of 0.1N oxidant solution were taken in a titration vessel and the contents diluted to 40 ml to produce the acetate acid concentration of 2M (in the case of vanadate), 4M (in the case of dichromate) or 6M (in the case of Fe(III)). Carbon dioxide was passed through the solutions for 10 min, and the titration carried out against V(III) solution adding 0.5 ml of cacothelinc solution (0.2%) near the end-point (pink colour). The results are given in Table 1.

The indicator correction in all the above cases was 0.03 ml of 0.1M reductant solution.

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**References**


**Extractive Spectrophotometric Determination of Ce(IV) with p-Anisidine**

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A new extractive spectrophotometric method for the determination of Ce(IV) with p-anisidine is proposed. The reddish-violet complex can be quantitatively extracted at pH 2 (KCl-HCl buffer) by isoamyl alcohol in which solution it shows maximum absorbance at 510 nm. The complex has a molar composition of 1:1 and obeys Beer’s law up to 20 ppm of Ce(IV).

SUTEU has reported that p-anisidine forms a violet complex with V(V) in the presence of HCl (2.21M). We have observed that Ce(IV) also forms a violet complex at pH 2 with this reagent. The complex is stable in aqueous solution for 1 hr but if extracted in organic solvents it is stable for a longer time. This property has been utilized to develop an extractive spectrophotometric method for the determination of Ce(IV).

The system attains maximum absorbance ($\lambda_{max}$ 510 nm) between pH 2 and 2.5 beyond which the $\lambda_{max}$ is changed. Subsequent experiments were done at pH 2. Amongst the buffers tried KCl-HCl buffer gave better results. The extraction of the complex was tried in various organic solvents. It was found that the complex is extractable in chloroform, isooamyl alcohol, amyl acetate and isobutyl alcohol. The choice of the solvent was made by finding the distribution coefficient and percentage extraction in each solvent. It was found that percentage extraction and distribution coefficient are highest in the case of isoamyl alcohol.

The linearity between absorbance and metal ion concentration was observed up to 20 ppm of Ce(IV). The sensitivity of the colour reaction as calculated from Beer’s law plot was found to be 0.1 $\mu$g of Ce(IV)/cm$^2$ for $\log$ $E_0$ = 0.001. The molar extinction coefficient for the complex is $1.68 \times 10^3$.

Job’s method of continuous variation was applied to find out the composition of the complex. The complex has 1:1 stoichiometry. The suggested method though tedious is justified by the higher extinction coefficient and greater stability of the complex. This method can also be used for the separation of Ce(IV) from other lanthanides.

**Procedure** — Ce(IV) solution (500 ppm) was prepared by dissolving Ce(SO$_4$)$_2$ in distilled water after adding appropriate amount of H$_2$SO$_4$ and was standardized by the usual method. Commercial grade p-anisidine was purified by recrystallization from water and its 1% solution was prepared in ethanol.

To a solution containing up to 20 $\mu$g of Ce(IV), 5 ml of 1% p-anisidine was added. The pH of the solution was adjusted to 2 with KCl-HCl buffer and volume made up to 25 ml. The complex was extracted in 10 ml of isoamyl alcohol and absorbance measured at 510 nm after filtering it through anhydrous sodium sulphate and appropriate dilution. The amount of Ce(IV) was then deduced from the calibration curve drawn under identical conditions.

**Effect of diverse ions** — The effect of diverse ions was studied by adding to the Ce(IV) solution (0.25 ml of 500 ppm) various cations and anions 10 times in excess. It was found that Cu$^{2+}$, Ni$^{2+}$, Co$^{2+}$, Mn$^{2+}$, Cl$^-$, Br$^-$, NO$_3^-$ do not interfere but MnO$_4^-$, Cr$_2$O$_7^{2-}$ and Fe$^{3+}$ interfere and hence should be absent.

**References**