Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

A Comparison between the Picrate and Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) Methods of Metal Assays in Solution for Calix[4]arene Amides and Amines as Extractants

H. Fred Koch[a]; D. Max Roundhill[a]
[a] DEPARTMENT OF CHEMISTRY AND BIOCHEMISTRY, TEXAS TECH UNIVERSITY, LUBBOCK, TEXAS, USA

Online publication date: 04 March 2000

To cite this Article Koch, H. Fred and Roundhill, D. Max(2000) 'A Comparison between the Picrate and Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) Methods of Metal Assays in Solution for Calix[4]arene Amides and Amines as Extractants', Separation Science and Technology, 35: 5, 779 — 784
To link to this Article: DOI: 10.1081/SS-100100191
URL: http://dx.doi.org/10.1081/SS-100100191

SEPARATION SCIENCE AND TECHNOLOGY, **35**(5), pp. 779–784, 2000

TECHNICAL NOTE

A Comparison between the Picrate and Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) Methods of Metal Assays in Solution for Calix[4]arene Amides and Amines as Extractants

H. FRED KOCH and D. MAX ROUNDHILL*
DEPARTMENT OF CHEMISTRY AND BIOCHEMISTRY
TEXAS TECH UNIVERSITY
LUBBOCK, TEXAS 79409-1061, USA

ABSTRACT

A comparison has been made between the picrate and the inductively coupled plasma-atomic emission spectroscopy methods for detection of the metals UO_2^{2+}, Cu^{2+}, Eu^{3+}, Cd^{2+}, Cr^{3+}, and Pb^{2+} after extraction from aqueous solution into chloroform with a series of calix[4]arene amide and amines. These data reveal that the picrate method gives consistently higher analytical results because of salt formation between the picrate anion and the protonated amide or amine cation. By comparison, a calix[4]arene ester that has no centers that can be protonated by picric acid shows no difference between the two methods.

Key Words. ICP-AES; Picrate; Calix[4]arene; Amide; Amine

INTRODUCTION

The selective extraction of metal cations and anions from aqueous solution into an organic phase is an important process if the ions are toxic and present in the environment in significant quantities (1, 2). An important aspect of achieving this goal is being able to rapidly and accurately estimate the amount of metal present in the two phases after extraction by a complexant. In previous studies we and others have employed inductively coupled plasma-atomic

* To whom correspondence should be addressed. E-mail: ULDMR@ttacs.ttu.edu

emission spectroscopy (ICP-AES), tuned to the emission wavelength of the particular metal, to determine metal concentrations in the aqueous phase. This method, therefore, gives a direct measure of the metal content in the aqueous layer, as would atomic absorption spectroscopy. One indirect method involves the addition of picric acid or picrate salts to the aqueous layer, with the metal concentrations being determined from the intensities of absorption bands of the metal picrate salts that are extracted into the organic layer. Since this picrate method has been used in the extraction of metals by calixarenes, we have carried out experiments to compare results obtained by both the ICP-AES and the picrate methods of metal analysis.

EXPERIMENTAL SECTION

Materials

The compounds $Cu(NO_3)_2$, $Cd(NO_3)_2$, $Cr(NO_3)_3$, and $Pb(NO_3)_2$, and the chloroform (HPLC grade), were purchased from Fisher Scientific. The compounds $UO_2(NO_3)_2$ and $EuCl_3$ were purchased from Strem Chemicals. Picric acid was purchased from Aldrich Chemical Co. High purity water was produced by passing distilled water through a Milli-Q deionizing system. Compounds **1–6** were prepared according to literature methods (3, 4).

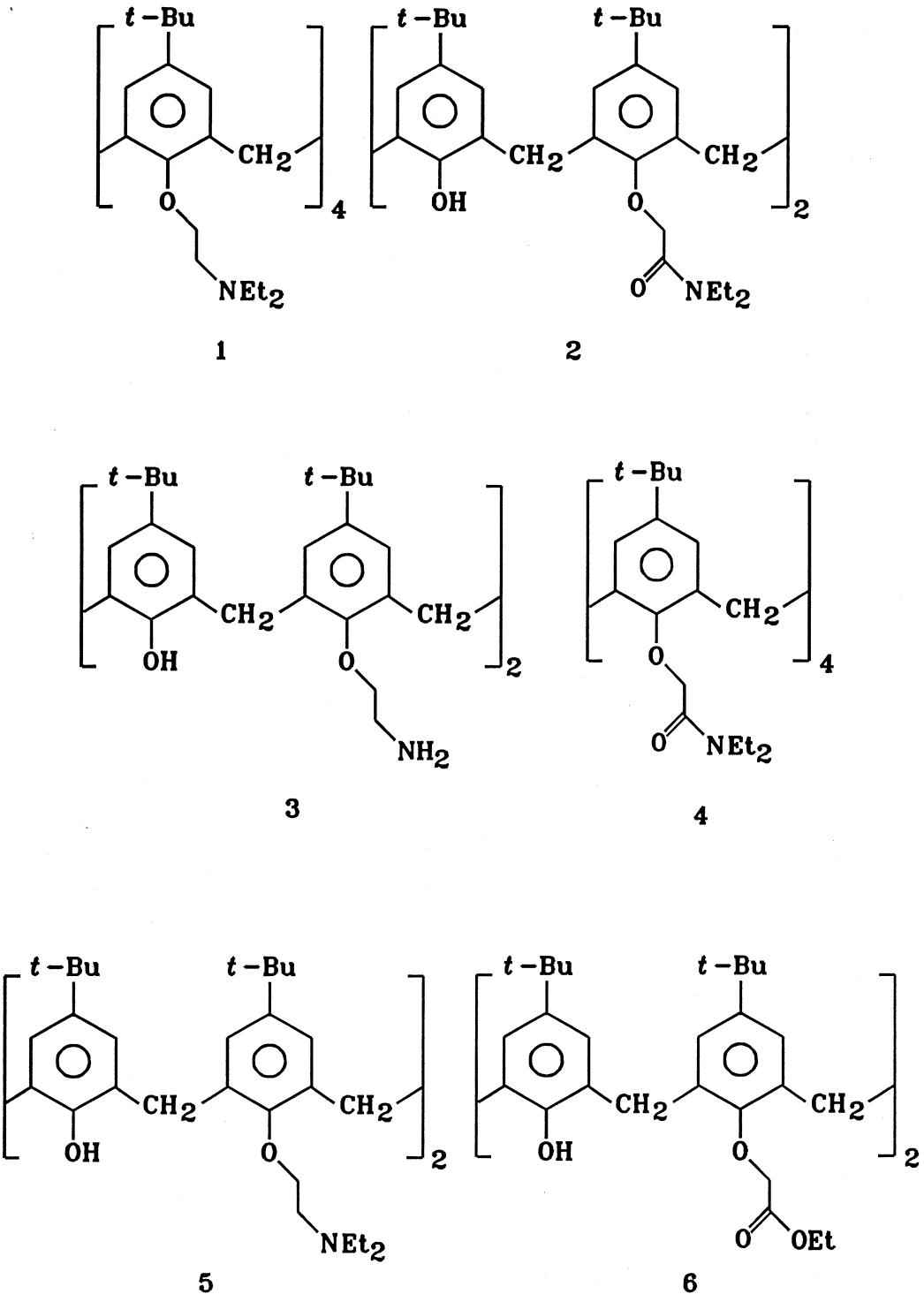
Determination of Extraction Ability

Ten milliliters of an aqueous metal picrate solution (10^{-3} M) was added to 10 mL of an extractant solution (10^{-3} M in $CHCl_3$), and the two phases were shaken together for 3 minutes. The layers were then allowed to separate, and each was individually collected for analysis. The organic layer was analyzed using a HP 8452A UV-Vis spectrophotometer. The concentration of the picrate anion was determined from the peak height at its maximum absorbance (368 nm). Metal assays of the aqueous layer were obtained by ICP-AES analysis using a Perkin-Elmer Plasma 400 spectrophotometer. Separate determinations of the individual metal concentrations were made at the following emission wavelengths (nm): U, 385.958; Cu, 221.458; Eu, 281.394; Cd, 214.438; Cr, 205.552; Pb, 220.353.

RESULTS AND DISCUSSION

Calix[4]arene Amides and Amines

We recently synthesized a series of calix[4]arene amides and amines **1–5** for use as potential extractants for heavy metals, lanthanides, and actinides (Fig. 1) (3, 4). We previously successfully used the ICP-AES method for metal analysis, but it is plausibile to use the picrate method with these amides



1 2 3 4 5 6

FIG. 1 Structures of extractants used.

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

and amines (5–9). We have now used both of these methods of metal analysis with these compounds to compare the relative effectiveness of our calix[4]arene amides and amines **1–5** as phase transfer agents for metals from aqueous solution into chloroform.

Comparison of the ICP-AES and Picrate Methods

The comparative data for individual aqueous solutions containing UO_2^{2+}, Cu^{2+}, Eu^{3+}, Cd^{2+}, Cr^{3+}, and Pb^{2+} by use of these two methods are collected in Table 1. These data were obtained by using the ICP-AES method with the aqueous phase, and the picrate absorption method with the chloroform layer. The measurements were made after shaking the phases together, and then allowing them to separate again.

The picrate method has been previously used with solutions that range from metal:complexant:picric acid ratios of 1000:5:1 to those of 500:500:1. Since it is unclear how compositions with such high metal:picrate ratios can give a true estimate of the total percent of metal extracted into the organic phase by the complexant, for our comparison between the picrate and ICP-AES methods we used concentration ratios of 1:1:*X*, where *X* is the charge on the metal cation, with the picrate concentrations being measured by the intensity of the electronic absorption peak at 368 nm. Details of the conditions used for the

TABLE 1
Comparative Extraction of Metals as Determined by ICP-AES and the Picrate Method

Compound	Metal	% Metal (ICP)	% Metal (picrate)	Compound	Metal	% Metal (ICP)	% Metal (picrate)
1	UO_2^{2+}	<1	99	**1**	Cd^{2+}	<1	100
2	UO_2^{2+}	<1	49	**2**	Cd^{2+}	<1	39
3	UO_2^{2+}	<1	147	**3**	Cd^{2+}	<1	127
4	UO_2^{2+}	<1	101	**4**	Cd^{2+}	<2	111
5	UO_2^{2+}	<2	102	**5**	Cd^{2+}	<1	107
6	UO_2^{2+}	<2	<1	**6**	Cd^{2+}	<1	<1
1	Cu^{2+}	<2	101	**1**	Cr^{3+}	<1	98
2	Cu^{2+}	4	52	**2**	Cr^{3+}	<1	49
3	Cu^{2+}	4	115	**3**	Cr^{3+}	<1	102
4	Cu^{2+}	6	106	**4**	Cr^{3+}	<1	105
5	Cu^{2+}	4	100	**5**	Cr^{3+}	<1	105
6	Cu^{2+}	<1	<1	**6**	Cr^{3+}	<1	<1
1	Eu^{3+}	<1	102	**1**	Pb^{2+}	<2	103
2	Eu^{3+}	<1	28	**2**	Pb^{2+}	9	67
3	Eu^{3+}	<1	110	**3**	Pb^{2+}	7	102
4	Eu^{3+}	<1	106	**4**	Pb^{2+}	48	112
5	Eu^{3+}	<1	102	**5**	Pb^{2+}	<1	101
6	Eu^{3+}	<1	<1	**6**	Pb^{2+}	<1	<1

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

ICP-AES method have been published previously (4, 10). Essentially, we measured the amount of metal extracted into the chloroform layer by taking the difference between its initial and final concentrations in the aqueous layer. The method is therefore a *direct* measurement of the individual metal concentrations in the solutions.

Our extraction data for UO_2^{2+}, Cu^{2+}, Eu^{3+}, Cd^{2+}, Cr^{3+}, and Pb^{2+} in Table 1 imply that each of the calix[4]arene amides and amines studied apparently yields a much higher analytical value for the metals when the picrate method rather than the ICP-AES method is used. This is clearly unreasonable.

Salt Formation

These widely divergent analytical values between the two methods can be explained on the basis that the picrate method gives unrealistically high values because these calix[4]arenes act as a base to picric acid, and it is the amide and amine salt, rather than the metal picrate, that is extracted into chloroform. As a test of this premise, we find that the calix[4]arene amide and amine picrate salts in the absence of metal ion are also extracted into chloroform from an aqueous phase. By contrast, the calix[4]arene diester **6** (11), which has no sites available for protonation by picric acid (pK_a 0.38), shows no metal extraction by either method.

CONCLUSION

Although the picrate method is generally problematic for quantitative estimations because of inherent uncertainties of concentration ranges and the stoichiometries of the metal picrates (12), the method appears to be particularly unreliable for calix[4]arene amide and amine extractants because of their formation of picrate salts that are preferentially dissolved in the chloroform phase rather than in the aqueous one, thereby giving false readings for the extraction percentages of metals by this method. In such cases a more direct metal assay must be used.

ACKNOWLEDGMENTS

We thank the US Army Research Office, the Robert A. Welch Foundation, and the US Department of Energy, through the Pacific Northwest Laboratory, for financial support. We thank Bruce Moyer and Karsten Gloe for helpful comments.

REFERENCES

1. W. Salomons, U. Förstner, and P. Mader (Eds.), *Heavy Metals*, Springer, New York, NY, 1995.
2. A. T. Yordanov and D. M. Roundhill, *Coord. Chem. Rev.*, *170*, 93 (1998).

3. O. M. Falana, H. F. Koch, D. M. Roundhill, G. J. Lumetta, and B. Hay, *J. Chem. Soc., Chem. Commun.*, p. 503 (1998).
4. N. J. Wolf, E. M. Georgiev, A. T. Yordanov, B. R. Whittlesey, H. F. Koch, and D. M. Roundhill, *Polyhedron*, *18*, 885 (1999).
5. N. N. L. Kirsch, R. J. J. Funck, and W. Simon, *Helv. Chim. Acta*, *61*, 2019 (1978).
6. S. Kumar, R. Singh, and H. Singh, *J. Chem. Soc., Perkin Trans. I,* p. 3049 (1992).
7. A. P. Marchand, S. Alihodzic, A. S. Mckim, K. A. Kumar, K. Mlinaric-Majerski, T. Sumanovac, and S. G. Bott, *Tetrahedron Lett.*, *39*, 1861 (1998).
8. P. D. Beer, M. G. B. Drew, M. Kan, P. B. Leeson, M. I. Ogden, and G. Williams, *Inorg. Chem.*, *35*, 2202 (1996).
9. U. Olsher, H. Feinberg, F. Frolow, and G. Shoham, *Pure Appl. Chem.*, *68*, 1195 (1996).
10. A. T. Yordanov and D. M. Roundhill, *Inorg. Chem.*, *37*, 3526 (1998).
11. R. Ungaro, A. Pochini, and G. D. Andreetti, *J. Incl. Phenom.*, *2*, 199 (1984).
12. J. E. Barry, M. Finkelstein, and S. D. Ross, *Tetrahedron*, *32*, 223 (1976).

Received by editor April 7, 1999
Revision received August 1999

Request Permission or Order Reprints Instantly!