DETERMINATION OF SMALL QUANTITIES OF $^{51}\text{Cr}(\text{III})$ IN THE PRESENCE OF LARGE QUANTITIES OF $^{51}\text{Cr}(\text{VI})$ BY COPRECIPITATION WITH ZINC HYDROXIDE


Institute of Nuclear Science, National Tsing Hua University, Hsinchu, Taiwan (Republic of China)

(Received May 18, 1971)

A procedure is described for the determination of $^{51}\text{Cr}(\text{III})$ in $^{51}\text{Cr}(\text{VI})$ samples having a $^{51}\text{Cr}(\text{VI})$ to $^{51}\text{Cr}(\text{III})$ ratio of $10^5$, by means of a single zinc hydroxide coprecipitation at a pH of ca. 13. Acceptable precision (standard deviation of 10–15%) is possible with solid $^{51}\text{Cr}(\text{VI})$ samples containing 10 ppm of $^{51}\text{Cr}$ as $^{51}\text{Cr}(\text{III})$.

Introduction

Many different procedures have been developed for the separation and subsequent analysis of $^{51}\text{Cr}(\text{III})$ and $^{51}\text{Cr}(\text{VI})$ when similar quantities of radioactivity are present in both species. However, these procedures cannot generally be applied to the separation and determination of small amounts of $^{51}\text{Cr}(\text{III})$ in the presence of much greater amounts of $^{51}\text{Cr}(\text{VI})$, i.e. when the $^{51}\text{Cr}(\text{VI})/^{51}\text{Cr}(\text{III})$ ratio is greater than $10^3$. This is due to the $^{51}\text{Cr}(\text{VI})$ contamination (0.1% or more) which tends to follow the $^{51}\text{Cr}(\text{III})$ under typical analytical conditions.

Cline, Simmons and Rossmassler have used Al(III) as coprecipitant-carrier for the hydroxide separation of (non-labelled) Cr(III) from Cr(VI) when the ratio of Cr(VI) to Cr(III) is of the order of $10^3$. This procedure requires a double precipitation of the aluminium–chromium hydroxide to attain an efficient separation. The reported precision of this method is reasonably good (+10%); however, the level of Cr(VI) contamination of the separated aluminium–chromium hydroxide is significant. More recently, coprecipitation of Cr(III) with zinc hydroxide was investigated by Fuhrman and Latimer for the separation of (non-labelled) Cr(III) from chromic acid. With a Cr(VI)/Cr(III) ratio of ca. $10^4$, the standard deviation of the Cr(III) measurement after two precipitations is also approximately ±10%. However, no indication of the amount of Cr(VI) contamination of the hydroxide precipitate, if any, was reported.

* International Atomic Energy Agency Expert, on leave from the Western New York Nuclear Research Center, Buffalo, N. Y., USA.

J. Radioanal. Chem. 10 (1972)
The success of these coprecipitation procedures for the separation of 'micro' quantities of Cr(III) from much greater quantities of Cr(VI) suggested that a coprecipitation procedure could be developed for the separation of \(^{51}\text{Cr(III)}\) from \(^{51}\text{Cr(VI)}\) when the Cr(VI)/Cr(III) ratio is at least of the order of \(10^4\). We report here a modification of the zinc hydroxide coprecipitation procedure with which we have routinely and accurately determined small (<0.01 \%) amounts of \(^{54}\text{Cr(III)}\) in \(K_2^{51}\text{CrO}_4\) or \(K_2^{51}\text{Cr}_2\text{O}_7\).

**Experimental**

*Solutions.* (A) Zinc nitrate hexahydrate \([\text{Zn(NO}_3\text{)}_2 \cdot 6\text{H}_2\text{O}]\) and chromium trioxide \((\text{CrO}_3)\) are dissolved in redistilled water to give a solution containing 1 mg \(\text{Zn}^{2+}\) per ml and 10 mg \('\text{CrO}_3'\) per ml. (B) Zinc nitrate hexahydrate is dissolved in redistilled water to give a solution containing 1 mg \(\text{Zn}^{2+}\) per ml.

Others: 1.0N KOH, \(\text{pH} 10\) KOH, 1.0N HCl and ca. 1N HNO\(_3\).

*Filtration column.* A short (5–10 mm) bed of alumina or Celite (Johns-Manville Co.) is prepared in a 6 mm I.D. glass column. The bed is prewashed with 5 ml of 1.0N KOH and with 5 ml of \(\text{pH} 10\) KOH wash solution, then kept wetted with \(\text{pH} 10\) solution until the sample is added.

*Analysis.* Typically, a 10–60 mg solid sample of \(K_2^{51}\text{CrO}_4\), \(K_2^{51}\text{Cr}_2\text{O}_7\) or other water-soluble Cr(VI) salt is dissolved in 5.0 ml of solution (A). After complete dissolution, 3.0 ml of 1.0N KOH is added, and the solution is heated to near boiling (90–95 °C) for about 30 min. While the solution is still hot, 1.0 ml of solution (B) is added, with stirring. The resulting suspension may be filtered immediately or after cooling.

In our filtration procedure, the suspension is stirred as needed to suspend the precipitate, and a small amount (several mg is adequate) of Celite is added to decrease the time required for filtration and subsequent washing. The contents of the precipitation tube are then poured onto the prepared filtration column, with the eluate being collected in a 100 ml volumetric flask containing 5 ml of ca. 1N HNO\(_3\). Several 1–2 ml amounts of \(\text{pH} 10\) KOH wash solution are used to complete the transfer of the precipitate to the filtration column. After the precipitation solution and these washes have passed through, the glass walls and bed are meticulously washed free of Cr(VI) with several 1–2 ml portions of \(\text{pH} 10\) KOH wash solution and then with two additional 10 ml portions of wash solution. The eluate wash solutions are also collected in the volumetric flask. When the washings are completed, the contents of the volumetric flask are diluted to the mark, mixed thoroughly and a carefully measured aliquot is transferred to a counting tube.

The precipitate is dissolved from the column with about 5 ml of 1.0N HCl. This eluate is collected directly in a second counting tube.

The volumes (heights) of the solutions in the two counting tubes are made equal, each solution is thoroughly mixed and the \(^{51}\text{Cr(III)}\) and \(^{51}\text{Cr(VI)}\) activities