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NUCLEAR SCIENCE SERIES

The Radiochemistry of Chromium

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The Radiochemistry of Chromium

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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 nuclear chemistry and analytical chemistry.

The Subcommittee has concerned itself with those areas of nuclear science which involve the chemist, such as the collection and distribution of radiochemical procedures, the establishment of specifications for radiochemically pure reagents, the problems of stockpiling uncontaminated materials, the avaialbility of cyclotron time for service irradiations, the place of radiochemistry in the undergraduate college program, etc.

This series of monographs has grown out of the need for up-to-date compilations of radiochemical information and procedures. The Subcommittee has endeavored to present a series which will be of maximum use to the working scientist and and which contains the latest available information. Each monograph collects in one volume the pertinent information required for radiochemical work with an individual element or a group of closely related elements.

An expert in the radiochemistry of the particular element has written the monograph, following a standard format developed by the Subcommittee. The Atomic Energy Commission has sponsored the printing of the series.

The Subcommittee is confident these publications will be useful not only to the radiochemist but also to the research worker in other fields such as physics, biochemistry or medicine who wishes to use radiochemical techniques to solve a specific problem.

W. Wayne Meinke, Chairman
Subcommittee on Radiochemistry

CONTENTS

INTRODUCTION

This volume which deals with the radiochemistry of chromium is one of a series of monographs on radiochemistry of the elements. There is included a review of the nuclear and chemical features of particular interest to the radiochemist, a discussion of problems of dissolution of a sample and counting techniques and finally, a collection of radiochemical procedures for the element as found in the literature.

The series of monographs will cover all elements for which radiochemical procedures are pertinent. Plans include revision of the monograph periodically as new techniques and procedures warrant. The reader is therefore encouraged to call to the attention of the author any published or unpublished material on the radiochemistry of chromium which might be included in a revised version of the monograph.

I. General Reviews of the Inorganic and Analytical Chemistry of Chromium

Handbuch der Analytischen Chemie
Ed. R.Fresenius und G.Jander, Springer Verlag Berlin 1948.
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 b α : Elemente der Sechsten Nebengruppe: CHROM
Dr.H.Garschagen, Dr.W.Kimpel und Dr.J.Weise
p. 1- 411

G.Charlot et D.Bézier
Analyse quantitative Minérale.
Masson et Co. Paris 1955
p. 488-494

G.Charlot and D.Bézier
Modern Methods of Quantitative Inorganic Analysis
Trad.By R.C.Murray
J.Wiley and Sons N.Y. 1957

Colorimetric Determination of Traces of Metals
E.B.Sandell (1959)
p.388-408

Analytical Chemistry of the Manhattan Project
Ed. Cl.J.Rodden
Mc.Graw-Hill 1950
p.445 : CHROMIUM

Solvent Extraction in Analytical Chemistry
G.H.Morrison and H.Freiser
J.Wiley and Sons (1957)

II. General Reviews of the Radiochemistry of Chromium

none

III. Table of Isotopes of Chromium

(with decay-schemes and
activation cross-sections).

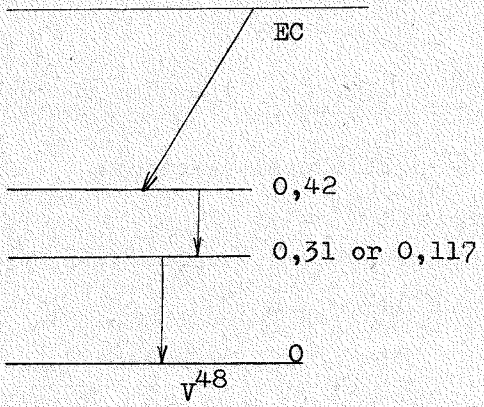
1.Table of Isotopes.

isotope	% abund.	half-life	decay	energy	method of preparation
Cr^{46}		1,1 s			
Cr^{47}		0,4 s			
Cr^{48}		23 h	EC, no β^+		
			γ_1	0,116	
			γ_2	0,31	
Cr^{49}		41,9m	β^+	1,54	Ti^{46} (α;n)
				1,39	
				0,73	Cr^{50} (n;2n)
			γ	0,063	
				0,089	
				0,150	
Cr^{50}	4,31				
Cr^{51}		27,8d	no β^+		V^{51} (d;2n)
			γ	0,323	Ti^{48} (α;n)
				0,320	V^{51} (p;n)
				0,65	Cr^{50} (n;γ)
Cr^{52}	83,76				
Cr^{53}	9,55				
Cr^{54}	2,38				
Cr^{55}		3,52m	β^-	2,85	Cr^{54} (n;γ)
			no γ		Cr^{54} (d;p)
					Mn^{55} (n;p)

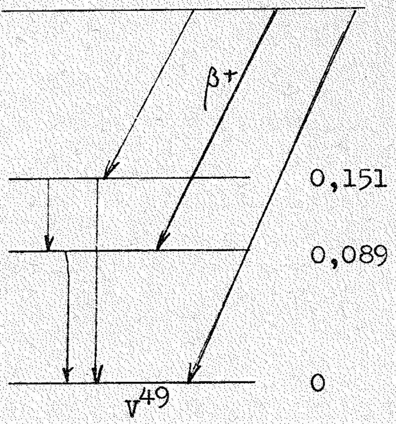
For more complete information on the radiations of chromium isotopes and references to the original literature, see "Table of Isotopes" by D.Strominger, J.M.Hollander and G.T.Seaborg, Rev.Mod.Phys., 30 No.2, Part II, April 1958 pages 625-627.

2. Decay-schemes of some chromium isotopes.

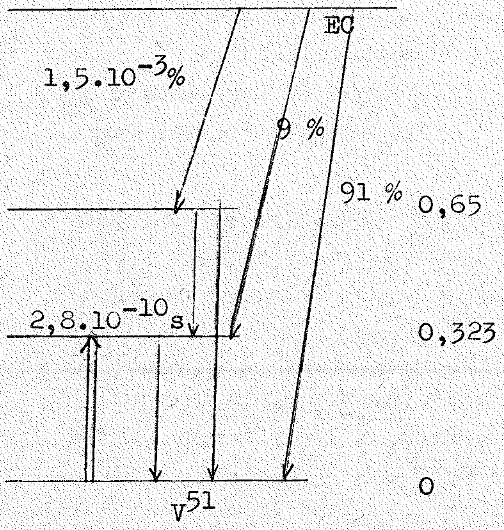
Cr^{48} (23 h)



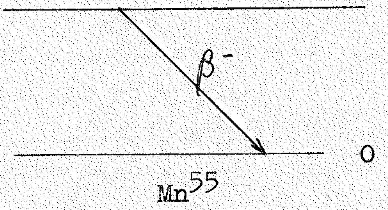
Cr^{49} (42 m)



Cr^{51} (28 d)



Cr^{55} (3,5 m)



3.Activation cross-sections of chromium isotopes

Absorption cross-sections are given below:

natural element:		2,9
Cr^{50}		16
Cr^{52}		0,73
Cr^{53}		18
Cr^{54}	less than	0,3

The cross section for the less common reaction:

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

is given by Mellish,Payne and Otlet (M 1) as 0,37 millibarns.

IV. Review of those Features of Chief Interest to Radiochemists.

1. Metallic Chromium

Chromium is a very hard steel-gray metal (density 7,2088) with cubic cristalline form. Depending on the way of preparation,it can attain a hardness of 9 (R 1). It melts at 1890 °C and has a boiling point of 2200 °C.

Readily soluble in hydrochloric acid and in diluted sulfuric acid,it is nevertheless insoluble in nitric acid. Rendered passive,it is very resistent towards 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.

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 analogue behaviour of chromium with the elements of the entire group 6 is furthermore illustrated by the isomorphous cristallisation 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 sulfur and selenium.

2. 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.

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

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 little interest. The +5 state is only found in the red perchromates of the type Me_3CrO_8, whereas the +2 state is readily oxidized by atmospheric oxygen.

For analytical purposes, 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 alcaline medium

concentrated NaOH and H_2O_2 (W 1)(B 1)
Na_2O_2 (M 2)
concentrated NaOH and bromine (J 1)(H 1)(M 3)
concentrated NaOH and Sn^{IV} oxide (K 1)
$KMnO_4$ and NaOH (K 1) (L 1)
alcaline oxidation by electrolysis
persulfate in alcaline medium (O 1) (J 1)

b. Wet oxidation in acid medium

persulfate with catalysator (Ag^+) (P 1)
persulfate without catalysator (V 2) (K 2)
permanganate (H 2)
$KBrO_3$ (K 3)(H 3) (D 1)
$HClO_4$ (W 1) (S 1) (B 2)
Cl_2 (S 2)
Pb-IV-oxide (T 1)
Ce-IV-sulfate (W 2)
sodiumbismuthate (B 3) (C 1)
silverperoxide (T 2)

c. Oxidizing melt

This method, which will be discussed in chapter V, 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 : seldom used
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 (S 3),SO_2 , hydrazinesulfate (B 4), $NH_2OH.HCl$ (J 2), KNO_2 (S 4) or even H_2S (F 1)

Transition to oxidation state + 2

This transition can be achieved by energetic reduction with hydrogen or by making use of a Jones reductor.

Chromium can be determined volumetrically by a large number of methods,most of which are based upon the oxido-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+} (S 5), $KMnO_4$ (S 5), $K_2Cr_2O_7$ (S 5), methylene blue (S 5), I_2 (S 6), $KBrO_3$ (S 6) and KIO_3 (S 6).

Determination of chromium 3+

oxidative determination: with $KMnO_4$ (D 2) (B 4), potassium hexacyanoferrate (B 5) or Ce-IV sulfate (W 2).

precipitative or complexometric determination: with arsenate (F 2),diammoniumphosphate (K 4) or with Complexon III (S 7).

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) (Z 1)
- excess of Fe 2+ and back-titration with $KMnO_4$ or $K_2Cr_2O_7$ (S 8)(F 3) or with Ce-IV-sulfate (S9)(B 6).
- direct titration with Fe 2+ (F 2,pag.95)
- titration with arsenic acid (F 2,pag.146)
- titration with Sn 2+ chloride solution (F 2,pag.162)
- titration with Ti 3+ salt (F 2,pag.174)
- titration with chromium-2+-sulfate (Z 2)

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

3.Insoluble salts and compounds of chromium. Precipitation and co-precipitation characteristics of chromium.

The more common insoluble compounds of chromium are listed in the following table:

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 decomposes in alcali
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
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,alcohol,alcali
oxide	$Cr_2O_3xH_2O$	insol.cold and hot water sol.acids,alcali 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,alcali 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

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+ hydroxides and the phosphates.

The most common gravimetric determination of chromium 3+ is based upon the precipitation as chromium oxyhydrate, with subsequent ignition to Cr_2O_3 (F 2, 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, Tl, 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. (G 1)

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.

Precipitation and co-precipitation characteristics of chromium.

Tracer amounts of chromium 3+ will co-precipitate quantitatively with a number of hydroxides, such as for instance $Fe(OH)_3$, $La(OH)_3$ or $Al(OH)_3$

Chromium hydroxide however often remains in a colloïd 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 separation.

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.(F 4, pag.157).Other specific precipitation reactions for Cr 2+ ions use acetate or oxalate,with formation of respectively red and yellow precipitates.(F 4,p.157).

A number of more complex organic chelating reagents can be used as precipitating agents for chromium, and will be discussed under IV/5.

4.Complex ions of chromium

Chromium,with its coördination number 6, forms hexacoördinate 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.

5. Chelate compounds of chromium

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 in the following table:

- Disodium dihydrogenium ethylene diamino tetraacetate. (E D T A) (Complexon III) (D 3)
- Ammoniumtriacetic acid. Quantitative data and stability constant are given by Schwarzenbach and Biederman (S 10).
- Oxine derivatives. Irving,Butler and Ring (I 1) 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 pp.of unknown composition (J 3)
- *thiodiphenyl carbohydrazide* (P 2)
- *sodium alizarine sulphonate* gives a yellow pp. of unknown composition,which is insoluble in 1 % acetic acid. (G 2).
- *Resorufine*. An ammoniacal solution of this reagent gives a violet pp.with Cr 3+ ions.The reaction is not specific for chromium. (E 1).
- *Double salt of methylenblue and zincchloride* Formation of a red brown colour or pp. in the presence of pyrochromates.(P 3).
- Coloured *lakes* are formed with *acid alizarine yellow-RC* (F 5) and with *acid alizarine red* (F 5).
- *Coloured chelate-complexes* are furthermore formed by a number of reagents such as:

orcine (G 3)
dimethylether of pyrogallol (M 4)
chromotropic acid (K 5)
serichrome blue R (S 11)
haematoxyline (W 3)
m-phenylene diamine (K 6)
diphenylcarbazide (F 2 p.220).
α-naphtylamine (V 3)
diphenylcarbazone (G 4)

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 of these reagents is diphenylcarbazide (F 2,p.220),which has the advantage of being rather selective for the element chromium.

6. Extraction of chromium into organic solvents.

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 (M 5)(M 6)(S 12):
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 3 N, and extracted with the acetylacetone in chloroform.

The complex has its absorption maximum at 560 mμ.

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 an excess of reagent (2 % aqueous solution) to avoid decomposition. (L 2).

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.

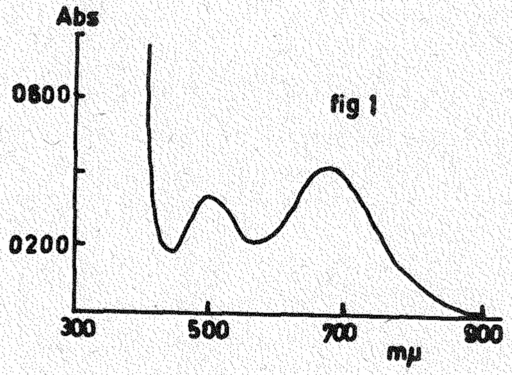


fig 1

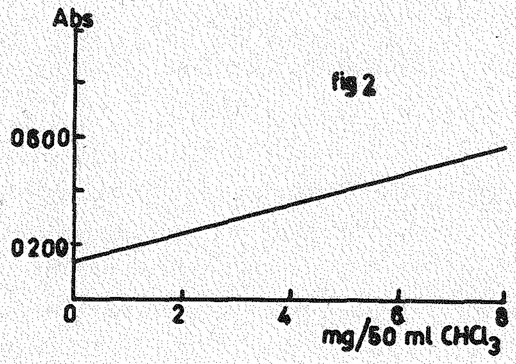


fig 2

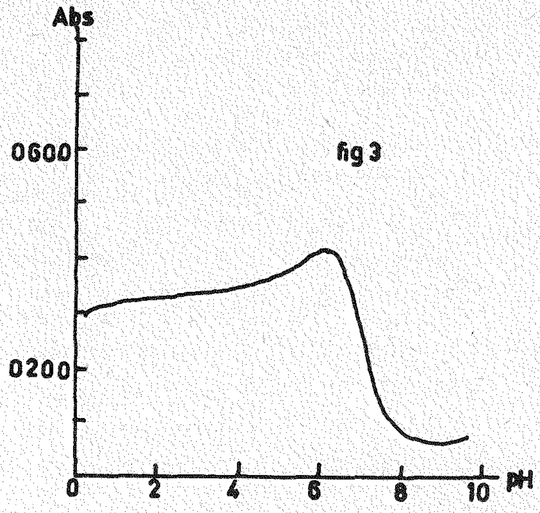


fig 3

Diphenylcarbazide

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

The following procedure can be used (D 4): To about 10-15 ml of a solution containing microgram amounts of Cr 6+ in 0,4 N 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 isoamylalcohol.

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 (F 2,p.220-253).

Extraction of Cr 3+ with high molecular weight amines,as methyldioctylamine in 2 N HCl,is not quantitative (31,8 %).The same is the case with nitrate extraction of Cr 6+ in 8 M HNO_3 with ethylether.Only 15 % of the chromium is removed by one extraction. (B 7)

Perfluorobutyric acid (C_3F_7COOH) in ethyl ether can be used for the separation of Cr 3+ from monovalent and divalent ions.Extractions are optimum at a pH just less than that at which the metal hydroxide would precipitate. (M 7).

J.C.White (W 4) claims that in 7 M 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 conditions cited.

An interesting separation method involving the use of liquid-liquid extraction,is the peracid method for the separation of chromium from vanadium.(B 8).
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 mixture and add 1 ml of 1 M (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.

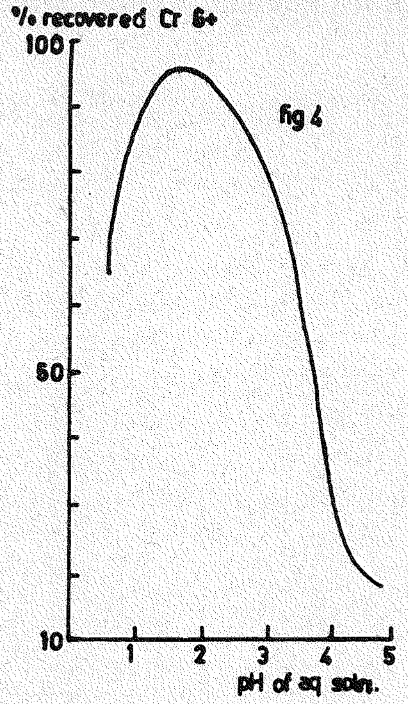
Extract the yellow chromate with water and boil the solution for 10 minutes. Dilute to 50 ml and determine the chromium content with diphenylcarbazide. The effect of the pH upon the recovery of chromium is given in figure 4.

Alternatively, a photometric determination of the blue perchromic acid can be made directly on the organic phase at a wavelengh of 565 mμ (G 5).

Chromium-vanadium separations can also be carried out by extraction of the vanadium-oxinate with chloroform at a pH of 4 (S 13).

7. Ion-exchange behaviour of chromium.

Relatively little is known about the anion-exchange behaviour of chromium. Kraus and Nelson, in their ion exchange studies of the fission products (K 7), note slight adsorption of Cr 3+ in 12 M HCl, but strong adsorption of Cr 6+ in the same medium.



Considerably more data are available on <u>cation - exchange</u> resins.
The formation of a coördinate 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 (G 6). The same author (G 7) 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 (sulfurated 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 (S 14) noted quantitative exchange of the cation with the hydrogen ions of the column. The acid liberated can be determined by simple titration with standard alcali. 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 (S 15), 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 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 5 N 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. (F 6), (G 8), (G 9), (G 10), (G 11), (G 12), (K 8), (K 9), (P 4), (T 3).

Lur'e and Filippova (L 3) 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 alcaline 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.

V. Solubilisation of Samples Containing Chromium

Metallic chromium,prepared by aluminothermic reaction (G 13) (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+ halogenides,the double chromium oxides (chrome spinels such as for instance Chromite), the anhydrous chromium sulfate (the so-called Cr 3+ heptasulfate-dihydrate : $2\ Cr_2(SO_4)_3 \cdot H_2SO_4$) and ignited chromium phosphate and oxide are insoluble in water,acids and alcali.

Nitride,carbide,silicide and boride are less likely to be encountered in common practice.

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

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 ultramicroscale (P 5).

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.

VI.Counting Techniques Pertinent to Chromium Isotopes

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.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).

3.Scintillation counting for multiple-tracer studies

G.H.Hine,B.A.Burrows,L.Apt,M.Pollycove,J.Ross and L.A.Sarkes.
Nucleonics 13 no 2 23-5 (1955).
Scintillation counting for Fe^{59} and Cr^{51} are described.

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 furthermore 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 determinated.
The calculation is discussed.

6. The preparation of Cr 51 of high specific activity: 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 Electronics 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.

VII.Collection of Detailed Radiochemical Procedures for Chromium

Procedure 1.

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

Distillation of carrier-free chromium as chromylchloride.

Several authors (F 2,pag.406),(S 16),(W 5) 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, distil under these conditions.They can be removed,if

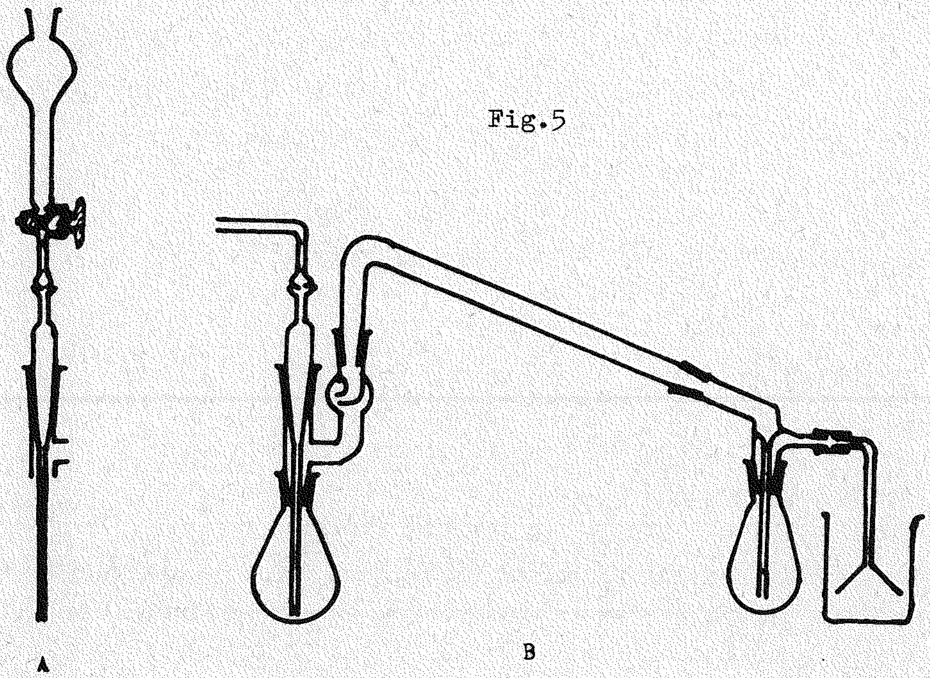
necessary, prior to the chromium distillation, by the procedure of Scherrer (S 17).
Tracer experiments using As^{76}, Sb^{124} and Cr^{51} indicated that the removal of the arsenic, antimony and tin is quantitative, whereas the chromium does not distil under these conditions. Experiments using V^{48} and Fe^{59} showed that these elements do not distil 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 with 10 ml of concentrated H_2SO_4, whereafter the sulfuric solution is quantitatively transferred into the distillation apparatus represented in Fig.5.

Fig.5



Apparatus for the distillation of Chromium

The rinsing water used is removed by distillation, whereafter 50 ml of concentrated HCl are added dropswize 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 dropswize 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 chromylchloride is collected in approximately 5-10 ml water. This solution can be taken to dryness, without chromium losses, after the addition of a small excess hydrazine hydrate. The excess hydrazine is finally destroyed with 6 N 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

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

Chemical separation of carrier-free chromium after bombardment of iron target.

Reaction: Fe^{54} (n;α) 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 alcaline 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 6 N and saturated with SO_2 to insure the reduction of Cr 3+
Fe 3+ and La 3+ is added and the solution is made alcaline with Na_2CO_3 .

V is oxidised to soluble vanadate by air in alcaline 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 1 N 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 2 N sulfuric acid,the solution diluted three times and the aluminiumhydroxide 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 aluminiumhydroxide was dissolved in a caustic solution prepared by the addition of five or

six pellets of sodiumhydroxide to 10 ml of water and the solution oxidized by the addition of about 100 mg of sodiumperoxide. The peroxyde 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 asecond volumetric flask. The second aliquot portion was made basic with NaOH, oxidized with Na_2O_2, heated to destroy excess of sodiumperoxide, 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 6 N 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 sodiumvanadate.

The final $Fe(OH)_3$ precipitate containing the Cr-51 was dissolved in 6 N 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 1 N 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 6 N 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 give 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 0,008 M 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 orth to the azo group,which yields a chromium complex from 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.

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Ch.Z	Chemiker Zeitung
Fr	Zeitschrift für analytische Chemie (Fresenius)
G	Gazzetta chimica italiana
J.pr	Journal für praktische Chemie

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