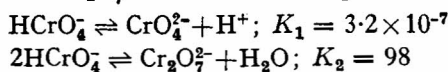distribution of activity of ^{32}P in the organic phase as a function of Cr(VI) concentration in the aqueous phase. It is seen that as long as the Cr(VI) concentration is significantly less than that required for 1:1 salt formation, the ^{32}P activity remains unaltered in the organic phase. However, as the Cr(VI) concentration in the aqueous phase approaches the amine concentration, the ^{32}P activity in the organic phase shows a decrease and finally as the Cr(VI) concentration becomes equal or greater than the amine concentration, all the ^{32}P activity is found in the aqueous phase. This experiment clearly confirms the absence of phosphate in the Cr(VI) species extracted into amine.

In aqueous systems Cr(VI) exhibits[8-10] various equilibria giving rise to different species. Under the experimental conditions the predominant species $HCrO_4^-$ and $Cr_2O_7^{2-}$ arise from the equilibria:

$$HCrO_4^- \rightleftharpoons CrO_4^{2-} + H^+; \quad K_1 = 3\cdot 2 \times 10^{-7}$$
$$2HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + H_2O; \quad K_2 = 98$$

These two species can be extracted as $(R_3NH^+HCrO_4^-)$ or $(R_3NH^+)_2Cr_2O_7^{2-}$ respectively by the extractant. In both the cases the extraction isotherm is expected to give a Cr(VI)-amine ratio of 1:1.

The UV spectrum of the extracted species shows maxima at 280 and 355 nm with a peak ratio of 1·8 (approximately two). These spectral characteristics are attributed to $Cr_2O_7^{2-}$ (ref. 2, 3).

References

1. (a) Sastri, M. N., Sundar, D. S. & Prasada Rao, T. S. R., *Curr. Sci.*, **35** (1966), 307. (b) Prasada Rao, T. S. R., *Studies on the blue peroxychromic acid and its derivatives*, Ph.D. thesis, Andhra University, 1967.
2. Tuck, D. G. & Walters, R. M., *J. chem. Soc.*, (1963), 1111.
3. Deptula, C., *J. inorg. nucl. Chem.*, **30** (1968), 1309.
4. Deptula, C., *Chem. Abstr.*, **69** (1968), 62035.
5. Moore, F. L., *Analyt. Chem.*, **29** (1957), 1660.
6. Coleman, C. F., Brown, K. B., Moore, J. G. & Allen, K. A., *Proceedings of second int. conf. on peaceful uses of atomic energy, Geneva* (United Nations Publications), 1958, C-10, paper 510.
7. Hesford, E. & Mckay, H. A. C., *Trans. Faraday Soc.*, **54** (1958), 573.
8. Davies, W. G. & Prue, J. E., *Trans. Faraday Soc.*, **51** (1955), 1, 45.
9. Neuss, J. D. & Rieman, W., *J. Am. chem. Soc.*, **56** (1934), 2238.
10. Tong, J. Y. & King, E. L., *J. Am. chem. Soc.*, **51** (1955), 1045.

Extractive Titrimetric Determination of Hg(II), Cu(II) & Ag(I) Using Lead Diethyldithiocarbamate

A. L. J. Rao & Chander Shekhar

Department of Chemistry, Punjabi University
Patiala 147002

A procedure for the selective determinations of Hg, Ag, Hg-Cu and Ag-Cu is described. Lead diethyldithiocarbamate [Pb(DDC)₂] undergoes quantitative, stoichiometric and fast exchange reactions with Hg(II), Ag(I) and Cu(II), even near the equivalence point, making it a suitable reagent for their determinations. Cobalt does not interfere in the determination of these cations.

KREIMER *et al.*[1] used chloroform solution of Cu(DDC)₂ for extractive titration of Ag(I). Lead diethyldithiocarbamate has also been used by many workers[2-5] for the spectrophotometric determination of Cu(II). In this note Pb(DDC)₂ has been used as a potential extractive titrimetric reagent for the selective determination of Hg(II) and Ag(I) alone and in binary combinations with Cu(II).

A stock solution of Pb(DDC)₂ ($2 \times 10^{-4}M$) was prepared by dissolving 101 mg/litre of Pb(DDC)₂ in chloroform and diluting with carbon tetrachloride (1:20, v/v) to make up to the mark. Similarly, its $1 \times 10^{-3}M$ solution was prepared. Dissolving Pb(DDC)₂ in carbon tetrachloride takes a long time and chloroform makes the preparation of titrant solution easy.

Metal ion solutions were prepared by dissolving analytical grade metal salts, standardizing by volumetric methods and then preparing more dilute solutions from these standardized solutions.

Acetate buffer was prepared by mixing $2M$ solutions of sodium acetate and acetic acid in the ratio 4:1 (v/v).

Erma photoelectric colorimeter AE-II was used for absorbance measurements. Titrations were performed using a specially constructed titration apparatus similar to that proposed by Galik[6].

Determination of Hg and Ag can be done by locating the end points visually, and also colorimetrically. The diethyldithiocarbamate of Hg and Ag formed during the titrations does not give any absorbance changes with the filter 420 nm used for measuring absorbance due to Cu(DDC)₂ formed during titrations.

Procedure for Hg(II) and Ag(I) — An appropriate amount of the metal ion to be analysed was taken, diluted to 20 ml with distilled water and the pH adjusted to 4·0-5·5 by adding 2 ml of acetate buffer. About 2 μg of Cu was added as indicator. Titrant ($2 \times 10^{-4}M$) was added in 1 ml portions, shaking for half a minute each time and separating the extract after each addition. The titration was continued until the extract showed brownish colouration due to the formation of Cu(DCC)₂. The titration was repeated, adding in one lot the reagent solution (1 ml less than that is required in the first titration), retaining about 0·5 ml of the organic phase, then continuing with the addition of reagent in 0·1 ml portions until the extract showed brownish colouration.

For locating the end points colorimetrically, about 50 μg of copper was added to the aqueous phase taken in the titration apparatus containing 20 ml of CCl₄. Aqueous phase made nearly 20 ml and the pH adjusted to 4·0 to 5·5 as before. The titrant solution ($1 \times 10^{-3}M$) was added in 0·1 ml portions with shaking of about 1 min each time. After setting the phases, absorbance of the organic phase was measured against CCl₄ blank. Absorbance of the organic phase does not change during the exchange of Hg or Ag with the titrant. After the end point, absorbance of the organic phase, started increasing owing to the formation of Cu(DCC)₂ giving a break in the titration curve.

Procedure for Hg-Cu and Ag-Cu — Simultaneous determinations of Hg-Cu and Ag-Cu were done by locating the end points colorimetrically and adopting the procedure as given for single cations. After
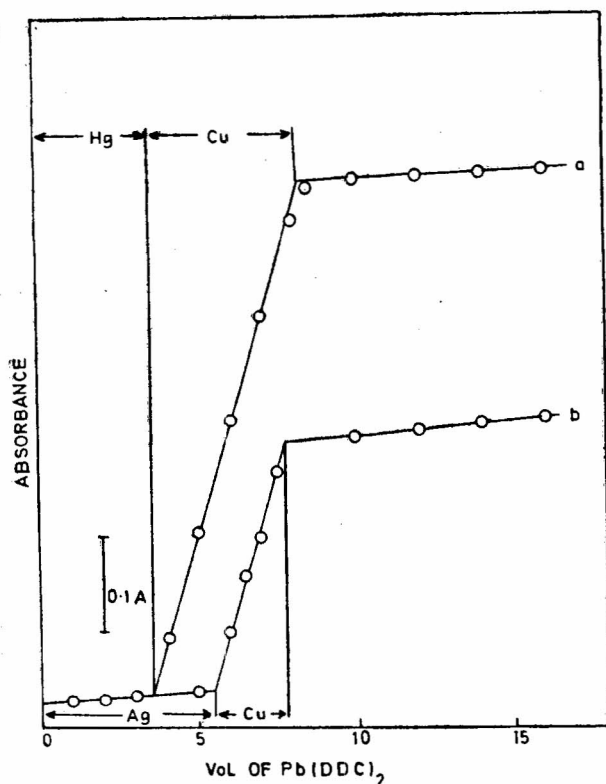
Fig. 1 — Simultaneous determination of Hg-Cu and Ag-Cu
[(a) Hg (100 μg) + Cu (57·2 μg); (b) Ag (194 μg) + Cu (31·8 μg)]

the first break in the titration curve, the absorbance of the organic phase would go on increasing until the whole of Cu has been exchanged, and after that the addition of colourless $Pb(DDC)_2$ titrant would not change the absorbance of organic phase giving a second break in the titration curve.

For plotting the titration curves, absorbance values were corrected to the initial volume of the solution by multiplying the absorbance readings by the factor $(v+V)/V$, where V is the initial value of the organic phase and v is the volume of titrant added for the particular absorbance reading being considered. Typical titration curves are shown in Fig. 1.

For the determination of Hg and Ag using visual extractive titrations, two titrations have to be performed, the first to find the approximate volume of the titrant and the second to find the exact volume of the titrant. In spite of this drawback, visual location of the end points is recommended for the determination of Hg or Ag because the results obtained are always better than those obtained by the location of end points colorimetrically. However, for binary solutions visual spotting of the end point is not helpful and the location of end point colorimetrically gives better results. For the visual and colorimetric location of end point the amount of copper needed is 2 and 50 μg respectively.

The pH effect was studied in the range 2-6 so that no auxiliary masking agent would be required to keep the metal ions in solution. The separation of the organic and aqueous phase becomes clear if the pH is more than 3·5 and so a pH range of 4·0-5·5 was selected for the determinations. The exchanges

in this pH range are very fast and stoichiometric even near the equivalence point and the conditions for performing extractive titrations are satisfied. The stoichiometries of exchange reactions between $Pb(DDC)_2$ and Hg, Ag and Cu have always been found out to be 1:1, 1:2 and 1:1. Twelve replicate determinations of 240 μg of Hg(II) and 259 μg of Ag(I) never gave a deviation of more than 1·7% or the relative standard deviation of 0·85%.

Interferences — Under the selected conditions, Ni, Co, Fe(II, III), Mn, Zn, Pb, Cd and Al do not interfere even if present up to 50 mg each, making the method selective for determining the cations, and also, Cu does not interfere at all in the determination of Hg. The stabilities of the complexes of these metals are less than those of Hg, Ag and Cu, and so, these metals are not expected to interfere. If NaDDC is used as titrant and cobalt is present in 0·1 mg amounts or more, it also reacts with the titrant during the course of titration and the cobalt diethyldithiocarbamate formed does not participate in exchanges with Hg, Ag or Cu present in the aqueous solution resulting its interference. While using $Pb(DDC)_2$ as titrant, cobalt diethyldithiocarbamate is not formed at all and so cobalt does not interfere.

References

1. KREIMER, S. E., LOMOKHOV, A. S. & STOGOVA, A. V., *Chem. Abstr.*, **58** (1963), 6186a.
2. KREIMER, S. E. & BUTYLKIN, L. P., *Chem. Abstr.*, **54** (1960), 8452a.
3. VASAK, V. & SEDIVEC, V., *Chem. Listy*, **45** (1951), 435.
4. TERTOOLEN, J. F. W., DETMAR, D. A. & BUIJZE, C., *Z. analyt. Chem.*, **167** (1959), 401.
5. ADAMIEC, I., *Chem. Abstr.*, **60** (1964), 4b.
6. GALIK, A., *Talanta*, **13** (1966), 109.

Separation & Quantitative Determination of Be(II) & Ce(IV) with N-*m*-Tolyl-*m*-nitrobenzohydroxamic Acid

PRAKASH C. VERMA*, P. V. KHADIKAR & Y. K. AGRAWAL†

School of Studies in Chemistry, Vikram University, Ujjain

Quantitative gravimetric determination and separation of Be(II) and Ce(IV) in the presence of Ag(I), Pd(II), Mn(II), Ni(II), Zn(II), Cu(II), Hg(II), Ga(III), Sb(III), As(III), Bi(III), Ti(IV) and Zr(IV) have been made by selective precipitation of Be(II) and Ce(IV) with N-*m*-tolyl-*m*-nitrobenzohydroxamic acid (N-*m*-T-*m*-NBHA) from the solution containing about 2·22 mg of Be(II) and 3·35 mg of Ce(IV) at pH 7·9 to 8·9 and 3·8 to 4·1 respectively. Be(II) and Ce(IV) complexes of this ligand have been isolated as dirty white and white granular solids respectively and analysed to have the composition $[C_{14}H_{11}N_2O_4]_nM$ (where $n=2$ if M=Be and $n=4$ if M=Ce).

*To whom all correspondence should be made at the Department of Chemistry, Model Science College, Ujjain, MP.
†Present address: Health Physics Division, BARC, Bombay 400085.