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Stable Isotope Separation
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CHEMISTRY ASSOCIATED WITH THE ELECTROMAGNETIC SEPARATION OF CHROMIUM ISOTOPES

Boyd Weaver
R. L. Bailey
W. C. Davis
F. M. Scheitlin
C. W. Sheridan
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ISOTOPES DIVISION

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INTRODUCTION

Chemical research and production efforts supporting the electromagnetic separation of the stable isotopes of chromium include the preparation of charge material, removal of separated material from collectors, and product purification.

PREPARATION OF CHARGE MATERIAL

Chromium trichloride, the only compound considered satisfactory for charge material, has been prepared by two methods (though the first is no longer used):

Reaction of Chromium Metal with Chlorine. – The reaction of chromium and chlorine is slow, even at 1000°C, but its speed is increased by pulverization of the metal with a stainless steel mortar and pestle. A quartz tube, in which chlorine gas is passed over the crushed metal, makes a suitable reactor when heated by a somewhat shorter tube furnace. Anhydrous, water-insoluble $CrCl_3$ collects as pink-to-violet flakes in the cooler part of the tube. This deposit must be scraped out occasionally to prevent formation of a solid block. The usual batch was made from about 160 g of chromium metal.

Reaction of Cr_2O_3 with CCl_4 at 575°C. – The most reactive form of Cr_2O_3 is made by thermal decomposition of $(NH_4)_2Cr_2O_7$. The salt is poured into a heated stainless steel beaker in portions of a few grams at a time. Decomposition is violent and gives an oxide of a very low density. This Cr_2O_3 is placed in a boat which in turn is inserted in a pyrex tube heated to 575°C. Carbon tetrachloride contained in a gas-washing bottle is vaporized by a stream of nitrogen and by heat from infrared lamps, and the vapors are passed over the Cr_2O_3. A loose block of glass wool wrapped around a beaker and inserted at the end of the tube helps to develop a slight CCl_4 back pressure, which is conducive to chlorination. Chromium trichloride remains in the boat, usually along with some unreacted Cr_2O_3, which must be separated mechanically. The $CrCl_3$ is freed of residual Cl_2 and CCl_4 by evacuation at 50 to 100 μ for 8 hr at 450°C. The resulting $CrCl_3$ has such a low bulk density that it is usually pressed into pellets before being loaded into charge bottles.

CHEMICAL RECOVERY AND REFINEMENT

Summary of Recommended Procedure

The following procedure is recommended for the chemical treatment of chromium isotopes:

1. Collect isotopes only in purified graphite receivers.
2. Ignite collectors at 800°C in an oxygen atmosphere.
3. Heat ash with 20 ml of 70% $HClO_4$ per gram of Cr_2O_3 until all the green color disappears.
4. Cool to room temperature quickly, and filter by suction on sintered glass.
5. Dissolve CrO_3 through filter with water.
6. Heat filtrate, make ammoniacal, and filter.
7. Acidify solution with H_2SO_4 and reduce with $(NH_2OH)_2 \cdot H_2SO_4$.
8. Heat to near boiling and adjust to near neutral with dilute NH_4OH; add $(NH_2)_2CO$ and keep hot until precipitation is complete.
9. Filter on paper as soon as precipitate has settled; wash thoroughly with hot 1% aqueous solution of NH_4NO_3.
10. Dry and ignite at 1000°C for at least 2 hr.

Recovery from Collectors

Copper Collectors. – Chromium may be recovered from copper collectors (where it appears as massive deposits of a chromium-copper alloy in the copper pockets) by treatment with either hydrochloric or nitric acid. The outsides of the collectors must first be freed of all unenriched chromium contamination by washing with HCl and H_2O_2 solution. Recovery is accelerated by cutting the pockets open and mounting the pieces so that acid can be applied only to areas containing chromium. The chromium-copper deposit dissolves slowly in 12 *N* HCl, crumbling first to a black powder. Mechanical scraping and the addition of H_2O_2 to the HCl are helpful, but boiling is necessary to bring about complete solution. The pure copper of the collector dissolves somewhat more slowly. Complete removal of chromium is indicated by the absence of black stain when HCL is applied.

Nitric acid has been used to dissolve away copper from beneath the chromium deposit. Here too, recovery can be accelerated by scraping away the loosened film. When the deposit is massive, the amount of copper dissolved is many times that of chromium, resulting in a large volume of concentrated copper nitrate solution. Although chromium is usually considered to be insoluble in HNO_3, and most of the metal can be recovered as a metallic sludge containing a considerable amount of copper, significant quantities of chromium have always been observed in the nitrate solutions from collector washes. This fact precludes discarding such solutions after filtering out the metallic chromium.

Graphite Collectors. – When graphite collectors are used, the chromium may be recovered by simply burning away the graphite. The exterior of the collector must first be freed of chromium. This can be done by scraping with a half watch glass or by the use of emery cloth, although the latter may introduce more impurities. Collectors contained in flat quartz trays will burn in a muffle furnace at 600 to 800°C within 48 hr if the door is held partly open (higher temperatures make the resulting oxide more difficult to dissolve). Use of a combustion tube and oxygen speeds up the ignition. More protection from airborne losses is given by Vycor dishes, but ignition is slower. The oxide always contains ash from the graphite and a mixture of contaminants derived from the calutron, such as copper and the constituents of stainless steel. The mechanism by which most of the foreign matter enters the collectors is unknown.

Chemical Purification

A variety of methods have been applied to the purification of chromium isotopes, but in all cases use has been made of the fact that chromium may exist in aqueous solution as a cation with a valence of 3+ or as an anion in which the chromium has a valence of 6+. The latter forms insoluble chromates with a few cations, permitting its separation from most metals.

When the copper content of the chromium solution is high, separation from the copper is carried out by heating the solution, making it ammoniacal, and filtering out the chromium as the hydroxide. However, if the solution contains enough ammonia to keep the copper as a soluble complex, the chromium precipitation is likely to be incomplete and at best rather slow. Furthermore, $Cr(OH)_3$ always carries copper, and this requires an additional separation step. There is no simple test for completeness of precipitation.

A more complete separation can be attained by electroplating the copper, using platinum (if chloride is absent) or graphite anodes. (The necessity for redissolving the copper deposit from a platinum cathode with HNO_3 has been very effectively obviated by using as the cathode a copper collector which has been used for collection of the same isotope. The collector can be discarded after plating is complete. Before use, the collector must be thoroughly cleaned of all external contamination. A plain copper sheet would also be satisfactory.) It is advisable first to convert to copper sulfate by adding H_2SO_4 and evaporating to fumes of SO_3. Dilution to a suitable concentration has given volumes of 20 liters or more for a 40-g lot of Cr^{52}. (Pocket leaching with HCl gives somewhat smaller volumes.) Since it is desirable that the copper plate be firm and adherent enough to prevent occlusion of solution and redissolving of copper, the presence of some HNO_3 is helpful. Excessive current density can be avoided by diluting the solution or by reducing the electrode potential to near the minimum of about 2 v. Periods up to three days have been required for the removal of all the copper from a single 4-liter beaker of solution.

Chromium metal which has been removed from copper collectors with HNO_3 can be dissolved in a solution of HCl and H_2O_2 and converted to sulfate, and any occluded copper separated by electrolysis. This procedure is preferable to ignition of the metal followed by solution of the oxide in some acid. At this point, chromium from copper sources is concentrated and partially purified, especially from residual copper, by precipitation from dilute solution with NH_4OH. The following rules have been found useful in making hydroxide precipitations:

1. Addition of NH_4OH to solutions near the boiling point results in the most rapid and complete precipitation. Periods as long as three days on a steam bath have been required for quantitative precipitation when the NH_4OH was added to cool solutions.

2. There must be only a very small excess of NH_4OH beyond the neutral point. (Excess NH_3 can be boiled off.)

3. Concentrations of chromium above about 2 g/liter yield precipitates which settle only slowly and are especially difficult to filter; on the other hand, concentrations of the order of 0.1 g/liter tend to remain unprecipitated unless temperature and alkalinity are closely controlled.

4. Precipitates are filtered and washed with hot distilled water.

Although fluted filters give the most rapid filtration, at best there is still a high retention of liquid. Vacuum filtration has been used, but the pores of sintered glass filters usually become plugged, and the hydroxide cannot be quantitatively recovered. The hydroxide is dried and ignited in Vycor or porcelain at 600 to 800°C.

From this point on, the crude oxides obtained from the ignition of graphite collectors or from the laborious treatment required for copper-collected chromium are treated identically. Hence it is obvious that collection on graphite is far more efficient.

An early procedure included oxidation of the chromium by boiling with $HClO_4$. The solution was diluted, filtered, made alkaline, and filtered again. The chromium was precipitated as $BaCrO_4$ by adding $Ba(NO_3)_2$; $BaCrO_4$ was dissolved in 10% $HClO_4$, and the barium removed as $BaSO_4$ by addition of H_2SO_4. A second $BaCrO_4$-$BaSO_4$ precipitation cycle was usually necessary to give complete purification. The chromium was then reduced with H_2S and filtered, or reduced with $NH_2OH{\cdot}HCl$, treated with H_2S, and filtered. The purified chromium was precipitated as hydroxide by NH_4OH, dried, and ignited. The chief difficulty was that the separation of barium is slow, and some chromium is held up in the $BaSO_4$, even though $HClO_4$ improves its crystallization.

There is now a much simpler process, also based on $HClO_4$, which gives very satisfactory purification. When 70% $HClO_4$ is boiled with Cr_2O_3, the oxide slowly dissolves and is oxidized to CrO_3. Volumes of 20 ml of 70% $HClO_4$ per gram of Cr_2O_3 are usually sufficient. The green color of Cr^{+++} will have disappeared when oxidation is complete. Part of the CrO_3 precipitates from the hot solution, and the remainder precipitates as the solution is cooled to room temperature.

The orange-red crystals are filtered on sintered glass by suction, washed with 70% $HClO_4$, and suction-dried. (Long exposure to air must be avoided because moisture is readily absorbed.) This step removed only those metals which form perchlorates soluble in $HClO_4$. (It was originally thought that the only other chemical operation necessary would be for the purpose of recovering the chromium in a useful form. However, it was found that in certain instances considerable amounts of aluminum were carried into the final products. The aluminum is removed by making an ammonia precipitation from the hot H_2CrO_4 solution, whose color changes from orange to yellow as the solution becomes alkaline. In some cases there is a considerable precipitate; in others no visible indication of solids.) The suction flask is emptied, washed, and returned to receive the CrO_3, which is dissolved and washed through the filter with distilled water. Silica remains with the water-insoluble materials on this filter.

The $(NH_4)_2CrO_4$ solution from the separation of aluminum is adjusted to an acidity of about 1 *N* with H_2SO_4, and the chromium is reduced to the 3+ state by the addition of $(NH_2OH)_2{\cdot}H_2SO_4$. The completely reduced solution has a very deep green color, entirely free of chromate orange. The chromium is finally precipitated as $Cr(OH)_3$ from the reduced solution by carefully raising the pH of the gently heated solution to near the neutralization point with 1:1 filtered NH_4OH and by the addition of sufficient urea to completely precipitate all the chromium.

Since $Cr(OH)_3$ precipitates usually do not settle well enough for decantation without loss, filtration is carried out on a fast paper. For large precipitates, fluted paper is preferable. High retention of water by the precipitate requires numerous washings with hot water containing a small amount of NH_4NO_3. Drainage is incomplete even after long standing.

The precipitate on the paper is transferred to a porcelain or Vycor crucible or dish, dried in an oven, and ignited for several hours by gradually increasing the temperature to 1000°C. The highly ignited Cr_2O_3 is difficult to dissolve if further treatment is required, but significant weight reductions have been observed at 1000°C after previous ignitions at 800°C. The product has a bright green color and is easily crushed to a fine powder.

RECOVERY OF SPECIAL CHARGE MATERIAL

One lot of Cr^{52} was used as charge material for the production of Cr^{52} of very high isotopic purity. It was desirable to recover this material from the calutron equipment, although it was known that contamination with normal chromium in stainless steel had occurred. The principles of purification were the same as those previously described, although the quantities of material involved were greater than in any other lot, and the impurities were different.

Some special difficulties were encountered. In general, the starting material was a solution of chloride and nitrate. Chromium was concentrated by NH_4OH precipitation. The filtered precipitate was dissolved directly in $HClO_4$. Residual ammonium salts in the voluminous precipitate appeared later as slightly soluble NH_4ClO_4. The presence of iron and nickel made it difficult to determine when both the hydroxide precipitation and the oxidation were complete. Addition of NH_4OH to a solution containing chromium in both valence states gives a precipitate resembling hydrated ferric oxide.

The $HClO_4$ solution was boiled for several hours after strong fuming began; it was then cooled and was filtered to recover CrO_3. Colored filtrates were boiled further and cooled to make certain that all chromium had been removed. The remaining steps taken to obtain pure Cr_2O_3 were similar to those used in the standard refinement procedure.

PURITY OF PRODUCT

The purity of the refined product is determined by a semiquantitative spectrochemical analysis of small samples. The usual analytical sampling techniques, including grinding, mixing, and dividing, cannot be applied because of the certainty of losses of valuable material and the possibility of contamination. Only a few milligrams of material thought to be fairly representative of the whole lot are taken as a sample. Analysis is by a procedure developed to apply to most elements. The sample is diluted ten times with graphite as a matrix material and burned in an arc. Spectrographic lines are compared with standards prepared stepwise. The only elements for which a search is made are those considered most likely to be present. A separate analysis of another sample is required for determination of the alkali metals. These elements and the usual lower limit of determination are listed in Table 1. Analyses are on a metal-to-metal basis. The quantities of Cr_2O_3 and impurities determined in several recent lots of separated chromium isotopes are listed in Table 2.

Table 1. Spectrographic Limits

Element	Limit (%)	Element	Limit (%)
Al	0.05	Mo	0.02
Ba	0.02	Na	0.01
Be	0.001	Nb	0.1
Ca	0.1	Ni	0.05
Co	0.05	Pb	0.1
Cu	0.05	Si	0.05
Fe	0.02	Ti	0.02
K	0.01	V	0.02
Li	0.01	Zn	0.2
Mg	0.01	Zr	0.1
Mn	0.01		

Isotopes purified before development of the current procedure usually contained a greater variety of impurities, although they were also near the lower limit of estimation. It is probable that a higher degree of purity than that indicated by these analyses could be attained by further modifications of the purification procedure. Thus the remaining copper might be removed by an H_2S precipitation after the $(NH_2OH)_2 \cdot H_2SO_4$ reduction. Higher purity of water and reagents might be helpful. However, the detection and measurement of impurities at a much lower level would require the development of new spectrographic techniques and the use of larger samples.

ACKNOWLEDGMENTS

A very important contribution was made by H. H. Willard, who pointed out that CrO_3 is insoluble in cold $HClO_4$. All analyses were performed in the Spectroscopy Laboratory of the Analytical Chemistry Division under the supervision of J. A. Norris.

Table 2. Production Data on Chromium Isotopes

Isotope	Lot No.	Weight of Cr_2O_3 (g)	Impurities Found (%)			
			Al	Cu	Mg	Si
50	GR 836(a)	2.640			0.01	0.05
52	GR 837(a)	91.360		0.01		0.02
53	GR 838(a)	6.837		None detected		
52	GS 841(a)	8.910				0.05
50	GZ 868(a)	2.062		0.02	0.03	0.02
52	GS 869(a)	56.733		0.01		0.02
53	GZ 870(a)	6.043		0.01	0.02	0.01
54	GZ 871(a)	1.377			0.05	0.02
52	HA 872(a)	5.813	<0.05			0.1
52	HA 872(b)	12.581	<0.05		<0.01	0.1
52	HA 872(c)	0.765	<0.05		<0.01	0.05

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