the presence of 40% acetonitrile. Very poor extractability necessitated the use of calcium nitrate as the salting out agent.

In the present note, an efficient method for extraction and spectrophotometric determination of La(III), Pr(III), Nd(III), Sm(III), Gd(III) and Tb(III) from nitric acid media by 2-mercapto-4, 4, 6-trimethyl-(1H, 4H)-pyrimidine-1-acetic acid (MTPAcH) is presented. Very poor extractability necessitated the use of calcium nitrate as the salting out agent. The common solvents studied include acetonitrile, acetone, methanol, dioxane, ethanol, and *iso*-propanol. Attempts were also made to understand the nature of the metal ion species extracted.

Experimental procedure—All the chemicals used were of AR grade and their solutions always were prepared afresh. MTPAcH was prepared by a reported method¹ and used as 0.2% solution in admixture of chloroform-butanol-1 (4:1v/v). Naphthalene was checked spectrophotometrically before use. A 20% naphthalene solution in acetone was used.

A Shimadzu (UV 160 A) UV-visible and Chemito 215 D visible spectrophotometer were used for recording absorption spectra of organic extractants.

A suitable aliquot of the individual lanthanide (4.5×10^{-5} M) was added to the aqueous phase containing conc. HNO₃ (0.04M) and Ca(NO₃)₂ (4M), and shaken mechanically with an equal volume of the pre-equilibrated solution of MTPAcH diluted with 40% acetonitrile. After setting for

half an hour, suitable aliquots from both the phases were withdrawn and analyzed spectrophotometrically² for the determination of *D* and *E* %³.

Results and Discussion

Dependence of *D*_{Ln} on nitric acid concentration—Extraction of lanthanides was found to be very poor from aqueous nitric acid solution tested even upto 8M. The value of *D*_{Ln} decreased rapidly with increasing acidity from 10⁻⁴ to 0.8M. This necessitated the use of the salting out agent.

Dependence of *D*_{Ln} on salting out agent concentration—Addition of calcium nitrate to the aqueous phase resulted in increased extraction of lanthanides with MTPAcH. Taking 0.04 M HNO₃ in aqueous phase and by varying the concentration of Ca(NO₃)₂ upto 6 M, the values of *D*_{Ln} and *E*% are calculated and presented in Table 1.

Variation of *D*_{Ln} values with MTPAcH concentration—The extractibilities of lanthanides from 0.04 M HNO₃ containing 4 M Ca(NO₃)₂ as salting out agent into chloroform by varying amount of MTPAcH from 0.2 to 0.8 M have been studied and results are presented in Table 2. A 0.6 M MTPAcH extracted more than 95% in a single step.

The extraction of lanthanides by MTPAcH from nitrate solution can be separated by the reaction



The equilibrium constant, *K*_{ex}, is given by

$$K_{\text{ex}} = \frac{[\text{Ln}(\text{NO}_3)_3 \cdot n\text{MTPAcH}]_{(o)}}{[\text{Ln}^{3+}]_{(a)} [\text{NO}_3^-]_{(a)} [\text{MTPAcH}]_{(o)}^n} \quad \dots (2)$$

Introducing the distribution ratio as

$$D_{\text{Ln}} = \frac{[\text{Ln}(\text{NO}_3)_3 \cdot n\text{MTPAcH}]_{(o)}}{[\text{Ln}^{3+}]_{(a)}} \quad \dots (3)$$

Assuming that [NO₃⁻] is constant and taking logarithms of both sides of the Eq. (1) and rearranging gives,

$$\log D_{\text{Ln}} = \log K_{\text{ex}} + n \log [\text{MTPAcH}] + 3 \log [\text{NO}_3^-] \quad \dots (4)$$

The plot of log *D*_{Ln} vs log [MTPAcH] in the or-

Table 1—Extraction of lanthanides from aqueous nitrate medium as a function of $\text{Ca}(\text{NO}_3)_2$ concentration

[$\text{Ca}(\text{NO}_3)_2$], M	Organic phase : 0.4 M MTPAcH in CHCl_3 Aqueous phase : 0.04 M HNO_3 + 4.5×10^{-5} Lanthanides + $\text{Ca}(\text{NO}_3)_2$											
	La		Pr		Nd		Sm		Gd		Tb	
	D	E, %	D	E, %	D	E, %	D	E, %	D	E, %	D	E, %
0.0	<0.01	Poor	<0.01	Poor	ND	ND	ND	ND	<0.01	Poor	ND	ND
1.5	0.08	7.41	0.08	7.41	0.20	16.67	0.32	24.24	0.45	31.03	0.58	36.71
3.0	1.05	51.22	0.85	45.95	0.98	49.50	1.05	51.22	1.75	63.64	2.10	67.74
4.0	6.63	86.89	8.00	88.89	9.06	90.06	9.34	90.33	10.00	90.91	11.05	91.70
5.0	24.58	96.09	30.00	96.77	35.05	97.23	38.15	97.45	40.68	97.60	40.80	97.61
6.0	95.45	98.96	98.03	98.99	98.50	98.99	110.0	99.10	132.0	99.25	140.0	99.29

ND = Not determined

Table 2—Extraction of lanthanides as a function MTPAcH concentration

[MTPAcH] M	Organic phase : MTPAcH in CHCl_3 Aqueous phase : 4.0 M $\text{Ca}(\text{NO}_3)_2$ + 0.04 M HNO_3 + 4.5×10^{-5} Lanthanides											
	La		Pr		Nd		Sm		Gd		Tb	
	D	E, %	D	E, %	D	E, %	D	E, %	D	E, %	D	E, %
0.2	0.90	47.37	1.02	50.50	1.25	55.56	1.30	56.52	1.48	59.68	1.50	60.00
0.4	6.35	86.40	8.00	88.89	9.06	90.06	9.34	90.33	10.00	90.91	11.80	92.19
0.6	18.50	94.87	20.60	95.37	21.83	95.62	24.34	96.05	31.05	96.88	33.40	97.09
0.8	50.00	98.58	58.15	98.31	60.02	98.36	ND	ND	60.90	98.39	62.00	98.41

ND = Not determined

Table 3—Effect of organic solvents on the extraction of lanthanides into chloroform by MTPAcH from aqueous phase

Metals	Organic additives, %	Organic phase : 0.4 M MTPAcH in CHCl_3 Aqueous phase : 0.04 M HNO_3 + 4.0 M $\text{Ca}(\text{NO}_3)_2$ + 4.5×10^{-5} Lanthanides + solvents					
		D_{Ln} in the presence of organic solvents*					
		A	B	C	D	E	F
La	20	7.42	7.28	6.25	6.00	5.35	0.77
	30	9.40	9.00	8.05	7.62	7.00	0.90
	40	16.55	16.00	14.20	13.00	12.15	1.62
Pr	20	9.15	8.98	8.00	7.67	7.00	0.80
	30	10.20	9.16	8.67	8.50	8.00	0.80
	40	18.10	16.25	15.00	14.15	14.10	1.70
Nd	20	10.08	9.80	9.70	9.00	8.70	1.00
	30	12.98	11.00	10.05	9.65	9.00	1.35
	40	20.00	18.15	16.10	15.00	14.12	1.50
Sm	20	10.28	10.00	9.80	9.50	9.00	1.60
	30	14.00	13.12	12.00	11.50	10.00	1.68
	40	20.00	18.00	16.15	15.12	14.70	2.78
Gd	20	12.00	11.12	10.00	9.06	8.60	0.98
	30	14.60	12.00	11.67	11.00	10.00	1.05
	40	22.00	20.60	18.50	15.80	14.20	1.60
Tb	20	12.10	11.75	11.00	10.85	10.55	0.98
	30	15.00	12.78	11.80	11.50	11.28	2.07
	40	24.06	22.00	20.50	18.12	15.20	3.28

* Dielectric constant: Acetonitrile (A) = 37.50, acetone (B) = 20.70, methanol (C) = 32.60, dioxane (D) = 2.20, ethanol (E) = 24.30 and *iso*-propanol (F) = 18.30

ganic phase gives the value of $n=3$. This indicates that the extracted species is predominantly of the type $\text{Ln}(\text{NO}_3)_3 \cdot 3 \text{MTPAcH}$.

Influence of solvents—The extractability and selectivity for the extraction of lanthanides by organic solvents are greatly affected. The value of D_{Ln} with 0.4 M MTPAcH and varying amount of solvents in chloroform from an aqueous phase [0.04 M HNO_3 + 4.0 M $\text{Ca}(\text{NO}_3)_2$] presented in Table 3 indicates that the maximum enhancement² in the extraction was obtained in the presence of 40% acetonitrile. It was also observed that at the same solvent percentage, value of D_{Ln} follow the sequence : acetonitrile > acetone > methanol > dioxane > ethanol > *iso*-propanol.

Acknowledgement—The author thanks Dr. J P Shukla, Radiochemistry Division, BARC, Mumbai and Dr. Y K Agrawal, Head, Department of Chemistry, Gujarat University, Ahmedabad for their keen interest and suggestions in this work. Thanks are also due to University Grants Commission, New Delhi, for financial support.

References

- 1 Mathes R A, *J Am Chem Soc*, 75 (1983) 1747.
- 2 Kumar Ashok, *Anal Sci*, 11 (1995) 281.
- 3 Shukla J P & Kedari C S, *J Radial Chem*, 157 (1992) 355.