

NOTE

Amperometric Trace Determination of V(V) and Cr(VI) with Ethanethioic Acid

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Ethanethioic acid (thioacetic acid, ETA) has been employed for the amperometric determination of V(V) in 0.1 M KCl and Cr(VI) in acetate buffer medium of pH 4.99 at d.m.e. While Cr(VI) method involves no chemical interaction and is based on the phenomenon of mutual compensation of cathodic current of metal species and anodic current of ETA, V(V) method seems to be the consequence of complexation reaction. Metal species-ETA titrimetric ratio has been found to be 1 : 2 for V(V) and 1 : 3.32 for Cr(VI). Solutions as dilute as 5.09 ppm [V(V)] and 0.52 ppm Cr(VI) have been estimated with high degree of accuracy. Tolerance limits for foreign ions have also been worked out.

Ethanethioic acid (thioacetic acid, ETA) has sometimes been used as a complexing agent for metals¹⁻³ though its capacity to act as analytical reagent remains largely unexamined. The work was undertaken with a view to unravel this aspect of the acid and a unique amperometric method was evolved for estimating trace amounts of V(V) and Cr(VI) at d.m.e.

All the titrations were performed at d.m.e. vs. s.c.e. employing a manual polarograph (Toshniwal, India, model CL02A). Only analytical grade chemicals and doubly distilled water were used. NH_4VO_3 and $\text{K}_2\text{Cr}_2\text{O}_7$ were used as source compound of V(V) and Cr(VI) respectively. ETA solution was prepared afresh daily and was used as such. Amperometric determination of metal solution of any particular concentration was carried out at least thrice. Purified nitrogen was employed for deaeration. Titration potential (-0.10 V) was selected in the anodic limiting region of ETA in case of both the metal ions and metal ion solutions were used as titrant in case of V(V). Cr(VI) titrations at 0.10 V were performed using ETA solution as well as Cr(VI) solution as titrant.

Determination of V(V): Amperometric determination of V(V) was carried

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out in 0.1 M KCl medium. VO_3^- has been reported⁴ to give an irreversible wave in this medium with an extremely ill-defined limiting region spread over the potential range of -1.55 V through -1.70 V and $E_{1/2}$ as -1.26 V. ETA also gave its one-electron anodic wave in this medium with the limiting region from 0.00 to -0.15 V, $E_{1/2}$ being -0.22 V. Anodic titrations using metal ion solution as titrant were carried out at -0.10 V which fell in the limiting region of ETA wave. The titration resulted in upside-down L-shaped curve and the null point corresponded to the metal-ligand molar ratio of 1 : 2. The method enabled the estimation of V(V) in the concentration range of 254.70 ppm through 5.09 ppm. Maximum error (less than 2%) was encountered in the case of most dilute solutions only.

Determination of Cr(VI): Amperometric titrations were performed at 0.10 V. Cr(VI) gives a single reduction wave⁵ in acetate buffer of pH 4.99 + 0.005% gelatin medium, with the limiting region starting from 0.00 V to -1.40 V. ETA is known to undergo reversible, one-electron oxidation at d.m.e. in various supporting electrolytes. In acetate buffer of pH 4.99 also, a similar anodic wave of the acid with the limiting region stretching from 0.00 to -0.14 V is obtained. Titration voltages thus fall in the limiting regions of the metal species as well as the ligand.

On titrating Cr(VI) solution with ETA at 0.10V, cathodic current was progressively compensated by the anodic current of the wave of ETA until it reached zero value and this arm touched the residual current line. Addition of more ETA now led to the appearance of anodic current with slight change in the slope of the curve. The two arms of the titration curve thus intersected each other at the residual current line and Cr(VI) : ETA molar concentration ratio at this point was found to be 1 : 3.32. Similarly when ETA solution was titrated with Cr(VI) solution, same titrimetric molar ratio was obtained. The method enabled the estimation of Cr(VI) solutions in the concentration range of 259.95 ppm through 5.2 ppm (anodic) and 0.52 ppm (cathodic titration). When the titration was carried out at more negative potential (-0.80 V), addition of ETA did not bring about any reduction in the cathodic current of the metal species, thus indicating that the titration was not a consequence of any chemical interaction. It may further be mentioned that Cr(VI) : ETA titrimetric molar ratio (1 : 3.32) was found to be the same as the reverse ratio of i_d/c values of the two species. This confirms the current compensation phenomenon.

Checking of interference of foreign ions and selectivity: Study of interference of foreign ions in the new amperometric methods was carried out for three concentrations of each metal species, viz., 5.00 mM, 1.00 mM and 0.50 mM. Table-1 includes safe limits of foreign ions in the cell solution. Non-interfering species did not interfere even when present simultaneously in the cell solution. However, for these selectivity tests, the maximum concentration of each species taken was 0.25 mM to avoid supersaturation.

TABLE-1
SAFE LIMIT OF THE CONCENTRATION OF FOREIGN IONS
IN THE CELL SOLUTION WITH RESPECT TO THE
CONCENTRATION OF THE METAL SPECIES

Foreign ions	Determination of V(V)	Determination of Cr(VI)
NO ₃ ⁻	B	B
SO ₄ ²⁻	B	B
SCN ⁻	A	B
CH ₃ COO ⁻	B	B
WO ₄ ²⁻	A	B
Ox ²⁻	A	B
S ₂ O ₃ ²⁻	1/10	1/10
Mg(II)	B	B
Al(III)	B	B
Mn(II)	A	B
Cr(III)	A	A
Cr(VI)	Equal	—
Mn(VII)	A	A
Fe(II)	A	1/10
Fe(III)	Equal	A
Co(II)	A	B
Cu(II)	A	A
Cd(II)	A	A
Mo(VI)	10 times	A
Ni(II)	B	B
V(V)	—	A
Hg(II)	A	A
Cl ⁻	A	A

A: Serious interference even when the conc. foreign ion is 1/20 of the metal
B: No interference even when foreign ion is 20 times that of ion.

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