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.

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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$_2$O$_4$]$_n$M (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.

GRAVIMETRIC estimation of Be(II) with N-phenylbenzohydroxamic acid (N-PBHA) is reported in the literature[1]. Introduction of a bulky group into N-PBHA is expected to give a larger molecular weight and hence better conversion factor[2] and may improve the selectivity and sensitivity of the reagent. With this in view the efficiency of N-*m*-tolyl-*m*-nitrobenzohydroxamic acid has been tested for the gravimetric estimation and separation of Be(II) and Ce(IV) in the presence of several commonly occurring metal ions and the results of this study are presented in this note.

N-*m*-Tolyl-*m*-nitrobenzohydroxamic acid was synthesized using the method described by Agrawal and Tandon[3], m.p. 118° (lit. m.p. 118°). A 0·01M solution of the reagent in ethanol was used.

Aqueous stock solutions of Be(II) and Ce(IV) ($10^{-3}M$) were prepared by dissolving 0·1771 g of beryllium sulphate and 0·3333 g of cerium sulphate respectively in a litre of doubly distilled water and standardized[45].

Solutions of masking reagent (1%) were prepared in doubly distilled water.

Procedure—Beryllium or cerium salt solution (25 ml) and water (500 ml) were heated to 60° on a steam-bath and to this was added the reagent solution (25 ml) dropwise with constant stirring, followed by the addition of 0·01M ammonia until complete precipitation. Quantitative precipitation of Ce(IV) occurred between pH 3·8 and 4·1 and that of Be(II) between pH 7·9 and 8·9. Desired pH was adjusted using 0·1M ammonium chloride and sulphuric acid solutions. The granular complex thus obtained was digested for 2-3 hr on a steam-bath, filtered, washed thoroughly with hot water and finally with aq. ethanol (10 ml, 20%). The complex was dried at 110-20° and weighed directly as $(C_{14}H_{11}N_2O_4)_nM$ [$n = 2$ for Be(II) and $n = 4$ for Ce(IV)]. The results of estimation are presented in Table 1.

Taking advantage of wide variation in the pH of precipitation of Be(II) and Ce(IV), these two metals have been separated and estimated from their binary mixture. Following the above procedure and in the presence of KCN solution Be(II) and Ce(IV) could be separated from Ag(I) (60 mg), Pd(II) (80 mg), Mn(II) (80 mg) Ni(II) (80 mg), Cu(II) (80 mg), Zn(II) (80 mg), and Hg(II) (60 mg). The interference of Ga(III) (100 mg), Sb(III) (80 mg), As(III) (80 mg), Bi(III) (80 mg), Ti(IV) (100 mg), Zr(IV) (100 mg) can be avoided by using 1% citrate-oxalate solution as a masking agent instead of KCN. Al(III) (100 mg) and Mo(VI) (100 mg) can be masked by the addition of Mg-EDTA.

Both the complexes were found soluble in chloroform, benzene and ethanol but sparingly soluble in carbon tetrachloride, ether and gl. acetic acid. Complexes decompose if treated with conc. sulphuric, nitric or perchloric acid.

It is interesting to note that the presence of excess of cyanide and Mg-EDTA does not interfere with the precipitation of Be(II) and Ce(IV), but the excess of citrate-oxalate inhibits the precipitation.

The complexes analysed for: (A) $(C_{14}H_{11}N_2O_4)_2$ Be: (Found: C, 61·04; H, 4·01; N, 10·16; Be, 1·63. Reqd: C, 61·02; H, 4·02; N, 10·17; Be, 1·62%). (B) $(C_{14}H_{11}N_2O_4)_4$Ce: (Found: C, 54·96; H, 3·62; N, 9·16; Ce, 11·39. Reqd: C, 54·94; H, 3·62; N, 9·17, Ce, 11·37%).

The IR spectrum (nujol) of the reagent N-*m*-T-*m*-NBHA showed peaks at 3289, 1600 and 917 cm^{-1}, due to stretching vibrations of O—H, C=O and N—O groups respectively. On complex formation the peak at 3289 cm^{-1} disappeared owing to the replacement of H^+ by the metal ion, indicating the co-ordination of oxygen atom to the metal ion. If the hydroxyl group were bonded to the metal through a lone pair of electron and still retained the hydrogen atom, the O—H stretching frequency at 3289 cm^{-1} would have been altered. The νCO in the complexes appeared at lower frequency (1560 cm^{-1}), indicating bonding of the carbonyl oxygen atom to the metal ion. The N—O stretching vibration at 917 cm^{-1} was unaltered except for its intensity, which was increased.

TABLE 1 — ESTIMATION OF Ce(IV) AND Be(II)

Cerium (mg)		Error	Beryllium (mg)		Error
Taken	Found		Taken	Found	
3·50	3·52	+0·02	2·25	2·26	+0·01
7·00	7·01	+0·01	4·50	4·49	−0·01
7·00	7·02	+0·02	4·50	4·51	+0·01
17·50	17·48	−0·02	11·25	11·24	−0·01
35·00	35·02	+0·02	22·50	22·42	−0·08

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