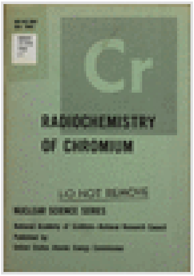

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Radiochemistry of Chromium

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Radiochemistry of chromium.

FOREWORD

The Subcommittee on Radiochemistry is one of a number of subcommittees working under the Committee on Nuclear Science within the National Academy of Sciences - National Research Council. Its members represent government, industrial, and university laboratories in the areas of radiochemistry and nuclear chemistry.

The Subcommittee has concerned itself with preparation of publications, encouraging and supporting activities in nuclear education, sponsoring symposia on selected current topics in radiochemistry and nuclear chemistry, and investigating special problems as they arise. A series of monographs on the radiochemistry of essentially all the elements and on radiochemical techniques is being published. Initiation and encouragement of publication of articles on nuclear education in various subject areas of chemistry have occurred, and development and improvement of certain education activities (e.g., laboratory and demonstration experiments with radioactivity) have been encouraged and assisted. Radioactive contamination of reagents and materials has been investigated and specific recommendations made.

This series of monographs has resulted from the need for comprehensive compilations of radiochemical and nuclear chemical information. Each monograph collects in one volume the pertinent information required for radiochemical work with an individual element or with a specialized technique. The U. S. Atomic Energy Commission has sponsored the printing of the series.

Comments and suggestions for further publications and activities of value to persons working with radioactivity are welcomed by the Subcommittee.

N. E. Ballou, Chairman
Subcommittee on Radiochemistry

INTRODUCTION

This monograph on the radiochemistry of chromium is one in a series covering the radiochemistry of essentially all the elements. It is a revised and expanded version of an earlier monograph. In it are included reviews of nuclear and chemical properties of chromium, discussions of methods of sample dissolution and of separation reactions, descriptions of counting techniques, and a compilation of radiochemical separation procedures.

As new information accumulates on chemical and nuclear properties of chromium and on separation and measurement techniques, consideration will be given to further revision of this monograph. Consequently as additional information becomes available in both published and unpublished form, readers are encouraged to bring it to the attention of the author for possible inclusion in future editions of this monograph.

Radiochemistry of Chromium

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I. GENERAL REVIEWS OF THE INORGANIC AND ANALYTICAL CHEMISTRY OF CHROMIUM.

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Teil II : Qualitative Nachweisverfahren.
Band VI : Elemente der Sechsten Gruppe.
p. 142-190 : Dr Otto Schmitz-Dumont : CHROM.

Handbuch der Analytischen Chemie.
Ed. R. Fresenius und G. Jander, Springer Verlag Berlin 1958.
Teil III : Quantitative Analyse.
Band VI bα : Elemente der Sechsten Nebengruppe : CHROM.
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II. GENERAL REVIEWS OF THE RADIOCHEMISTRY OF CHROMIUM.

"The Radiochemistry of Chromium".
NAS-NS 3007 Jan. 1960 J. Pijck.
Superseded by the present revised monograph.

III. TABLE OF ISOTOPES OF CHROMIUM.

(with decay-schemes, activation cross-sections and other nuclear data).

For more complete information on the radiations of chromium isotopes and references to the original literature, see (1), (2).

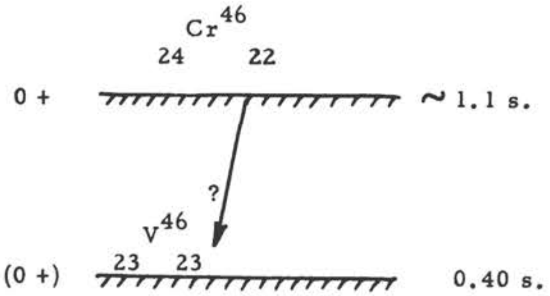
1. Table of isotopes.

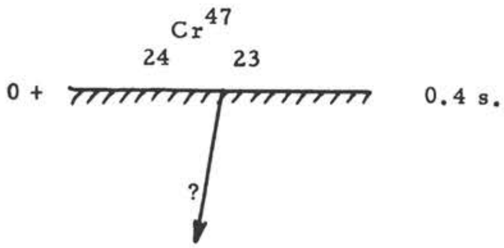
TABLE I.

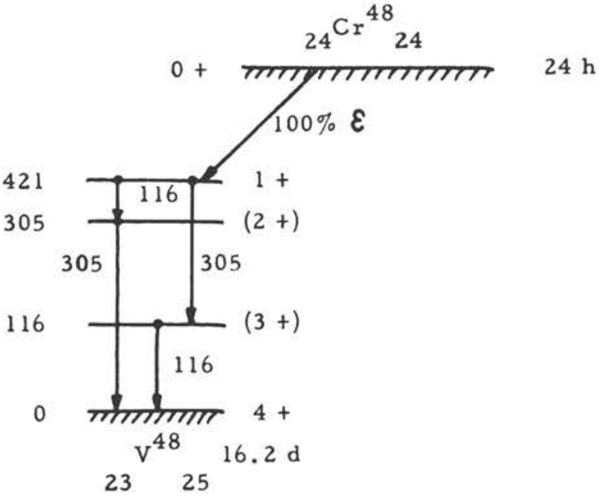
Table of Isotopes.

isotope	% abund.	isotopic mass.	half-life	decay	energy	methods of preparation	literature
Cr^{46}			~1.1 s				3
Cr^{47}			0.4 s				3
Cr^{48}			23 h	EC, no β^+			4, 5, 6
				$\gamma 1$	0.116		
				$\gamma 2$	0.31		
Cr^{49}		48.966794	41.9 m	β^+	1.54	Ti^{46} (α,n)	7, 8, 9
					1.39	Cr^{50} (n,2n)	
					0.73	Cr^{50} (γ,n)	
				γ	0.063		
					0.089		
					0.150		
Cr^{50}	4.31	49.961640					
Cr^{51}		50.960844	27.8 d	no β^+		V^{51} (d,2n)	8, 9, 10 through 27
				γ	0.323	Ti^{48} (α,n)	
					0.320	V^{51} (p,n)	
					0.65	Cr^{50} (n,γ)	
						Cr^{52} (p,pn)	
						Cr^{50} (d,p)	
Cr^{52}	83.76	51.956990					
Cr^{53}	9.55	52.957460					33 through 37
Cr^{54}	2.38	53.956020					38
Cr^{55}		54.958430	3.52 m	β^-	2.85	Cr^{54} (n,γ)	
				no γ		Cr^{54} (d,p)	
						Mn^{55} (n,p)	

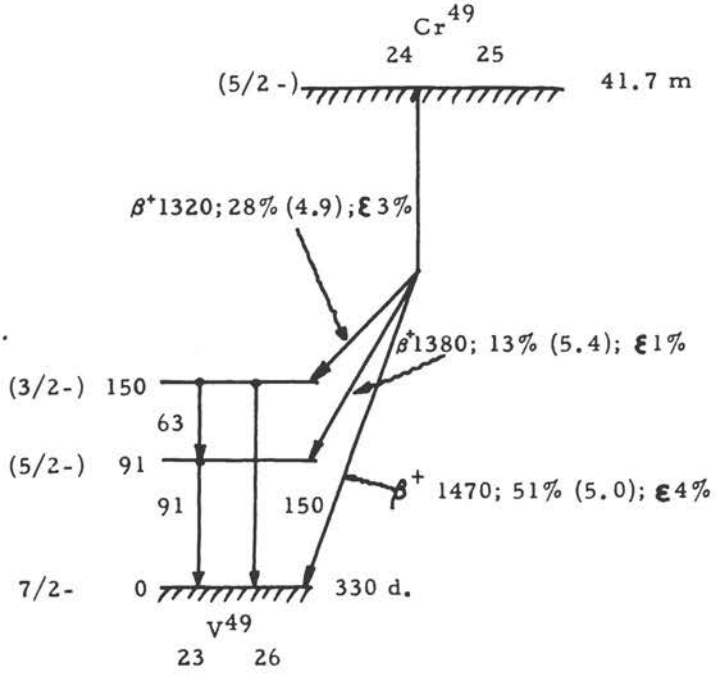
2. Decay-schemes of chromium isotopes.



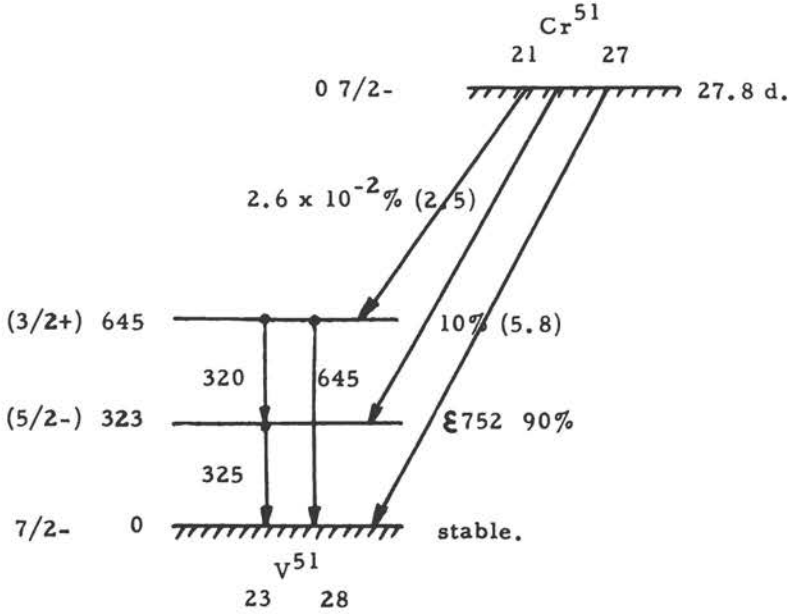


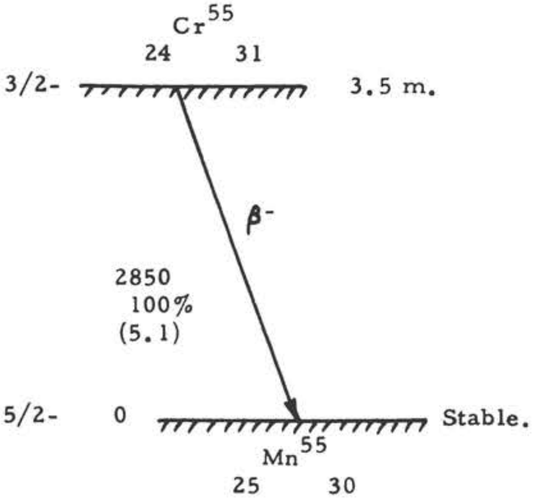


$_{24}Cr^{48}{}_{24}$
0 +
24 h
100% ε
421
1 +
116
305
(2 +)
305
305
116
(3 +)
116
0
4 +
V^{48}
16.2 d
23 25



Cr^{49}
24 25
(5/2 -)
41.7 m
β^+1320; 28% (4.9); ε 3%
β^+1380; 13% (5.4); ε1%
(3/2-) 150
63
(5/2-) 91
91
150
β^+ 1470; 51% (5.0); ε4%
7/2- 0
330 d.
V^{49}
23 26


Cr^{51}
21 27
0 7/2-
27.8 d.
2.6 x 10^{-2}% (2.5)
(3/2+) 645
10% (5.8)
320
645
(5/2-) 323
ε752 90%
325
7/2- 0
stable.
V^{51}
23 28


Cr^{55}
24 31
3/2-
3.5 m.
β-
2850
100%
(5.1)
5/2- 0
Stable.
Mn^{55}
25 30

3. Activation cross-sections of chromium isotopes.

Absorption cross-sections (in barn) are given in table II.

TABLE II.

reference :	(40)	(39)
natural element :	2.9	
Cr^{50}	16	17.0 ± 1.4 13.5 ± 1.4
Cr^{52}	0.73	0.76 ± 0.06
Cr^{53}	18	18.2 ± 1.5
Cr^{54}	< 0.3	0.38 ± 0.04

The cross section for the less common reaction :

$$Fe^{54}\,(n,\alpha)\,Cr^{51}$$

is given by Mellish, Payne and Otlet (41) as 0.37 millibarns. (n,α) and (n,p) cross sections for production of chromium isotopes are given by Neuert and Pollehn (171).

4. Neutron Activation Reactions.

$Cr^{50}(n,\gamma)Cr^{51}$: calculated sensitivity 2.0×10^{-5} µg.

Applications for neutron activation analysis :

Detn. of Cr in Si with a sensitivity of 0.1 ppm; flux $2 \times 10^{14}\ n.cm^{-2}.sec^{-1}$ (42)
Detn. of Cr in Al with a sensitivity of 2.5 µg ; flux $3.4 \times 10^{12}\ n.cm^{-2}.sec^{-1}$ (43)
Detn. of Cr in liquid metals with a sensitivity of 0.2 ppm (44)
Detn. of Cr in Mg with a sensitivity of 5 µg; flux $5 \times 10^{11}\ n.cm^{-2}.sec^{-1}$ (45)
Other applications : (46) (47) (48) (49)
Detn. of Cr in human blood serum (50)

Possible interference from

$Fe^{54}(n,\alpha)Cr^{51}$ with an Fe matrix.
$V^{51}(p,n)Cr^{51}$ $E_{th} = 1.56$ MeV (E_{th} = threshold energy) (59)
$Cr^{52}(p,pn)Cr^{51}$.
$Fe^{54}(p,\alpha)Mn^{51} \xrightarrow{\beta^+} Cr^{51}$
$Cr^{54}(n,\gamma)Cr^{55}$.
possible interference from $Mn^{55}(n,p)Cr^{55}$ with a Mn matrix.
possible interference from $Fe^{58}(n,\alpha)Cr^{55}$ with an Fe matrix.

$Cr^{52}(n,p)V^{52}$ E_{th} = 2.8 MeV $\sigma(14.5)$ = 77.7 mb. (51) (52)
possible interference from $V^{51}(n,\gamma)V^{52}$.
possible interference from $Mn^{55}(n,\alpha)V^{52}$.

$Cr^{50}(n,2n)Cr^{49}$.
E_{th} = 13.4 MeV.
no apparent interference at $E<20$ MeV.

5. Charged Particles and Photon activation reactions.

$Cr^{52}(p,n)Mn^{52}$.
E_{th} = 5.4 MeV ; thick target yield from natural chromium at 22 MeV = 80 mc/ma.h. (53) (54)
no apparent interference at $E<20$ MeV.

$Cr^{54}(p,n)Mn^{54}$.
thick target yield from natural Cr at 22 MeV = 0.5 mc/ma.h (54)
possible interference from $Fe^{57}(p,\alpha)Mn^{54}$.
$Mn^{55}(p,pn)Mn^{54}$ at $E>12$ MeV.
possible interference from secondary reaction $Fe^{54}(n,p)Mn^{54}$.

$Cr^{52}(p,2n)Mn^{51}$.
E_{th} = 16 MeV : $\sigma(21.5)$ = 155 mb. (55)
possible interference from $Fe^{54}(p,\alpha)Mn^{51}$.

$Cr^{52}(p,pn)Cr^{51}$.
E_{th} = 12 MeV : $\sigma(21.5)$ = 425 mb. (55)
possible interference from $V^{51}(p,n)Cr^{51}$.
$Fe^{54}(p,\alpha)Mn^{51} \xrightarrow{\beta^+} Cr^{51}$.
possible interference from secondary reaction $Fe^{54}(n,\alpha)Cr^{51}$.

$Cr^{53}(d,n)Mn^{54}$.
Excitation function from E_{th} ($\sim$0.5 MeV) to 15 MeV.
E_d = 5.5 MeV ; $\sigma(5.5)$ = 0.26 b.
$\sigma(15)$ = 0.17 b.

thick target yields for less than 15 MeV. (56)

calculated sensitivity : 6.1×10^{-2} µg.

possible interference from $Mn^{55}(d,dn)Mn^{54}$.

$Fe^{54}(d,2p)Mn^{54}$.

$Fe^{56}(d,\alpha)Mn^{54}$.

from secondary reactions : $Fe^{54}(n,p)Mn^{54}$.

$Fe^{57}(p,\alpha)Mn^{54}$.

$Cr^{50}(d,p)Cr^{51}$.

Excitation function from E_{th} ($\sim$0.5 MeV) to 15 MeV.

E_d = 5.2 MeV ; $\sigma(5.2) = 0.66$ b.

$\sigma(15) = 0.33$ b.

thick target yield for $E < 15$ MeV. (56)

possible interference from $V^{50}(d,n)Cr^{51}$.

$V^{51}(d,2n)Cr^{51}$.

from secondary reactions : $Fe^{54}(n,\alpha)Cr^{51}$.

$V^{50}(p,\gamma)Cr^{51}$.

$V^{51}(p,n)Cr^{51}$.

calculated sensitivity : 4.9×10^{-3} µg.

$Cr^{50}(d,\alpha)V^{48}$.

Excitation function from E_{th} ($\sim$ 1 MeV) to 15 MeV.

$E_d \sim 9$ MeV $\sigma(9) = 70$ mb.

thick target yields for $E < 15$ MeV. (56)

possible interference from $Ti^{47}(d,n)V^{48}$.

$Ti^{48}(d,2n)V^{48}$.

from sencondary reactions: $Ti^{47}(p,\gamma)V^{48}$.

$Ti^{48}(p,n)V^{48}$.

$Cr^{52}(d,2n)Mn^{52}$.

Excitation function from E_{th} ($\sim$6.5 MeV) to 20 MeV.

E_d = 18.5 MeV ; $\sigma(18.5) = 0.9$ b.

thick target yields for $E < 15$ MeV = 80 µc/µa.h at 14 MeV. (56) (57)

$Cr^{50}(\gamma,n)Cr^{49}$.

Excitation function from E_{th} (13.4 MeV) to 22 MeV.

E_γ = 19 MeV ; $\sigma(19) = 52$ mb. (58)

no apparent interference.

$Cr^{53}(\gamma,p)V^{52}$.
Excitation function from E_{th} ($\sim$12 MeV) to 22 MeV.
E_{γ} = 19.7 MeV ; $\sigma(19.7) \sim 27$ mb. (58)

IV. REVIEW OF THOSE FEATURES OF CHROMIUM CHEMISTRY OF CHIEF INTEREST TO THE RADIOCHEMIST.

A. GENERAL.

1. Introduction.

Pertinent data on chromium isotopes, their natural abundance, and isotopic mass are already given in III/1. The atomic volume, deduced from specific gravity data was found to be 7.286 at 25° and 7.268 at -50°C respectively. The calculated atomic radius is listed by different authors as 1.44, 1.40 to 1.42 Å. For hexavalent chromium atoms the effective atomic radius is 0.52 to 0.65 Å and for typical atoms this value varies between 1.17 and 1.54 Å.

The ionisation potential is 6.7 volts whereas the first resonance potential was found to be 2.89 volts.

Abundant data and references on other physical properties of chromium can be found in the excellent monograph of Mellor (60), who gives data in connection with : crystallographic structure, allotropy, specific gravity, hardness, viscosity, compressibility, diffusion, thermal expansion, atomic heat, boiling point, vapour pressure, heat of fusion, entropy, index of refraction, reflecting power, refraction equivalent, specific refraction, flame spectrum, spark spectrum, arc spectrum, ultra-violet spectrum, infra-red spectrum, Stark effect, Zeeman effect, absorption spectrum, fluorescence spectrum, series spectrum, X ray spectrum, absorption of X ray, vibration frequency, emission of anode rays, atomic moments, photo electric effect, triboelectricity, electrical conductivity and magnetic susceptibility.

The electronic configuration of chromium in its normal atomic state is $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^5\,4s$ (62).

2. Metal and Oxides.

Metallic Chromium.

Chromium is a very hard steel-gray metal (density 7.2088) with a cubic crystalline form.

Electro-deposited chromium may exhibit allotropy (α and β chromium) and have an hexagonal structure as well as the cubic structure.

Depending upon the way of preparation, chromium can attain a hardness of 9 (61). It melts at 1890°C and has a boiling point of 2200°C. It is readily soluble in HCl, HF, HBr, HI, CH_3COOH, oxalic acid, H_2SO_4 and hydrofluosilicic acids, with liberation of hydrogen.

Chromium is passive, thus insoluble, in chlorine and bromine water, in conc. HNO_3, chromic, phosphoric, chloric, perchloric, citric, formic and tartaric acid.

Rendered passive, it is very resistant to a great number of chemicals. Its use as anti-corrosive coating of other metals is based upon this property. This covering can be obtained by electrodeposition.

The difference in behaviour between active and passive chromium is associated with the difference in electrode potential.

In the electrochemical series, active Cr is close to zinc, and passive chromium is near to platinum.

Passive chromium behaves like a noble metal. Detailed discussion of these phenomena are to be found in literature (60).

Metallic chromium is only rarely found in nature. It is one of the elements of sub-group 6/b of the periodic system of elements. Its highest oxidation state is 6+, illustrated by the tri-oxide CrO_3, which is a true acid anhydride, the salts of which are the chromates of the type Me_2CrO_4.

Chromium has a behaviour very similar to that of the elements U, W and Mo (which are homologues), but furthermore shows some similarities with the elements of sub-group 6/a, of which sulfur is a characteristic example. The analogous behaviour of chromium with the elements of the entire group 6 is furthermore illustrated by the isomorphous crystallisation of the chromates, as compared with the molybdates, tungstates, sulfates and selenates.

The greater similarity of chromium with Mo and W however, as compared with S and Se, is demonstrated by the fact that the first three elements form iso- and hetero-polyacids, which is not the case with sulphur and selenium.

Chromium alloys.

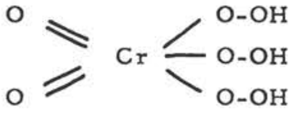
References on alloys of chromium with copper, silver, zinc, cadmium, mercury, aluminium, tin, lead and tantalum are given by Mellor (60). It should be remembered that chromium is part of many ferrochromium alloys and special steels, which are hard, tough and resistant to oxidation and various chemical agents.

Chromium Oxides.

The different chromium oxides : CrO, CrO_2, $CrO.Cr_2O_3$, Cr_2O_3, CrO_3, Cr_5O_9, Cr_3O_5, Cr_3O_6, Cr_5O_{13}, Cr_5O_{12}, Cr_6O_{15} and hydrated oxides as $Cr_2O_3.H_2O$, CrO(OH), $Cr_2O_3.CrO_3.9H_2O$, etc... are of limited interest to the radiochemist, with the exception of CrO_3 as acid anhydride and Cr_2O_3 which is used as an analytical weighing form. Some properties of these oxides are discussed further (4,a and 4,b).

3. Oxidation states and general remarks about solution chemistry.

The chemistry of the aqueous solutions of chromium salts is somewhat complicated by the different oxidation states of chromium (+2 +3 +5 and +6) as reduction-oxidation reactions are to be expected. The +2 and +5 states are of less interest than the +3 and +6 states. The +5 state is only found in the red perchromates of the type Me_3CrO_8, although a septivalent state has been hypothetically assumed too :



The +2 state is readily oxidized by atmospheric oxygen.
For analytical purposes, only the +3 and the +6 oxidation states are to be considered. The transition of one state to another can be achieved by different means, as given below.

Transition to oxidation state +6.

a. Wet oxidation in alkaline medium.

concentrated NaOH and H_2O_2	(63) (64)
Na_2O_2	(65)
concentrated NaOH and bromine	(66) (67) (68)
concentrated NaOH and Sn(IV) oxide	(69)
$KMnO_4$ and NaOH	(69) (70)
alkaline oxidation by electrolysis	
persulfate in alkaline medium	(71) (66)

b. Wet oxidation in acid medium.

persulfate with catalyst (Ag^+)	(72)
persulfate without catalyst	(73) (74)
permanganate	(75)
$KBrO_3$	(76) (77) (78)
$HClO_4$	(63) (79) (80)
Cl_2	(81)
Pb(IV) oxide	(82)
Ce(IV) sulfate	(83)
sodium bismuthate	(84) (85)
silver peroxide	(86)

c. Oxidizing melt.

This method, which will be discussed in the chapter on dissolution (C) can be used for the solubilisation of chromium-iron, ferrochromium, high alloy steels and some very insoluble chromium oxides.

Simultaneously with solubilisation, oxidation to the +6 state is achieved.

Transition to Oxidation State +3.

transition from +2 to +3 : provides a strong reducing potential.
transition from +6 to +3 : this transition can be achieved by active hydrogen. In many cases however, chromium 3+ is further reduced to the +2 state.

Other methods make use of alcohol (87), SO_2, hydrazine sulfate (88), $NH_2OH.HCl$ (89), KNO_2 (90) or even H_2S (91).

Transition to oxidation state +2.

The transition from the higher valency states to + 2 can be achieved by energetic reduction with hydrogen or by making use of a Jones reductor.

4. Salts of chromium.

Several chromium salts exist in a water-soluble and insoluble form. This is for instance the case of the bromide $CrBr_3$ and the sulfate $Cr_2(SO_4)_3$.

a. Soluble salts of chromium.

Some of the water-soluble salts of chromium are : the acetate (Cr VI), the bromide, the chloride (Cr III and Cr VI), the fluoride, the iodide, the nitrate, the tri-oxide, the sulfate (Cr III and Cr VI) and the oxychloride. The latter decomposes on contact with water. The aqueous chloro-complexes are equally soluble in water.

b. Insoluble salts and compounds of chromium.

The more common insoluble compounds of chromium are listed in Table III.

TABLE III.

Insoluble compounds of chromium.

acetate	$Cr(C_2H_3O_2)_2.H_2O$	red crist.pp.
arsenide	CrAs	insol. cold and hot water insol. acids.
boride	CrB	insol. cold and hot water sol. fusion Na_2O_2.
bromide	$CrBr_2$	insol. cold and hot water very sol. alcohol decompose in alkali.
carbide	Cr_3C_2	insol. cold and hot water sol. dil. HCl.
carbide	Cr_5C_2	insol. cold and hot water
carbonate	$CrCO_3$	amorph. green-white pp.
carbonate		basic Cr-III-carbonate.
carbonyl	$Cr(CO)_6$	subl. room temp. insol. benz., eth., alcohol, acetic acid. sl. sol. $CHCl_3$, CCl_4.
chloride	$CrCl_3$	insol. cold and hot water insol. acids, CS_2, acet., alcohol.
chromate	$(CrO)_2CrO_4$	chromichromate, yellow-brown pp.
fluoride	CrF_3	insol. cold water sl. sol. acids insol. alcohol, NH_3.
hydroxide	$Cr(OH)_2$	soluble acids.
hydroxide	$Cr(OH)_3$	soluble acids.
nitride	CrN	insol. cold and hot water insol. dil. HNO_3.

TABLE III (continued).

oxalate	$Cr(C_2O_4).H_2O$	yellow crist. pp. sol. hot water.
oxide	CrO	insol. cold and hot water insol. dil. HNO_3.
oxide	Cr_2O_3	insol. cold and hot water insol. acids, acohol, alkali.
oxide	$Cr_2O_3.x\ H_2O$	insol. cold and hot water sol. acid, alkali sl. sol. NH_3.
oxide	CrO_2	insol. cold water sol. HNO_3.
phosphate	$Cr(PO_4).2H_2O$	sl. sol. cold water sol. acids, insol. acet.acid.
phosphate	$Cr(PO_4).4H_2O$	sl. sol. cold water sol. acids.
phosphate	$Cr(PO_4).6H_2O$	sl. sol. cold water sol. acids, alkali insol. acetic acid.
phosphate	$Cr_3(PO_4)_2$	blue pp.
phosphide	CrP	insol. cold water sol. HNO_3, HF. insol. acids.
selenide	basic selenide	
silicide	Cr_3Si_2	insol. cold and hot water sol. HCl, HF. insol. HNO_3, H_2SO_4.
sulfate	$Cr_2(SO_4)_3$	insol. cold water sl. sol. alcohol insol. acids.
sulfate	$2Cr(SO_4).H_2SO_4$	insol. cold water.
sulfide	CrS	black pp. insol. cold water very sol. alcohol.
sulfide	Cr_2S_3	insol. cold water decomposes with hot water and in alcohol, sol. HNO_3.
barium chromate	$BaCrO_4$	sl. sol. cold and hot water sol. min. acids.
barium dichromate	$BaCr_2O_7$	sl. sol. cold water sol. hot conc. H_2SO_4.
basic bismuth dichromate	$(BiO)_2Cr_2O_7$	insol. cold and hot water sol. acids, insol. alkali.
cobaltous chromate	$CoCrO_4$	insol. cold water, sol. acids and NH_4OH.

TABLE III (continued).

basic copper chromate	$CuCrO_4 \cdot 2CuO \cdot 2H_2O$	insol. cold water, sol. HNO_3 dil. acids, NH_4OH.
lead chromate	$PbCrO_4$	slightly sol. cold, insol. hot water sol. acids, alkali.
basic lead chromate	$Pb_2(OH)_2CrO_4$	insol. cold water.
lead dichromate	$PbCr_2O_7$	decomposes cold water sol. acids, alkali.
mercurous chromate	Hg_2CrO_4	slightly sol. cold and hot water, sol. HNO_3, KCN.
mercuric chromate	$HgCrO_4$	slightly sol. cold water decomposes hot water decomposes acids, sol. NH_4Cl.
silver chromate	Ag_2CrO_4	slightly sol. cold and hot water sol. acids, NH_4OH, KCN.
silver dichromate	$Ag_2Cr_2O_7$	slightly sol. cold water decomposes hot water sol. acids, NH_4OH, KCN.
thallium dichromate	$Tl_2Cr_2O_7$	insol. cold water decomposes acids.
zinc chromate	$ZnCrO_4$	insol. cold water decomposes hot water sol. acids, insol. aceton.

This table lists a number of precipitates of possible analytical interest in separation and precipitation work, as the chromium 2+ acetate and oxalate, the chromium 3+ hydroxide and the phosphates.

c. Non-isotopic carriers/coprecipitation.

Tracer amounts of chromium 3+ will co-precipitate quantitatively with a number of hydroxides, such as $Fe(OH)_3$, $La(OH)_3$ or $Al(OH)_3$. Chromium hydroxide however often remains in a colloidal state and can only be flocculated with an excess of the aforementioned hydroxides.

This co-precipitation is far from specific, and can only be used as a preliminary group-separation, to be followed by more specific separations.

5. Complex Ions.

Chromium, with its coordination number 6, forms hexacoordinate complexes with a large number of ions and molecules, such as aquo-, chloro-, sulfato-, oxalato-, and ammoniaco-complexes.

These complexes have an octahedral configuration and can give rise to cis- and trans-isomerism. They are mostly easily soluble in water.

A comprehensive discussion on many complex chromium ions can be found in Mellor (60). They are however of no direct interest to the radiochemist.

6. Chelates.

A number of organic compounds give rise to chromium chelates. Some of these chelates are insoluble, others form characteristic colours. Nevertheless only a limited number are used for current analytical purposes.
They are listed below :

- Disodium dihydrogenium ethylene diamino tetraacetate. (E D T A) (Complexon III) (108).
- Ammoniumtriacetic acid. Quantitative data and stability constant are given by Schwarzenbach and Biederman. (109).
- Oxine derivatives. Irving, Butler and Ring (110) give detailed descriptions of the following compounds :

oxine
2-methyloxine
5-methyloxine
6-methyloxine
7-methyloxine
2-phenyloxine.

The same authors describe the use of 1-hydroxy-acridine, 9-hydroxy-tetrahydro-acridine, p-tolyl-5-azo-8-oxychinoline and o-carboxyphenyl-5-azo-8-oxychinoline as reagents for chromium.

- triethanolamine gives a blue-green precipitate of unknown composition (111).
- thiodiphenyl carbohydrazide (112).
- sodium alizarine sulphonate gives a yellow precipitate of unknown composition, which is insoluble in 1% acetic acid (113).
- resorufine. An ammoniacal solution of this reagent gives a violet precipitate with Cr 3+ ions. The reaction is not specific for chromium (114).

- double salt of methylenblue and zinc chloride.
  Formation of a red brown colour or precipitate in the presence of pyrochromates (115).
- coloured lakes are formed with acid alizarine yellow-RC (116) and with acid alizarine red (116).
- coloured chelate-complexes are furthermore formed by a number of reagents such as :

orcine	(117)
dimethylether of pyrogallol	(118)
chromotropic acid	(119)
serichrome blue R	(120)
haematoxyline	(121)
m-phenylene diamine	(122)
diphenylcarbazide	(97, p. 220)
α-naphthylamine	(123)
diphenylcarbazone .	(124)

Less common colorimetric reagents for chromium (because of their lack of specificity) are diphenylamine, pyrrol, plasmochine, strychnine, methylen-blue leukobase, tincture of guaiac, and o-oxychinoline derivatives.

The most sensitive and most widely used reagent is diphenylcarbazide (97, p. 220), which has the advantage of being rather selective for the element chromium.

7. Others.

Volatile compounds.

The only compound of interest here is the chromylchloride $CrO_2.Cl_2$ which can be volatilised in $HClO_4$ medium (see chapter VII).

Organic compounds.

None of the 35 organic chromium compounds described in Kaufman's "Handbook of organometallic compounds" (92) has any analytical or radiochemical application.

8. Principal Methods of Determination.

a. Volumetric determinations of chromium compounds.

Chromium can be determined volumetrically by a large number of methods, most of which are based upon the oxidation-reduction properties of the different chromium ions.

A survey of these methods is given below. Detailed procedures are found in literature.

Determination of chromium 2+.

Chromium is quantitatively reduced to the +2 state, which is then oxidized back to the +3 state with one of the following reagents : Fe^{3+} (93), $KMnO_4$ (93), $K_2Cr_2O_7$ (93), methylene blue (93), I_2 (94), $KBrO_3$ (94) and KIO_3 (94).

Determination of chromium 3+.

oxidative determination : with $KMnO_4$ (95) (88), potassium hexacyanoferrate (96) or Ce(IV) sulfate (83).

precipitative or complexometric determination : with arsenate (97), diammoniumphosphate (98) or with Complexon III (99).

Determination of chromium 6+.

All these determinations are based upon the reduction of the chromium 6+ ions. This reduction can be achieved by a number of reducing agents such as :

- iodide (with subsequent titration of the I_2) (100)
- excess of Fe 2+ and back-titration with $KMnO_4$ or $K_2Cr_2O_7$ (101) (102)
  or with Ce(IV) sulfate (103) (104)
- direct titration with Fe 2+ (97, pag. 95)
- titration with arsenic acid (97, pag. 146)
- titration with Sn 2+ chloride solution (97, pag. 162)
- titration with Ti 3+ salt (97, pag. 174)
- titration with chromium-2+-sulfate (105)

The end-point of a number of these reactions can be determined potentiometrically.

b. Gravimetric determinations of chromium compounds.

The most common gravimetric determination of chromium 3+ is based upon the precipitation as chromium oxyhydrate, with subsequent ignition to Cr_2O_3 (97, pag. 19). Electrodeposition of metallic chromium is equally possible.

Gravimetric determination of chromium 6+ can be achieved by precipitating chromium in the form of the chromate of a heavy metal as Ba, Pb, Ti, Ag or Hg^+.

These chromates are however easily transformed into their basic salts. Another gravimetric determination of chromium 6+ uses the Hg^+-chromate as precipitation form, which is then transformed to Cr_2O_3 by ignition. (106).

Other very insoluble compounds of chromium are its bichromates of lead, barium and silver. Most of the complex ions of chromium are readily soluble in water, and are of little interest for gravimetric work. They will be discussed later, as will be the organometallic chromium chelate-compounds.

A number of organic reagents give more or less specific precipitation of the chromium ion. Addition of sodium benzoate or sodium succinate to a chromium 2+ salt for instance, gives a red precipitate. (107, pag. 157).

Other specific precipitation reactions for Cr 2+ ions use acetate or oxalate, with formation of respectively red and yellow precipitates. (107, p. 157).

A number of more complex organic chelation reagents can be used as precipitating agents for chromium, and are already discussed under IV/A/6.

c. Miscellaneous.

The spectrophotometric determination of chromium is discussed in the chapter on solvent extraction (IV B 2). The most used and most sensitive reagent for this determination is diphenylcarbazide.
The activation analysis procedures will be discussed in detail in chapter VII.

B. SEPARATION REACTIONS.

1. Precipitation.

Attention was already drawn to the insoluble inorganic chromium salts, the organic insoluble chromium chelates, the non-isotopic carrier and co-precipitation characteristics of chromium.

None of the precipitation reactions however seems to be selective for chromium, and in the current determination procedures, preference is given to solvent extraction procedure or volatilisation techniques.

2. Solvent extraction.

a. Acetylacetone.

Acetylacetone forms well-defined chelates with over 60 different metals. A great number of these chelates are soluble in organic solvents. The solubility of the acetylacetonates in organic solvents is of a much higher order of magnitude than the solubilities of most analytically used chelates. Macro-as well microscale separations are feasible.

For extraction of chromium, the following procedure can be used (125) (126) (127).

Extract a solution containing Cr 3+ with a 50 vol. % acetylacetone solution in $CHCl_3$, at a pH of 3-4, to remove other metals. Separate the aqueous phase, which still contains the Cr 3+, adjust its pH to 6, add 10 ml acetylacetone and heat under reflux for an hour to permit the formation of the chromium acetylacetonate to proceed to completion. Once formed, this acetylacetonate remains in the organic phase, even at very high acidities. The solution is cooled, acidified to between 1 and 3N, and extracted with the acetylacetone in chloroform.

The complex has its absorption maximum at 560 mμ.

b. Diethyldithiocarbamate.

A systematic investigation of the behaviour of sodium diethyldithiocarbamate has shown that the extraction of chromium 6+ is best performed with chloroform as solvent at a pH of 0-6.

Extractions at low pH should be performed without delay and with excess of reagent (2% aqueous solution) to avoid decomposition (128). The absorption spectrum, Beer's Law relationship and the effect of the pH of the aqueous phase are shown in figures 1, 2 and 3.

c. Diphenylcarbazide.

This very sensitive reagent for chromium can be used for the extraction of chromium 6+.

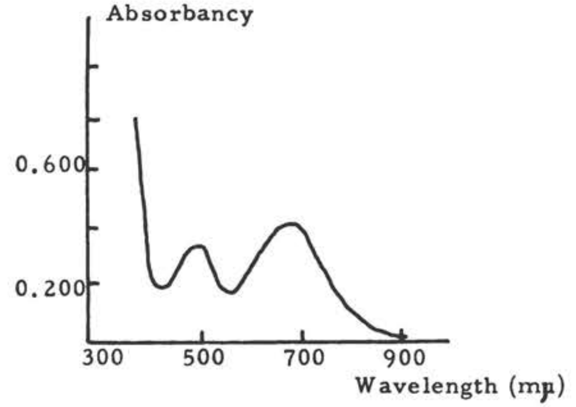


Fig. 1. Diethyldithiocarbamate:absorption spectrum.

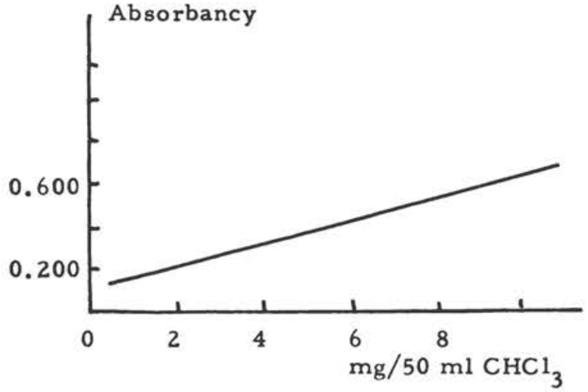


Fig. 2. Diethyldithiocarbamate:Beer's law relationship.

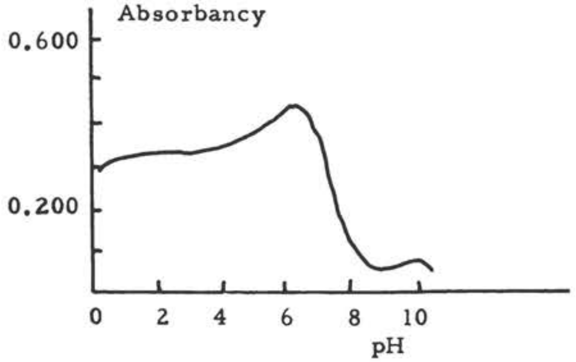


Fig. 3. Diethyldithiocarbamate:effect of pH.

The following procedure can be used (129) : to about 10-15 ml of a solution containing microgram amounts of Cr 6+ in 0.4N H_2SO_4, add 1 ml 0.25% diphenylcarbazide solution (reagent 1/1 acetone-water). Add 15 ml of a saturated NaCl solution and extract with isoamyl alcohol.

The complex has a maximum absorbancy at a wavelength of 543 mμ. The coloured complex may be used for the spectrophotometric determination of chromium. Previous to the extraction, chromium may be oxidized by boiling briefly with a small amount of a $KMnO_4$ solution. The excess $KMnO_4$ is destroyed in the cold solution by the addition of sodium azide. For a more elaborate description of this method, see (97, p. 220-253).

d. Miscellaneous.

Extraction of Cr 3+ with high molecular weight amines, as methyldioctylamine in 2N HCl, is not quantitative (31.8%). The same is the case with nitrate extraction of Cr 6+ in 8M HNO_3 with ethyl-ether. Only 15% of the chromium is removed by one extraction (130). Perfluorobutyric acid (C_3F_7COOH) in ethyl ether can be used for the separation of Cr 3+ from monovalent ions. Extractions are optimum at a pH just less than that at which the metal hydroxide would precipitate (131).

J.C. White (132) claims that in 7M HCl Cr 3+ can be extracted quantitatively with tri-n-octylphosphine oxide. Sb 3+, Ga 3+, Au +, Hf 4+, Fe 3+, Mo 6+, Sn 4+, Ti 4+, U 6+, V 4+, and Zr 4+ have a similar behaviour under the given conditions.

An interesting separation method involving the use of liquid-liquid extraction, is the peracid method for the separation of chromium from vanadium (133). After removing small amounts of Fe by precipitation from alkaline solution, neutralize the filtrate containing Cr 6+ and V 5+ with H_2SO_4 and evaporate the solution to 15-20 ml. If large amounts of iron are present, acidify the sample solution with H_2SO_4 and oxidize the chromium with ammonium persulfate if necessary. This will prevent loss of chromium during the precipitation of iron. Cool the solution and carefully buffer to a pH of 1.7 ± 0.2. Transfer this buffered solution to a separatory funnel, dilute to 50 ml and add 75 ml of ethyl acetate. Cool the nixture and add 1 ml of 1M (3.8%) H_2O_2.

After shaking the funnel vigorously for 30 seconds, allow the layers to separate and then draw off the aqueous solution. Repeat the extraction of the aqueous layer at least twice, using 15 ml of ethyl acetate each time. Combine the organic fractions.

Add 1 ml of 10% KOH solution to the blue solution of perchromic acid and shake until the blue color is replaced by yellow.

Extract the yellow chromate with water and boil the solution for 10 minutes. Dilute to 50 ml and determine the chromium content with diphenylcarbazide.

Alternatively, a photometric determination of the blue perchromic acid can be made directly on the organic phase at a wavelength of 565 mμ (134). Chromium-vanadium separations can also be carried out by extraction of the vanadium-oxinate with chloroform at a pH of 4 (135).

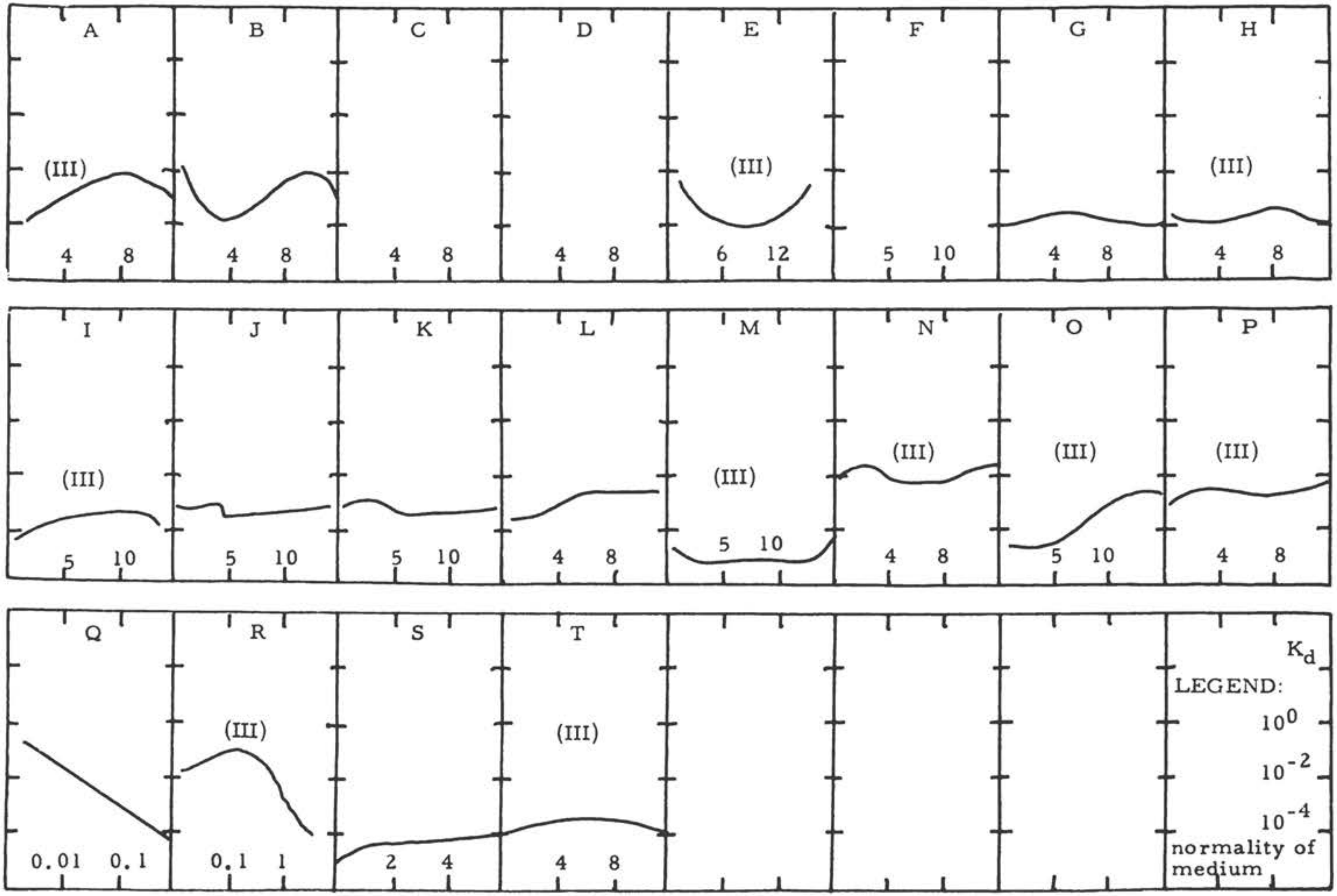
A series of extensive studies by Japanese authors (ref. 136 through 144) on the extractability of inorganic ions by organic solvents is summarized in table IV, the results being graphically represented in fig. 4.

TABLE IV.

Solvent Extraction : Chromium.

Extraction system	Fig. 4
100% TBP - HCl	A
50% TBP - HCl	B
25% TBP - HCl	C
10% TBP - HCl	D
100% TBP - HNO_3	E
25% TBP - HNO_3	F
1% TBPO - HCl	G
5% TOPO - HCl	H
5% TOPO - HNO_3	I
10% tetrabutylmethylenediphosphonate - HNO_3	J
10% tetrabutylethylenediphosphonate - HNO_3	K
5% TIOA - HCl	L
5% TIOA - HNO_3	M
10% amberlite LA-1 - HCl	N
10% amberlite LA-1 xylene - HNO_3	O
10% primene JM-T - HCl	P
50% HDEPH - HCl	Q
HCl - 3% DBSA	R
0.1 N triethylbenzyl NH_4Cl - NH_4SCN	S
0.1 M dimethylbenzylphenyl NH_4Cl - HCl	T

Fig. 4. Solvent Extraction of Chromium.



3. Volatilization.

One of the most selective separation procedures for the element chromium is the distillation technique developed by De Soete et.al.(145). This technique, based upon the volatilization of chromium as chromylchloride, $CrO_2.Cl_2$, will be discussed in detail in chapter VII as a separate radioactivation procedure. The procedure allows carrier free separation.

4. Ion Exchange Behaviour.

Relatively little is known about the anion-exchange behaviour of chromium. Kraus and Nelson, in their ion exchange studies of the fission products (146), note slight adsorption of Cr 3+ in 12M HCl, but strong adsorption of Cr 6+ in the same medium. Their data are graphically represented in fig. 5.

Considerably more data are available on cation-exchange resins. The formation of a coordinate bond between the sulfonic acid group of the resin (cation exchanger of the sulfonic acid type) and basic chromium ions has been reported by Gustavson (147).

The same author (148) had already observed difficulties for the complete removal of chromium retained from a complex solution and ascribed them to secondary reactions of the complex with the phenolic structure of the resin (sulfonated phenol-formaldehyde type).

Especially after contact with solutions of hexaurea chromic chloride, chromium is bound so strongly that hardly any chromium at all can be removed by treatment with HCl (1 : 1).

In his studies of the cation exchange behaviour of the bromide, chlorate, chloride, iodide, nitrate and perchlorate of the element chromium, Samuelson (149) noted quantitative exchange of the cation with the hydrogen ions of the column. The acid liberated can be determined by simple titration with standard alkali. The absorption however is not complete with certain solutions containing basic chromium chloride. In the case of the chromium phosphate, a considerable amount of chromium passes through the column. The same effect was noted with chromium sulfate (150) where no quantitative exchange occurs with the green complex chromium sulfate. The experiment showed that, while part of the chromium remained on the column as complex cations, part of the

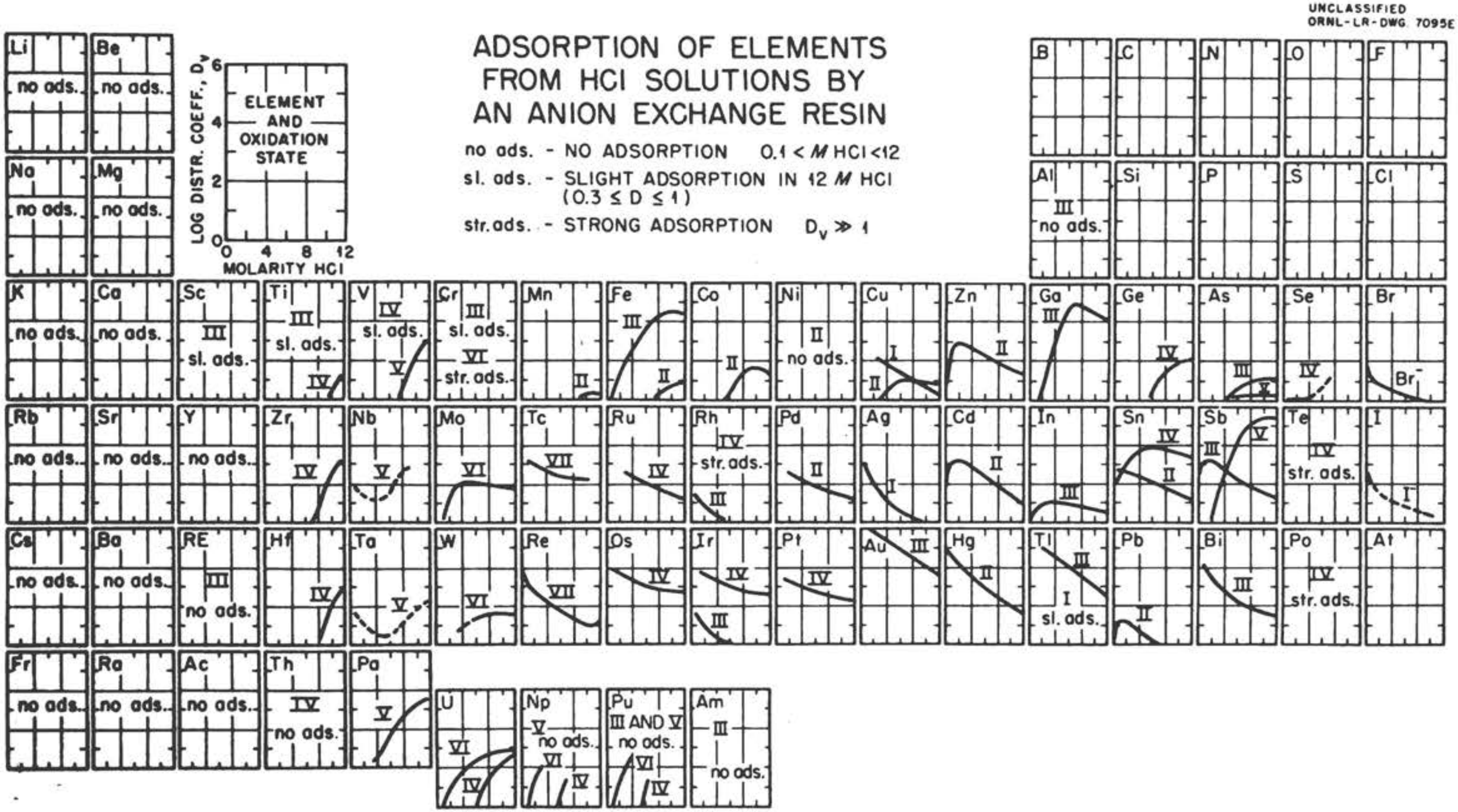


Fig. 5. Ion Exchange Behaviour.

chromium passed through the resin bed in the form of complex anions. The amount of sulfate taken up by the resin or the amount passing through the column depends among other things, on the time taken for filtration or washing, the amount of ion exchanger, the concentration of the solution, etc... No difficulties arise in the presence of the violet hexaquo ions.

Retention of chromium is equally incomplete when a solution of Na $[Cr(C_2O_4)_2]$ is passed through the column. Here again, strong anionic complexes are formed, and little or no chromium is taken up from the solution. On the other hand, the elution of the adsorbed chromium can be sometimes extremely difficult.

This is for instance the case with the complex chromium thiocyanate anion $[Cr(CNS)_6]^{3-}$ when retained on a weakly basic resin. Only a small part can be eluted by the use of 5N HCl.

This is again explained by secondary reactions taking place between the chromic complex and the resin. Ion exchange studies of chromium were mostly carried out to recover chromium from electro-plating baths or from solutions used in the leather industry. A large number of papers dealing with this subject are to be found in literature (151) (152) (153) (154) (155) (156).

Lur'e and Filippova (157) describe the following method for the separation of chromium from large amounts of nickel : chromium may be taken up as chromate on an anion exchange column in acid as well as in alkaline medium (pH 1-12). Elution is performed by means of 2% NaOH solution. Some reduction of the chromate may occur, and therefore a final extraction of the resin with diluted sulfuric acid (1 : 9) may be recommended. Nickel is not retained in ammoniacal solution, and it is possible to separate chromate from nickel in ammoniacal solution in which the ratio Ni/Cr may be as high as 60/1.

5. Rapid radiochemical separation procedures.

In work involving the use of short-lived radioisotopes the time required for separation is very important and should be kept as short as possible. Special techniques were developed for many elements and are critically reviewed by Kusaka and Meinke (158).

The specific rapid separation methods for chromium reported by these authors, are reproduced below.

a. Rapid procedure 1. (159)

nuclide: Cr^{55} (3.52 m).

reaction: $Cr^{54}(n,\gamma)$.

target material: $Cr(OH)_3$.

type of separation : precipitation.

procedure : The sample (0.3 g) is dissolved in conc. HCl. 5 ml of V carrier and H_2O are added to the soln. After boiling, V is precipitated and separated as V-cupferrate.

After filtering, the chromium-activity is precipitated as silver chromate and filtered.

b. Rapid procedure 2.

nuclide: Cr^{55} (3.52 m).

reaction: Mn^{55} (n,p).

target material: $MnSO_4$.

type of separation : precipitation.

procedure : The 0.3 g target is dissolved in 30 ml hot 0.1N HNO_3. 70 mg $K_2Cr_2O_7$ and 30 mg $Cr(OH)_3$ are added as carriers. After cooling, the V-activity is precipitated by 60 mg cupferron. After a double V-separation, the solution is made alkaline and H_2O_2 is added. After boiling and separating Mn-hydroxide, Cr is precipitated as $BaCrO_4$ and filtered.

c. Rapid procedure 3.

nuclide: Cr^{55} (3.51 m).

reaction: Mn^{55} (n,p).

target material: $MnSO_4$.

type of separation : extraction.

procedure : To the irradiated $MnSO_4$, Cr and V carriers are added. The Cr in the solution is oxidized by H_2O_2 to perchromate and extracted into ether at pH = 1.7. The organic layer is measured.

Or the Cr activity can be back-extracted by 1N KOH and precipitated as $BaCrO_4$ in acetic acidic soln., and filtered.

6. Low-level Radiochemical Separation.

Special low-level techniques, developed in work on environmental studies, naturally occuring radioisotopes, trace analysis, etc., are reviewed by Sugihara (160). From his tabulated data it appears, that specific low-level procedures were developed for the determination of chromium in rocks and minerals (161), in meteorites (162) and in irradiated targets (163) (164).

C. DISSOLUTION.

Metallic chromium, prepared by aluminothermic reaction (170) (99% Cr) is readily soluble in HCl and in diluted H_2SO_4. The solubilisation of the chromium salts (Cr 2+, Cr 3+ and the chromates) offers no special difficulties. Many of these substances are water-soluble or can be brought into solution by means of diluted or concentrated acids. Only the anhydrous Cr 3+ halides, the double chromium oxides (chrome spinels such as for instance Chromite), the anhydrous chromium sulfate (the so-called Cr 3+ heptasulfate-dihydrate : $2\ Cr_2(SO_4)_3 . H_2SO_4$) and ignited chromium phosphate and oxide are insoluble in water, acids and alkali. Nitride, carbide, silicide and boride are less likely to be encountered in common practice.

All these compounds however can be solubilized by alkaline oxidative melt. Alkali carbonates or alkali hydroxides may be used, but addition of sodium peroxide speeds up the process. At the same time, chromium is transferred to its 6+ oxidation state and a number of insoluble hydroxides are precipitated.

Chromic oxide is incompletely soluble in fused potassium pyrosulphate. To open up the oxide for analysis, it is preferable to fuse the substance with a mixture of 2 parts of Na_2CO_3 and 1 part of KNO_3 for 10 min. The mass is dissolved in water and the insoluble residue fused with pyrosulphate.

Chromium alloys, of which the chromium steels are important representatives, are mostly solubilized by diluted H_2SO_4 (1 + 5) or HCl (1 + 1) or with mixtures of H_2SO_4 (1 + 5) with HNO_3 (1 + 1).

Chromium nickel alloys are treated with aqua regia and tungsten alloys with phosphoric acid, mixed with other mineral acids.

In this way no precipitate of tungstic acid occurs but complex and soluble heteropolyacids are formed. High alloy steels may be treated with perchloric acid mixtures. If on the other hand, high concentration of carbon is to be expected (steel or cast iron) diluted $HClO_4$ is to be preferred. Ferrochrome alloys are solubilized by HCl, diluted H_2SO_4 or mixtures H_2SO_4-H_3PO_4.

Organic matter containing chromium can be destroyed, prior to determination, by dry or wet oxidation. This last method is to be preferred, and mixtures of HNO_3-$HClO_4$-H_2SO_4 have been used with success. It has been proved that this destruction method using the ternary acid mixture allows quantitative recovery of the element chromium, even on micro- or ultra-microscale (165).

The dry ashing method, on the other hand, may give rise to important losses at high temperature due to reaction of chromium with materials of the crucibles in which the ashing is performed.

V. HAZARDS AND PRECAUTIONS.

Refering to the nuclear data of chapter III and the radiation properties of the different chromium isotopes, it appears that no special precautions are necessary, other than the usual safety rules observed when handling radioisotopes.

From the different isotopes, chromium-51 is the most widely used. It has a biologically "effective" energy of 0.01 MeV, a half life of 26.5 days and is selectively deposited in the human body in the kidneys and the gastro-intestinal tract. The maximum admissible concentration in the kidneys is given as 600 microcuries, against 17 to 240 microcuries for the gastro-intestinal tract. The maximum admissible concentration in water is 0.72×10^{-2} microcuries/ml and 10^{-5} to 4×10^{-6} microcuries/ml in air. Chromium is normally ingested in daily trace quantity.

The chemical toxicity of chromium compounds is only observed at rather massive doses or after a prolonged exposure.

VI. COUNTING TECHNIQUES.

The different chromium isotopes emit gamma or beta rays of sufficiently high energy to be counted by conventional GM or scintillation detector equipment. The gamma ray pulse height spectrum of the Cr-51 isotope is reproduced in fig. 6.

The special counting techniques described below are concerned with the measuring of chromium in mixtures or with the determination of the absolute counting rate.

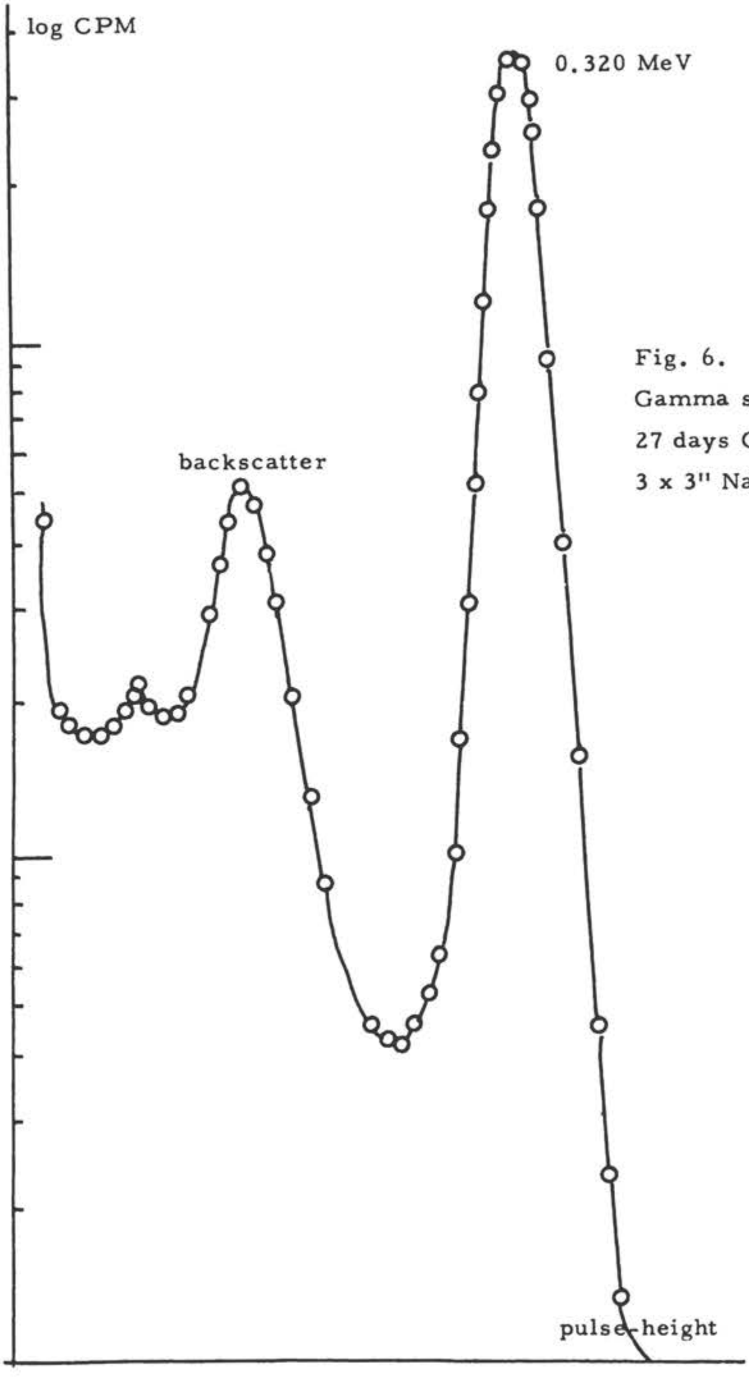


Fig. 6.
Gamma spectrum of Cr-51
27 days Cr^{51}
3 x 3" NaI(Tl) detector

1. The detection of soft X-rays in the presence of hard gamma-radiation. A possible application to reactor technology.

B.T.Price and E.Healy AERE-RP/M- 29 Jan. 11, 1954.
Nuclear Science Abstracts 11, 4535, 1957.

The 5 KeV X-ray of chromium can in principle be used to detect corrosion of a stainless steel reactor tube by a liquid metal coolant. The design of counting equipment for the efficient detection of such X-rays in the presence of large gamma-ray backgrounds is discussed.

2. Scintillation counting for multiple-tracer studies.

G.H.Hine, B.A.Burrows, L.Apt, , M.Pollycove, J.F.Ross and L.A.Sarkes.
Nucleonics 13 no.2, 23-5 (1955).

By using an appropriate, high base line sitting of the discriminater, it is possible to obtain the relative Fe^{59} content, independently from the Cr^{51} content. At a low bias setting, a mixture Cr^{51} - Fe^{59} is counted. By using a standard Fe^{59} source, free from Cr^{51}, and counting this at the low and the high bias setting, the activity ratio between the two settings is determined for radio-iron.

The ratio is used to compute the Fe^{59} contribution in the mixture at low bias setting. By difference the Cr^{51} contribution at the low bias setting is computed.

3. Procedure for estimating the composition of Fe-59/Cr-51 mixtures.

S.A.Lough and G.I.Hertsch.
Nucleonics 13 no 7, 66-7 (1955).

A method similar to the previous one described, is used. Counts from the mixture Cr^{51} - Fe^{59} were obtained at discriminator setting 16 and from Fe^{59} alone on setting 37.

The counts Cr^{51} at setting 16, or D were obtained from the formula.

$$D = A - B \times C.$$

where A = cpm Fe^{59} - Cr^{51} mixture at 16
B = cpm Fe^{59} - Cr^{51} mixture at 37
C = (cpm Fe^{59} at 16/cpm Fe^{59} at 37).

A - D = Fe^{59} in mixture at setting 16.

C is determined on a pure Fe^{59} sample.

Possible interference by Fe^{55} was proved to be negligible, as this isotope has a K-capture X-ray of only 70 KeV, way below the 320 KeV used for the Cr^{51} counting.

4. Tracer problem : Counting of Cr^{51}.

Tracerlog no. 67 Tracerlab Inc., Waltham Mass.
p. 9-10 (1955).

The decay of chromium-51 occurs through orbital electron capture with emission of K-capture X-rays and also with emission of soft gamma rays (0.323 MeV) in about 8-10% of the desintegrations.

It is thus possible to measure a sample of Cr^{51} either by gamma- or by K-capture X-ray assay.

For the measurement of the gamma-ray, a well-type scintillation counter is the most efficient detector. This detector has a total efficiency of about 4% (i.e. 4% of all desintegrations occuring in the sample are counted).

For the measurement of the K-capture X-rays, a Geiger proportional counter filled with a heavy gas and provided with a thin window is the most suitable detector. Under good working conditions, the total efficiency of this setup is of the order of magnitude of about 1%. It is furtheremore calculated, that a 5 ml sample, containing less than about 2.2×10^{-3} microcuries, is more efficiently measured with the Geiger counter, whereas samples of greater activity are best measured with a well-type scintillation detector.

5. Differentiation of Fe^{59} and Cr^{51} in mixture.

R. L. Libby and K. Hand.
J. Lab. Clin. Med., 48, 289-93 (1956).

Criteria for the construction of a simple lead absorber for any type of scintillation counter are described, whereby the Fe^{59} and Cr^{51} activities in mixtures may be easily determined.

The calculation is discussed.

6. The preparation of Cr^{51} of high specific acitivity : Determination of absolute desintegration rate of Cr-51.

G. Harbottle and A. G. Maddock.
J. Chem. Phys. 21, 1686 (1953).

Aliquot portions of solutions containing the enriched Cr-51 were evaporated on foils, and the emitted X-rays were counted in a proportional counter of known geometry. The counter was filled with two atmospheres of argon and 0.2 atmosphere of methane, and was operated at 2900 volts. The counter tube was of such dimensions, that all X-rays passing the window, were absorbed. The pulses from the counter were amplified and analysed by a sliding-channel pulse height analyser of Oak Ridge design, constructed by the Brookhaven Electronic Division. The X-ray counting rate was obtained by numerically summing the area under the X-ray peak, and this figure was corrected for geometry, absorption by air, and absorption by the beryllium window of the counter. The desintegration rate was obtained by an additional correction for the fluorescence yield.

7. Two-channel Gamma Counting of Cr^{51} and I^{131}.

R. Adams, I. C. Woodward, M. C. Crane and J. E. Holloway.
International J. Appl. Rad. and Isotopes 3/2, 156 (1958).

Use is made of two single channel pulse height analyzers. The no 1 channel, for Cr^{51} is centered toward the low energy side of the 0.32 MeV photopeak. No 2 channel, for I^{131}, is shifted toward the high energy portion of the 0.364 MeV photopeak (fig. 7).

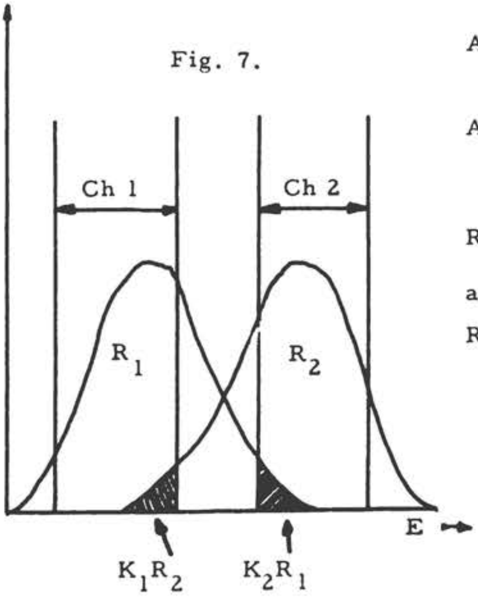


Fig. 7.

A_1 = total activity in channel 1 = $R_1 \cdot K_1R_2$.

$A_2 = R_2 + K_2R_1$ = total activity counted in channel 2.

$$R_1 = \frac{A_1 - K_1A_2}{1 - K_1K_2} = Cr^{51} \text{ in channel 1}$$

and

$$R_2 = \frac{A_2 - K_2A_1}{1 - K_1K_2} = I^{131} \text{ in channel 2.}$$

K_2 is obtained by dividing the counting rate in channel 2 by that in channel 1, if a pure Cr^{51} source is counted. K_1 is obtained by dividing activities of channel 1 by channel 2 when counting a pure I^{131} source. With proper channel adjustment, the K values can be kept within 0.06 - 0.08.

As $K_1 \times K_2$ is <0.01, the denominator of the equations may be considered as unity and

$$R_1 \approx A_1 - K_1A_2$$

$$R_2 \approx A_2 - K_2A_1.$$

8. Production of radioisotopes with charged particles.

H.H.Ph.Moeken.
Thesis Univ. Amsterdam, 10 July 1957.

Reaction: $V^{51}(d,2n)Cr^{51}$.

Cr^{51} was produced by bombarding a thick vanadium sheet.

The chromium fraction was separated by co-precipitation and extraction.

The Cr^{51} activity was calibrated in two ways : measurement of the K X-rays following the electron capture and measurement of the 320 KeV γ-rays from Cr^{51} on a scintillation spectrometer.

These two methods agree if 8% of the Cr^{51} disintegrations are taken to occur with emission of the 320 KeV gamma-ray.

Lyon and Bunker found a value in agreement within 10% by measurement of the decay scheme. The thick target yield was found to be 185 $\mu C/\mu Ah$ or 2.3×10^{13} $N/\mu Ah$.

Lyon, W.S. : Phys.Rev., 87, 1126 (1952).
Bunker, M.E. & Starner J.W. : Phys.Rev., 97, 1272 (1955).

VII. SEPARATION PROCEDURES.

Procedure 1.

Source : De Soete, Thesis Univ. of Ghent, Belgium (1959).
D.De Soete, J.Hoste and G. Leliaert (145).

Distillation of carrier-free chromium as chromyl chloride.

Several authors (97)(167) (168) have already described the separation of chromium as CrO_2Cl_2 by distillation from a perchloric acid solution in the presence of hydrochloric acid. Experiments demonstrated that this procedure is suitable for the quantitative distillation of tracer amounts of chromium.

The basic procedure was slightly modified by using gaseous HCl instead of an aqueous solution, so as to avoid the dilution of the perchloric acid. It also ensures a smoother distillation in the presence of solid materials in the perchloric acid.

Other volatile chlorides as those from arsenic, antimony and tin, possibly present due to the use of solder, used for fixation to the target holder of the cyclotron, distill under these conditions. They can be removed, if necessary, prior to the chromium distillation, by the procedure of Scherrer (169).

Tracer experiments using As^{76}, Sb^{124} and Cr^{51} indicated that the removal of the arsenic, antimony and tin is quantitative, whereas the chromium does not distill under these conditions. Experiments using V^{48} and Fe^{59} showed that these elements do not distill throughout the whole proposed procedure.

Chromium-51 was produced by deuteron bombardment of a vanadium target at energies of 11 and 25 MeV.

Procedure.

The irradiated vanadium target is transferred into a platinum dish and dissolved by heating in approximately 5 ml conc. HF. The excess HF is removed by fuming down 10 ml of concentrated H_2SO_4, whereafter the sulfuric solution is quantitatively transferred into the distillation apparatus represented in fig. 8.

The rinsing water used is removed by distillation, whereafter 50 ml of concentrated HCl are added dropwise at a bath temperature of 250°C. After complete distillation of arsenic and antimony as their chlorides, a mixture of 50 ml HCl/HBr (1/3) was also added dropwise at the same bath temperature to insure removal of tin as $SnBr_4$. The separatory funnel A is now replaced by the HCl inlet tube B. The formed bromine is swept from the solution by the gaseous dry HCl stream. 30 ml 70% $HClO_4$ are added and the chromium tracer is distilled as CrO_2Cl_2 after approximately 30 minutes at a bath temperature of 250°C. A slow dry HCl stream is maintained throughout the distillation.

The chromyl chloride is collected in approximately 5-10 ml water. This solution can be taken to dryness, without chromium losses, after

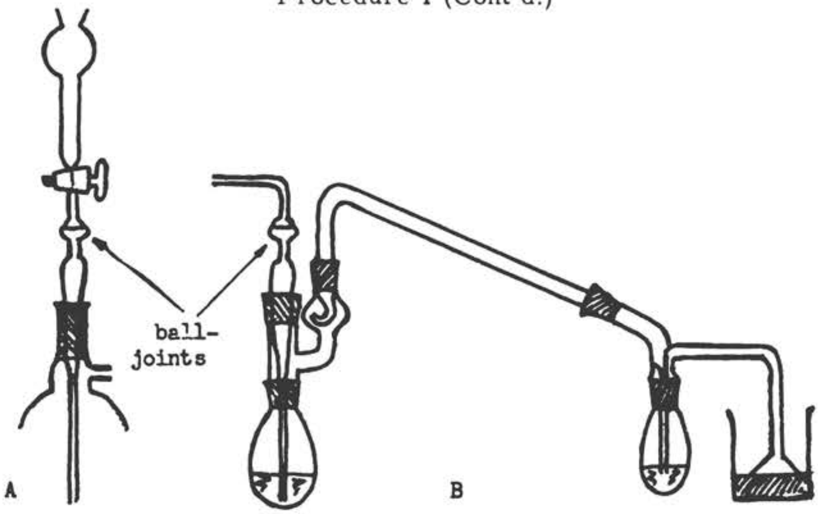


Fig. 8. Apparatus for the distillation of chromium.

the addition of a small excess hydrazine hydrate. The excess hydrazine is finally destroyed with 6N HNO_3.

Discussion.

Typical distillation in the presence of As^{76}, Sb^{124}, Sn^{121}, V^{48} and Fe^{59} is represented in the following table :

TABLE V.

Distillation of volatile element	% distilled
As	99.7
Sb	99.1
Sn	98.6
Fe	0
V	0.02
Cr	0.03
Distillation of CrO_2Cl_2	
Sn	0.03
Fe	0
V	0.02
Cr	99.93

As can be seen from the table, the removal of As and Sb is practically quantitative, whereas 1.4% of the Sn does not distil. Only 0.03% of the total tin however distills in the subsequent chromium distillation. Both iron, which can also be present as trace element, and vanadium, which forms the bulk of the solution, do not distil to an appreciable amount throughout the whole procedure. It is also apparent that the chromium yield is quantitative.

The thick target yields, computed from the 0.323 MeV gamma, were found to be 4.4 µC/µAh and 10 µC/µAh for deuteron energies of respectively 11 and 25 MeV.

Procedure 2.

Source : The production of Threshold Reactions in a Graphite Reactor.
C.E.Mellish, J.A.Payne and R.L.Otlet - AERE Harwell.
Vol. I, Proceedings, 1st UNESCO Intern.Conf., Paris (1957).

Chemical separation of carrier-free chromium after bombardment of iron target.
Reaction : $Fe^{54}(n,\alpha)Cr^{51}$.

Procedure : Pass SO_2 in HCl solution to reduce all Cr to Cr 3+, extract iron into isopropylether, precipitate $Cr(OH)_3$ with NaOH, boil with alkaline H_2O_2, precipitate $BaCrO_4$, dissolve in acid and extract Cr into ether in presence of H_2O_2 ; re-precipitate $BaCrO_4$.

Procedure 3.

Source : Production and Isolation of Carrier-free Isotopes.
W.M.Garrison and J.G.Hamilton.
Chem.Rev. 49, 237-72 (1951) p. 259.

Target material : V.
Type of bombardment : (d,2n) or (p,n).

Procedure: The V target is dissolved in HNO_3. The solution is diluted to 6N and saturated with SO_2 to insure the reduction of Cr to 3+.

Fe 3+ and La 3+ is added and the solution is made alkaline with Na_2CO_3 . V is oxidised to soluble vanadate by air in alkaline solution and Cr^{51} is carried quantitatively on the $La(OH)_3$. Cr^{51} is separated from the $La(OH)_3$ by a second precipitation in the presence of Br_2, which oxidizes the Cr^{51} to chromate.

Procedure 4.

Source : A.G. Maddock and G. Harbottle.
J. Chem. Phys. 21, 1686 (1953).

The preparation of chromium-51 of high specific activity.

Procedure for the separation of enriched Cr-51.

The 12.4 hr potassium-42 activity in the bombarded salt (potassium chromate) was allowed to decay for a week, and the irradiated material was dissolved in approximately 1N sulfuric acid. 100 ml of acid was used per 10 grams of salt. Twenty milligrams of aluminium carrier was added (as aluminium nitrate). Aluminium hydroxide, which carries trivalent chromium, was precipitated by the addition of concentrated ammonia, centrifuged down and washed four times by centrifugation with water containing a trace of ammonia. The aluminium hydroxide was then dissolved in about 10 ml of 2N sulfuric acid, the solution diluted three times and the aluminium hydroxide reprecipitated with ammonia and washed once with H_2O. This cycle of reprecipitation was repeated a total of four times and served to free the precipitate completely of hexavalent chromium. An additional 10 milligrams of Al was added after the second reprecipitation. Finally the aluminium hydroxide was dissolved in a caustic solution prepared by the addition of five or six pellets of sodium hydroxide to 10 ml of water and the solution oxidized by the addition of about 100 mg of sodium peroxide. The peroxide was destroyed by heating on a hot water bath. The solution now contained only Al, Cr (as chromate) and NaOH.

The chromium was estimated colorimetrically by the use of the absorption band shown by chromate in basic solution at 366 mμ (molar extinction coefficient $\varepsilon = 4670$).

Al does not interfere in this determination. If it is desired to obtain the Cr free of Al, the solution may be adjusted to pH 2.5 and lead chromate precipitated and centrifuged out.

Procedure 5.

Source : G. Harbottle.
J. Chem. Phys., 22, 1083 (1954).

Szilard-Chalmers reaction in crystalline compounds of Chromium.

Radiochemical analysis.

The bombarded crystals were dissolved in aqueous solutions, previously adjusted to pH 2, which contained trivalent chromium carrier in the case of hexavalent chromium compounds, and hexavalent carrier when trivalent salts had been bombarded. Two aliquot portions were then removed. To the first was added an excess of lead nitrate : lead chromate was filtered off and the filtrate, which contained trivalent Cr, was collected in a volumetric flask. The lead chromate was dissolved in concentrated nitric acid and collected in a second volumetric flask. The second aliquot portion was made basic with NaOH, oxidized with Na_2O_2, heated to destroy excess of sodium peroxide, adjusted to pH 2.5 ± 0.5 and lead chromate precipitated, filtered off, washed and dissolved as before.

Three solutions were then counted, representing trivalent and hexavalent fractions and total chromium.

The agreement between the sum of the first two and the third was usually better than two percent, and constituted a check on the absence of foreign activities. This procedure had been previously tested and found to give a clean separation, not subject to serious errors due to coprecipitation or induced exchange.

Procedure 6.

Source : J.D. Gile and W.M. Garrison and J.G. Hamilton.
J. Chem. Phys., 19, 1217 (1951).

Carrier-free radioisotopes from cyclotron targets. Separation of Chromium-51 from Vanadium.

The bombarded vanadium was dissolved in a minimum volume of 6N HNO_3. 10 mg of Fe 3+ were added, and the solution was slowly poured into an excess of boiling 10% naOH solution. The Cr-51 carried quantitatively on the $Fe(OH)_3$ precipitate which was then redissolved and reprecipitated as above. Three such cycles were required to remove the last traces of sodium vanadate. The final $Fe(OH)_3$ precipitate containing the Cr-51 was dissolved in 6N HNO_3 previously saturated with Br_2 and reprecipitated by the addition of dilute NaOH. The temperature of the solution was maintained at approximately 90°C. Under these conditions, the carrier-free chromium as chromate was retained in the solution, which was then made 1N in HNO_3 and saturated with SO_2.

2 mg of Fe 3+ was added and precipitated by the addition of dilute ammonia.

The $Fe(OH)_3$ precipitate containing the Cr-51 was washed, dissolved in 6N HCl, and Fe was extracted with ether. The HCl solution was evaporated to dryness on 20 mg of NaCl. The carrier-free Cr-51 was redissolved quantitatively in 2 ml of water at pH 5 to given an isotonic saline solution for biological investigation.

Procedure 7.

Source : J. H. Green and A. G. Maddock.
Nature , 164, 788 (1949).

(n, γ) recoil effects in potassium chromate and dichromate.

The authors have irradiated solid potassium dichromate, sealed in silica ampoules, with thermal neutrons.

Aqueous solutions of the dichromate of 0.008M concentrations were used in the subsequent chemical manipulations. To aliquots of the various solutions were added measured volumes of the same solution of chrome alum as carrier; chromic hydroxide was precipitated, the activity of the precipitate was determined and the % of Cr-51 present in the solutions as trivalent ions, calculated.

Precipitates were uniformly deposited on hard filter paper held in polystyrene holders and measured directly in the holder. Results indicate that a small, but definite Szilard-Chalmers separation occurs.

Procedure 8.

Source : V. I. Kutznetsov
C. A. 111i, (1956) 50.

Organic coprecipitants in analytical chemistry.

Chromium is coprecipitated by heating with sulfonic acids of azo compounds having 2 HO groups in position ortho to the azo group, which yields a chromium complex with Cr 3+ and chromates. Addition of methylviolet leads to precipitation of a solid which quantitatively coprecipitates chromium.

To separate chromium from other elements, the slow formation of the complex from Cr 3+ in the cold is used.

Procedure 9.

(courtesy N. V. Philips-Duphar
Apollolaan, 151, Amsterdam
The Netherlands. Europe).

Production of Carrier-free Cr^{51}.

Deuteron irradiated vanadium is dissolved in concentrated nitric acid. Several mg of iron carrier are added. This solution is slowly added to a hot solution of NaOH, iron is precipitated, co-precipitating the chromium. After cooling, the precipitate is centrifuged and washed. The hydroxydes are dissolved in 6N HCl and the iron extracted with diethyl ether. The solution is taken to dryness in the presence of NaOH and H_2O_2, chromium is transformed to chromate and the excess of H_2O_2 is eliminated by boiling. The solution is made 3N with HCl, and the chromate is extracted with methyl isobutylketone. The chromate is re-extracted into the aqueous phase by rinsing with water and taken to dryness after addition of a few drops of HCl. A calculated aliquot of NaOH and a little H_2O_2 are added, the solution is boiled and again taken to dryness.

After dissolution in water and adjustment of the pH to 8, the solution is filtered through paper and made up to a calculated volume.

Procedure 10.

J. Pijck, J. Gillis, J. Hoste.
Intern. J. Applied Rad. Isotopes, 10, 149-57 (1961).

Procedure 10 (Cont'd.)

The determination of Cu, Cr, Zn and Co in human blood serum by radioactivation.

Serum sample of 250 λ are irradiated in polyethylene vials during 3 days at a neutron flux of 5.10^{11} $n.cm^{-2}.sec^{-1}$, together with metallic chromium standards. After mineralisation of the organic matter with a mixture H_2SO_4-$HClO_4$-HNO_3 (1 : 1 : 3), the rest is submitted to the distillation procedure of De Soete (see procedure 1).

Chemical yield is determined by spectrophotometry with 1;5 diphenylcarbazide (166).

Procedure 11.

Procedure given in : "Chemical Procedures Used in Bombardment Work at Berkeley".

Compiled by W. W. Meinke, UCRL-432, August 30, 1949.

Element separated	: Chromium	Procedure by : H. Hopkins, Jr
Target material	: As	Time for sep'n : 3/4 hr.
Type of bbdt	: 190 MeV D^+	Equipment required : standard.

Yield : 60%

Degree of purification : ∼ factor of 50 from other activities.

Procedure :

(1) Dissolve As in HNO_3. Add 10 mg Cr carrier and evaporate to ∼ 2 cc.

(2) Add 1 cc fuming HNO_3 and several crystals $KClO_3$. Boil several minutes, adding more $KClO_3$.

(3) Cool, add KOH and water to about 25 cc of 1N H^+. Chill in ice salt bath to near freezing, add 10 cc cold ether. Add 1 dp H_2O_2 and extract deep blue color into ether.

(4) Add a second portion of ether and H_2O_2. Wash the cold ether layers with four quarter volumes of water containing 1 drop conc. HNO_3.

(5) Extract chromate out with dilute KOH, add other hold-back carriers and HAc to slightly acid.

(6) Add Ba dropwise to precipitate $BaCrO_4$.

Remarks : Procedure should be practiced so success of the oxidation and extraction can be recognized.

Procedure 12.

Procedure given in : "Chemical Procedures Used in Bombardment Work at Berkeley".

Compiled by W. W. Meinke, UCRL-432, August 30, 1949.

Element separated : Chromium

Procedure by : Goeckerman

Target material : approx. 1 g Bi metal

Time for sep'n : 1-2 hrs.

Type of bbdt : 184" all particles

Equipment required : centrifuge, cones, 110° oven.

Yield : approx. 50%.

Degree of purification : Few c/m separated from several million counts of fission and spallation products.

Advantages : Fair yield of pure Cr.

Procedure :

(1) To aliquot of HNO_3 soln. of target add 10 mg Cr as $Cr_2O_7^=$. Add HCl & HCOOH to reduce to Cr^{+3}. Ppt Bi_2S_3 & Sb_2S_3 scavenger from 1N HCl soln.

(2) Ppt $Cr(OH)_3$ with $K_2CO_3 + H_2S$, by long boiling.

(3) Oxidize in 10 ml 0.5 N NaOH with H_2O_2, scavenge with $Fe(OH)_3$ & destroy H_2O_2.

(4) Make slightly acid with 6N H_2SO_4 & wash with ether.

(5) Add H_2O_2 & extract H_3CrO_8 into about equal volume of ether.

(6) Re-oxidize & re-extract aqueous phase.

(7) Evaporate ether over H_2O & repeat H_3CrO_8 extrn.

(8) Evap. ether over H_2O, oxidize with H_2O_2 in alkaline soln, scavenge with $Fe(OH)_3$.

(9) Acidify with 6N HNO_3, add 1 ml 6N HAc & 2 ml 6N NH_4Ac, heat, add several ml 50 g/l Ba soln. Filter, wash with hot H_2O & EtOH, dry 10 min. at 110°C. Weigh as $BaCrO_4$ (48.7 mg per 10 mg Cr).

Remarks : H_3CrO_8 extrn.tricky, easy to lose Cr by reduction before extraction.

Procedure 13.

Procedure given in : "Chemical Procedures Used in Bombardment Work at Berkeley".

Compiled by W. W. Meinke, UCRL-432, August 30, 1949.

Element separated : Chromium Procedure by : Batzel
Target material : Copper Time for sep'n : 40 minutes
Type of bbdt : all 184" and 60" Equipment required : standard
Yield : 50%
Degree of purification : 10^2 - 10^3
Advantages : very specific - no interfering ions.

Procedure :

(1) Dissolve the copper in the minimum amount of concentrated HNO_3. Boil almost to dryness, add carriers (Zn and below) and make 1N in HCl.

(2) Precipitate the copper as sulfide, make the supernate alkaline with NH_4OH and precipitate the sulfides including Cr with H_2S.

(3) The Mn is usually removed at this point. Neutralize the HNO_3 and make 1N in HNO_3.

(4) Cool in an ice bath to 5°C and add 0.5 cc of 30% H_2O_2. Extract the blue peroxychromic acid with ethyl ether (two 4 ml portions).

(5) Wash the ether layer with three 4 ml portions of water acidified with a drop of HNO_3.

(6) Extract the chromium from the ether layer with 3 cc of distilled water made distinctly alkaline with NH_4OH.

(7) The Cr may be precipitated and weighed as $BaCrO_4$.

Remark : The Mn is usually removed (step 3) so that an estimate can be made of the amount of Cr^{51} formed by decay of the 42 minute Mn^{51}.

Procedure 14.

Procedure given in : "Chemical Procedures Used in Bombardment
Work at Berkeley".
Compiled by W. W. Meinke, UCRL-432, August 30, 1949.

Element separated : Chromium   Procedure by : D. B. Stewart

Target material : Alumium alloy 95% Al, 2.25% Mg, 0.25% Cr (+ Fe & Cu)   Time for sep'n : 1 hr

Type of bbdt : 184" deuterons   Equipment required : standard

Yield : 60-80%

Degree of purification : 10^4 from Al, others unknown.

Procedure :

(1) Dissolve aluminium in 6N HCl. Add 25-50 mg Cr carrier, 5 mg Cu carrier.

(2) Oxidize Cr to dichromate by boiling with 1 g ammonium persulfate and 2-3 drops of 2% $AgNO_3$ solution.

(3) Remove Al, Mg, Fe by precipitation with excess NH_4OH. Centrifuge & decant supernatant. Dissolve precipitate in HCl and repeat to get out more of the Cr which can be occluded.

(4) Acidify the combined supernatants with HCl (0.1 - 0.3N acid). Saturate with H_2S to precipitate CuS and reduce chromium to Cr^{+3}. Centrifuge or filter off the CuS.

(5) Boil filtrate to expel H_2S and reduce volume as far as possible. Make solution basic with NH_4OH. A gelatinous green precipitate of $Cr(OH)_3$ forms on boiling off the excess NH_3.

Procedure 15.

Procedure given in : "Collected Radiochemical Procedures" (Radiochemistry Group J-11), LA-1721, 2nd ed., August 18, 1958.
W. H. Burgus.

1. Introduction.

In the analysis for radiochromium, exchange between active chromium and dichromate carrier is promoted by reduction of the latter to the +3 state. Some decontamination of the sample is then effected by acid sulfide scavenging when chromium is in the +3 state. After sulfide scavenging chromium is oxidized to the +6 state and precipitated as barium chromate, which is then converted to the blue peroxy compound CrO_5, by treatment with hydrogen peroxide in hydrochloric acid medium, in the presence of ethyl ether. The peroxy compound is extracted into the ether layer (effecting further decontamination), back-extracted into aqueous ammonia, and barium chromate again precipitated. After removal of any remaining radiobarium as the sulfate, followed by ferric hydroxide scavenging steps and precipitation of excess sulfate as barium sulfate, chromium is finally precipitated and counted as barium chromate. The chemical yield is 40 to 50%, and the time for a single analysis is 2 to 2 1/2 hours.

2. Reagents.

Cr carrier : 10 mg Cr/ml (56.6 mg $K_2Cr_2O_7$ per liter - primary standard)
Pd carrier : 10 mg Pd/ml (added as $PdCl_2 \cdot 2H_2O$ in very dilute HCl)
Cu carrier : 10 mg Cu/ml (added as $CuCl_2 \cdot 2H_2O$ in H_2O)
Fe carrier : 10 mg Fe/ml (added as $FeCl_3 \cdot 6H_2O$ in very dilute HCl).
HCl : conc.
HCl : dilute (3 ml conc. HCl/liter)
H_2SO_4 : 3M
$HC_2H_3O_2$: 1M
NH_4OH : conc.
H_2S : gas
H_2O_2 : 30%
$Ba(NO_3)_2$: saturated solution
$NaBrO_3$: 1M
$NH_4C_2H_3O_2$: 1M
Aqueous SO_2 solution : saturated
Ethanol : 95%
Ethyl ether.

3. Equipment :

Drying oven
Centrifuge
Fisher burner
Block for holding centrifuge tubes

Forceps
Mounting plates
Tongs for holding Erlenmeyer flasks
Ground-off Hirsch funnels : Coors 000A (one per sample)
Filter chimney (one per sample)
Pipets : 2 ml
125 ml separatory funnels (one per sample)
Wash bottle
125 ml Erlenmeyr flasks (one per sample)
2", 60° short stem glass funnels (two per sample)
40 ml conical centrifuge tubes : Pyrex 8320 (10 per sample)
100 ml graduated cylinder
Pharmaceutical graduated cylinders : 5, 10 and 30 ml
No 42 Whatman filter paper (tared for mounting) : 7/8" diameter
No 40 Whatman filter paper (9 cm)
Stirring rods
Ice bath.

4. Procedure.

(1) To the sample in a 40 ml centrifuge tube, add 2 ml of standard Cr carrier. Dilute the solution to 15 ml, add 3 ml of conc. HCl and heat to boiling. Add saturated SO_2 solution dropwise until all of the $Cr_2O_7^=$ has been reduced to Cr^{+3} ion. Boil off the excess SO_2.

(2) To the hot solution add conc. NH_4OH dropwise to precipitate $Cr(OH)_3$. Caution.. Do not use a great excess of NH_4OH (Note 1). Centrifuge the $Cr(OH)_3$ and discard the supernate.

(3) Dissolve the $Cr(OH)_3$ in 6 to 8 drops of conc. HCl, dilute to 20 ml, heat to boiling, and reprecipitate $Cr(OH)_3$ with conc. NH_4OH. Centrifuge and discard the supernate.

(4) Dissolve the $Cr(OH)_3$ in 6 to 8 drops of conc. HCl, dilute to 20 ml, and add 4 drops each of Pd and Cu carriers. Heat to boiling and pass in H_2S for 5 min. Filter and discard the sulfide scavenger precipitate, retaining the Cr^{+3}-containing filtrate in a 40 ml centrifuge tube.

(5) Precipitate $Cr(OH)_3$ from the filtrate (step 2), centrifuge and discard the supernate.

(6) Dissolve the $Cr(OH)_3$ in 8 drops of conc. HCl, boil out remaining H_2S, and dilute to 20 ml. Add 4 drops each of Pd and Cu carriers and remove another sulfide scavenging precipitate as before (step 4). Filter and collect filtrate in a 40 ml centrifuge tube.

(7) Repeat step 5.

(8) Redissolve the $Cr(OH)_3$ from step 7 in 8 drops of conc. HCl, heat to boiling to remove H_2S, and reprecipitate $Cr(OH)_3$ with conc. NH_4OH. Centrifuge and discard the supernate.

(9) Dissolve the $Cr(OH)_3$ in only 4 to 6 drops of conc. HCl (Note 2). Add 15 ml of H_2O and about 6 ml of 1M $NaBrO_3$. Transfer quantitatively to a 125 ml Erlenmeyer flask and heat over a flame until all the Cr^{+3} ion is oxidized to $Cr_2O_7^{=}$. (If the oxidation does not appear to be complete, additional $NaBrO_3$ should be added (Note 3).

(10) Add 3 to 4 ml of saturated $Ba(NO_3)_2$ solution and 3 to 4 ml of 1M $NH_4C_2H_3O_2$. This will result in the precipitation of $BaCrO_4$. If precipitation appears to be incomplete, a drop of conc. NH_4OH should be added. Transfer to 40 ml centrifuge tube, centrifuge and discard the supernate. Wash the precipitate with 30 ml of H_2O, centrifuge and discard the washings.

(11) Dissolve the $BaCrO_4$ in about 6 drops of conc. HCl and 10 ml of H_2O. (Heat may be required.) Dilute to about 30 ml and reprecipitate $BaCrO_4$ with 1M $NH_4C_2H_3O_2$ as before (step 10). Centrifuge, wash the precipitate with 30 ml of water, centrifuge and discard the washings.

(12) Dissolve the $BaCrO_4$ in 10 ml of H_2O and 5 drops of conc. HCl. Cool to 0 to 5° in an ice bath. Transfer to a 125 ml separatory funnel to which 90 to 100 ml of cold ethyl ether has been added. Add 3 drops of cold 30% H_2O_2 and immediately extract the blue peroxy compound CrO_5 into the cold ether (Note 4). Discard the aqueous layer.

(13) Wash the ether layer four times with 10 ml portions of cold (about 5°) H_2O containing 3 ml of conc. HCl per liter. Discard the washings.

(14) Back-extract into H_2O by shaking the ether with about 15 ml of H_2O containing 3 to 4 drops of conc. NH_4OH. Transfer the aqueous layer to a 40 ml centrifuge tube.

(15) Add 2 to 3 ml of saturated $Ba(NO_3)_2$ solution to precipitate $BaCrO_4$. Centrifuge and wash with 30 ml of H_2O, discarding the supernate and washings.

(16) Dissolve the $BaCrO_4$ in 15 ml of H_2O and 8 drops of conc. HCl. Heat to boiling and add 3 (only 3) drops of 3M H_2SO_4. Centrifuge and discard the $BaSO_4$ precipitate. Transfer the supernate to a 40 ml centrifuge tube.

(17) Add 6 drops of Fe carrier to the supernate containing the $Cr_2O_7^=$ ion and precipitate $Fe(OH)_3$ with conc. NH_4OH. Centrifuge and discard the $Fe(OH)_3$, transferring the supernate to a 40 ml centrifuge tube. Acidify the supernate with HNO_3.

(18) Repeat step 17 and heat the supernate to boiling.

(19) Add about 3 ml of saturated $Ba(NO_3)_2$ solution to remove $SO_4^=$ ion. Centrifuge the $BaSO_4$, discard the precipitate, and transfer the supernate to a 40 ml centrifuge tube.

(20) Precipitate $BaCrO_4$ from the supernate by the addition of conc. NH_4OH. Dissolve in 6 to 8 drops of conc. HCl and reprecipitate from 20 ml of solution by adding 3 to 4 ml of 1M $NH_4C_2H_3O_2$. Centrifuge and discard the supernate.

(21) Dissolve the $BaCrO_4$ in 5 drops of conc. HCl. Dilute to 30 ml and add 1 ml of 1M $HC_2H_3O_2$. Heat to boiling and add 2 ml of 1M $NH_4C_2H_3O_2$ dropwise to precipitate $BaCrO_4$. Filter on a tared No. 42 Whatman circle, using a ground-off Hirsch funnel and a chimney. Wash the precipitate with three 15 to 20 ml portions of hot H_2O and then with ethanol. Dry for 10 min. at 110°. Weigh, mount, and count immediately.

Notes.

1) It is important to avoid the use of a large excess of conc. NH_4OH to precipitate $Cr(OH)_3$, inasmuch as some of the latter will complex with NH_3 and go into solution.

2) The Cl^- and H^+ ion concentrations must be kept low to avoid reduction of the $Cr_2O_7^=$ which is formed by oxidation of Cr^{+3} ion with BrO_3^-.

3) It is possible, visually, to determine whether oxidation of Cr^{+3} ion to $Cr_2O_7^=$ is complete.

4) The formation and ether extraction of the blue peroxy compound CrO_5 must be carried out in the cold, otherwise the $Cr_2O_7^=$ will merely oxidize the H_2O_2. Only a transient blue color is then observed.

Procedure 16.

Procedure given in R.R.Smith, T.O.Passell, and S.D.Reeder, "Radiochemical Analyses for Fe, Cr, Ni and Co corrosion Products". AECD-3889, Sept. 9, 1955.

The step by step procedure used to separate and to decontaminate Cr from Zr and gross fission products is given below. In this particular case a 15 ml aliquot of the stock solution containing an equivalent of 2.47 mg of the salt mixture was used.

Equipment : 40 ml centrifuge cones, centrifuge, separatory funnel, filter chimney.

Reagents : $K_2Cr_2O_7$ carrier, 6M NH_4Ac, conc. NH_4OH, Fe, Pd, and Cu carriers, H_2SO_4, 30 per cent H_2O_2, sat. $Ba(NO_3)_2$, conc. HCl, H_2SO_3, ether, 6M NaOH, H_2S gas (lect.bot.).

(1) Add 20 mg of standardized Cr carrier as $K_2Cr_2O_7$ and evaporate sample in a 40 ml centrifuge cone with HCl to remove nitric acid.

(2) Add sufficient 6M NaOH to dissolve the chromium and aluminum. Dilute to 15 ml.

(3) Add 2 or 3 drops of 30 per cent H_2O_2 and boil the solution for several minutes.

(4) Scavenge with 4 mg of Fe and centrifuge.

(5) To the filtrate in a new cone, add sat. $Ba(NO_3)_2$ to precipitate $BaCrO_4$. Digest in a hot bath, centrifuge, and discard the filtrate.

(6) Wash $BaCrO_4$ with hot water. Dissolve in a minimum of conc. HCl and add 20 ml of water. Add 2 ml of 6M HAc and reprecipitate $BaCrO_4$. Wash.

(7) Dissolve $BaCrO_4$ in 2 ml of conc. HCl and dilute to 20 ml. Heat to boiling and reduce Cr^{+6} to Cr^{+3} by dropwise addition of sulfurous acid. Some $BaSO_4$ will form. Precipitate $Cr(OH)_3$ by the careful addition of NH_4OH. Avoid excess...

(8) Centrifuge $Cr(OH)_3$. Wash. Dissolve in 8 drops of HCl, and one drop of H_2SO_4. Dilute to 15 ml and add Pd and Cu carriers. Pass in H_2S and centrifuge.

(9) Remove the supernate and from it precipitate $Cr(OH)_3$ with ammonia; wash with hot water.

(10) Add 6-8 drops of 6N NaOH and dilute to 15 ml. Add 2-3 drops of H_2O_2. Boil to oxidize Cr^{+3} to Cr^{+6}, scavenge with $Fe(OH)_3$.

(11) Acidify the filtrate, add 2 ml of NH_4Ac and precipitate $BaCrO_4$. Wash the centrifuged $BaCrO_4$ and dissolve in 6 drops of HCl and dilute to 15 ml.

(12) Cool to 0-5°C and transfer the Cr to a separatory funnel. Add 50 ml of 0-5°C ether. Add 3 drops of 30 per cent H_2O_2 and immediately extract the H_3CrO_8 into the ether. Discard the water layer. Wash ether with 3 portions (10 ml) of cold water acidified with HCl. (3 ml HCl/liter).

(13) Add 15 ml of water to the ether in the funnel and 4 drops of conc. ammonia. Shake and transfer water layer of $CrO_4^{=}$ to a 40 ml cone.

(14) Boil off ether in a water bath. Add NH_4Ac and precipitate $BaCrO_4$. Filter into a weighed filter disc and wash with hot water, and then with absolute alcohol. Dry at 110°C for 10 minutes. Weigh, compute chemical yield, and count.

Procedure 17.

Extraction of high specific activity chromium-51 from pile-irradiated potassium chromate.

R.S. Mani, Intern. J. Appl. Rad. Isotopes, 14, 327 (1963).

The absorption properties of hydrous aluminium oxide are used for extracting high specific activity chromium-51 from irradiated potassium chromate.

Preparation of the column.

The column (10 cm x 1 cm^2) is prepared by filling it with Merck chromatographic grade alumina (standardized according to Brockman) with a mesh size of 100-200. The alumina is previously digested with dilute HCl for 4 hours and washed with water before being transferred to the column.

A flow rate of 10 $ml/cm^2/min$ is maintained throughout the operation.

Procedure.

Reagent grade potassium chromate is irradiated for one week at a neutron flux of 1.5 to 3×10^{12} $n.cm^{-2}.sec^{-1}$. The irradiated potassium chromate is transferred to the top of the alumina column (conditioned with dilute ammonia solution) and dissolved with dilute ammoniasolution.

The column is washed with dilute ammonia solution, followed by water, untill the effluent is free from chromate. The retained chromium (III) activity is eluted with 0.1N HCl.

The acid solution is concentrated by slow evaporation to dryness and the activity is leached out with alkaline peroxide solution. Excess peroxide is destroyed by boiling,the solution is cooled and the pH is adjusted to 7.4 - 7.8 by addition of dilute HCl. The solution is allowed to stand for one hour and is then filtered through a sintered glass filter.

The radiochemical purity of the product exceeds 99% and it is possible to obtain a specific activity of 25 to 60 mc/mg.

Procedure 18.

Solvent extraction of chromium(VI) with tribenzylamine (applied to neutron activation analysis).

G.B.Fasolo, R.Malvano and A.Massaglia

Anal.Chim.Acta 29, 569 (1963).

Procedure.

Weighed samples (0.2 to 1 g of aluminium alloys) are irradiated in sealed quartz vials together with standard Al-Cr alloys for 50-200 hours at thermal fluxes of 5×10^{12} to 4×10^{13} $n.cm^{-2}.sec^{-1}$. After a 10-day cooling time, the samples are chemically treated ; chromium(III) carrier is added (20 mg) and the samples are dissolved in NaOH, oxidized with $KMnO_4$ and acidified with HCl, whereas organic substances are fused with an oxidizing alkaline flux and then leached out with HCl.

The acidity is adjusted to give an approximately 1N HCl solution and this solution is shaken in a separatory funnel with two successive 5 ml portions of a 1% chloroform solution of tribenzylamine (analytical grade, recrystallized from ethanol and free from any solvent residues). The combined $CHCl_3$ extracts are diluted to 25 ml.

Gammaspectrometric measurements are performed on this solution, which is at the same time used for spectrophotometric yield determination by absorbance measurement at 355 or 458 mμ. Anhydrous sodium sulphate is used to dry the organic extracts. All measurements can however also be made on aqueous solutions after an alkaline stripping.

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