Titrimetric Determination of Thallium

By

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Literature has cited several methods concerning the titrimetric determination of thallium(I). Some workers have determined it with potassium permanganate\(^1\) in alkaline medium at 40\(^\circ\)C; potassium ferrocyanide\(^2-4\) in the presence of sodium hydroxide; potentiometrically\(^5\) with periodato cuprate(III); potassium manganate\(^6\); a standard solution of bromine\(^7\) in glacial acetic acid. The present method deals with titrimetric determination by redox process: thallium(I) sulphate is reduced with D-glucose (or D-fructose) in alkaline medium. The reaction mixture, consisting of thallous sulphate, known volume of a standard solution of D-glucose and sodium hydroxide, is either kept at room temperature or heated to boiling. Potassium chloride is added to protect the precipitated metal from aerial effects. After cooling to room temperature the metal is filtered, washed and oxidised with an excess of ferric ammonium sulphate. The ferrous ion formed is titrated against a standard solution of ceric sulphate using N-phenyl anthranilic acid as indicator. It is observed that the results agree with those obtained by standard method\(^1\) and give concordant and precise values. It is also observed that Li\(^+\), Ca\(^{2+}\), Ba\(^{2+}\), Sr\(^{2+}\), Mg\(^{2+}\), Cd\(^{2+}\), Zn\(^{2+}\), Ni\(^{2+}\), Co\(^{2+}\), Al\(^{3+}\), and Zr\(^{4+}\) interfere but Pb\(^{2+}\) and Th\(^{4+}\) do not.

Experimental

Reagents

Thallous sulphate (Riedel de Haen Ag. grade); D-glucose (Analar B. D. H. grade); sodium hydroxide (Analar B. D. H. grade); sodium carbonate (Analar B. D. H. grade); potassium chloride (Analar B. D. H. grade); ferrous ammonium sulphate (Analar B. D. H. grade); ferric ammonium sulphate (Indian grade); ceric sulphate (Technical B. D. H. grade); sulphuric acid (Analar B. D. H. grade); and N-phenyl anthranilic acid (B. D. H. grade).
0.02 \textit{N} Ceric sulphate (in 8 \textit{N} H\textsubscript{2}SO\textsubscript{4}) is standardised by titrating against a standard solution of ferrous ammonium sulphate (in 1 \textit{N} H\textsubscript{2}SO\textsubscript{4}) using N-phenyl anthranilic acid as indicator.

\textbf{Procedure}

To a known solution of thallous sulphate are added measured standard solutions of D-glucose and sodium hydroxide respectively (see Table I). This reaction mixture is boiled for 2 to 4 minutes after adding 10 ml of \textit{N} potassium chloride solution. After cooling at room temperature the metal in the powdered state is collected on a filter, washed and transferred to a beaker. Oxidation is then carried out by adding an excess of ferric ammonium sulphate (needs no standardisation but must be tested for any ferrous ion present). The ferrous ion produced, corresponding to the metal oxidised, is titrated against a standard solution of ceric sulphate (in 8 \textit{N} H\textsubscript{2}SO\textsubscript{4}) using N-phenyl anthranilic acid as indicator. At the end point a red brown colour appears.

\textbf{Results and Discussion}

The results are shown in Table I. The range in which thallium is estimated vary from 10.2 mg/l to 50.9 mg/l.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|}
\hline
\text{TI\textsubscript{2}SO\textsubscript{4}} & \text{D-glucose} & \text{NaOH} & \text{H\textsubscript{2}O} & \text{Co(SO\textsubscript{4})\textsubscript{2}} & \text{Amount of thallium} \\
\text{ml} & \text{0.2 M} & \text{3 \textit{N}} & \text{ml} & \text{ml} & \text{mg/l} \\
\hline
1.0 & 10 & 4 & 5.0 & 2.50 & 10.2 \\
2.0 & 10 & 4 & 4.0 & 4.92 & 20.1 \\
2.5 & 10 & 4 & 3.5 & 6.20 & 25.3 \\
3.0 & 10 & 4 & 3.0 & 7.42 & 30.3 \\
4.0 & 10 & 5 & 1.0 & 9.94 & 40.6 \\
5.0 & 10 & 5 & 0.0 & 12.46 & 50.9 \\
\hline
\end{tabular}
\caption{Table I}
\end{table}

The reaction that occurs between metallic thallium and ferric ammonium sulphate is:

\[ \text{Tl} + \text{Fe}^{3+} \rightarrow \text{Tl}^+ + \text{Fe}^{2+}. \]

It is observed that the metal exists in the three forms viz., cloth like (in alkaline medium) and in sheet or solid mass (in acid medium), in powdered state, and in brittle form. The metal exists cloth like in alkaline medium when the reaction mixture is left as such for more than 24 hours at room temperature; but the metal becomes a sheet or a solid mass when acid neutralises the alkali. In the powdered form the metal is obtained by boiling the reaction mixture with potassium chloride from 2–4 minutes. In brittle state the metal is obtained by slowly evaporating