ENVIRONMENTAL CONTAMINANTS ENCYCLOPEDIA

CHROMIUM III (TRIVALENT CHROMIUM) ENTRY

July 1, 1997

COMPILERS/EDITORS:

ROY J. IRWIN, NATIONAL PARK SERVICE

WITH ASSISTANCE FROM COLORADO STATE UNIVERSITY
STUDENT ASSISTANT CONTAMINANTS SPECIALISTS:

MARK VAN MOUWERIK
LYNETTE STEVENS
MARION DUBLER SEESE
WENDY BASHAM

NATIONAL PARK SERVICE
WATER RESOURCES DIVISIONS, WATER OPERATIONS BRANCH
1201 Oakridge Drive, Suite 250
FORT COLLINS, COLORADO 80525

WARNING/DISCLAIMERS:

Where specific products, books, or laboratories are mentioned, no official U.S. government endorsement is implied.

Digital format users: No software was independently developed for this project. Technical questions related to software should be directed to the manufacturer of whatever software is being used to read the files. Adobe Acrobat PDF files are supplied to allow use of this product with a wide variety of software and hardware (DOS, Windows, MAC, and UNIX).

This document was put together by human beings, mostly by compiling or summarizing what other human beings have written. Therefore, it most likely contains some mistakes and/or potential misinterpretations and should be used primarily as a way to search quickly for basic information and information sources. It should not be viewed as an exhaustive, "last-word" source for critical applications (such as those requiring legally defensible information). For critical applications (such as litigation applications), it is best to use this document to find sources, and then to obtain the original documents and/or talk to the authors before depending too heavily on a particular piece of information.

Like a library or most large databases (such as EPA's national STORET water quality database), this document contains information of variable quality from very diverse sources. In compiling this document, mistakes were found in peer reviewed journal articles, as well as in databases with relatively elaborate quality control mechanisms [366,649,940]. A few of these were caught and marked with a "[sic]" notation, but undoubtedly others slipped through. The [sic] notation was inserted by the editors to indicate information or spelling that seemed wrong or misleading, but which was nevertheless cited verbatim rather than arbitrarily changing what the author said.

Most likely additional transcription errors and typos have been added in some of our efforts. Furthermore, with such complex subject matter, it is not always easy to determine what is correct and what is incorrect, especially with the "experts" often disagreeing. It is not uncommon in scientific research for two different researchers to come up with different results which lead them to different conclusions. In compiling the Encyclopedia, the editors did not try to resolve such conflicts, but rather simply reported it all.

It should be kept in mind that data comparability is a major problem in environmental toxicology since laboratory and field methods are constantly changing and since there are so many different "standard methods" published by EPA, other federal agencies, state agencies, and various private groups. What some laboratory and field investigators actually do for standard operating practice is often a unique combination of various standard protocols and impromptu "improvements." In fact, the interagency task force on water methods concluded that [1014]:

> It is the exception rather than the rule that water-quality monitoring data from different programs or time periods can be compared on a scientifically sound basis, and that...
>
> No nationally accepted standard definitions exist for water quality parameters. The different organizations may collect data using identical or standard methods, but identify them by different names, or use the same names for data collected by different methods [1014].

Differences in field and laboratory methods are also major issues related to (the lack of) data comparability for chromium in media other than water: soil, sediments, tissues, and air.

In spite of numerous problems and complexities, knowledge is often power in decisions related to chemical contamination. It is therefore often helpful to be aware of a broad universe of conflicting results or conflicting expert opinions rather than having a portion of this information arbitrarily censored by someone else. Frequently one wants to know of the existence of information, even if one later decides not to use it for a particular application. Many would like to see a high percentage of the information available and decide for themselves what to throw out, partly because they don't want to seem uniformed or be caught by surprise by potentially important information. They are in a better position if they can say: "I knew about that data, assessed it based on the following quality assurance criteria, and decided not to use it for this application." This is especially true for users near the end of long decision processes, such as hazardous site cleanups, lengthy ecological risk assessments, or complex natural resource damage assessments.

For some categories, the editors found no information and inserted the phrase "no information found." This does not necessarily mean that no information exists; it simply means that during our efforts, the editors found none. For many topics, there is probably information "out there" that is not in the Encyclopedia. The more time that passes without encyclopedia updates (none are planned at the moment), the more true this statement will become. Still, the Encyclopedia is unique in that it contains broad ecotoxicology information from more sources than many other reference documents. No updates of this document are currently planned. However, it is hoped that most of the information in the encyclopedia will be useful for some time to come even with out updates, just as one can still find information in the 1972 EPA Blue Book [12] that does not seem well summarized anywhere else.

Although the editors of this document have done their best in the limited time available to insure accuracy of quotes as being "what the original author said," the proposed interagency funding of a bigger project with more elaborate peer review and quality control steps never materialized.

> The bottom line: The editors hope users find this document useful, but don't expect or depend on perfection herein. Neither the U.S. Government nor the National Park Service make any claims that this document is free of mistakes.

The following is one chemical topic entry (one file among 118). Before utilizing this entry, the reader is strongly encouraged to read the README file (in this subdirectory) for an introduction, an explanation of how to use this document in general, an explanation of how to search for power key section headings, an explanation of the organization of each entry, an information quality discussion, a discussion of copyright issues, and a listing of other entries (other topics) covered.

See the separate file entitled REFERENC for the identity of numbered references in brackets.

HOW TO CITE THIS DOCUMENT: As mentioned above, for critical applications it is better to obtain and cite the original publication after first verifying various data quality assurance concerns. For more routine applications, this document may be cited as:

> **Irwin, R.J., M. VanMouwerik, L. Stevens, M.D. Seese**, and **W. Basham.** 1997. Environmental Contaminants Encyclopedia. National Park Service, Water Resources Division, Fort Collins, Colorado. Distributed within the Federal Government as an Electronic Document (Projected public availability

on the internet or NTIS: 1998).

Chromium III (Trivalent Chromium Ion, CAS number 16065-83-1)

NOTE: This entry contains information on primarily Chromium III, although some information on elemental chromium and chromium VI is also included when it was deemed helpful relative to Chromium III. For much more detailed information on elemental chromium and chromium VI, see the entries entitled Chromium and Chromium VI.

Brief Introduction:

Br.Class: General Introduction and Classification Information:

Chromium (Cr) is a metallic element which is listed by the Environmental Protection Agency as one of 129 priority pollutants [58]. Chromium is considered one of the 14 most noxious heavy metals [83]. Chromium is also listed among the 25 hazardous substances thought to pose the most significant potential threat to human health at priority superfund sites [93].

Chromium does not occur free in nature; in bound form it makes up 0.1-0.3 parts per million of the Earth's crust [343]. Trace quantities of certain forms of chromium are considered helpful or necessary [366,483].

Elemental chromium is very stable, but is not usually found pure in nature [24]. Chromium can exist in oxidation states ranging from -2 to +6, but is most frequently found in the environment in the trivalent (Cr+3) and hexavalent (Cr+6) oxidation states [24]. The +3 and +6 forms are the most important because the +2, +4, and +5 forms are unstable and are rapidly converted to +3, which in turn is oxidized to +6 [24].

Chromium compounds are stable in the trivalent state and occur in nature in this state in ores, such as ferrochromite (FrCr2O4). The hexavalent state is the second most stable state. However, hexavalent chromium rarely occurs naturally, but is produced from anthropogenic sources [927].

Trivalent chromium (Chromium III, Cr3+, chromium +3) is an essential element for fungi and vertebrates in general [366,483]. Trivalent chromium is considered essential for glucose and lipid metabolism in mammals, and a deficiency of it produces symptoms of diabetes mellitus [483]. Trivalent chromium is essential for the maintenance of normal glucose tolerance in animals and man, and the factor or the group of factors containing trivalent chromium, called GTF (glucose tolerance factor) has been suggested to be responsible for this favorable action of chromium [366].

Trivalent chromium is the most common form in rocks of the earth's crust, but both trivalent and hexavalent chromium occur as dissolved chromium [190].

Br.Haz: General Hazard/Toxicity Summary:

Potential Hazards of Chromium III:

In general, the toxicity of trivalent chromium to mammals is low because membrane permeability is poor and it is noncorrosive [24]. However, chromium deficiency is unknown, and too much chromium can be harmful to humans [173]. Sensitivity to chromium varies widely, even among closely related species (that is, biota) [24].

Chromium III, the naturally occurring form, has low toxicity due to poor membrane permeability and noncorrosivity, while Cr VI, from industrial emissions, is highly toxic due to strong oxidation characteristics and ready membrane permeability (Nat'l Research Council Canada; Effects of Chromium in the Canadian Envir p.15 (1976) NRCC No.15017) [940].

Since the valence states are subject to change, tissues are often analyzed for total chromium rather than only chromium III or VI. During the laboratory digestion of tissue samples, most chromium is changed to the trivalent form.

There may be some partial exceptions to the generalization that hexavalent chromium is more hazardous than trivalent. One author stated that fish are sometimes more sensitive to Cr+3 than to Cr+6 [926]. Another stated that in soft water, trivalent chromium is more toxic to fish than Cr+6 [445]. The mean 96-h LC50 for Cr+3 has been reported to be about four-fold lower than that for Cr+6 in salmonid fish, with their reproductive cycles being particularly sensitive to Cr+3 [926]. However, the data are mixed and there appear to cases where chromium 6 is as hazardous or more hazardous to fish (and certainly to aquatic life other than fish) as chromium 3:

A comparison of the lowest EC20 value for fish in general shows that the value for chromium 6 (51 ug/L) is lower than the value for chromium 3 (89 ug/L [649]. The lowest chronic values for fish in general shows little difference

> between chromium 6 (73.18 ug/L) vs. chromium 3 (68.63 ug/L), and both the acute and chronic national ambient water quality criteria for chromium 6 are much lower concentrations than the equivalent concentrations for chromium 3 [649].
>
> Because trivalent chromium in natural waters is frequently found in particulate form, ingestion is a common route of exposure in aquatic species [445].

There appear to be some exceptions to the generalization that hexavalent chromium is more hazardous than trivalent. One author stated that fish are sometimes more sensitive to Cr+3 than to Cr+6 [926]. Another stated that in soft water, trivalent chromium is more toxic to fish than Cr+6 [445]. For more details, see W.Fish section below.

The USEPA regards all chromium compounds as toxic, although the most toxic and carcinogenic chromium compounds tend to be the strong oxidizing agents with an oxidation state of +6 [751]. Divalent and trivalent forms of chromium often (not always) have a lower order of toxicity or hazard [445,480]. The overall toxicity, carcinogenicity, and general hazard of chromium is highly related to chemical speciation [233,751]. The biological effects of chromium depend on chemical form, solubility and valence [24,751].

As in the case of other metals, the overall hazard presented by chromium may be partly related to the solubility of the specific form of chromium [751]. Substances having a low solubility in water are often not as easily absorbed through the gastrointestinal tract as are those substances with higher solubilities [751]. Thus, chromium III fluoride, which is very insoluble (sic, actually "relatively insoluble") in water, is far less toxic than chromium III sulfate, which is much more soluble [751]. In the same way, some hexavalent chromium compounds tend to be more toxic than the +3 forms not only because the oxidizing potential of +6 compounds is high [24,751,929], but also because some of the +6 forms more easily penetrate biological membranes [24].

Chromium III, the naturally occurring form, has low toxicity due to poor membrane permeability and noncorrosivity, while Cr VI, from industrial emissions, is highly toxic due to strong oxidation characteristics and ready membrane permeability

(Nat'l Research Council Canada; Effects of Chromium in the Canadian Envir p.15, 1976, NRCC No.15017) [609].

The toxic mechanism of action differs for hexavalent versus trivalent chromium [445]. Hexavalent chromium causes cellular damage via its role as a strong oxidizing agent, whereas trivalent chromium can inhibit various enzyme systems or react with organic molecules [445]. In mammalian species, chromium is considered one of the least toxic trace elements, as normal stomach pH converts hexavalent chromium to trivalent chromium [445]. One hundred to two hundreds times the normal total body load of chromium can usually be tolerated in mammals without evidence of negative effects [445]. The therapeutic:toxic dose ratio for trivalent chromium in rats has been calculated at approximately 1:10,000 [445].

Both chromium III and VI (especially hexavalent) are significant from the standpoint of potential impacts to fish and wildlife [24,57]. However, although chromium in general has some notoriety as a potentially harmful environmental contaminant, most of that notoriety is due to the toxic, carcinogenic, oxidizing agent, general, and reproductive risk hazards of hexavalent chromium (Cr6+, chromium +6, chromate) compounds [366,480,483,751,929].

Chromium toxicity to aquatic biota is significantly influenced by abiotic variables such as hardness, temperature, pH, and salinity of water; and biological factors such as species, life stage, and potential differences in sensitivities of local populations [24]. For many metals, alkalinity is sometimes a more important co-factor for toxicity than hardness (Pat Davies, Colorado Division of Wildlife, personal communication, 1997).

Potential Benefits of Chromium III:

Small amounts of trivalent chromium are considered essential in animals and man [366]. Trivalent chromium (Cr3+) is an essential human and animal nutrient at levels of 50 to 200 micrograms/day [929].

Trivalent chromium is the only form of chromium known to play a beneficial biological role. The form must be supplied as a stable complex, as trivalent chromium exists a an insoluble (sic, actually "relatively insoluble") macro-molecule at normal blood pH. The known biological effect of trivalent chromium is the maintenance of normal glucose tolerance [445].

Trivalent chromium (Cr3+, chromium +3) is an essential element for fungi and vertebrates in general [366,483,940]. Trivalent chromium is considered essential for glucose and lipid metabolism in mammals, and a deficiency of it produces symptoms of diabetes mellitus [483,940]. Trivalent chromium is essential for the maintenance of normal glucose tolerance in animals and man, and the factor or the group of factors containing trivalent chromium, called GTF (glucose tolerance factor) has been suggested to be responsible for this favorable action of chromium [366].

Chromium(III) may stabilize biological proteins in their proper configurations. /Cr III/ (Mertz W; Physiol Rev 49: 165-239, 1969, as cited in Nat'l Research Council Canada; Effects of Chromium in the Canadian Envir p.67 (1976) NRCC No.15017) [940].

Trivalent chromium is essential in mammals. Adequate trivalent chromium nutrition improves growth and longevity and, along with insulin, helps to maintain correct glucose, lipid, and protein metabolism. /Trivalent chromium/ (Nat'l Research Council Canada; Effects of Chromium in the Canadian Environment p.94, 1976, NRCC No 15017) [940].

Studies with mammals have suggested that trivalent chromium is not well absorbed from the intestinal tract. For example, rat studies have indicated that only a few percent of an oral chromium+3 dose crosses the intestinal wall, regardless of previous dietary history. However in studies of small intestinal absorption in black ducks (Anas rubripes), Eastin et al. (1980) measured equal rates of absorption of trivalent chromium (as chromium potassium sulfate [CrK(SO4)2]) and hexavalent chromium (as chromium trioxide [CrO3]). They noted that the ionic form of chromium influenced the degree of its absorption, with anionic chromium complexes being better absorbed [445].

See also: Chromium, General and Chromium VI entries.

Br.Car: Brief Summary of Carcinogenicity/Cancer Information:

EPA 1996 IRIS database information [893]:

Evidence for classification as to human carcinogenicity; weight-of-evidence classification

Classification: Under Review [893]. No classification given for Chromium(III), insoluble salts or soluble salts [893].

BASIS: Results of occupational epidemiologic studies of chromium-exposed workers are consistent across investigators and study populations. Dose-response relationships have been established for chromium exposure and lung cancer. Chromium-exposed workers are exposed to both chromium III and chromium VI compounds. Because only chromium VI has been found to be carcinogenic in animal studies, however, it was concluded that only chromium VI should be classified as a human carcinogen.

Human carcinogenicity data: Sufficient. [893].

Chromosomal effects produced by treatment with chromium compounds have been reported by a number of authors; for example, both Cr VI and Cr III salts were clastogenic for cultured human leukocytes [893].

Under appropriate conditions, Cr is a human and animal carcinogenic agent; its biological effects depend on chemical form, solubility and valence [24]. In general, Cr+6 compounds are hazardous to animals, whereas metallic Cr and Cr+3 are essentially non-toxic; however, exposure to water solubilized Cr+3 has caused cancers and dermatitis in workers, and toxicity in rabbits [24].

There is little consistent convincing evidence of associations between exposure to trivalent chromium and cancer [926].

Classification of carcinogenicity for trivalent chromium: 1) evidence in humans: inadequate; 2) evidence in animals: inadequate. Overall summary evaluation of carcinogenic risk to humans is group 3: The chemical is not classifiable as to its carcinogenicity to humans. /From table, trivalent chromium cmpd/ (IARC. Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man. Geneva: World Health Organization, International Agency for Research on Cancer,1972-present. (Multivolume work).,p. S7 60, 1987) [609].

Experiments in mice, rats, hamsters, guinea pigs and rabbits to investigate the carcinogenicity of chromic(iii) acetate, chromic(iii) oxide ... Chromium(vi) trioxide, chromium metal ... Sodium chromate(vi) ...

Sodium dichromate(vi) ... Chromium(iii) sulfate ... Were inadequate to evaluate the carcinogenicity of these chromium compounds (IARC. Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man. Geneva: World Health Organization, International Agency for Research on Cancer,1972-PRESENT, Multivolume work, p. V23 302, 1980) [609].

More than 100 years have passed since the first cancer case in a chromium worker was reported in Scotland....All chromium VI compounds should be considered carcinogenic, but no evidence has been presented indicating that human exposure to chromium III is associated with increased cancer risk [Langard S. 1990. One hundred years of chromium and cancer: a review of epidemiological evidence and selected case reports. Am-J-Ind-Med 17(2); P 189-215, Department of Occupational Medicine, Telemark Central Hospital, Porsgrunn, Norway].

Br.Dev: Brief Summary of Developmental, Reproductive, Endocrine, and Genotoxicity Information:

Exposure of eggs and spermatozoa of rainbow trout (Oncorhynchus) to 5 ug/L of Cr+3 reduced the fertilization rate by 60 to 70 % [926].

Turkey hens fed 10 ug/g wet weight of Cr+3 in their diet produced significantly fewer eggs than controls; however, egg fertility and hatchability were unaffected [926].

The reproductive effects seen in mice after oral dosing suggest a potential for chromium VI and chromium III to produce reproductive effects in humans exposed by the oral route. Levels of chromium found in drinking water and food, however, are probably not high enough to elicit reproductive effects in humans [927].

In a study of a freshwater fish, Clarias batrachus, chromium did not cause any changes of protein concentration in the kidney and testis. In general, the biochemical parameters of the organs were affected by treatments of cations in the following order: cadmium > copper > chromium over control values of Clarias batrachus (Jana S, Sahana SS; Physiol Bohemoslov 37, 1: 79-82, 1988) [366].

While a variety of genetic effects have been induced by trivalent chromium in subcellular or acellular systems, in general, trivalent compounds have not been genotoxic in cultured animal or human cells [926].

One article reviewed approximately 700 results reported in the literature with 32 chromium compounds assayed in

130 short-term tests, using different targets and/or genetic end-points. The large majority of the results obtained with Cr VI compounds were positive, as a function of Cr VI solubility and bioavailability to target cells. On the other hand, Cr III compounds, although even more reactive than Cr VI with purified nucleic acids, did not induce genotoxic effects in the majority of studies using intact cells. Coupled with the findings of metabolic studies, the large data-base generated in short-term test systems provides useful information for predicting and interpreting the peculiar patterns of Cr VI carcinogenicity [De Flora S; Bagnasco M; Serra D; Zanacchi P, 1990. Genotoxicity of chromium compounds. A review. Mutat-Res; 1990 Mar; 238(2); P 99-172. Institute of Hygiene and Preventive Medicine, University of Genoa, Italy].

Br.Fate: Brief Summary of Key Bioconcentration, Fate, Transport, Persistence, Pathway, and Chemical/Physical Information:

Most of the chromium in surface waters may be present in particulate form as sediment; some of the particulate chromium would remain as suspended matter and ultimately be deposited in sediments [366].

In natural waters, chromium is commonly precipitated as insoluble (sic, actually "relatively insoluble") chromium hydroxide, formed from the reaction of trivalent chromium with aqueous hydroxide ion [445]. In waters where conditions favor the formation of hexavalent chromium, chromium will remain in solubilized form [445].

There is little tendency for chromium (+3) to biomagnify in food chains in the inorganic form. However, organo-trivalent chromium compounds may have significantly difference accumulation tendencies although little is know about these compounds [24]. Organic forms of chromium with toxicological significance have not been found in nature [445].

Since Cr+3 forms highly insoluble (sic, actually "relatively insoluble") oxides, hydroxides, and phosphates, and is adsorbed by suspended particles, dissolved Cr+3 is removed rapidly from surface waters by settling particulate matter. However, Cr+3 can also form stable complexes with many dissolved or colloidal organic, and inorganic ligands. This complexed Cr+3 is relatively unaffected by adsorbtion and precipitation reactions, and can thus remain in the water column [926].

Although there are few oxidants capable of converting Cr+3 to Cr+6, and the oxidation kinetics are normally very slow, it has recently been suggested that unstable (including dissolved and colloidal) forms of Cr+3 can be converted to Cr+6 relatively quickly by strong oxidants such as H2O2 that are produced photochemically in aerobic surface waters [926].

Due to its association with suspended particulate phases, a large proportion of the Cr+3 discharged to surface water is transferred to sediment. In aerobic sediments, some Cr+3 can be oxidized by manganese oxides and hydroxides present at the sediment-water interface. It has been suggested that the resulting Cr+6 can be released to the overlying waters, especially by bioturbation processes [926].

In contrast to Cr+3, Cr+6 is not readily adsorbed to surfaces and, since most of its salts are soluble, much of the Cr+6 released to aerobic surface waters is present in a soluble form as hydrochromate, chromate, and dichromate ionic species [926]. However, dissolved Cr+6 can be converted to Cr+3 by a host of reducing agents such as S(2-), Fe(II), fulvic acid, low molecular weight organic compounds, and proteins, and is thus removed from solution, especially in deeper anaerobic waters [926]. Effectiveness of reducing agents varies with pH, redox conditions, and total concentrations of chromium. A small amount of Cr+6 can also be taken up by plankton and released as Cr+3 at lower depths where oxygen is depleted [926].

Chromium is released to the atmosphere primarily in particulate form [926]. Since airborne chromium is associated mostly with the particulate phases, it is removed from the atmosphere by both dry fallout and wet precipitation. The residence time of chromium in the atmosphere is estimated to be less than 14 days [926].

One strategy for remediation of hexavalent chromium in soils or sediments is to provide additional reducing agents (such as organic matter) to facilitate the conversion of relatively soluble Chromium +6 to essentially insoluble (and thus less mobile) chromium +3 [445].

Synonyms/Substance Identification:

Chromium (III) [617]
Chromium (III) ion [617]
Cr+3 [617]
Chromium (+3)
Chromium (+3) ion [617]
Chromium trivalent ion [617]
Chromic ion [617]

Associated Chemicals or Topics (Includes Transformation Products):

See also individual entries:

Chromium
Chromium VI

Water Data Interpretation, Concentrations and Toxicity (All Water Data Subsections Start with "W."):

W.Low (Water Concentrations Considered Low):

No information found.

W.High (Water Concentrations Considered High):

No information found.

W.Typical (Water Concentrations Considered Typical):

California, 1986: Ambient background level for water concentrations of chromium +3 was 5 ug/l [222].

W.Concern Levels, Water Quality Criteria, LC50 Values, Water Quality Standards, Screening Levels, Dose/Response Data, and Other Water Benchmarks:

W.General (General Water Quality Standards, Criteria, and Benchmarks Related to Protection of Aquatic Biota in General; Includes Water Concentrations Versus Mixed or General Aquatic Biota):

EPA Water Quality Criteria are as low as 57 ug/L [1001,1003].

Notes on total vs. acid soluble vs. dissolved metals:

Although most of the lab tests done to develop water quality criteria and other benchmarks were originally based on "total" values rather than "dissolved" values, some regulatory authorities nevertheless recommend comparing criteria with dissolved or acid soluble metals concentrations. EPA gave many reasons why water quality criteria should be compared to acid soluble values. For detailed discussion, see the Laboratory and/or Field Analyses section (far below) and USEPA 1984 Ambient Water Quality Criteria Document for Chromium.

EPA 1996 IRIS information [893]:

Ambient Water Quality Criteria for Aquatic Organisms

Acute Freshwater: 9.8E+2 ug/L hardness dependent criteria for Chromium (III), insoluble salts CASRN: 16065-83-1 [893]. No criteria given for soluble salts [893].

Older reference: Water Quality Criteria in ug/L for CHROMIUM (III) (CAS# 1308-14-1)[446]: Freshwater Acute Criteria: 1700 is the hardness dependent criterion rounded to two digits (100 mg/L CaCO3 used) [446,689]. The equation is acute = e(0.8190[ln(hardness)+3.688) [445,689]. Further clarification:

e is the base of natural logarithms and numerically equals 2.72 (rounded), and In(hardness) equals the natural logarithm of the measured hardness (Gary Rosenlieb, National Park Service, Personal Communication, 1997).

Chronic Freshwater: 1.2E+2 ug/L hardness dep. criterion for Chromium (III), insoluble salts CASRN: 16065-83-1. No criteria given for soluble salts [893].

Older reference [446]: Freshwater Chronic Criteria: 210 is the hardness dependent criterion rounded to two digits (100 mg/L CaCO3 used) [46,689]. The equation is chronic = e(0.8190[ln(hardness)+1.5161) [445,649]. Further clarification:

e is the base of natural logarithms and numerically equals 2.72 (rounded), and In(hardness) equals the natural logarithm of the measured hardness (Gary Rosenlieb, National Park Service, Personal Communication, 1997).

Marine Acute Criteria: 1.03 ug/L LEC [893]. No criteria given for soluble salts [893].

Older references: Marine Acute Criteria: Insufficient data to develop criteria. Lowest Observed Effect Level: 10,300 ug/L [446,928].

Marine Chronic Criteria: None Published [893].

Note: Before citing a concentration as EPA's water quality criteria, it is prudent to make sure you have the latest one. Work on the replacement for the Gold Book [302] was underway in March of 1996, and IRIS is updated monthly [893]..

Adverse effects of chromium to sensitive species have been documented at 10.0 ug/L (ppb) of Cr+6 and 30.0 ug/L of Cr+3 in freshwater and 5.0 of Cr+6 in saltwater [24].

Oak Ridge National Lab, 1994: Ecological Risk Assessment Freshwater Screening Benchmarks for concentrations of contaminants in water [649]. To be considered unlikely to represent an ecological risk, field concentrations should be below all of the following benchmarks [649]:

For CAS 16065-83-1 CHROMIUM III (ug/L):

NATIONAL AMBIENT WATER QUALITY CRITERION - ACUTE: 1700

NOTE: The above is a hardness dependent criterion (100 mg/L CaCO3 was used to calculate the above concentration). For sites with different water hardness, site-specific criteria should be calculated with the following formula:

The equation for freshwater acute criteria = e(0.8190[ln(hardness)]+3.688) [649], where "e" = exponential.

NATIONAL AMBIENT WATER QUALITY CRITERION CHRONIC: 210

NOTE: The above is a hardness dependent criterion (100 mg/L CaCO3 was used to calculate the above concentration). For sites with different water hardness, site-specific criteria should be calculated with the following formula:

The equation for freshwater acute criteria = e(0.8190[ln(hardness)]+1.5161) [649], where "e" = exponential.

SECONDARY ACUTE VALUE: no information found.

SECONDARY CHRONIC VALUE: no information found.

LOWEST CHRONIC VALUE - FISH: 68.63

LOWEST CHRONIC VALUE - DAPHNIDS: <44

LOWEST CHRONIC VALUE - NON-DAPHNID INVERTEBRATES: no information found.

LOWEST CHRONIC VALUE - AQUATIC PLANTS: 397

LOWEST TEST EC20 - FISH: 89

LOWEST TEST EC20 - DAPHNIDS: no information found.

SENSITIVE SPECIES TEST EC20: 8.44

POPULATION EC2O: 126

A State of California recommendation based on direct toxicity was that 24 ug/L be the water quality criteria for chromium +3 (116 ug/l was an adverse effects level) [222].

W.Plants (Water Concentrations vs. Plants):

No information found.

W.Invertebrates (Water Concentrations vs. Invertebrates):

No information found.

W.Fish (Water Concentrations vs. Fish):

There appear to be some exceptions to the generalization that hexavalent chromium is more hazardous than trivalent. One author stated that fish are sometimes more sensitive to Cr+3 than to Cr+6 [926]. Another stated that in soft water, trivalent chromium is more toxic to fish than Cr+6 [445]. The mean 96-h LC50 for Cr+3 has been reported to be about four-fold lower than that for Cr+6 in salmonid fish, with their reproductive cycles being particularly sensitive to Cr+3 [926]. However, the data are mixed and there appear to cases where chromium 6 is as hazardous or more hazardous to fish (and certainly to aquatic life other than fish) as chromium 3:

> A comparison of the lowest EC20 value for fish in general shows that the value for chromium 6 (51 ug/L) is lower than the value for chromium 3 (89 ug/L [649]. The lowest chronic values for fish in general shows little difference between chromium 6 (73.18 ug/L) vs. chromium 3 (68.63 ug/L), and both the acute and chronic national ambient water quality criteria for chromium 6 are much lower concentrations than the equivalent concentrations for chromium 3 [649].

Exposure of eggs and spermatozoa of rainbow trout (Oncorhynchus) to 5 ug/L of Cr+3 reduced the fertilization rate by 60 to 70 % [926].

W.Wildlife (Water Concentrations vs. Wildlife or Domestic Animals):

Oak Ridge National Lab, 1994: Risk Assessment Screening Benchmarks for Wildlife derived from No-Observed-Adverse-Effect (NOAEL) levels (see Tis.Wildlife, B) section below for these). To be considered unlikely to represent an ecological risk, water concentrations should be below the following benchmarks for each species present at the site [650]:

CAS 16065-83-1 CHROMIUM III (AS CHROMIC OXIDE)

SPECIES	WATER CONCENTRATION (ppm)
Rat (test species)	0.000
Short-tailed Shrew	35179.034
Little Brown Bat	60803.310
White-footed Mouse	22735.073
Meadow Vole	39790.415
Cottontail Rabbit	18854.438
Mink	19551.580
Red Fox	13953.622
Whitetail Deer	7807.2560

Comment: Actually, the number of significant figures for a benchmark value should never be more than one; even if these values have been taken directly from another report, they should be rounded; otherwise the impression is given of a level of accuracy that is simply unwarranted. The uncertainties are too large to justify such a fine distinction (Owen Hoffman, SENES Oak Ridge, Personal Communication, 1997).

W.Human (Drinking Water and Other Human Concern Levels):

Water health based limits (HBL) for Chromium III, EPA 1996: 40 mg/L, based on RfD [952].

Ambient Water Quality Criteria for Human Health, IRIS 1996 EPA information listed for Chromium III [893]:

Water & Fish: 1.7E+5 ug/liter for Chromium (III), insoluble salts CASRN: 16065-83-1 [893]. No criteria given for soluble salts [893].

Older references to Human Health (10-6 Risk Level for Carcinogens) in ug/L [446]: Published Criteria for Water and Organisms: 170,000. IRIS Recalculated (9/90) Criteria for Water and Organisms: 33,000 [446].

Fish Only: 3.433E+6 ug/liter for Chromium (III), insoluble salts CASRN: 16065-83-1 [893]. No criteria given for soluble salts [893].

Older reference to Human Health (10-6 Risk Level for Carcinogens) in ug/L [446]: Published Criteria for Organisms Only: 3,433,000. IRIS Recalculated (9/90) Criteria for Organisms Only: 670,000.

Reference: 45 FR 79318 (11/28/80); 50 FR 30784 (07/29/85) [893].

Contact: Criteria and Standards Division / OWRS / (202)260-1315 [893].

Discussion: The WQC of 1.7E+5 ug/L is based on consumption of contaminated aquatic organisms and water. A WQC of 3.433E+6 ug/L has also been established based on consumption of contaminated aquatic organisms alone. [893].

EPA has set the maximum level of Cr+3 and Cr+6 allowed in drinking water at 100 ug Cr/L [927]. According to the EPA, the following levels of Cr+3 and Cr+6 in drinking water are not expected to cause effects that are harmful to health: 1400 ug/L for 10 days of exposure to children, 240 ug/L for longer-term exposure to children, 840 ug/L for longer-term exposure for adults, and 120 ug/L for lifetime exposure of adults [927].

Most other benchmarks are for total chromium not for Chromium III:

EPA 1996 IRIS information [893] listed under Chromium (III), insoluble salts CASRN: 16065-83-1:

Maximum Contaminant Level Goal

Value: 0.1 mg/L total chromium Status/Year: Final 1991 Econ/Tech?: No, does not consider economic or technical feasibility Reference: 56 FR 3526 (01/30/91) [893].

Note : No MCLG given for soluble salts [893].

Contact: Health and Ecological Criteria Division / (202)260-7571 Safe Drinking Water Hotline / (800)426-4791 [893].

Discussion: An MCLG of 0.1 mg/L for total chromium (Cr III and Cr VI) is based on the EPA's RfD methodology for Cr VI, the more toxic chromium species. The MCLG is based upon a DWEL of 0.17 mg/L calculated from available human and animal data and an assumed drinking water contribution of 20 percent. An uncertainty factor of 500 was applied. The MCLG also falls into the safe and adequate daily dietary intake range of 50 to 200 mg/day for Cr III established by the National Research Council in the National Academy of Sciences (NAS, 1989).

[893].

Maximum Contaminant Level (MCL)

Value: 0.1 mg/L total chromium [893] Status/Year: Final 1991 Econ/Tech?: No, does not consider economic or technical feasibility Reference: 56 FR 3526 (01/30/91) [893].

Note : No MCL given for soluble salts [893].

Contact: Drinking Water Standards Division / OGWDW / (202)260-7575 Safe Drinking Water Hotline / (800)426-4791 [893].

Discussion: The EPA has established an MCL equal to the MCLG of 0.1 mg/L [893].

Note: Before citing a concentration as EPA's water quality criteria, it is prudent to make sure you have the latest one. Work on the replacement for the Gold Book [302] was underway in March of 1996, and IRIS is updated monthly [893].

W.Misc. (Other Non-concentration Water Information):

There appear to be some exceptions to the generalization that hexavalent chromium is more hazardous than trivalent (see W.Fish and W.Invertebrates sections above).

A potential complication in comparing contaminants data is that different investigators have sometimes meant different things when they put the words "dissolved" or "total" in front of a reported measurement. In the case of nutrients, the "dissolved" portion is usually simply that portion which has passed through a 0.45-micrometer membrane filter and the "total" measurements implies that it was not filtered and includes both dissolved and other forms of the nutrient [141]. However, usage of the words dissolved and total has not been uniform in the past and there is still considerable debate about which methods should truly be considered "dissolved" or "total" (Merle Schlockey, USGS, personal communication).

Water bodies are often marked by heterogeneity of the distribution of undissolved materials [691]. The size of any effects depends on the difference in density of the undissolved materials and the water, the size of the particles or bubbles of the materials, and various hydrodynamic factors such as the degree of turbulence in the water. Thus, undissolved inorganic materials in rivers and other natural water-bodies tend to increase in concentration with increasing depth because the particles tend to settle [691]. On the other hand, certain biological detritus may tend to rise towards the surface of the water because its density is less than that of water; oils also commonly demonstrate this effect markedly [691]. The surface microlayer is usually higher in concentration of many metallic and organic contaminants than the water column further down.

If the only change one makes is to use the prefix "dissolved" rather than the prefix "total" in an otherwise identical water quality standard, the effect can be a weakening of the standard related to total loading of a system. Many contaminants which are not currently dissolved can become dissolved at a later time, when encountering different conditions (perhaps downstream), such as changes in pH, additions of surfactants or humic substances, bioturbation, methylating organisms, and various other physical, chemical, or biological changes.

One problem with relying too heavily on dissolved fractions of metals is that the dissolved fraction misses the metals carried by colloids. Colloids were found to carry toxic metals 140 miles downstream of mining sources in Leadville, Colorado, to be repeatedly washed from flood deposited lowlands back into the river year after year in spring runoff (Briant Kimball, USGS Salt Lake City, as quoted in U.S. Water News, April 5th, 1995).

See Laboratory section below for EPA generic (guesstimate) conversion factors to convert total to dissolved concentrations.

Some environmental toxicologists make the argument that dissolved metals in surface water and porewaters represent most of what is bioavailable and thus "total" metals parameters are not good as a measure of potential biological effects. This is mostly true in many situations, but it should be kept in mind that fish and other aquatic organisms do not typically live in filtered water and that many fish and other aquatic organisms live in the sediments and in other situations in which they come in contact with toxic or otherwise harmful compounds (as certain colloids, precipitates, oxides, adsorbed metals), etc. Sometimes the effect of total metals is partially related to physical or chemical aspects, such as when ferric oxide coats or covers benthic organisms. Another factor to consider: contaminants carried downstream by erosion of bottom sediments or colloids can be mobilized when they come in contact with different physical/chemical environments downstream (for example, a tributary bringing low pH into the system).

Misc. Notes on colloids (Briant Kimball, USGS, Salt Lake City Office, Personal Communication, 1995):

> There is no question that dissolved metals are critical to fish and invertebrates, but less well recognized is the potential impact and movement of metals in colloids. The possibility of having colloidal material present means there is a readily available supply of metals in a state in which the metals can quickly be reduced and mobilized. In river banks, reducing environments form just under the surface quickly. Toxic metals of concern would include zinc, lead, copper, and cadmium.
>
> Colloids do move in surface water (for example, transport of metal in colloids 140 miles downstream of Leadville, CO), but also in groundwater, especially related to radionuclides.
>
> Colloidal metals may effect biota more than is widely recognized. Brown trout are effected by colloids which travel kind of like dissolved fractions, don't settle out. There may be little understood colloidal pathways of metals to fish, for example. Colloidal metals become part of the caddis cast which are ingested, once part of acid gut, metals can be released. On the Arkansas River of Colorado below Leadville, the dissolved metals have gone down with treatment, but Will Clements of CSU has discovered the toxicity has not been reduced to the same extent as have the

dissolved metals. Treatment has not eliminated colloidal fractions loaded with cadmium and copper, and this is possibly impacting the fish.

In rivers, there is annual flushing of the colloids, loads are much greater during runoff.

Sediment Data Interpretation, Concentrations and Toxicity (All Sediment Data Subsections Start with "Sed."):

Sed.Low (Sediment Concentrations Considered Low):

No information found.

Sed.High (Sediment Concentrations Considered High):

No information found.

Sed.Typical (Sediment Concentrations Considered Typical):

No information found.

Sed.Concern Levels, Sediment Quality Criteria, LC50 Values, Sediment Quality Standards, Screening Levels, Dose/Response Data and Other Sediment Benchmarks:

Sed.General (General Sediment Quality Standards, Criteria, and Benchmarks Related to Protection of Aquatic Biota in General; Includes Sediment Concentrations Versus Mixed or General Aquatic Biota):

No information found.

Sed.Plants (Sediment Concentrations vs. Plants):

No information found.

Sed.Invertebrates (Sediment Concentrations vs. Invertebrates):

No information found.

Sed.Fish (Sediment Concentrations vs. Fish):

No information found.

Sed.Wildlife (Sediment Concentrations vs. Wildlife or Domestic Animals):

No information found.

Sed.Human (Sediment Concentrations vs. Human):

No information found.

Sed.Misc. (Other Non-concentration Sediment Information):

No information found.

Soil Data Interpretation, Concentrations and Toxicity (All Soil Data Subsections Start with "Soil."):

Soil.Low (Soil Concentrations Considered Low):

No information found.

Soil.High (Soil Concentrations Considered High):

No information found.

Soil.Typical (Soil Concentrations Considered Typical):

No information found.

Soil.Concern Levels, Soil Quality Criteria, LC50 Values, Soil Quality Standards, Screening Levels, Dose/Response Data and Other Soil Benchmarks:

Soil.General (General Soil Quality Standards, Criteria, and Benchmarks Related to Protection of Soil-dwelling Biota in General; Includes Soil Concentrations Versus Mixed or General Soil-dwelling Biota):

No information found.

Soil.Plants (Soil Concentrations vs. Plants):

Levels of 200 ug/g dry wt of Cr+3 in soils resulted in a significant (23 to 36%) reduction in the yields of grass, lettuce, and radish. Other studies reported that levels of Cr+3 of 150 ug/g dry wt or more in soil can inhibit the growth of sensitive plant species depending on the nature of the soil [926].

Soil.Invertebrates (Soil Concentrations vs. Invertebrates):

No information found.

Soil.Wildlife (Soil Concentrations vs. Wildlife or Domestic Animals):

No information found.

Soil.Human (Soil Concentrations vs. Human):

EPA 1996 National Generic Soil Screening Level (SSL) designed to be conservative and protective at the majority of sites in the U.S. but not necessarily protective of all known human exposure pathways, land uses, or ecological threats [952]:

SSL = 78000 mg/kg for ingestion pathway [952].

SSL = none given for inhalation pathway [952].

SSL = none given for protection from migration to groundwater at 1 to 20 Dilution-Attenuation Factor (DAF) [952].

EPA 1995 Region 9 Preliminary remediation goals (PRGs), 1995 [868]:

Residential Soil: none given
Industrial Soil: none given

NOTE:
1) PRGs focus on the human exposure pathways of ingestion, inhalation of particulates and volatiles, and dermal absorption. Values do not consider impact to groundwater or ecological receptors.
2) Values are based on a non-carcinogenic hazard quotient of one.
3) PRGs for residential and industrial landuses are slightly lower concentrations than EPA Region III RBCs, which consider fewer aspects [903].

EPA 1995 Region 3 Risk based concentration (RBC) to protect from transfers to groundwater [903]: None given.

Soil.Misc. (Other Non-concentration Soil Information):

The greatest chromium toxicity risk to plants is posed in acidic sandy soil with low organic content [366]. In plants, chromium interferes with uptake translocation, and accumulation by plant tops of calcium, potassium, magnesium, phosphorus, boron, copper and aggravates iron deficiency chlorosis by interfering with iron metabolism [366].

Tissue and Food Concentrations (All Tissue Data Interpretation Subsections Start with "Tis."):

Tis.Plants:

A) As Food: Concentrations or Doses of Concern to Living Things Which Eat Plants:

No information found.

B) Body Burden Residues in Plants: Typical, Elevated, or of Concern Related to the Well-being of the Organism Itself:

No information found.

Tis.Invertebrates:

A) As Food: Concentrations or Doses of Concern to Living Things Which Eat Invertebrates:

No information found.

B) Concentrations or Doses of Concern in Food Items Eaten by Invertebrates:

No information found.

C) Body Burden Residues in Invertebrates: Typical, Elevated, or of Concern Related to the Well-being of the Organism Itself:

No information found.

Tis.Fish:

A) As Food: Concentrations or Doses of Concern to Living Things Which Eat Fish (Includes FDA Action Levels for Fish and Similar Benchmark Levels From Other Countries):

No information found.

B) Concentrations or Doses of Concern in Food Items Eaten by Fish:

No information found.

C) Body Burden Residues in Fish: Typical, Elevated, or of Concern Related to the Well-being of the Organism Itself:

No information found.

Tis.Wildlife: Terrestrial and Aquatic Wildlife, Domestic Animals and all Birds Whether Aquatic or not:

A) As Food: Concentrations or Doses of Concern to Living Things Which Eat Wildlife, Domestic Animals, or Birds:

No information found.

B) Concentrations or Doses of Concern in Food Items Eaten by Wildlife, Birds, or Domestic Animals (Includes LD50 Values Which do not Fit Well into Other Categories, Includes Oral Doses Administered in Laboratory Experiments):

Turkey hens fed 10 ug/g wet weight of Cr+3 in their diet produced significantly fewer eggs than controls; however, egg fertility and hatchability were unaffected [926].

Adverse effects of chromium to sensitive species of wildlife have been documented at 5.1 and 10.0 mg/kg of diet (ppm) of Cr+6 and Cr+3, respectively [24].

Oak Ridge National Lab, 1994: Risk Assessment Screening Benchmarks for Wildlife derived from No-Observed-Adverse-Effect (NOAEL) levels (mg contaminant per kg body weight per day). To be considered unlikely to represent an ecological risk, wet-weight field concentrations should be below the following (right column) benchmarks for each species present at the site [650]:

CAS 16065-83-1 CHROMIUM III (AS CHROMIC OXIDE)

SPECIES	NOAEL (mg/kg/day)	FOOD CONCENTRATION (ppm)
Rat (test species)	2737.0000	0.000
Short-tailed Shrew	7739.3880	12898.979
Little Brown Bat	9728.5300	29185.589
White-footed Mouse	6820.5220	44132.789
Meadow Vole	5425.9660	47748.498
Cottontail Rabbit	1822.5960	9228.3330
Mink	1935.6060	14128.514
Red Fox	1178.3060	11783.059
Whitetail Deer	511.27200	16601.635

Comment: Actually, the number of significant figures for a benchmark value should never be more than one; even if these values have been taken directly from another report, they should be rounded; otherwise the impression is given of a level of accuracy that is simply unwarranted. The uncertainties are too large to justify such a fine distinction (Owen Hoffman, SENES Oak Ridge, Personal Communication, 1997).

C) Body Burden Residues in Wildlife, Birds, or Domestic Animals: Typical, Elevated, or of Concern Related to the

Well-being of the Organism Itself:

No information found.

Tis.Human:

A) Typical Concentrations in Human Food Survey Items:

No information found.

B) Concentrations or Doses of Concern in Food Items Eaten by Humans (Includes Allowable Tolerances in Human Food, FDA, State and Standards of Other Countries):

Crit. Dose: 1468 mg/kg-day for insoluble salts of Chromium III [Study 1 NOAEL(adj)] UF: 100 MF: 10 [893].

Note : No Crit. Dose given for soluble salts [893].

RfD for insoluble salts of Chromium III: 1E+0 mg/kg-day Confidence: Low [893,952].

Note : No RfD given for soluble salts [893].

C) Body Burden Residues in Humans: Typical, Elevated, or of Concern Related to the Well-being of Humans:

No information found.

Tis.Misc. (Other Tissue Information):

In the body, chromium +6 can be reduced to chromium +3, but the reverse reaction does not occur (in the body) [483].

Freshwater fish can regulate chromium over a wide range of ambient concentrations [180]. Some have even stated that freshwater fish seem to be relatively tolerant of chromium, although some aquatic invertebrates are very sensitive [302,375].

Bio.Detail: Detailed Information on Bioconcentration, Biomagnification, or Bioavailability:

No information found.

Interactions:

No information found.

Uses/Sources:

Chromium is used in a wide variety of industrial applications in Canada including the production of stainless and heat-resistant steels, refractory products such as bricks and mortars, and in pigments, metal finishing, leather tanning, and wood preservatives [926]. Both trivalent and hexavalent forms of chromium are released into the environment in Canada as a result of these industrial uses, as well as from the production and combustion of fossil fuels, and the smelting and refining of nonferrous base metals [926].

Information from HSDB [609]:

> Drinking water generally contains the same chromium levels as the surface and groundwaters, which serve as its source. Although some piping materials contain significant levels of chromium (corrosion resistant steel, 8-14%; cement, 5-120 ppm chromium), little is leached into the water. However, it should be noted that Cr III may be oxidized to Cr VI during the chlorination process. /Total chromium/ [Nat'l Research Council Canada; Effects of Chromium in the Canadian Environment p.36 (1976) NRCC No 15017].
>
> Occupational exposure: Chromium & its compounds are found in 3 main types of indust activity: (I) most Cr deriv are used in metallurgical indust ... (II) chromium compounds are ... Component of refractory materials ... & (III) many of highly colored chromate salts ... Are used in pigment, paint, tanning & dyeing industries. [IARC. Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man. Geneva: World Health Organization, International Agency for Research on Cancer,1972-present. (Multivolume work).,p. V23 243 (1980)].

Forms/Preparations/Formulations:

No information found.

Chem.Detail: Detailed Information on Chemical/Physical Properties:

No information found on Cr+3. See sources such as ATSDR for chemical/physical information of a variety of Cr+3 compounds [927].

Fate.Detail: Detailed Information on Fate, Transport, Persistence, and/or Pathways:

See Br.Fate section above for information on chromium III. Additional information on chromium in general [609]:

> TERRESTRIAL FATE: In order to decide on a suitable sampling depth for grassland soil treated with sewage sludge and to assess implications for grazing animals, a field trial on two soils was designed to estimate the

distribution of metals in grassland soil profiles following surface applications of sludge. Soil cores were taken using specialized equipment to 30 cm depth and divided into seven sections. Movement from the soil surface to a depth of 10 cm was observed for all of the seven metals; cadmium, chromium, copper, molybdenum, nickel, lead and zinc, but most of the metal (60%-100%, mean 87%) remained in the upper 5 cm of soil. Sampling to a depth of 5 or 7.5 cm would be most suitable for monitoring long-term grassland treated with surface applications of sludge. [Davis RD et al: Environ Pollut 49 (2): 99-116 (1988)].

TERRESTRIAL FATE: Uptake is greater from ultrabasic soils by a factor of 5-40 than on calcarious or silica-based soils. /Total chromium/ [Schroeder HA et al; J Chron Dis 15: 941-4 (1962) as cited in NAS; Medical and Biological Effects of Environmental Pollutants: Chromium p.12 (1974)].

Aquatic Fate: ... Most of the chromium in surface waters may be present in particulate form as sediment. Some of the particulate chromium would remain as suspended matter and ultimately be deposited in sediments. ... The exact chemical forms of chromium in surface waters are not well defined. Although most of the soluble chromium in surface waters may be present as Cr VI, a small amount may be present as Cr III organic complexes. Hexavalent chromium is the major stable form of chromium in seawater; however, Cr VI may be reduced to Cr III by organic matter present in water, and may eventually deposit in sediments. /Chromium/ [USEPA; Health Assessment Document: Chromium p.3-18 (1984) EPA 600/8-83-014F].

Atmospheric Fate: Under normal conditions, chromium(III) and Cr (0) are relatively unreactive in the atmosphere. Cr VI in air may react with particulate matter or gaseous pollutants to form Cr III. However, these atmospheric reactions have not been extensively studied. ... Chromium is removed from air through wet and dry depositions. The total yearly deposition of chromium in urban areas may vary from 0.12 ug/sq m to 3 ug/sq m. In general, urban areas have higher total deposition than rural areas. Chromium concentration in a wet deposition may vary from 0.004 to 0.060 ug/ml and 0.0006 to 0.034 ug/l for urban and rural areas, respectively. The precipitated chromium from the air enters surface water or soil. /Chromium/ [USEPA; Health Assessment Document: Chromium p.3-17 (1984) EPA 600/8-83-014F].

ATMOSPHERIC FATE: Chromium is associated with particulate matter in the air, and is not expected to exist in gaseous form. /Total chromium/ [Nat'l Research Council Canada; Effects of Chromium in the Canadian Envir p.22

(1976) NRCC No.15017].

Atmospheric Fate: Chromium (Cr) is most highly concn in the smallest particles collected from ambient air. Bulk analysis does not allow adequate characterization of these particles. /Total chromium/ [Natusch DFS et al; Science 183: 202-4 (1974)].

Laboratory and/or Field Analyses:

Determination of chromium has been done many ways [861], often by an atomic absorption technique using either direct aspiration into a flame or a furnace [893]. EPA Method 1639 is a relatively new (1996) lab protocol for trivalent chromium and several other metals. Method 1639 is supposed to be used along with EPA Field Method 1669 for Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels [1003].

In some situations (as when background concentrations are low), water detection limits as low as 0.10 ug/L may be necessary for Chromium III, using EPA method 1639; EPA Water Quality Criteria are as low as 57 ug/L [1001,1003].

Acceptable Containers:

Acceptable containers (after proper cleaning per EPA protocols) for Chromium III: 500-mL or 1-L fluoropolymer, conventional or linear polyethylene, polycarbonate, or polypropylene containers with lid [1003].

Filtration and Preservation (Acidification) of Water Samples:

Only chromium rather than trivalent chromium seems to be addressed in 40 CFR Part 136, Appendix C, pertaining to ICP analyses using method 200.7, 1994 edition of CFR Part 40).

In more recent (1996) guidance related to the more rigorous method 1639, EPA specified:

> For dissolved metal determinations, samples must be filtered through a 0.45-um capsule filter at the field site [1003]. The filtering procedures are described in the Sampling Method 1669 [1003]. Except for trivalent chromium, the filtered samples may be preserved in the field or transported to the laboratory for preservation [1003]. Nitric acid—concentrated (sp gr 1.41), Seastar or equivalent" is specified [1003]. Procedures for field preservation are detailed in the Sampling Method 1669; procedures for laboratory preservation are provided in this method [1003]. To determine trivalent chromium, a field preparation step, which is described in the Sampling Method 1669, is used

to isolate the trivalent chromium [1003]. Related specifications from method 1669:

> For dissolved metal determinations, samples must be filtered through a 0.45-um capsule filter at the field site [1003]. The filtering procedures are described in this method [1003]. The filtered samples may be preserved in the field or transported to the laboratory for preservation [1003].
>
> Nitric acid, "ultrapure" — For use when field-preserving samples for trivalent chromium determinations is specified [1003]. Although seastar brand nitric acid is recommended for Chromium III work in method 1639, no mention of it is made in method 1669 [1003].

Other preservation details for Chromium III: "Preserve on-site immediately after collection [1003]. Chromium (III) extraction solution—For use when field-preserving samples for trivalent chromium determinations [1003]. Prepare this solution by adding 100 mL of ammonium iron (II) sulfate solution to a 125-mL polyethylene bottle [1003]. Adjust pH to 8 with approximately 2 mL of ammonium hydroxide solution [1003]. Cap and shake on a wrist-action shaker for 24 h [1003]. This iron (III) hydroxide solution is stable for 30 days [1003].

Notes on total vs. acid soluble vs. dissolved metals:

There are many things to be considered when interpreting metals data expressed as "dissolved" vs. "total" or "total recoverable" (see W.Misc. Section above).

Although most of the lab tests done to develop water quality criteria and other benchmarks were originally based on "total" values rather than "dissolved" values, the lab settings were typically fairly clean and the numbers generated by the lab tests are therefore often even more comparable to field "dissolved" values than to field "total" values (Glen Suter, Oak Ridge National Lab, Personal Communication, 1995). As of January 1995, the U.S. EPA was recommending that states use dissolved measurements in water quality standards for metals, in concert with recommendations EPA previously made for the Great Lakes [672]. The conversion factors recommended by EPA for converting total recoverable metals criteria to dissolved metal criteria were given as follows [672]:

> Chromium +3 conversion for acute and chronic criteria are 0.333 and 0.860, respectively (for

example, total recoverable metals acute criteria x 0.333 = dissolved metals acute criteria).

The conversion factors recommended by EPA for converting total recoverable Chromium III to dissolved concentrations in the January 1997 draft EPA Guidelines for 5 year 305(B) assessments were:

Criterion Maximum Concentration: 0.316

Criterion Continuous Concentration: 0.860

Note: None of these "generic" conversion factors work well for all areas. Both total and dissolved concentrations should be checked at new locations before relying on generic conversion factors (Pat Davies, Colorado Division of Wildlife, personal communication, 1997).

Sources of potential variation in contaminants data:

Variation in concentrations of contaminants may sometimes be due to differences in how individual investigators treat samples in the field and lab rather than true differences in environmental concentrations. See also, notes in disclaimer section at the top of this entry. It was recognition that collectors and labs often contaminate samples that led EPA to develop the 1600 series of water protocols for low detection limit applications [1001,1002,1003,1004]. In comparing contaminants data from different labs, different states, and different agencies, one should keep in mind that they are often not very comparable. They may be as different as apples and oranges since:

1) Different Agencies (EPA, USGS, NOAA, and various State Agencies) publish different lab and field protocols. Each of these protocols is different and has typically changed over time.

Note: Even "Standard EPA Methods" which are supposedly widely used by consultants, industry, and academia, have been variable over time and between application category (Drinking Water vs. NPDES, vs. RCRA, vs. CERCLA, vs. Water-Quality Based permits, etc.).

Preservation and other details of various EPA lab and field protocols have changed over the years, just as they have at USGS and various States and other agencies. USGS data from 30 years ago may be different than USGS data today due to differences (drift) in lab and field protocols rather than differences in environmental concentrations.

2) Independent labs and field investigators are not always using "the latest and greatest methods," and it is difficult for them to keep up with all the changes from various agencies in the midst of their "real world" busy lives. Updates are not always convenient to obtain. For example, EPA changes are scattered through various proposed Federal Register Notices, various updates of CFRs, and numerous publications originating in many different parts of EPA and their contractors. The wording is sometimes imprecise and is often inconsistent between EPA methods for different applications.

3) The details of the way one person collects, filters, and acidifies water samples in the field may be different than the way another does it. Sources of potential variation include the following:

A) The protocol phrases "As soon as practical or as soon as possible." Different situations can change the elapsed time considered by the field collector to be "as soon as practical." It may take different amounts of time to get to a safe or otherwise optimum place to filter and/or acidify and cool the samples. In one case precipitation and other changes could be going on in the collection bottle while the bottle is on the way to filtration and acidification. In other cases, the field collector filters and acidifies the samples within minutes. Weather, safety concerns, and many other factors could play a role.

B) Differences in numerous other details of the method used can drastically change the results. Some cold, wet, hurried, or fire ant-bitten collectors might decide that it is not "practical" to filter and acidify quite so immediately in the field, and may decide the shore, a vehicle, a motel room, or even a remote lab are more "practical" locations. Filtering and acidifying in the field immediately has been thought of as a better option for consistency (see copper and silver entries for examples of what can happen if there is a delay). However, in recent methodology designed to prevent some the contamination and variability listed above, EPA has recently suggested that waiting until the sample arrives at the lab before acidifying is OK [1003].

C) What kind of .45 micron filter was used? The flat plate filters that were used for years tended to filter .45 micron sizes at first and then smaller and smaller sizes as the filtering proceeded and the filter loaded up with particulate matter. As the filter clogged, the openings grew smaller and colloids and smaller diameter matter began to be trapped on the filter. For this reason, both the USGS and EPA 1600 series protocols have gone to tortuous-path capsule filters that tend to filter .45 micron sizes more reliably over time. Example of specifications from EPA method 1669:

> Filter—0.45-um, 15-mm diameter or larger, tortuous-path capsule filters, Gelman Supor 12175, or equivalent [1003].

D) "Normally 3 mL of (1+1) of nitric acid per liter should be sufficient to preserve the (water) sample" (40 CFR Part 136, Appendix C, pertaining to ICP analyses using method 200.7, 1994 edition of CFR Part 40). Sometimes it is not, depending on alkalinity and other factors. What field collectors sometimes (often?) do is just use pop tabs of 3 mL of nitric acid and hope for the best rather than checking to see that the acidity has been lowered to below a pH of two. EPA CFR guidelines just call for a pH of below two, whereas samples meant to be "acid soluble" metals call for a pH of 1.5 to 2.0 [25]. See also, various USEPA 1984 to 1985 Ambient Water Quality Criteria Documents for individual metals.

> Note: Some shippers will not accept samples with a pH of less than 1 for standard shipping (John Benham, National Parks Service Personal Communication, 1997).

E) One person might use triple distilled concentrated nitric acid rather than reagent grades of acid to avoid possible contamination in the acid, while another may not. When using very low detection limits, some types of acid may introduce contamination and influence the results. Using a 10% dilution of nitric acid as called for by EPA [1003] is another potential source of contamination, since the dilution water and/or containers may be contaminated. Sometimes people may be incorrectly determining that background concentrations are high due to contamination sources such as these (Pat Davies, Colorado Division of Wildlife, personal communication, 1997).

> Note: Just using triple distilled nitric acid may not be the total answer to potential contamination. The key issue to be sure that the acid used is free of the metals being analyzed. In guidance for EPA method 1669, the use of "ultrapure nitric acid; or Nitric acid, dilute, trace-metal grade" is specified [1003]. In guidance for EPA method 1639 but not 1669), the use of "Nitric acid—concentrated (sp gr 1.41), Seastar or equivalent" is specified [1003].

F) Holding times can strongly influence the results and there can be quite a bit of variation even within EPA recommended 6 month limits (see Silver entry for details). Holding times recommended for EPA for water samples of metals other than mercury or chromium VI have usually been listed as 6 months (Federal Register, Volume 49, No. 209, Friday, October 28, 1984, page 43260). In the 1994 version of the CFR, NPDES holding times for mercury and Chromium VI are the same ones listed in 1984, but no EPA holding times are given for other metals (40 CFR, Part 136.3, Table 2, page 397, 1994). EPA sources stated this was a typo, that no one else brought it to their attention in the last 3 years, that 6 months is still an operable holding time for "other metals" including this one, and that 6 months is actually an artifact from the days when 6 month composite samples were used for NPDES permits rather than having been originally scientifically derived.

> Counterpoint: Although some information suggests that 6 months is probably too long for some contaminants in some scenarios (see silver and copper entries), not all of the information in the literature casts the 6 month metals holding time in such questionable light. In one study, two EPA research chemists found that preservation under certain conditions of drinking water (EPA Method 200.8) metals samples to a pH of less than 2 effectively stabilized the metal concentrations for 6 months. They found that trace metal standards in the 10 to 50 ug/L concentration could be held in 1% nitric acid if a 5% change of concentration was acceptable [1009]. Some metal concentrations changed more than 5% (Zinc up to 24%, Selenium up to 23%) [1009]. Vanadium, Manganese and Arsenic changed up to 5-7% [1009]. In some of the trials, metals were higher after 6 months due to leaching from containers, while in some they were lower [1009]. The changes were nevertheless considered not of great consequence related to drinking water MCLs and EPA method 200.8 [1009]. However, it is not clear that the careful measures utilized (like rechecking to make sure the pH was less than 2, the use of particular kinds of water samples, the use of particular acids, etc.) in this one study replicates what goes on in day to day ("real world") contaminants lab work around the country.
>
> Some EPA sources state that 6 months

> should be OK if the sample bottle is vigorously shaken and re-acidified in the lab prior to lab analyses, a practice not universally or even particularly commonly done in labs today. The degree to which a water sample is re-acidified, re-checked for pH, shaken before analysis, and the length of time it sits before and after these steps, seems to vary a lot between laboratories, and EPA guidance for various methods is not consistent. Some labs recheck pH, some don't. Some shake, some don't, etc. For chromium III by method 1639, preservation is considered complete after the sample is held in pH of less than 2 for at least 16 hours [1003].
>
> For many other methods, the minimum holding time in acid is not stated or is different (see various EPA and other Agency methods).

G) If present, air in head space can cause changes in water sample concentrations (Roy Irwin, National Park Service, Personal Communication, based on several discussions with EPA employees and various lab managers in February 1997).

> Note: air from the atmosphere or in headspace can cause oxidation of anaerobic groundwater or anaerobic sediment samples. This oxidation can cause changes in chemical oxidation states of contaminants in the sample, so that the results are not typical of the anaerobic conditions which were present in the environment prior to sampling (John Benham, National Park Service, Personal Communication, 1997).

H) When is the sample shaken in the lab or the field? If the filter is acidified in the field, it will be shaken on the way back to the lab. If lab acidified, how much and when is the sample shaken and then allowed to sit again for various times periods before analyses? Many methods treat this differently, and what many field collectors and labs actually do before analyzing samples is different as well. For EPA method 1638, the word shake appears in the "Alternate total recoverable digestion procedure":

> "..Tightly recap the container and shake thoroughly" [1003].

I) If one field filters and acidifies, one often changes metal concentrations and colloidal content compared to samples not treated in this manner. Acidifying effects microbial changes. If one holds the samples a while before filtering and acidifying, the situation changes. In collection bottles, there are potential aging effects: temperature changes, changes in basic water chemistry as oxygen and other dissolved gasses move from the water into the headspace of air at the top, potential aggregation of colloidal materials, precipitation of greater sizes over time, development of bigger and more colloids, and more sorption (Roy Irwin, National Park Service, personal communication, 1997).

4) The guidance of exactly where to take water samples varies between various state and federal protocols. Taking water samples at the surface microlayer tends to increase concentrations of various contaminants including metals. Other areas of the water column tend to produce different concentrations. Large quantities of anthropogenic substances frequently occur in the surface microlayer at concentrations ranging from 100 to 10,000 times greater than those in the water column [593]. These anthropogenic substances can include plastics, tar lumps, PAHs, chlorinated hydrocarbons, as well as lead, copper, zinc, and nickel [593]. Sometimes a perceived trend can be more the result of the details of the sample micro-location rather than real changes in environmental concentrations (Roy Irwin, National Park Service, personal communication, 1997).

5) Although the above examples are mostly related to water samples, variability in field and lab methods can also greatly impact contaminant concentrations in tissues, soil,

and sediments. Sediment samples from different microhabitats in a river (backwater eddy pools vs. attached bars, vs. detached bars, vs. high gradient riffles vs. low gradient riffles, vs. glides, etc.) tend to have drastically different concentrations of metals as well as very different data variances (Andrew Marcus, Montana State University, personal communication, 1995). Thus, data is only optimally comparable if both data collectors were studying the same mix of microhabitats, a stratified sampling approach which would be unusual when comparing random data from different investigators.

6) Just as there are numerous ways to contaminate, store, ship, and handle water samples, so are there different agency protocols and many different ways to handle samples from other media. One investigator may use dry ice in the field, another may bury the samples in a large amount of regular ice immediately after collection in the field, while a third might place samples on top of a small amount of ice in a large ice chest. The speed with which samples are chilled can result in different results not only for concentrations of organics, but also for the different chemical species (forms) of metals (Roy Irwin, National Park Service, personal communication, 1997).

7) In comparing contaminants metals data, soil and sediment contaminant concentrations should usually be (but seldom has been) normalized for grain size, total organic carbon, and/or acid volatile sulfides before biologically-meaningful or trend-meaningful comparisons are possible (Roy Irwin, National Park Service, Personal Communication, 1997).

8) There has been tremendous variability in the precautions various investigators have utilized to avoid sample contamination. Contamination from collecting gear, clothes, collecting vehicles, skin, hair, collector's breath, improper or inadequately cleaned sample containers, and countless other sources must carefully be avoided when using methods with very low detection limits [1003].

As of 1997, the problem of lack of data comparability (not only for water methods but also for soil, sediment, and tissue methods) between different "standard methods" recommended by different agencies seemed to be getting worse, if anything, rather than better. See also: discussion of comparability of data in the disclaimer section at the top of this entry.

In 1997, the trend in quality assurance seemed to be for various agencies, including the EPA and others, to insist on quality assurance plans for each project. In addition to quality control steps (blanks, duplicates, spikes, etc.), these quality assurance plans call for a step of insuring data comparability [1015,1017]. However, the data comparability step is often not given sufficient consideration. The tendency of agency guidance (such as EPA SW-846 methods and some other new EPA methods for bio-concentratable substances) to allow more and more flexibility to select options at various points along the way, makes it harder in insure data comparability or method validity. Even volunteer monitoring programs are now strongly encouraged to develop and use quality assurance project plans [1015,1017].

At minimum, before using contaminants data from diverse sources, one should determine that field collection methods, detection limits, and lab quality control techniques were acceptable and comparable. The goal is that the analysis in the concentration range of the comparison benchmark concentration should be very precise and accurate.

It should be kept in mind that quality control field and lab blanks and duplicates will not help in the data quality assurance goal as well as intended if one is using a method prone to false negatives. Methods may be prone to quality assurance problems due to the use of detection limits that are too high, the loss or addition of contaminants through inappropriate handling, or the use of inappropriate methods.

> Highlights from EPA Method 1639: Determination of trace elements in ambient waters by stabilized temperature graphite furnace atomic absorption:
>
>> This 1996 proposed EPA method provides procedures to determine dissolved elements in ambient waters at EPA water quality criteria (WQC) levels using stabilized temperature graphite furnace atomic absorption (GFAA) [1003]. It may also be used to determine total recoverable element concentrations in these waters [1003].
>>
>> This method was developed by integrating the analytical procedures contained in EPA Method 200.9 with the stringent quality control (QC) and sample handling procedures necessary to avoid contamination and ensure the validity of analytical results during sampling and analysis for metals at EPA WQC levels [1003]. This method contains QC procedures that will ensure that contamination will be detected when blanks accompanying samples are analyzed [1003]. This method is accompanied by Method 1669: Sampling Ambient Water for Determination of Trace Metals at EPA Water Quality Criteria Levels (the "Sampling Method") [1003]. The Sampling Method 1669 is

necessary to ensure that contamination will not compromise trace metals determinations during the sampling process [1003].

As of March 1997, the EPA 1600 series methods had not yet been officially approved in 40 CFR for use in NPDES permits, but the improvements in these methods were suggested by EPA staff to be wise practice when attempting low detection limit analyses for metals.

Many of the requirements for this method are similar to those for other EPA 1600 series methods [1003].

This method may be used with the following metals [1003]:

Antimony (Sb), CAS 7440-36-0
Cadmium (Cd), CAS 7440-43-9
Trivalent Chromium, CAS 16065-83-1
Nickel (Ni), CAS 7440-02-0
Selenium (Se), CAS 7782-49-2
Zinc (Zn), CAS 7440-66-6

For dissolved metal determinations, samples must be filtered through a 0.45-um capsule filter at the field site [1003]. The filtering procedures are described in the Sampling Method 1669 [1003]. Except for trivalent chromium, the filtered samples may be preserved in the field or transported to the laboratory for preservation [1003]. Nitric acid—concentrated (sp gr 1.41), Seastar or equivalent" is specified [1003]. Procedures for field preservation are detailed in the Sampling Method 1669; procedures for laboratory preservation are provided in this method [1003]. To determine trivalent chromium, a field preparation step, which is described in the Sampling Method 1669, is used to isolate the trivalent chromium [1003].

To determine total recoverable analytes in ambient water samples, a digestion/extraction is required before analysis when the elements are not in solution (e.g., aqueous samples that may contain particulate and suspended solids) [1003].

Construction materials—Only the following materials should come in contact with samples: fluoropolymer (FEP, PTFE), conventional or linear polyethylene, polycarbonate, polypropylene, polysulfone, or ultrapure quartz [1003]. PTFE is less desirable than FEP because the sintered material in PTFE may contain contaminates and is susceptible to serious memory contamination [1003]. Fluoropolymer or glass containers should be used for samples that will be analyzed for mercury because mercury vapors can diffuse in or out of the other materials resulting either in contamination or low-biased results [1003]. All materials, regardless of construction, that will directly or indirectly contact the sample must be cleaned with EPA protocols and must be known to be clean and metal free before proceeding [1003].

The following materials have been found to contain trace metals and must not be used to hold liquids that come in contact with the sample or must not contact the sample itself, unless these materials have been shown to be free of the metals of interest at the desired level: Pyrex, Kimax, methacrylate, polyvinylchloride, nylon, and Vycor [1003]. In addition, highly colored plastics, paper cap liners, pigments used to mark increments on plastics, and rubber all contain trace levels of metals and must be avoided [1003].

Serialization—It is recommended that serial numbers be indelibly marked or etched on each piece of Apparatus so that contamination can be traced, and logbooks should be maintained to track the sample from the container through the labware to injection into the instrument [1003]. It may be useful to dedicate separate sets of labware to different sample types; e.g., receiving waters vs. effluents [1003]. However, the Apparatus used for processing blanks and standards must be mixed with the Apparatus used to process samples so that contamination of all labware can be detected [1003].

Do not dip pH paper or a pH meter into the sample; remove a small aliquot with a clean pipet and test the aliquot [1003]. When the nature of the sample is either unknown or known to be hazardous, acidification should be done in a fume hood [1003].

Store the preserved sample for a minimum of 48 h at 0–4°C to allow the acid to completely dissolve the metal(s) adsorbed on the container walls [1003]. The sample should then verified to be pH < 2 just before withdrawing an aliquot for processing or direct analysis [1003]. If for some reason such as high alkalinity the sample pH is verified to be > 2, more acid must be added and the sample held for 16 h until verified to be pH < 2 [1003].

One of the requirements for the alternate total recoverable digestion procedure is to tightly recap the container and shake thoroughly [1003].

Field and Quality Control Protocol: Highlights from EPA Method 1669 for Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels [1003]:

This "field method details" protocol is for the collection and filtration of ambient water samples for subsequent determination of total and dissolved Antimony, Arsenic, Cadmium, Copper, Chromium III, Chromium VI, Lead, Mercury, Nickel, Selenium, Silver, Thallium, and Zinc, at low (Water Quality Criteria Range) concentrations [1003]. It is designed to support the implementation of water quality monitoring and permitting programs administered under the Clean Water Act [1003].

This method is not intended for determination of metals at concentrations normally found in treated and untreated discharges from industrial facilities [1003]. Existing regulations (40 CFR Parts 400–500) typically limit concentrations in industrial discharges to the mid to high part-per-billion (ppb) range, whereas ambient metals concentrations are normally in the low part-per-trillion (ppt) to low ppb range [1003]. This guidance is therefore directed at the collection of samples to be measured at or near the water quality criteria levels [1003]. Often these methods will be necessary in a water quality criteria-based approach to EPA permitting [1001]. Actual concentration ranges to which this guidance is applicable will be dependent on the sample matrix, dilution levels, and other laboratory operating conditions [1003].

The ease of contaminating ambient water samples with the metal(s) of interest and interfering substances cannot be overemphasized [1003]. This method includes sampling techniques that should maximize the ability of the sampling team to collect samples reliably and eliminate sample contamination [1003].

Clean and ultraclean—The terms "clean" and "ultraclean" have been used in other Agency guidance [1004] to describe the techniques needed to reduce or eliminate contamination in trace metals determinations [1003]. These terms are not used in this sampling method due to a lack of exact definitions [1003]. However, the information provided in this method is consistent with summary guidance on clean and ultraclean techniques [1004].

Preventing ambient water samples from becoming contaminated during the sampling and analytical process is the greatest challenge faced in trace metals determinations [1003]. In recent years, it has been shown that much of the historical trace metals data collected in ambient water are erroneously high because the concentrations reflect contamination from sampling and analysis rather than ambient levels [1003]. Therefore, it is imperative that extreme care be taken to avoid contamination when collecting and analyzing ambient water samples for trace metals [1003].

There are numerous routes by which samples may become contaminated [1003]. Potential sources of trace metals contamination during sampling include metallic or metal-containing sampling equipment, containers, labware (e.g. talc gloves that contain high levels of zinc), reagents, and deionized water; improperly cleaned and stored equipment, labware, and reagents; and atmospheric inputs such as dirt and dust from automobile exhaust, cigarette smoke, nearby roads, bridges, wires, and poles [1003]. Even human contact can be a source of trace metals contamination [1003]. For example, it has been demonstrated that dental work (e.g., mercury amalgam fillings) in the mouths of laboratory personnel can contaminate samples that are directly exposed to exhalation [1003].

For dissolved metal determinations, samples must be filtered through a 0.45-um capsule filter at the field site [1003]. The filtering procedures are described in this method [1003]. The filtered samples may be preserved in the field or transported to the laboratory for preservation [1003].

This document is intended as guidance only [1003]. Use of the terms "must," "may," and "should" are included to mean that EPA believes that these procedures must, may, or should be followed in order to produce the desired results when using this guidance [1003]. In addition, the guidance is intended to be performance-based, in that the use of less stringent procedures may be used so long as neither samples nor blanks are contaminated when following those modified procedures [1003]. Because the only way to measure the performance of the modified procedures is through the collection and analysis of uncontaminated blank samples in accordance with this guidance and the referenced methods, it is highly recommended that any modifications be thoroughly evaluated and demonstrated to be effective before field samples are collected [1003].

The method includes a great many details regarding prevention of field contamination of samples, including clothing needed, clean hands vs. dirty hands operations, and numerous other details [1003].

Trivalent Chromium Statements from Method 1669:

> If samples are to be collected for determination of trivalent chromium, the sampling team processes additional QC aliquots are processed [1003].
>
> Field preservation is necessary for determinations

of trivalent chromium [1003].

Special methods are specified for preservation of aliquots for trivalent chromium [1003].

If samples will be processed for trivalent chromium determinations, the sampling team shall also prepare method blank, OPR, and MS/MSD samples [1003]. Special blanks and other data quality checks are specified for chromium III analyses using method 1669 [1003].

Among the items needed for trivalent chromium analyses using method 1669:

> Nitric acid, ultrapure—For use when field-preserving samples for trivalent chromium determinations [1003]. Although seastar brand nitric acid is recommended for Chromium III work in method 1639, no mention of it is made in method 1669 [1003].
>
> Hydrochloric acid—High-purity, 10% solution—shipped with sampling kit in fluoropolymer wash bottles for cleaning trivalent chromium sample preservation equipment between samples [1003].
>
> For preservation of trivalent chromium, the glove bag or designated clean area must be large enough to accommodate the vacuum filtration apparatus, and an area should be available for setting up the wrist-action shaker [1003].

Since the valence states are subject to change, tissues are often analyzed for total chromium. During the laboratory digestion of tissue samples, most chromium is changed to the trivalent form. Very few methods are available to selectively measure chromium(III) (Harzdorf AC; Int J Environ Anal Chem 29, 4: 249-61, 1987) [699].

Many labs simply analyze residues for total chromium rather than trying to separate chromium 3 and 6. The following information relates to total chromium:

Many methods have been used to monitor for chromium [861,927]. Low concentration criteria or benchmarks may require relatively rigorous methods, while routine applications may require only inductively coupled plasma (ICP) analyses. Detection limits should be no higher than comparison benchmarks or criteria for various media (water, sediments, soil, tissues, etc), some of which are low (see sections above).

Otherwise, in cases where low detecton levels are not needed, the detection limits should usually not exceed the following default concentrations often recommended by the Fish and Wildlife Service and the National Park Service: Total chromium detection limits of 0.50 ppm dry weight in tissues, 1.0 ppm in sediments and soils, 0.003 ppm (mg/L) in water (Roy Irwin, National Park Service, Personal Communication, 1996).

EPA 1996 IRIS information [893]:

> Drinking Water Monitoring Requirements
>
> > Ground water systems monitored every 3 years; surface water systems monitored annually; systems out of compliance must begin monitoring quarterly until system is reliably and consistently below MCL.
>
> Drinking Water Analytical Methods
>
> > Atomic absorption/furnace technique (EPA 218.2; SM 304); inductively coupled plasma (EPA 200.7): PQL= 0.01 mg/L.

See also: Chromium, General entry.