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The Chemistry of Chromium and Some Resulting Analytical Problems

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Chromium, named for its many-colored compounds, exists in the oxidation states of −2 to +6 inclusively. The compounds exhibit a wide range of geometries including square planar, tetrahedral, octahedral, and various distorted geometries. Chromium is found in nature principally as the chromite ore $FeCr_2O_4$ in which chromium is in the +3 state. The existence of a particular oxidation state is dependent on many factors including pH, redox potentials, and kinetics. Thermodynamically, +3 and +2 are the most stable states, while the +3 and +6 oxidation states are the most common ones found in aqueous solution. Kinetically, chromium +3 is substitutionally inert: for water exchange $k(sec^{-1}) = 2.5 \times 10^{-6}$, due to the presence of the half-filled $d(t_{2g})^{3,4}A_{2g}$ state. On the other hand, protonation/deprotonation is quite rapid. Polymerization is very slow but is promoted at higher pHs; acid cleavage of the protonated oligomers is also quite slow. Chromium +6 as the chromate ion is strongly oxidizing at low pHs and less so in basic solution. The chromate ion does form some polyacids and polyanions. These factors must be considered in analyzing samples for total chromium and for the amounts of each oxidation state.

General

Chromium was named for the many colors manifested by its compounds. As is seen in Figure 1, potassium dichromate, $K_2Cr_2O_7$, is red, potassium chromate, K_2CrO_4, is yellow, and chromium trichloride, $CrCl_3$, is green. The element (*1*) is found in the combined form mainly as the chromite ore, $FeCr_2O_4$, a spinel. Here chromium occupies octahedral sites and Fe^{II} occupies tetrahedral sites. Lower abundant ores are crocoite ($PbCrO_4$), chrome ochre (Cr_2O_3), and chromium in trace amounts is found in emerald and ruby. The main deposits are in southern Africa with 96% of the known reserves.

In the metallic form chromium is a white, hard, brittle, and lustrous metal that melts at 1903 ± 10°C. It dissolves easily in mineral acids that are nonoxidizing. It does not dissolve in nitric acid (concentrated or dilute) or cold aqua regia probably due to passivation (*2*); thus, the use of the metal as a protective corrosion inhibitor, *viz.*, chromium plating and metal finishing formulations. Other uses encompass pigments, tanning and textile chemicals, synthetic rubies for lasers, synthetic emeralds, wood preservatives, catalysts, stainless steels, chromium dioxide magnetic tapes, labeling of red blood cells, and as a fungicide (*3*). As Cr^{3+}, chromium (*4*) is an essential trace element in human nutrition. It is involved in glucose metabolism. The required amount has been variously reported to be from 50 to 200 µg per day.

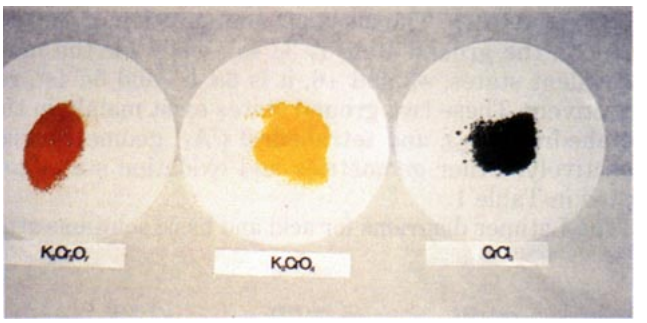

FIGURE 1. Examples of colored chromium compounds.

Most importantly, chromium(VI), the reason for this conference, has been implicated as cause of cancer (*5,6*) in animals and man. Therefore, the sources of the problem, the pertinent aqueous chemistry, and some related analytical problems will be discussed.

Source

Chromium is recovered directly from its ores by reduction. This is done (*1*) by using coke in an electric arc furnace to give an alloy, ferrochromium. However, pure chromium is typically obtained by first fusing the ore

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with lime and soda ash in air. The resultant yellow mixture is then leached with water and filtered, separating the aluminum impurities from the chromium by precipitating the aluminum hydroxide. The filtered solution is then acidified and concentrated to a red slurry and then dried to yield sodium dichromate. From this, chromium metal can be recovered by electrolytic reduction in plating bathes or reduced with carbon. World production of chromite ores is almost 9.5×10^6 tons.

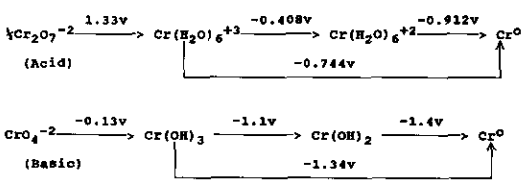
The residues, in the extraction process, can be recycled, but the spent ores must be disposed of eventually. Herein lies the source of the problem because the residues have been used as landfill in residential areas, becoming part of the dust carried by the wind or stirred up by traffic. Furthermore, these residues contain chromium salts that are leached out by rain (acid rain) and are even carried by capillary action or by ion exchange up the sides of houses. The spent material has also been dumped in places where the leachate enters the aquifer or local water systems. Changes in oxidation state can often accompany these movements.

Aqueous Chemistry

General

The inorganic chemistry of chromium is not only rich in its variety of colors, but also in its many oxidation states and the geometries of its many compounds. As seen in Table 1, the oxidation states of chromium can go from –2 to +6. The electron configuration of the element in the ground state is $3d^5 4s^1$, while for the most prevalent states, +3 and +6, it is $3d^3 4s^0$ and $3d^0 4s^0$, respectively. These two ground states exist mainly in the octahedral ($^4A_{2g}$), and tetrahedral ($^1A_1$) geometries respectively. Other geometries and oxidation states are listed in Table 1.

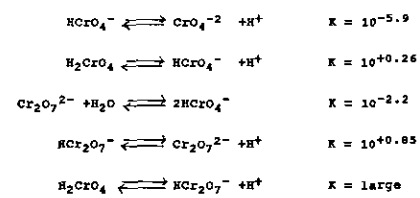
The Latimer diagrams for acid and basic solutions are:



The diagrams show that in aqueous solution the +3 state is most stable, followed by the +2 state. The +6 state is unstable in acid solution and goes to the +3 state. Furthermore, chromium in the +2 state is a good reducing agent, while in the +6 state it is a powerful oxidizing agent.

Chromium(VI)

The +6 oxidation state is of great interest because it is implicated in causing cancer in man and animals. Thus, its aqueous solution chemistry and methods for analytically determining its concentration are important. In aqueous solution, chromium(VI) may exist in a variety of oxospecies depending on pH. The structures of these anionic species are based on the sharing of a corner of the tetrahedral structure of the chromate ion as polymerization proceeds as pH is lowered. Figure 2 shows the structure of the chromate and dichromate anions where the Cr–O bond lengths are 166 pm (picometer) and 163 pm, respectively, and the bridge is 179 pm, while the Cr–O–Cr bond angle is 126°. As pH is lowered the familiar red dichromate $Cr_2O_7^{-2}$ forms, followed by formation of the tri- and tetra-anions $Cr_3O_{10}^{-2}$ and $Cr_4O_{13}^{-2}$, respectively. The small size and large charge of the chromium(VI) moiety enhances its liability and engenders Cr–O double bonding (infrared stretch at 730 cm^{-1}). Thermodynamically, the aqueous equilibria are as follows:



At pH < 1, the predominant species is H_2CrO_4, while as the pH is raised from pH 2 to 6, the $HCrO_4^-$ and $Cr_2O_7^{-2}$ anions prevail. At a pH > 8 only the yellow ion CrO_4^{-2} exists. Polymerization to the tri- and tetrachromates occurs at very low pH. The addition of concentrated

Table 1. Representative formal oxidation states and properties of chromium compounds.

Compound	Geometry	Oxidation state
$[Cr(CO)_5]^{-2}$	Trigonal bypyramid	–2
$[Cr_2(CO)_{10}]^{-2}$	Octahedron	–1
$[Cr(bipy)_3]$	Octahedron	0
$[Cr(CNR)_6]^+$	Octahedron	+1
$[Cr(CO)_2(diars)_2X]^+$	Capped trigonal prism	+2
$[CrCl_4]^{-1}$	Tetrahedron	+3
$[CrF_6]^{-2}$	Octahedron	+4
$[CrOCl_4]^{-1}$	Square pyramid	+5
$[CrO_4]^{-2}$	Tetrahedron	+6

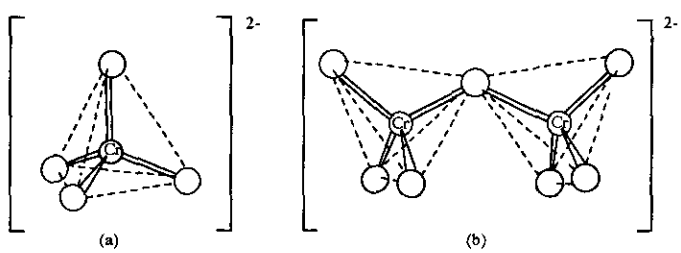


FIGURE 2. (*a*) CrO_4^{2-} ion; (*b*) $Cr_2O_7^{2-}$ ion.

sulfuric acid precipitates unstable red crystals of hydrated CrO_3. It should be noted that the Pourbaix diagram (*7*) (pH plotted against E°) clearly shows that at low pH, the +3 state, $Cr(H_2O)_6^{+3}$, is the predominant or stable species, and the +6 state, CrO_4^{-2}, is the predominant species at high pH. The presence of all of these species and their pH dependence poses a problem if one is interested in speciation as well as detection of a particular oxidation state.

The electronic spectrum of the chromate ion (*8*) arises from ligand to metal charge transfer bands only, since the chromium(VI) is d^0. It is its high charge-to-size ratio that enhances the process. Bands for the chromate ion in aqueous solution are 25,800 cm^{-1} (ε = 4,600), 37,000 cm^{-1} (ε = 3,800), and 55,560 cm^{-1} (ε = 28,000). Clearly, spectroscopic determination using these bands is either inconvenient or not sufficiently precise for current needs.

Attention should be given also to the oxyhalide, chromyl chloride, CrO_2Cl_2, a red liquid that boils at 117°C (*1*). Chromium analyses requiring high temperatures using, for example, inductively coupled plasma (ICP) or atomic absorption methods, can involve samples containing chlorides. This is especially true for tissue samples or others in which hydrochloric acid or sodium chloride has been used in the preparation of the sample. These samples would then give false results because some of the chromium(VI) would form the volatile chromium oxychloride.

To overcome this problem and the inconvenience of the band positions and intensities, the valence-specific diphenylcarbazide method (*9*) can be used readily since at λ_{max} = 546 nm, $\varepsilon = 3.4 \times 10^4$. In this case, care should be taken to avoid Hg, Fe, and V oxidants as well as too low a pH, as the unstable +6 state will undergo reduction to the +3 state.

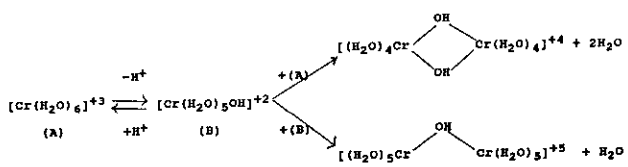
The analysis of total chromium is often carried out by using a nitric acid solution with hydrogen peroxide and heating (*5*). Under these conditions any chromate that may be present rapidly forms a deep violet-blue peroxo compound, $CrO(O_2)_2$, upon the addition of hydrogen peroxide. Addition of pyridine followed by extraction with ether affords the stable blue solid CrO_5(py), confirming the presence of a peroxy group as part of the structure (*1*). It is important to realize that this compound rapidly decomposes to chromium(III) and oxygen. Obviously, this method is only useful in determining total chromium.

Another problem that arises is whether or not chromium(III) can be oxidized to chromium(VI) in the soil. Because of the instability of chromium(VI) in the presence of organic matter, chromium(III) should be the only species present. However, Bartlett and James (*10*) have shown that chromium(III), added as salts or hydroxides, is rapidly oxidized to chromium(VI) if a fresh soil sample was moist. They attributed this to the presence of oxidized manganese. The oxidation of chromium(III) was found to be directly proportional to amount of the manganese(IV) reduced. The manganese is reoxidized by air.

Chromium(III)

In the cell (*6*), it is believed that the +3 oxidation state contributes to the carcinogenic activity of chromium. Thermodynamically, the +3 state is the most stable oxidation state of chromium, and it is represented by thousands of compounds. Kinetically, these compounds are inert in keeping with the half-filled t_{2g} level of the d^3 configuration in octahedral geometry. The violet hexaquo species is inert to water exchange, $k = 3.5 \times 10^{-6} sec^{-1}$ (*11*), i.e., a half-life of a few days.

The hexaquo species exhibits a $pK_a \approx 4$, comparable to formic acid. Upon heating, or with time, or by raising the pH, this species will hydrolyze to form polymers containing OH bridges as follows:



Aqueous chromium(III) chloride chemistry reflects the kinetic inertness of the violet hexaquo ion. $[Cr(H_2O)_6]Cl_3$ exists as three isomers: the dark green hydrate *trans*-$[CrCl_2(H_2O)_4]Cl \cdot 2H_2O$ and the pale green $[CrCl(H_2O)_5]Cl_2 \cdot H_2O$.

Chromium(III) is particularly difficult to analyze by using its electronic spectrum. The spectral data are as follows for the hexaquo species. It exhibits bands at 15,000 cm^{-1} (ε = 2), 17,400 cm^{-1} (ε = 3), 24,600 cm^{-1} (ε = 15), and 37,000 cm^{-1} (ε = 4) (*12*). These bands arise from the ground state electron configuration. They are all spin and/or LaPorte forbidden as indicated by the very low molar absorptivities.

Chromium(V)

The high oxidation state of +4 is most stable at high pH. It disproportionates easily to the chromium(III) and chromium(VI), especially in acid solution (*13*). See Table 2 for properties of $(CrO_4)^{-3}$. In studies with various cell systems, starting with chromate, chromium(V) has been shown to be present as an intermediate. The

Table 2. Some properties of $d^1(CrO_4^{-3})$.

Fairly stable at high pH but disproportionates as:
$3Cr^{V} \rightarrow 2Cr^{VI} + Cr^{III}$
d^1 Electron configuration
Electron spin resonance: g = 1.98, g = 1.97 at 20 K
Ultraviolet: 265 ± 5 nm (ε = 250 ± 50); 355 ± 5 nm (ε = 500 ± 50)
Chromate reduction in the presence of organics, effected by ester formation, light, media, concentrations, temperature.

mechanism of generation and carcinogenicity of chromium(V) was dealt with by Wetterhahn (*6*) at this conference.

Chromium(V) also can be found in the presence of naturally occurring organic matter such as humus. The ion is detected by a unique electron spin resonance (ESR) signal caused by its electron configuration that is d^1. The ESR signal is at g = 1.98. At this time chromium(V) has been analyzed only by ESR.

Boyko and Goodgame (*14*) reacted chromate with soil-derived fulvic acids over a pH range of 3 to 12 to produce chromium(V). As the chromium(V) signal decreased with increasing pH or time, chromium(III) was generated. Conventional wisdom would then lead one to believe that chromium(VI) in soil, containing organic matter, would have a short lifetime. This is because the organic matter would reduce it to at least chromium(V), and the natural acidity would make it unstable with respect to chromium(III). But, as mentioned previously, chromium(III) can be reoxidized in soils (*10*).

Analytical Chemistry of Chromium

General

Previous discussion showed that the use of the electronic spectrum of the +3 and +6 states is at best inconvenient and at worst impossible. Also, for analysis using high temperature methods such as ICP and atomic absorption, only total chromium can be determined. In addition, care should be taken with samples containing chlorides.

In general, for atomic absorption methods, matrix effects are important and subtle. The valence-specific diphenyl-carbazide method in testing for chromium(VI) is an excellent method, but the presence of various oxidants and a low pH interfere. The use of the nitric acid-hydrogen peroxide mixture and heating is a superb method, but only for total chromium, since all the chromium(VI) will be converted to chromium(III). A cursory search of the literature shows that there are many methods available for the determination of total chromium, and some can also evaluate oxidation state and species; Table 3 gives a nonexhaustive list (*15*). Two methods, however, will be described briefly, which also will reflect some of the difficulties in speciation.

Table 3. List of analytical methods.

Atomic absorption and emission spectroscopy
Inductively coupled plasma
X-ray fluorescence
X-ray photoelectron spectroscopy
Proton-induced X-ray emission (valence detection)
Neutron activation
Mass spectroscopy
Ion chromatography
UV visible spectroscopy
Electrochemical
Chromatography: high performance liquid chromatography, gas chromatography
Radioactivity, ^{51}Cr detection
Infrared and raman spectroscopy

Ion Chromatography

McLeod (*16*) has refined a flow injection (FI) system in combination with ICP instrumentation. The basic principle of FI systems is to control the dispersion of the sample in the carrier stream while the sample moves from injection port to detector. By exact synchronization and timing of the injection with the measurement routine, reproducibility is obtained. McLeod has found that activated alumina affords an excellent method for concentrating both anionic and cationic analytes as a function of pH (*16*). The alumina has a high affinity for oxyanions and cations. The procedure is to inject an analyte and concentrate it on a microcolumn. If the anion is retained on the acidic column, the cation can then be analyzed directly. Addition of strong base elutes the anion, which is then analyzed. For a 2-mL sample volume, limits of detection were 1.4 ppb for chromium(III), and 0.2 ppb for chromium(VI). Interferences were coeluting cations for chromium(III) such as calcium(II). Only the simple hexaquo and chromate species were studied.

Recently, Collins et al. (*17*) used column chromatographic methods combined with radiometric detection of ^{51}Cr. Radiolabeled chromium(VI) and chromium(III) of the mixture was placed on the cationic column and eluted with increasing concentrations of perchloric acid, followed by mixtures of $Ca(ClO_4)_2$ and $HClO_4$, and then a mixture of $La(ClO_4)_3$ and $HClO_4$. The chromium complexes were eluted giving peaks in the order of increasing charge as follows: $CrCl_3$ [and chromium(VI) if present], $[Cr(H_2O)_4Cl_2]^{+1}$, $[Cr(H_2O)_5Cl]^{+2}$, $[Cr(H_2O)_6]^{+3}$, $Cr_2(OH)_2^{+4}$ (dimer), $Cr_3(OH)_4^{+5}$ (trimer), and $Cr_4(OH)_6^{+6}$ (tetramer). Clearly, the assumption that the aqueous chemistry of chromium contains only simple ions is a dangerous one.

1,1,1,5,5,5-Hexafluoro-2,3-Pentanedione

Hexafluoropentanedione (Hf) forms volatile *tris*-Hf complexes with chromium(III) that can be detected with electron capture gas chromatography. This technique has the advantage that chromium(VI), being anionic, will not react with Hf, while chromium(III) reacts readily with it. Recently, Debetto and Luciani (*18*) used this method to quantify chromium(III) in mammalian cells to which chromate had been added. Chromium(V) was not determined.

Caveat

In a paper titled "The Inexact Imprecise Science of Trace Analysis," Rodgers (*19*) makes a number of important points concerning detection of species in the laboratory setting. Among these are two pertinent points.

First, as the concentration of the species of interest (e.g., impurity one is trying to detect) decreases, the number of interferences increases. Moreover, if the detection limits drop by two orders of magnitude, then "it is possible to include every substance that has ever been made in a laboratory" (*19*). Clearly, there must be agreed-upon limits.

The second point was made using the results of a Taft Engineering Center study in the early 1960s in which samples of the same chromium-spiked standard was sent to over 50 different laboratories. The amount of chromium in each sample was 0.18 mg/mL, but the mean value reported was 0.14 mg/mL. Rodgers concludes that since several different methods were used for analysis and each laboratory had its own calibration procedures, that the error was not in the analytical chemistry, "but a discrepancy arising from the handling of the sample before it was analyzed" (*19*). Indeed, the human factor must be carefully reckoned with in any analytical procedure.

Summary

Clearly, the aqueous chemistry of chromium is complicated. In analyzing for chromium many factors must be considered. These factors are the thermodynamic stability of each oxidation state as a function of pH and the kinds of species, i.e., anions, cations, and polymeric ions, that can form for each oxidation state as a function of conditions of the sample such as pH, lability, equilibria, temperature, and the presence of other reductants and oxidants. Other factors that should be considered are the volatility, geometry of its compounds, and the electronic state of the metal ion.

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