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Title: THE CONCENTRATION AND OXIDATION STATE OF CHRO-  
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The partitioning of chromium (III) and chromium (IV) between the dissolved and particulate phases of surface sea water off the coast of Oregon was examined. Independent measurements made on two aliquots of sea water allowed the determination of chromium (VI), and total chromium (the sum of chromium (VI) and any chromium (III)). Chromium (VI) was extracted and concentrated from one aliquot using a methyl isobutyl ketone extraction procedure, after acidification with hydrochloric acid. Total chromium was extracted and concentrated from the second aliquot using a similar procedure, after oxidation of any chromium (III) to chromium (VI) with potassium peroxydisulfate and a copper (II) catalyst. Both filtered and unfiltered samples were examined using these procedures. The chromium content of the ketone extracts was determined using neutron activation analysis.

Mean values for chromium (VI) and total chromium in filtered sea water were determined to be  $0.189 \pm 0.102 \mu\text{g}/\text{l}$  and  $0.246 \pm 0.127 \mu\text{g}/\text{l}$ , respectively. For unfiltered sea water, mean values for chromium (VI) and total chromium were found to be  $0.156 \pm 0.144 \mu\text{g}/\text{l}$  and  $0.194 \pm 0.186 \mu\text{g}/\text{l}$ , respectively. The precision of the analytical data proved to be poor, due to compounding of counting errors.

At the 68% confidence level, the presence of soluble chromium (III), particulate chromium (III), or particulate chromium (VI) could neither be confirmed nor disproved.

The Concentration and Oxidation State  
of Chromium in Sea Water

by

Harold Milford Stanford

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Assistant Professor of Oceanography

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Date thesis is presented October 13, 1970

Typed by Barbara Eby for Harold Milford Stanford

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# THE CONCENTRATION AND OXIDATION STATE OF CHROMIUM IN SEA WATER

## I. INTRODUCTION

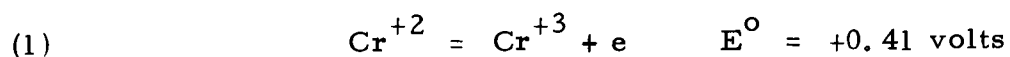
### General Statement

To understand the behavior of a trace element in sea water, it is necessary to know its chemical and physical states. Although difficult to distinguish operationally, "physical states" include: (1) true solution, (2) colloid (embracing sol and gel), and (3) solid. Operationally, dissolved or soluble matter, and particulate or solid matter are arbitrarily separated using membrane filters. The dividing line is often placed at  $0.45\mu$ . Fukai and Huynh-Ngoc (1968) define "chemical state" as the chemical bond characterizing the element or matrix materials involved. Their view of possible chemical states does not lend itself to experimental utilization in a complex medium like sea water, especially during initial attempts to determine the species of a particular trace element. Because of the complex matrix, and the possibility that an element is present in more than one chemical state, a more useful classification, during preliminary investigations, is by oxidation state

The primary purpose of this thesis is to investigate the distribution of oxidation states (chemical states) of the trace element chromium between the dissolved and particulate phases (physical states) in sea water.

## Aqueous Chemistry of Chromium

For chromium, oxidation states<sup>1</sup> from -2 to +6, inclusive have been reported in complexes and compounds. However, only the +2 through +6 have an associated aqueous chemistry. Sky-blue chromium (II) solutions are easily oxidized by molecular oxygen and can be preserved temporarily only by exclusion of air:



The oxidation states +4 and +5 are formed as transient intermediates during oxidation of Cr(III) to Cr(VI) or during the reverse reduction. Because of their ready disproportionation to Cr(III) and Cr(VI), these oxidation states have a highly transitory aqueous chemistry (Cotton and Wilkinson, 1966). Therefore, in natural aerobic aqueous systems, only the +3 and +6 oxidation states need be considered.

Aqueous solutions of Cr(III) salts are characterized by the formation of numerous hexacoordinate complexes which are relatively kinetically inert. Because of this inertness, few thermodynamic data for these complexes are available. Ligand displacement reactions of chromium (III) complexes generally have half-times of the order of

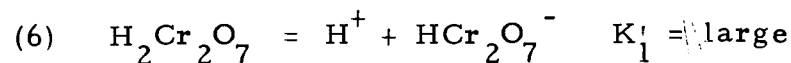
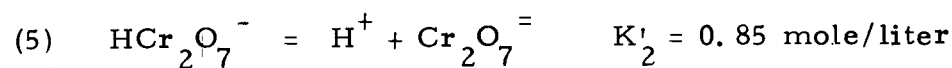
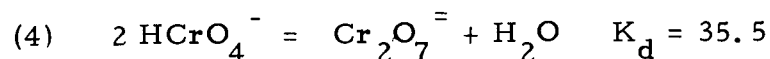
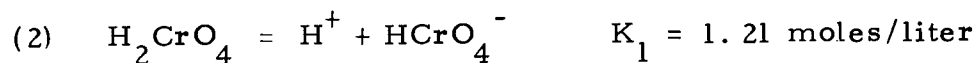
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<sup>1</sup>The term oxidation state is preferred over the term valency state since an element exhibits a valence only when it is combined with some other element--in other words, when it is part of a compound. The oxidation state or oxidation number is that assigned charge an element would have if it were electrovalent (King and Caldwell, 1967).

hours, days or even weeks at 25° C (Cotton and Wilkinson, 1966). As a result, many thermodynamically unstable species remain in solution for relatively long periods of time. The complexes present in solution at any time, therefore, are functions of original chromium salt composition, matrix composition, and past history of the solution. In moderately acidic solution violet hexaquo ions  $[\text{Cr}(\text{H}_2\text{O})_6]^{+3}$ , are present. Hunt and Taube (1951) investigated the rate of exchange of water between the hydrated chromium (III) ion and the solvent water as a function of acidity. In acid solution, at 25° C and 1 M salt concentration, they found the exchange to be independent of the acid concentration and to have a half-time of about 40 hours. In strongly basic solution chromites are formed; Cotton and Wilkinson (1966) suggested that the chromite species include  $[\text{Cr}(\text{OH})_6]^{-3}$  and, perhaps,  $[\text{Cr}(\text{OH})_5(\text{H}_2\text{O})]^{-2}$ . At intermediate pH values hydrous chromic oxide,  $\text{Cr}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ , is formed. This gelatinous, blue-green-gray precipitate, often and incorrectly called chromic hydroxide,  $\text{Cr}(\text{OH})_3$ , is actually a peptized negative sol (Wells, 1949; Weiser, 1933). These aqueous complex ions illustrate the effect of pH on Cr(III) chemistry in the absence of other complexing ions or molecules.

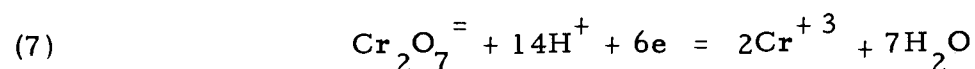
The aqueous chemistry of Cr(VI) is much simpler than that of Cr(III). In moderately acidic to moderately basic solutions,  $4 \leq \text{pH} \leq 10$ , hexavalent chromium has a coordination number of four and forms oxyanions. For solutions lacking other ions, the following equilibria,

at 25° C, are applicable (Wiberg, 1965):



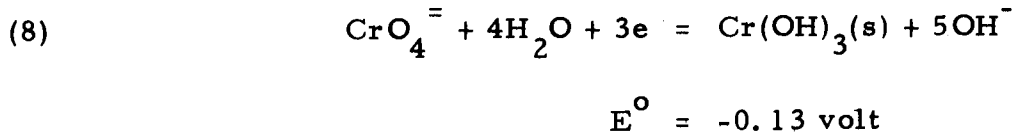
In dilute basic solution, yellow, tetrahedral chromate ion,  $\text{CrO}_4^{=}$ , is the predominant species. As the pH is lowered to about seven, acid chromate (bichromate ion), written as  $\text{HCrO}_4^-$  or as  $\text{CrO}_3(\text{OH})^-$ , forms approximately 25% of the Cr(VI) species (Howard, Nair and Nancollas, 1958; Neuss and Riemann, 1934). In concentrated solution, especially if acidic, orange dichromate ion,  $\text{Cr}_2\text{O}_7^{=}$ , and its protonated forms predominate. These reactions among the several chromium (VI) species are very labile (Cotton and Wilkinson, 1966).

The oxidizing ability of hexavalent chromium is a function of the acidity of the medium. In acid solution dichromate is a strong oxidizing agent:



$$E^{\circ} = 1.33 \text{ volts}$$

In basic solution, the ability of chromium (VI) to oxidize organic compounds virtually vanishes (Stewart, 1964):



Exchange reactions between Cr(III) and Cr(VI) are exceedingly slow in aqueous solution (Muxart et al., 1947; Menker and Garner, 1949; Aten et al., 1953; King and Neptune, 1955; Tong and King, 1960; Altman and King, 1961), due to: (1) the difference of three units of oxidation state, and (2) the difference of two in coordination number between the two chromium species.

#### Chromium in Crustal Rocks and River Water

Crustal Rocks. The average amount of chromium in crustal rocks, as restimated by various investigators, is listed in Table 1.

Table 1. Average crustal abundance of chromium.

<u>Reference</u>	<u>Amount (ppm)</u>
Rankama and Sahama (1950)	200
Barth (1952)	200
Goldschmidt (1954)	200
Turekian (1960)	111, 65
Mason (1966)	100

Turekian and Carr (1960) list the average abundances of chromium (ppm) in major igneous rock types as: (1) ultramafic, 1600; (2) basaltic, 170; (3) high-calcium granitic, 27; and (4) low-calcium granitic, 4.

Chromium is found primarily in the trivalent state in the earth's crust, where it substitutes for aluminum and ferric iron in spinels, simple silicates, aluminosilicates, and complex salts (Thayer, 1956). The most important of the chromium-bearing silicates include amphiboles, pyroxenes, and chlorites (Thayer, 1956). Minerals which contain Cr(VI) are quite rare and include exotic species like crocoite ( $\text{PbCrO}_4$ ), dietzeite ( $\text{Ca}(\text{IO}_3)_2 \text{CaCrO}_4$ ), and tarapacaite ( $\text{K}_2\text{CrO}_4$ ) (Barth, 1952). Consequently, little Cr(IV) is available for weathering in most drainage basins.

Weathering. Garrels and Christ (1965) indicate that for natural systems (at  $25^\circ \text{C}$ ) exposed to air the value for Eh (volts) follows the approximate relation

$$(9) \quad \text{Eh} = 0.70 - 0.06 \text{ pH},$$

in contrast to the theoretical equilibrium value of

$$(10) \quad \text{Eh} = 1.23 - 0.06 \text{ pH}.$$

If the system being weathered (while exposed to the air) is considered as being chemically ideal, then reference to Equations (7) and (8) indicates that Cr(VI) can be produced from Cr(III) only under basic conditions. Whether or not this happens depends on the myriad of physical

and biological factors controlling the pH. Chromium can be transported by rivers in the following modes: (1) in solution, (2) bound within the particulate load, and (3) adsorbed to solid material.

Dissolved Load. The concentration of total soluble chromium in rivers has been studied by a number of investigators (see Table 2).

Table 2. Total soluble chromium in rivers.

Location of rivers sampled	Number of rivers sampled	Chromium concentration range ( $\mu\text{g}/\text{l}$ )	Mean chromium concentration ( $\mu\text{g}/\text{l}$ )	Reference
North America	15	0.72 - 84	5.8*	(1)
United States	6	1 - 40	+	(2)
United States	**	1 - 112	9.7	(3)
United States - 7 France-1, Rhone Brazil-1, Amazon	9	0.10 - 3.08	1.3	(4)

(1) Durum (1960), Durum and Haffty (1961, 1963)

(2) Kroner and Kopp (1965)

(3) Kopp and Kroner (1969)

(4) Kharkar et al. (1968)

+ Data not given

\* Median

\*\* Many rivers, sampled more than once.

In the lower reaches of 15 North American rivers values ranged from  $0.72\mu\text{g}/\text{l}$  (Sacramento River) to  $84\mu\text{g}/\text{l}$  (Mississippi River), and indicated a median concentration of  $5.8\mu\text{g}/\text{l}$  (Durum, 1960; Durum and Haffty, 1961, 1963). In general, rivers draining into the Pacific Ocean had values below the median while rivers draining into the Atlantic Ocean had values above the median. Kroner and Kopp (1965)



investigated soluble chromium in six major United States rivers for the period 1958-1962. In composite samples (weekly samples combined over a three to four month period) they observed that the chromium concentration ranged from 1  $\mu\text{g}/\text{l}$  (Columbia River) to 40  $\mu\text{g}/\text{l}$  (Missouri River and Columbia River). The five year summary (1962-1967) of trace elements in rivers and lakes of the United States by Kopp and Kroner (1969) includes data on dissolved chromium. They detected chromium in 386 composite samples (24.5 percent of those analyzed for chromium), observed a range from 1  $\mu\text{g}/\text{l}$  to 112  $\mu\text{g}/\text{l}$ , and determined a mean value of 9.7  $\mu\text{g}/\text{l}$ . In a study of the composition of some of the world's rivers, Kharkar, Turekian and Bertine (1968) discovered soluble chromium to average 1.3  $\mu\text{g}/\text{l}$ , with a range from 0.10  $\mu\text{g}/\text{l}$  to 3.08  $\mu\text{g}/\text{l}$ .

Kharkar et al. (1968) were unable to correlate the dissolved chromium concentration with the superficially evident properties of the rivers, their sediments or their drainage basins. Two important features observed were: (1) the concentration of soluble chromium is independent of the concentration on particulate material, and (2) the concentration of dissolved chromium is independent of the total suspended load.

Suspended Load. Turekian and Scott (1967) examined the chromium concentration in suspended matter in 18 United States rivers plus the Rhone and Rio Maipo. The United States rivers were those

emptying into the Atlantic Ocean and the Gulf of Mexico. The Cr concentration in suspended material ranged from 37 ppm to 460 ppm, with a median of 170 ppm and a mean of 190 ppm. Using their values for the suspended load (mg/l), the particulate chromium concentration ranges from 2.5  $\mu\text{g}/\text{l}$  to 95  $\mu\text{g}/\text{l}$ , with a median of 12  $\mu\text{g}/\text{l}$  and a mean of 18  $\mu\text{g}/\text{l}$ . They indicate that the concentration of chromium in solution does not correlate with its concentration in the detrital load. In their analysis of Brazos River bottom sediment, Turekian and Scott (1967) found no significant differences in the chromium content of the 2- to 20-, 0.2- to 2-, and less than 0.2- $\mu$  size fractions, indicating, perhaps, little surface adsorption or cation exchange effect (finer material generally has a higher cation exchange capacity (Kennedy, 1965)). Kopp and Kroner (1968) analyzed 101 monthly composite samples from five eastern U. S. rivers and found that chromium in the suspended load ranged from 3 to 13  $\mu\text{g}/\text{l}$ . However, they detected chromium in only 38 percent of the samples. Analysis of 228 samples, from unspecified U. S. rivers, for suspended chromium yielded a mean concentration of 30  $\mu\text{g}/\text{l}$  (Kopp and Kroner, 1969). This value, however, was for only 18 of the samples which contained chromium detectable by their spectrographic procedure.

Pollution. Significant quantities of chromium may be contributed to rivers by industrial sources, particularly those industries involved in mining, alloying, and the cleaning or plating of metals.

Klein (1957, 1962) and McKee and Wolf (1963) summarized the primary sources of chromium contamination from waste waters. Hexavalent chromium is supplied by industries involved in manufacturing chromates, in chromium plating, in anodizing aluminum, in tanning leather, in manufacturing paints, dyes, explosives, ceramics and paper, and by plants which use potassium dichromate as a corrosion inhibitor in cooling system waters. Trivalent chromium is used much less extensively, primarily in the textile dyeing, leather tanning, ceramic, glass, and photographic industries.

Columbia River. Several investigators have examined the soluble chromium content of Columbia River water (see Table 3).

Table 3. Dissolved chromium in the Columbia River.

Date (s)	No. of samples	% of samples Cr detected	General Cr conc. range ( $\mu$ g/1)	Mean Cr conc. ( $\mu$ g/1)	Reference
11 Jun 58	1	100	9.2	9.2	(1)
1 Dec 58	1	100	18	18.	(1)
8 Sep 59	1	100	20	20	(1)
1958-1962	31	87	1-10	*	(2)
1962-1967	69	58	1-22	6	(3)

\* Data not provided

(1) Durum (1960), Durum and Haffty (1961, 1963)

(2) Kroner and Kopp (1965)

(3) Kopp and Kroner (1969)

Dissolved chromium in the Columbia River (below The Dalles Dam) ranged from 9.2  $\mu$ g/1 (11 Jun 1958) to 18  $\mu$ g/1 (1 Dec 1958) to 20  $\mu$ g/1 (8 Sep 1959) (Durum, 1960; Durum and Haffty, 1961, 1963).

No relation to stream flow was evident. For the period 1958-1962 Kroner and Kopp (1965) detected dissolved chromium in Columbia River water in 27 of 31 samples, and found a general range of  $1\mu\text{g}/\text{l}$  to  $10\mu\text{g}/\text{l}$ . They used composite samples (weekly samples from a three to four month period), with a lower detection limit of  $1\mu\text{g}/\text{l}$ . They found a maximum value of  $40\mu\text{g}/\text{l}$ . Sixty-nine composite samples were analyzed by Kopp and Kroner (1969) from six Columbia River stations during the period 1 Oct 1962 to 30 Sep 1967. They detected soluble chromium in 58.9 percent of the samples, and observed a mean concentration of  $6\mu\text{g}/\text{l}$  within a range from  $1\mu\text{g}/\text{l}$  to  $22\mu\text{g}/\text{l}$ .

At Hanford, Washington, Cr(VI) as the anion  $\text{Cr}_2\text{O}_7^{=}$ , is added to reactor coolant water as a corrosion inhibitor. The resultant  $^{51}\text{Cr}$  in the coolant water is introduced to the Columbia River (Perkins, Nelson and Haushild, 1966). At the pH of Columbia River water, generally from pH 7 to pH 8 (Keller, 1962; Nelson et al., 1966; Forster, Park and Renfro, 1969), and at the general chromium concentrations indicated above, the dichromate ion should dissociate to chromate ion,  $\text{CrO}_4^{=}$ . The distribution of  $^{51}\text{Cr}$  in dissolved and particulate phases has been determined between Hanford and Vancouver, Washington (Perkins et al., 1966, and Nelson et al., 1966), between Vancouver and Astoria, Oregon (Cutshall, 1967), and from The Dalles Dam to the Columbia River mouth (Forster et al., 1969). These studies indicate that the bulk of the transported  $^{51}\text{Cr}$  remains in

in solution. Nelson, Perkins and Nielsen (1965) and Nelson et al. (1966) passed 0.3  $\mu$  membrane-filtered Columbia River water samples (from Hanford downriver to Vancouver) through ion exchange columns. They concluded that most of the  $^{51}\text{Cr}$  remains in solution and that the  $^{51}\text{Cr}$  in solution persists in the anionic form.

Nelson et al. (1966) determined the  $^{51}\text{Cr}$  content of stream bed sediments from the Columbia River as a function of particle size. The fraction less than 74 $\mu$  ( $\leq 0.1\%$  of the sediment) contained more than 96% of the total chromium activity at each of three different depths. Since the fraction less than 74 $\mu$  was not further subdivided, it is not possible to compare these data directly with those of Turekian and Scott (1967), presented above.

Cutshall (1967) studied the uptake of  $^{51}\text{Cr(VI)}$  and  $^{51}\text{Cr(III)}$  on Columbia River sediments. Using a stable chromium carrier concentration of 80 $\mu\text{g/l}$ , he showed that Cr(III) was taken up rapidly, and that Cr(VI) was taken up much more slowly. He concluded that any  $^{51}\text{Cr(VI)}$  reduced in the river to  $^{51}\text{Cr(III)}$  would soon be removed from solution. Displacement experiments with Columbia River sediments (Johnson, Cutshall and Osterberg, 1967) suggest that  $^{51}\text{Cr}$  is not bound to the sediment by cation exchange.

Partitioning Experiments. The partitioning of Cr(III) and Cr(VI) between solution and particulate phases in distilled water, as a function of pH and concentration (100 $\mu\text{g/l}$  and 10 $\mu\text{g/l}$  for  $\text{Cr}^{+3}$  and

10  $\mu\text{g}/\text{l}$  for  $\text{Cr}^{+6}$ ) has been investigated by Fukai and Huynh-Ngoc (1968). Using radioactive tracers, at  $18 \pm 1^\circ \text{C}$ , they showed that the rate of  $\text{Cr}(\text{III})$  precipitation increases rapidly as the pH is raised from 7.2 to 8.5-9.0, and decreases with increasing pH thereafter. The percentage of  $\text{Cr}(\text{III})$  precipitated (including that retained on the 0.22  $\mu$  membrane filter and that adsorbed to the vessel) decreases with decreasing concentration at all pH's from approximately 7.0 to 10.0. They found no appreciable differences for periods of one, three and six hours. For  $\text{Cr}(\text{VI})$ , Fukai and Huynh-Ngoc (1968) found that after a three hour standing period only 3.1% had precipitated at pH 7.3 and 2.9% at pH 8.0.

Summary. In general, the concentration of dissolved chromium in river water is extremely variable ( $< 1 \mu\text{g}/\text{l}$  to  $112 \mu\text{g}/\text{l}$ ). The particulate concentration is nearly as variable and is of the same general magnitude ( $< 2.5 \mu\text{g}/\text{l}$  to  $95 \mu\text{g}/\text{l}$ ). However, the two do not appear to be correlated. Although the oxidation state of chromium in river water is not known with certainty,  $^{51}\text{Cr}$  experiments with river water and sediment suggest that soluble chromium is nearly all anionic  $\text{Cr}(\text{VI})$  and that any  $\text{Cr}(\text{III})$  formed in the rivers is rapidly taken up by sediment particles. Little can be said about the chemical state of the particulate chromium in river water. Since the concentration of dissolved chromium is not directly related to that of particulate chromium, chromium in the particulate phase probably occupies inert

positions (Turekian and Scott, 1967).  $^{51}\text{Cr}$  experiments tend to confirm this observation.

### Chromium in Sea Water

The changes in physical state accompanying the addition of Cr(III) and of Cr(VI) to samples of sea water previously filtered through 0.22 $\mu$  membrane filters have been examined by Chipman (1967). Using  $^{51}\text{Cr}$  solutions of "high specific activity" (value not stated), he added Cr(III) in the form of a chromic chloride solution, and Cr(VI) in the form of a sodium chromate solution. After allowing the spiked sea water samples to stand for 7-11 days, he determined the radioactivity in solution, in particulate form (defined by a 0.45 $\mu$  membrane filter), and adsorbed to the flask walls. Table 4 summarizes his results.

Table 4. Physical state changes of Cr solutions added to sea water.

Time after added (days)	Cr(VI)			Cr(III)		
	Percent soluble	Percent particulate	Percent adsorbed	Percent soluble	Percent particulate	Percent adsorbed
7				34	40	26
8	99.8	0.36	1.44			
11				10	46	44

From Chipman (1967)

Using radioactive chromium tracers, Fukai and Huynh-Ngoc (1968) examined the physical state changes of Cr(III) and Cr(VI) in 0.22 $\mu$ -filtered

sea water (at  $18 \pm 1^{\circ}$  C and at concentrations of  $10 \mu\text{g}/\text{l}$ ) as a function of pH and time. They state that there were no appreciable differences in their data for solutions allowed to stand for 1, 3 or 6 hours. Paying particular attention to the pH range of 7-9, their results include:

1. For Cr(III). The percentage of Cr(III) retained by a  $0.22 \mu$  membrane filter and adsorbed to the flask walls showed a rapid increase from around pH 7 to the maximum at about pH 9. According to their graphed data, approximately 22% of the Cr(III) would be retained and adsorbed at pH 8.2.
2. For Cr(VI). Under the same conditions, and in the same pH range, the amount of Cr(VI) retained by the filter and adsorbed to the sample container was independent of pH, and was 3.0% or less. At pH 8.2, for example, 2.4% of the Cr(VI) was removed from solution.

Sorption of  $^{51}\text{Cr}(\text{III})$  to glass beads and to living and dead phytoplankton from sea water has been examined by Curl, Cutshall and Ostenberg (1965). They found the uptake to be rapid and to be related directly to the surface area of the material. Krauskopf (1956) used a variety of substances to examine the removal of  $\text{CrO}_4^{=}$  from artificial sea water. He found that "clay", apatite and plankton were not effective removers over periods of two days to two weeks. In laboratory experiments, Johnson (1966) showed that  $^{51}\text{Cr}$  bound to Columbia



River sediments is not displaced by synthetic sea water in short periods of time.

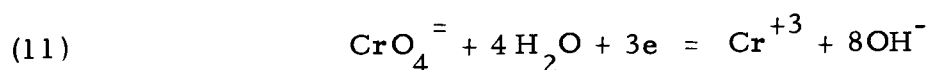
It should be pointed out that any experiments involving the addition of  $^{51}\text{Cr(III)}$  to sea water or even to river water are open to question. The ligand exchange reactions of Cr(III) in aqueous solution are rather slow (Cotton and Wilkinson, 1966). If Cr(III) does exist in solution in natural water systems, then for  $^{51}\text{Cr(III)}$  tracer experiments to be valid it is necessary that the same Cr(III) species be present in the tracer as in the system being analyzed. Since such information is not available,  $^{51}\text{Cr(III)}$  experiments have to be interpreted with care. Such is not the case for  $^{51}\text{Cr(VI)}$  experiments run in the same manner, because the reactions among the several possible Cr(VI) species are labile, and are controlled only by Cr(VI) concentration and pH.

Data on the concentration of chromium in sea water are somewhat limited. Tables 5 and 6 include compilations of available information. A total of 35 sea water samples have been analyzed for chromium by eight investigators. Of these 35 samples, 33 were from surface waters (including one each from 5, 20 and 63 m), one was from 500 m, and one was from 1,000 m. Only seven of the 35 samples have been examined for the partition of chromium between the dissolved and particulate phases (two by Loveridge et al., 1960, and five by Fukai and Vas, 1969).

Even fewer data exist on the oxidation state of chromium in sea water. Goldschmidt (1954) suggested Cr(VI). Krauskopf (1956) calculated that  $\text{CrO}_4^{=}$  is the thermodynamically stable state in aerated sea water, and concluded, upon adding "massive" amounts of potassium dichromate to sea water and observing no precipitate formation, that Cr(VI) should not be precipitated by the cations present in sea water. He suggested that chromium is controlled by local reduction and precipitation as  $\text{Cr}(\text{OH})_3$ . On the other hand, Sillen (1961) suggested that chromium is present in sea water as a hydroxide species.

The presence of measurable  $^{51}\text{Cr}$  many kilometers from the mouth of the Columbia River suggested to Cutshall, Johnson and Ostenberg (1966) that  $^{51}\text{Cr}$  is in solution as  $\text{CrO}_4^{=}$ . This conclusion is reinforced by the increase in recovery resulting from the use of Sn(II) and Sb(III) reducing agents during the coprecipitation of chromium with Fe(III). Since the  $^{51}\text{Cr}$  had been in contact with sea water for weeks or even months, Cutshall (1967) concluded that the reduction of  $^{51}\text{Cr}(\text{VI})$  to  $^{51}\text{Cr}(\text{III})$  must occur very slowly, if at all.

In a simple thermodynamic calculation, using Sillen's (1961) values of  $\text{pH} = 8.2$  and  $\text{pE} = 12.5$  for sea water, and the equation



$$\log K = -36.9$$

Fukai and Huynh-Ngoc (1968) obtained a value of  $10^{-28}$  for the ratio

of  $[\text{Cr}^{+3}]/[\text{CrO}_4^{=}]$ . In more extended equilibrium thermodynamic calculations, combined with an excellent discussion of some of the limitations of such calculations, Cutshall (1967) showed that the activity of  $\text{Cr}(\text{OH})_2^+$  is the greatest of the four trivalent species considered ( $\text{Cr}^{+3}$ ,  $\text{CrOH}^{+2}$ ,  $\text{Cr}(\text{OH})_2^+$  and  $\text{CrO}_2^-$ ). Considering two hexavalent chromium species, he showed the activity of  $\text{CrO}_4^{=}$  to be greater than that of  $\text{HCrO}_4^-$ . He then concluded that the activity of the most probable trivalent species,  $\text{Cr}(\text{OH})_2^+$ , is only  $10^{-22}$  of the activity of the most probable hexavalent species,  $\text{CrO}_4^{=}$ .

Cutshall et al. (1966), Chuecas and Riley (1966), and Fukai and Huynh-Ngoc (1968) have shown that coprecipitation of chromium from sea water is completely effective only when chromium is present in trivalent form. On this basis, Table 5 (Section B) lists the chromium species considered to have been analyzed by those investigators who have determined the chromium content of sea water. Assumptions for the construction of Table 5 (Section B) include: (1) no contamination problems, (2) 100% Cr(III) recovery, and (3) no Cr(VI) recovery during coprecipitation. The work of Fukai (1967), and Fukai and Vas (1967, 1969) is not included in Table 5, but will be considered later.

Chuecas and Riley (1966) repeated the coprecipitation methods used by previous investigators with  $^{51}\text{Cr}(\text{III})$  to check the percentage recovery. Their results indicate that the aluminum hydroxide coprecipitation used by Ishibashi and Shigematsu (1950), Ishibashi (1953),

and Loveridge et al. (1960) is quantitative only in a very small pH range, and that the coprecipitation method of Black and Mitchell (1952) may not be quantitative.

Chuecas and Riley (1966) attempted to determine the oxidation state distribution of soluble chromium in sea water. They concluded that chromium occurs mainly in the +3 oxidation state. However, their experimental treatment of sea water samples included acidification to a pH below 3 after filtration through a  $0.5\mu$  membrane filter, and before storage. At this pH any Cr(VI) initially present could have been reduced to Cr(III) during storage. Morris (1968), examining chromium in filtered sea water, tested his experimental procedure and found that it did not discriminate between trivalent and hexavalent chromium in solution, but was equally effective in removing either oxidation state from sea water spiked with  $0.63\mu\text{g/l}$ . The sampling, storage, and coprecipitation techniques of Chuecas and Riley (1966) were used by Chau, Sim and Wong (1968) on their South China Sea surface samples. Again, due to acid storage at pH 2, reduction of any Cr(VI) to Cr(III) would be expected. Thus their results probably indicate only total soluble chromium content.

Fukai (1967) and Fukai and Vas (1967, 1969) have made a concerted effort to examine the distribution of oxidation states of soluble chromium and the total chromium content of associated particulate matter in sea water. Table 6 summarises some of their findings.

They have developed a differential method of analysis for trivalent and hexavalent chromium which uses independent measurements on two aliquots of the same sample. One aliquot, used to determine Cr(III), is treated with iron hydroxide; the other, used to determine the sum of Cr(III) and Cr(VI), is first reduced with sodium sulfite in acid medium, and then treated similarly. The resulting precipitates are processed to eliminate chloride, oxidized, and determined spectrophotometrically with diphenylcarbazide. Recoveries were checked by using a Cr(III) radioactive tracer. Fukai (1967) commented that the Cr(III) estimated was within the range of analytical sensitivity for some of the samples. The standard deviation of the results for single analysis of Cr(III), in the presence of Cr(VI), was estimated by Fukai and Vas (1967) to be  $\pm 17\%$  in the  $\mu\text{g}$  range. They estimated a standard deviation of  $\pm 20\%$  for Cr(VI), determined as the difference between total chromium, Cr(T), and Cr(III). The relative errors involved in analyzing submicrogram amounts of chromium would be even larger, according to Fukai and Vas (1967).

It is believed that the values of Cr(T) in solution and in particulate material obtained by Fukai (1967), and Fukai and Vas (1967, 1969) are accurate within the limits set by Fukai and Vas (1967). However, their results for the distribution of Cr(III) and Cr(VI) may be open to question. That Cr(III) is almost completely coprecipitated by Fe(III) from sea water has been shown by Cutshall *et al.* (1966), Chuecas and

Riley (1966), Fukai and Vas (1967), and Fukai and Huynh-Ngoc (1968). However, Cr(VI) is also coprecipitated by Fe(III), the percentage of Cr(VI) removed increasing as the Cr(VI) concentration decreases. The adsorption experiments of Krauskopf (1956) illustrate this phenomenon well. He precipitated hydrous ferric oxide from sea water at 18-23° C and pH 7.7-8.2, and determined the amount of Cr(VI) adsorbed by 300 mg Fe(III)/l. At an initial chromium (VI) concentration of 490 µg/l, 22% was adsorbed, while at 95 µg/l, 47% was adsorbed, after a standing period of two days. Similar results were obtained after a nine day standing period. Cutshall et al. (1966) found that 27.3% and 72.4% of a <sup>51</sup>Cr(VI) spike was removed from two nominally duplicate sea water samples by coprecipitation with 45 mg Fe(III)/l. Using 10 µg/l Cr(VI), with a radioactive tracer, Fukai and Huynh-Ngoc (1968) showed that 50 µg Fe(III)/l coprecipitated 3.9% of the Cr(VI), at pH 8.1 after standing for three hours. Fukai and Vas (1967) found that about 1-2 mg Fe(III)/l coprecipitated an increasing percentage of Cr(VI) as the amount of Cr(VI) decreased. At 1.00 µg/l, an average of 19% of the Cr(VI) was removed with Fe(III). The precipitated hydrous ferric oxide, having a positive zeta-potential (positive "external surface charge") at pH < 8.3, may adsorb and/or occlude the anionic Cr(VI) (Cutshall et al., 1966). Column eight of Table 6 shows the percentage of soluble Cr(T) determined to be Cr(III) by Fukai (1967), and Fukai and Vas (1967, 1969). This percentage varies from

5.3 to 78, and, on the basis of the data just reviewed, could be due to contamination by Cr(VI). In other words, the results discussed so far do not preclude the possibility that chromium in solution in sea water exists solely as Cr(VI), as predicted by equilibrium thermodynamic calculations.

Table 5. A summary of existing data on the concentration of chromium in sea water.

Reference	No. Samples	Sample Location	Sample Depth	Section A			Section B		
				Cr Found $\mu\text{g}/\text{l}$	Method of Concentration	Method of Determination	Remarks	Cr Species Analyzed	Reason
Noddack and Noddack (1940)	1	Gullmarfjord, Sweden	Surface	<0.2	Coprecipitation	Spectrographic		Cr(T)	Sulfide treatment during preconcentration
Black and Mitchell (1952)	1	20 miles off Plymouth, England	20m	1.2	Coprecipitation with tannic acid plus 8-hydroxyquinoline with Fe(III) and Al(III) carriers	Spectrographic	Not filtered, stored in Pyrex bottle	Cr(III)	
				2.5					
	1	Inshore waters, Ardmcaph Bay, England	Surface	1.6	As above	As above	Not filtered, stored in Pyrex bottle		
	1	Inshore waters, Atlantic Bridge, England	Surface	1	As above	As above	Not filtered, stored in Pyrex bottle		
Ishibashi and Shigematsu (1950) Ishibashi (1953)	3	Offshore waters, Shirahama, Japan	Surface	0.04	Coprecipitation with aluminum hydroxide	Spectrophotometric with diphenylcarbazide		Cr(III)	
				0.05					
				0.07					
Loveridge <i>et al.</i> (1960)	6	Coastal waters	Surface?	0.13	Coprecipitation with aluminum hydroxide	Spectrophotometric with diphenylcarbazide	Not filtered, 3 or 4 replicate analyzes	Cr(T)	HNO <sub>3</sub> treatment prior to storage. Also use of sodium sulfite during coprecipitation
				0.17					
				0.18					
				0.22					
				0.25					
	2	Coastal waters	Surface?	0.14	As above	As above	Filtered (1 $\mu$ ), 4 replicate analyses. 0.20 $\mu\text{g}/\text{l}$ associated with suspended solids (single analysis)		



Table 5 continued.

Reference	No. Samples	Sample Location	Sample Depth	Section A			Section B		
				Cr Found $\mu\text{g/l}$	Method of Concentration	Method of Determination	Remarks	Cr Species Analyzed	Reason
				0.18	As above	As above	Filtered (1 $\mu$ ), 3 replicate analyses. 0.23 $\mu\text{g/l}$ associated with suspended solids (single analysis)		
Chuecas and Riley (1966)	2	Irish Sea	Surface	0.46 0.48	Coprecipitation with iron hydroxide	Spectrophotometric with diphenyl-carbazide	Filtered (0.5 $\mu$ ), stored in polyethylene, 4 or 5 replicate analyses	Cr(T)	HCl treatment prior to storage
Morris (1968)	1	Menai Straits	Surface?	0.29	Complex with ammonium pyrrolidine dithiocarbamate and extract into methyl isobutyl ketone	X-ray fluorescence spectrometry	Filtered (0.5 $\mu$ )	Cr(T)	Acid treatment and boiling during concentration
Chau <i>et al.</i> (1968)	1	100 miles off Hong Kong	Surface	1.59	Coprecipitation with iron (III) hydroxide	Atomic absorption spectrophotometry	Filtered (0.5 $\mu$ ), 5 replicate analyses	Cr(T)	Acid treatment after collection

Table 6. A summary of existing data on the distribution of oxidation states of soluble chromium and the total chromium content of associated particulate matter in sea water.

Sampling Date	Sample Location	Sample Depth	o/oo	Soluble Chromium				Particulate Chromium	Reference
				Cr(T) μg/l	Cr(VI) μg/l	Cr(III) μg/l	Cr(III)/Cr(T) %		
12 Jan 1966	Monaco Coast	Surface	---	0.43	0.29	0.14	37	---	(1)
1 Jun 1966	Monaco Coast	Surface	---	0.36	0.34	0.02	5.6	---	(1)
8 Jun 1966	2 km south of Monaco	Surface	---	0.38	0.36	0.02	5.3	---	(1)
19 Jul 1966	Cap d' Ail Coast	Surface	21.15	0.30	0.28	0.02	6.7	---	(1)
13 Sep 1966	Roquebrune Bay	Surface	20.95	0.23	0.05	0.18	78	---	(1)
30 Sep 1966	Cap d' Ail Coast	Surface	---	0.38	0.19	0.19	50	---	(1)
25 Oct 1966	42°47'N;72°29'E	5 m	20.92	0.39	0.16	0.23	59	---	(1)
		500 m	21.08	0.35	0.16	0.19	54	---	(1)
		1000 m	21.03	0.41	0.21	0.20	49	---	(1)
25 Apr 1967	Roquebrune Bay	Surface	---	0.57	0.32	0.25	44	---	(2)
		63 m	---	0.44	0.34	0.10	23	---	(2)
5 Jun 1967	1 km south of Monaco	Surface	20.56	0.96(0.35?)	0.79(0.19?)	0.17	18(47?)	.05	(3)
23 Oct 1967	1 km south of Monaco	Surface	21.00	0.35	0.25	0.10	29	.03	(3)
10 Jan 1968	1 km south of Monaco	Surface	21.03	0.27	0.17	0.10	37	.12	(3)
22 Apr 1968	1 km south of Monaco	Surface	20.78	0.25	0.21	0.04	16	.11	(3)
22 May 1968	1 km south of Monaco	Surface	20.90	0.26	0.19	0.07	27	.12	(3)

References: (1) Fukai (1967)

(2) Fukai and Vas (1967)

(3) Fukai and Vas (1969)

## II. EXPERIMENTAL

### Introduction

Total chromium, Cr(T), and Cr(VI) were determined from independent measurements made on two aliquots from a sample of sea water. Cr(VI) was extracted and concentrated from one aliquot, using a liquid extraction procedure. Cr(T), the sum of any Cr(III) plus Cr(VI), was extracted and concentrated from the second aliquot, using a similar procedure, after oxidation of any Cr(III) to Cr(VI). These procedures were applied to both filtered and non-filtered samples from the same station. The extracted chromium was determined using neutron activation analysis.

### Reagents

Analytical reagent grade chemicals were used without further purification throughout all experiments. Doubly-distilled, deionized water (DDDW) was used for the preparation of all solutions and for the final rinse when cleaning all apparatus. Tap distilled water was deionized on a mixed-bed column (Illco-Way Research Model), distilled through a continuous-flow glass still, and stored in a five-gallon, high-density, polyethylene carboy (Nalgene) until used.

Sodium Hydroxide Solution. A 1 M stock solution was prepared by dissolving 40.01 g of NaOH pellets in DDDW, and diluting to 1 l.

Copper Sulfate Solution. 2.185 g of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  were dissolved in DDDW and made to 1 l, producing a solution  $8.75 \times 10^{-3}$  M in Cu(II).

Potassium Peroxydisulfate Solution. A solution 0.175 M in peroxydisulfate was prepared using 47.31 g  $\text{K}_2\text{S}_2\text{O}_8$ , and diluting to 1 l with DDDW.

Cr(VI) Stock Solution. A stock solution of Cr(VI), containing 1,400  $\mu\text{g}/\text{ml}$ , was prepared by dissolving 3.961 g  $\text{K}_2\text{Cr}_2\text{O}_7$  in DDDW, and diluting to 1 l. From this stock solution, a 14.00  $\mu\text{g}/\text{ml}$  Cr(VI) solution was made by diluting the stock solution with DDDW.

$^{51}\text{Cr}$  Chromium Stock Solution. 2 ml of a  $^{51}\text{Cr}$ (VI) solution ( $\text{Na}_2\text{CrO}_4$  in a NaCl solution, at pH ~ 8, containing 0.620  $\mu\text{g}$  stable chromium), were obtained from New England Nuclear. This solution was diluted to 25 ml with DDDW, and used as a stock solution.

$^{51}\text{Cr}$ (VI) Tracer for Storage Experiments. Preparation of the  $^{51}\text{Cr}$ (VI) tracer solution used in the storage experiments included an alkaline oxidation step to ensure that all of the chromium was in the +6 state. Five ml of  $^{51}\text{Cr}$  stock solution were added to 50 ml of dilute NaOH, pH ~ 12, in a 100-ml volumetric flask, followed by one ml of 0.3%  $\text{H}_2\text{O}_2$ . The flask was placed on a hotplate and the temperature was raised slowly to about  $97^\circ\text{C}$ . The excess  $\text{H}_2\text{O}_2$  was decomposed by heating at  $97^\circ\text{C}$  for 16 hours (Bürki and Schaaf, 1921; Slater, 1945; Urone, Druschel and Anders, 1950; Rynasiewicz, 1954), and the solution made to 100 ml at pH ~ 8, using DDDW and HCl. Final

stable chromium concentration was 1.24  $\mu\text{g}/\text{l}$ .

$^{51}\text{Cr(VI)}$  Tracer for Extraction Experiments. Five ml of  $^{51}\text{Cr}$  stock solution were treated, through the peroxide addition step, in the same way as the  $^{51}\text{Cr(VI)}$  tracer used for storage experiments. Ten ml of the 14.00  $\mu\text{g}/\text{ml}$  stable Cr(VI) solution were added and the excess  $\text{H}_2\text{O}_2$  was removed by slowly raising the temperature to about 97° C and maintaining that temperature for 16 hours. The added Cr(VI), as chromate ion, accelerated the  $\text{H}_2\text{O}_2$  decomposition (Rynasiewicz, 1954). All the  $\text{H}_2\text{O}_2$  had to be destroyed to prevent reduction of the chromate ion when adding the concentrated HCl (just prior to extraction with MIBK), and to prevent possible oxidation of any Cr(III) present in the sample. After cooling to room temperature, DDDW and HCl were added to make 100 ml of solution at pH ~ 8. Final stable Cr(VI) concentration in the  $^{51}\text{Cr(VI)}$  tracer solution used for extraction experiments was 1.400  $\mu\text{g}/\text{ml}$ .

Cleaning Solution. All apparatus was cleaned with an acid mixture of one part concentrated  $\text{HNO}_3$ , three parts concentrated HCl, and four parts distilled water (Salzman, 1952). After cleaning, the apparatus was rinsed four times with tap distilled water, one time with DDDW, and drained or dried with Kimwipes.

### Apparatus

A Nuclear Data 512 Multichannel Analyzer (Series 130), coupled

to a 5" x 5" NaI(Tl) well crystal, was used to count the 0.320 MeV  $\gamma$ -activity of  $^{51}\text{Cr}$ . At no time during radioassay of the samples, including measurements made after neutron activation, did the dead time of the scalar unit exceed 2%. The counting efficiency for  $^{51}\text{Cr}$  was 6.2%. The readout was typed and computations were made using a desk calculator. When using  $^{51}\text{Cr}$  tracers, total photopeak areas were compared.

Neutron activation of the extracted chromium samples was accomplished using Oregon State University's TRIGA, Mark II, nuclear reactor. The extracts were placed in the reactor's rotating sample rack and irradiated at 500 KW (producing a neutron flux of approximately  $1.4 \times 10^{12}$  per  $\text{cm}^2$  per second) for three hours. After allowing 34 days for the decay of the shorter-lived (relative to the 27.8 day half-life of  $^{51}\text{Cr}$ ) interfering isotopes the samples were counted. Photopeak areas were obtained from the typed readouts using the method of Covell (1959). All counts and counting statistics were corrected for background (Wang and Willis, 1965).

#### Sampling Procedure

Surface sea water samples were taken from two stations, NH-5 and NH-10, located five and ten nautical miles off the coast, respectively, at Newport, Oregon (Latitude  $124^{\circ} 04' \text{W}$ , Longitude  $44^{\circ} 39' \text{N}$ ). The samples were taken using a large plastic bucket with a nylon

handle, attached to a polypropylene line. The water was transferred directly to 10-1 collapsible polyethylene containers and returned to the laboratory within six hours of sampling. The samples were stored at room temperature until analyzed, a period no longer than five days. Prior to analysis, some of the samples were filtered, under a partial vacuum, through a 0.45  $\mu$  membrane filter (Gelman, Type GM-6). The filters were placed in small glass bottles and retained for later examination.

In order not to disturb any relationship existing between any Cr(III) and Cr(VI) in solution and in particulate matter, acids or other preservatives were not added to the samples before analysis. Care was taken to prevent contamination during sampling. Oil slicks, which could have contained metallic chromium, were avoided. Samples were taken while the ship had a slight amount of way on, thereby minimizing the possibility of contamination from the ship's metallic hull and painted surfaces. All sampling apparatus and sample storage containers were acid cleaned, rinsed and drained. Just prior to use, they were rinsed with sea water from the station being sampled.

#### Sample Storage

<sup>51</sup>Cr(VI) tracer experiments were conducted to evaluate the effect of storage in the polyethylene containers on the measured chromium content of the sea water samples. Immediately after returning

to the laboratory, 50 ml of the  $^{51}\text{Cr(VI)}$  tracer were added to 10-1 aliquots of filtered (through a  $0.45\ \mu$  membrane filter) and non-filtered sea water from station NH-10. This addition resulted in an increase of  $1.24 \times 10^{-4}\ \mu\text{g/l}$  in the stable Cr(VI) content of each aliquot. A 10-ml portion of each of these two samples was removed immediately after spiking and shaking. Periodically, during the subsequent eight days, other 10-ml portions were removed and their activity compared to that of the first aliquots.  $^{51}\text{Cr(III)}$  storage experiments were not conducted. Because of slow ligand exchange reactions, any Cr(III) species added may not have been the same as those possibly present in the sea water.

### Analytical Method

Background. Since the chromium content of sea water is rather low, separation and concentration prior to analysis is necessary. Solvent extraction, using an aqueous-organic solvent pair, was adopted as the most practicable technique for the combined extraction and concentration of chromium from sea water. The undesirable features of coprecipitation methods, especially the possible contamination of Cr(III) by Cr(VI) and the extensive analytical schemes required were thereby eliminated. The analog of coprecipitation, coextraction, is almost unknown in solvent extraction (Morrison and Freiser, 1957; Stary, 1964).



Weinhardt and Hixson (1951), apparently, were the first to investigate the extraction of Cr(VI) from hydrochloric acid solution with 4-methyl-2-pentanone (methyl isobutyl ketone, MIBK). They extracted an aqueous solution containing  $\text{Cr}_2\text{O}_7^{=}$  or  $\text{CrO}_4^{=}$  and HCl into an equal volume of MIBK, and found a distribution that distinctly favored the organic phase. Their results showed an increase in distribution coefficient with: (1) decreasing Cr(VI) concentration, (2) increasing HCl concentration, and (3) decreasing temperature (measurements were made at 25° C and at 0° C). An apparent decrease in the distribution coefficient was noted in experiments where the ratio of the volume of the aqueous phase to the volume of the ketone phase increased. Such an apparent change can be attributed to the miscibility of methyl isobutyl ketone in the acidic aqueous phase (Pilloton, 1958). Chromic chloride, Cr(III), was found not to be extracted under similar conditions. Because of the reduction of Cr(VI) to Cr(III) at low pH, an acid concentration no greater than 3 M was recommended. Haight, Richardson and Hall (1964) found that solutions of Cr(VI) containing more than 1.0 M hydrogen ion slowly change to Cr(III), probably through oxidation of water.

The findings of Weinhardt and Hixson (1951), regarding the discrimination against Cr(III) during the extraction of Cr(VI), were confirmed by Doll and Specker (1958), and Goto and Kakita (1959). Specker and Arend (1961) examined the extraction of Cr(VI) from

aqueous HCl into MIBK, and determined by absorption spectrum analysis of both the aqueous and ketone phases that  $\text{HCrO}_3\text{Cl} \cdot 2\text{MIBK}$  was extracted. In their investigation of Cr(VI) in various acid solutions, Haight et al. (1964) determined that  $\text{HCrO}_4^-$  was converted to  $\text{CrO}_3\text{Cl}^-$  in 1.0 M HCl and that the Cr(VI) ultraviolet absorption spectrum remained essentially invariant between 1.0 and 8.0 M HCl. The MIBK extraction technique has been examined using trace amounts of chromium by Beyerman (1962a, b), Maeck, Kussy and Rein (1962), Dinstl and Hecht (1962), and many others since, and found to discriminate against the +3 state while extracting the +6 state. Because of this discrimination and because of the reduction of Cr(VI) to Cr(III) at low pH, it was decided to rid the MIBK of possible chromium contamination by equilibrating it with aqueous hydrochloric acid. Therefore, 2,000 ml of MIBK were placed with 500 ml of 2 M HCl, shaken thoroughly, and allowed to stand for 12 hours. The MIBK was then decanted off and used for all extraction experiments performed on the samples from stations NH-5 and NH-10.

Extraction and Counting Procedures. To a 2-l separatory funnel (total capacity about 2,400 ml) was added 1.75 l of sea water. This was followed by 1.00 ml of the  $^{51}\text{Cr(VI)}$  tracer solution. The mixture was then shaken for about 30 seconds. This sample was then put into a freezer for 30 minutes and cooled to approximately  $5^\circ\text{C}$ . After removal from the freezer, 350 ml of concentrated HCl, similarly chilled,

was added, and the mixture shaken for 30 seconds. Next, 62 ml of cooled MIBK was added, and the mixture was shaken for two minutes. After allowing five minutes for the aqueous and ketone layers to separate, the aqueous phase was drained off and discarded. The retained ketone layer was then washed three times with 15-ml aliquots of a 1.2 M HCl solution. Twelve ml of the washed ketone layer (usually 12-15 ml) were transferred by pipet to a polypropylene test tube (Falcon, 17 x 100 mm, with cap), which was placed in the NaI(Tl) well crystal for determination of the  $^{51}\text{Cr}$  activity. The volume of the remaining ketone layer was measured. The percentage  $^{51}\text{Cr(VI)}$  recovery in the 12-ml portion was determined by comparing the total photopeak area to that of an identical volume of solution containing 1.00 ml  $^{51}\text{Cr(VI)}$  tracer and 11.00 ml DDDW. Total extraction efficiencies were also computed.

Oxidation Procedure. The MIBK extraction and concentration procedure just described allows the determination of only the sum of the Cr(VI) species present in sea water. In order to ascertain the total chromium content of a sample, Cr(T), it is necessary to oxidize any Cr(III) present to Cr(VI), and to run a similar extraction.

The oxidant selected was potassium peroxydisulfate (peroxosulfate, persulfate),  $\text{K}_2\text{S}_2\text{O}_8$ . Peroxydisulfate has been generally recommended as the agent for oxidizing Cr(III) to Cr(VI) in acid solution (Kolthoff et al., 1969). Oxidation under basic conditions (with alkaline

$\text{H}_2\text{O}_2$ , for example) would have resulted in the precipitation of calcium carbonate. Despite a high oxidation potential (2.0 volts), peroxydisulfate ion oxidative reactions are slow in the absence of a catalyst. House (1962) reviews the kinetics and the mechanisms of oxidations by peroxydisulfate, including the effects of trace ion catalysis. The most commonly used catalysts for peroxydisulfate oxidations are Cu(II) and Ag(I). Examples of a noticeable catalytic effect of Cu(II) with little or no effect by Ag(I) are given by Ball, Chutchfield and Edwards (1960) and House (1962). This effect plus the potential problems associated with a silver halide precipitate led to the choice of copper (II) sulfate as the better catalyst. Also, excess peroxydisulfate decomposes by the oxidation of water when boiled for a few minutes (see House, 1962, for references). Decomposition of the excess peroxydisulfate is necessary to prevent oxidation of the methyl isobutyl ketone during the extraction procedure (Stewart, 1964; Turney, 1965).

Accordingly, a second 1.75-l aliquot of the sea water sample was placed in a 3-l erlenmeyer flask. To this was added 1.00 ml of  $^{51}\text{Cr(VI)}$  tracer, 1.75 ml of concentrated  $\text{HCl}$ , 1.00 ml of  $8.75 \times 10^{-3}$  M Cu(II), and 2.00 ml of  $0.175 \text{ M S}_2\text{O}_8^{=}$ . After thorough mixing and adding 12 glass beads (to prevent "bumping" of the solution), the solution was placed on a hotplate and the temperature was raised slowly until boiling commenced (approximately 30 minutes). Boiling was continued for 45 minutes. Then the flask and its contents were brought

to room temperature in a cold-water bath. The cooled contents, measuring about 1.5 l because of evaporation, were transferred to the 2-l separatory funnel, and then extracted in the same way as Cr(VI), described above. The only modifications in the Cr(T) extraction procedure, relative to that for the 1.75-l Cr(VI) extraction aliquot, were those dictated by the volume change of the sample: (1) only 300 ml of concentrated HCl, and (2) only 52 ml of MIBK were used.

Standards Preparation. Standards were prepared using a modified extraction procedure. The matrix from which the standards were extracted was 2 M HCl. The use of such a matrix, because of equilibrium thermodynamic, and kinetic considerations, ensured that extractable Cr(VI) was not present as a contaminant, just nonextractable Cr(III). A 1.00-ml aliquot of the  $^{51}\text{Cr(VI)}$  tracer used for extraction experiments was added to 10 ml of 2 M HCl, followed by thorough shaking. Then 14 ml of MIBK were added and the mixture shaken for two minutes. The solution was then allowed to stand for five minutes to enable the ketone and aqueous phases to separate. A 12-ml portion of the ketone phase, containing a measurable amount of  $^{51}\text{Cr(VI)}$  and therefore a measurable amount of stable Cr(VI), was removed and placed in a polystyrene test tube identical to those holding the sea water chromium extracts.

Blanks. In the entire analytical procedure, including the oxidation step, there are five areas of concern regarding blanks:

1. The concentrated hydrochloric acid. Since any chromium present will be in the +3 state and not in the +6 states, it is not extractable. Therefore, a blank correction for the HCl was not necessary.
2. The oxidizing reagents. A reagent blank was made by running an additional Cr(T) extraction on another 1.75-l aliquot from station NH-10. In this case, twice the amounts of Cu(II),  $S_2O_8^{=}$ , and HCl were used and the results compared to the original Cr(T) extraction.
3. The MIBK. Since the MIBK was stored over 2 M HCl, discussed previously, any chromium present should have been transferred to the acid phase (any Cr(VI) would have undergone reduction because of the low pH). However, as a check on this hypothesis 12 ml of the MIBK were placed in a test tube for neutron activation analysis of its chromium content.
4. The polystyrene test tubes. An empty test tube was also activated to determine the amount of chromium it contained.
5. The filtration apparatus. The filtration apparatus contains a glass frit having a very large surface area. In order to ascertain the effect of filtration on the soluble Cr(VI) and Cr(T) content of a sample, 4.00 l of sea water from station NH-10 were filtered three separate times (using three separate filters), and then analyzed; the results were compared

to those from a single filtration.

Neutron Activation of Chromium Extracts and Blanks. After all the chromium extracts, standards, and blanks had been made and the 12-ml portions counted to obtain extraction efficiencies, an additional treatment was required before the samples could be activated and analyzed for stable chromium content. This step was necessitated by the fact that MIBK decomposes with the production of gas (probably primarily  $\text{CO}_2$ ) when exposed to thermal neutrons and associated gamma-radiation in a nuclear reactor. The test tube samples were first placed in an oven at  $105^\circ \text{C}$ , under slight vacuum, and the MIBK evaporated. Air, filtered through glass wool, was allowed to enter and circulate in the oven to hasten the evaporation. The vaporized MIBK was condensed, collected in hydrochloric acid, and counted to determine if any  $^{51}\text{Cr}$  was coming off with the MIBK. In addition, two empty test tubes and the two with just MIBK in them (all four were activated later to determine their total chromium content) were placed in the oven with the other samples and counted later to see if any  $^{51}\text{Cr}$  might have collected on them. In all cases, the results were negative; the  $^{51}\text{Cr}$  in the test tubes did not escape during the evaporation procedure.

The evaporation step resulted in a change in counting geometry. Therefore, the  $^{51}\text{Cr}$  counts had to be determined once again. Since the test tubes containing only MIBK had no  $^{51}\text{Cr}$ , it was not possible

to obtain a geometry change correction for them. Instead, the average geometry change for all of the other samples was used.

After being recounted to correct for geometry changes, the test tubes were thoroughly cleaned three times using Kimwipes moistened with MIBK, acetone, and DDDW. The test tubes were then wrapped in a double layer of Glad Wrap, a household plastic wrap from Union Carbide. The evaporated chromium extracts, standards and blanks were then ready for neutron activation.

All of the samples were placed in the rotating sample rack in Oregon State University's TRIGA, Mark II, nuclear reactor and irradiated for three hours at a neutron flux of  $1.4 \times 10^{12}$  per  $\text{cm}^2$  per second. After the samples were removed from the rotating rack, they were stored in lead vaults for 34 days. This time allowed interfering isotopes having short half-lives, relative to the 27.8 day half-life of  $^{51}\text{Cr}$ , to decay. The plastic wrap was removed and replaced before counting to lessen the chance of contaminating the well detector. Once again, the samples were counted and the resulting gamma-ray spectra recorded as typed readout. In some cases, the readout was also recorded on a semi-log x-y plot. The spectrum of one of the evaporated extracts was examined periodically to determine the optimum decay time and counting times required.

Spectrum Analysis. Even after a 34-day decay period, the gamma spectra were complex. The Compton interference from higher



energy photopeaks was large in the low-energy 0.320 MeV region. Therefore, the method of spectrum analysis by Covell (1959), was utilized to determine that part of the spectrum due to  $^{51}\text{Cr}$  activity. This method involves the subtraction of the apparent continuum from the total photopeak, leaving the net photopeak area attributable to the radionuclide in question. An assumption inherent in this treatment is that there are no other photopeaks "hidden" within the region of concern. A more complete explanation of the method of spectrum analysis is contained in Appendix A.

Samples were counted for 20-400 minutes, depending on the  $^{51}\text{Cr}$  activity of the particular sample being examined. All gamma-ray spectra and all counting statistics were corrected for background. Background counts were for 400 minutes; this long counting period improved the counting statistics for the net photopeak area (Wang and Willis, 1965).

The net sample counts or net photopeak area contained not only the induced radioactivity from the  $^{50}\text{Cr}(n, \gamma)^{51}\text{Cr}$  reaction, but also the remaining  $^{51}\text{Cr}$  activity from the tracer. Therefore, it was necessary to subtract the  $^{51}\text{Cr}$  tracer activity from the net  $^{51}\text{Cr}$  activity to determine the net induced  $^{51}\text{Cr}$  activity resulting from the neutron activation of the stable  $^{50}\text{Cr}$ . It was assumed that none of the  $^{51}\text{Cr}$  tracer activity was affected by the neutron activation procedure. To accomplish this correction, all radioactivities were referenced to a

single time and to the original 12-ml counting geometry. Included in this treatment of the data was a "Covell correction" to the total phot-peak area of the  $^{51}\text{Cr}$  tracer.

## III. RESULTS AND DISCUSSIONS

Cr(III) Exclusion during Extraction

Many investigators have concluded that the methyl isobutyl ketone extraction of an acidic aqueous solution discriminates totally against Cr(III) while accepting Cr(VI) (see "Analytical Method", "Background"). However, none of these studies were concerned with a medium as complex as sea water. Therefore, it was deemed necessary to examine Cr(III) exclusion during extraction of sea water samples, as a function of salinity.

Duplicate extractions were run on three water samples: (1) a sea water of 32.35 ‰ salinity, (2) an aliquot of doubly distilled-deionized water, and (3) an equal-volume mixture of the sea water and the DDDW. A  $^{51}\text{Cr(III)}$  tracer solution was prepared by reducing a  $^{51}\text{Cr(VI)}$  aqueous solution (pH about six, specific activity unknown) with stannous chloride,  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ . The yellow  $^{51}\text{Cr(VI)}$  solution, upon the addition of stannous chloride, turned a turbid gray-green color, the resultant of the freshly formed Cr(III) cation and the flocculated excess of white hydrolyzed Sn(II). The excess Sn(II) ensured that the chromium remained in the +3 oxidation state when added to the water samples.

The extraction procedure followed was identical to that described previously, with two exceptions: (1) the volumes were different (but

still in the same ratios), and (2) the ketone extract was not washed with 2 M HCl. Only 1 l of water and 200 ml of hydrochloric acid were used. Upon addition of the concentrated HCl to the water sample, the flocculated excess of Sn(II) dissolved. The amount of MIBK (not equilibrated over 2 M HCl) was adjusted so that the volume of the resulting ketone extract was approximately 6 ml. Five ml of the extract were removed, placed in a counting tube, counted, and compared to 5 ml of aqueous solution containing the same amount of  $^{51}\text{Cr(III)}$  as introduced into the samples.

In a ten minute counting period, the photopeak of the comparison sample contained 19,202 net counts. None of the ketone extracts from the six samples produced counts outside of the statistical limits (at the 90% confidence level) of the background (585 counts per ten minutes). Therefore, it can be concluded that the  $^{51}\text{Cr(III)}$  introduced into the samples of various salinity was not extracted under the conditions described.

#### Oxidation Procedure Checks

The oxidation procedure includes (1) heating the sample for approximately 30 minutes to reach its boiling point, and then (2) boiling the sample for an additional 45 minutes. These two steps ensure (1) that any Cr(III) is rapidly oxidized to Cr(VI), and (2) that the excess peroxydisulfate is decomposed. If all of the excess oxidizing agent

decomposes, the conditions of high temperature and  $\text{pH} < 2$  would then favor the reduction of Cr(VI) to Cr(III). To ascertain the approximate percentage of peroxydisulfate remaining after the boiling step, experiments were conducted on 0.45- $\mu$ -filtered sea water which was oxidized using the standard procedure (except that no radioactive tracer was used). After the oxidized solution was cooled to room temperature and diluted with DDDW to the original 1.75-l volume, the remaining  $\text{S}_2\text{O}_8^{=}$  was determined using the method of Vogel (1961).

A 100-ml aliquot of the sample was put into a 250-ml erlenmeyer flask. To this was added 10 ml of 0.25 M  $\text{H}_2\text{SO}_4$ . An excess of ferrous ammonium sulfate, 10 ml of a  $5.00 \times 10^{-3}$  M solution made up in DDDW, was then added, and the resulting solution allowed to stand for 20 minutes. Three drops of a 0.010 M ferroin indicator were then added, and the excess of Fe(II) was titrated with  $5.00 \times 10^{-3}$  M cerium (IV) sulfate solution (in 1 M sulfuric acid) to the first color change from orange to yellow. Blanks of ferrous ammonium sulfate plus ferroin, and of the ferroin alone were also run, using a sea water matrix. Triplicate analyses showed 1.98%, 2.10% and 1.73% of the peroxydisulfate remaining at the end of the standard oxidizing procedure. Duplicate analyses of a slightly modified procedure, where boiling of the sample was continued for an additional 30 minutes, showed only 0.88% and 0.75% of the  $\text{S}_2\text{O}_8^{=}$  remaining.

Originally, it was planned to use atomic absorption spectrophotometry to measure the chromium content of the ketone extracts. Possible oxidation of the MIBK by excess peroxydisulfate during the extraction was then a point of great concern. Any change in the composition of the ketone extract might have changed its viscosity, thereby modifying the sample flow rate, and resulting in erroneous chromium values. The primary reason for not using an atomic absorption technique for chromium analysis was that the water content of the ketone extracts (Pilloton, 1958) was variable. This, in turn, caused either a variable flame temperature or a variable sample flow rate, or both. Cr(VI) extracts, as well as Cr(III) extracts, showed such inconsistencies. It was then decided to use neutron activation for analysis of the extracts. At that point, the presence of a small amount of  $S_2O_8^{2-}$ , remaining after oxidation of any Cr(III) to Cr(VI), was of little concern. Since some of the peroxydisulfate remained after completing the oxidation procedure, the reduction of Cr(VI) to Cr(III) was not a problem. However, the question of whether or not all of the Cr(III), if present, would have been oxidized to Cr(VI) was still open. Attempts to determine the effectiveness of the oxidation scheme only established that more than 90% of Cr(III) in a concentrated test solution was oxidized. A standard oxidation procedure, without the  $^{51}Cr(VI)$  tracer, was run on a 1.75-1 aliquot of 0.45- $\mu$ -filtered sea water, which was made  $5.0 \times 10^{-5}$  M in Cr(III) (approximately  $10^6$  x the total concentration of

chromium in sea water). After the oxidized solution was cooled to room temperature and diluted with DDDW to the original 1.75-l volume its Cr(VI) content was determined by absorption spectrophotometry (on a Hitachi-Perkin-Elmer Model UV-VIS spectrophotometer). The standard was a freshly-prepared solution of 0.45- $\mu$ -filtered sea water,  $5.00 \times 10^{-5}$  M in Cr(VI) (made using  $K_2Cr_2O_7$ ), containing the same concentrations of Cu(II) and HCl, but not containing  $K_2S_2O_8$ . Both standard and sample were compared against DDDW. Sea water alone, or sea water made  $5.0 \times 10^{-5}$  M in Cr(III), run against DDDW, gave a zero reading in that portion of the spectrum of concern (centered around 348 m $\mu$  - see Haight et al. (1964) and Haight (1966)). Duplicate analyses showed that 90.5% and 92.8% of the Cr(III) was oxidized to Cr(VI). However, these figures should be treated as minima because: (1) the Cr(III) used was in the form of  $CrCl_3 \cdot 6H_2O$ , a hygroscopic solid, which previously had been exposed to the air, and (2) the stock solution of sea water,  $5.0 \times 10^{-3}$  M in Cr(III), from which the  $5.0 \times 10^{-5}$  solutions were prepared, had been allowed to stand overnight. This time was ample for adsorption to the flask walls of, perhaps, all the "missing" Cr(III) (see the discussion of Cr(III) adsorption in the "INTRODUCTION", "Chromium in Sea Water").

#### Oxidation Checks for $^{51}Cr(VI)$ Tracers

To test the effectiveness of the oxidation procedure for the

$^{51}\text{Cr(VI)}$  tracers, six additional solutions were prepared in the same manner as the tracers, except that the 5 ml of a  $5.0 \times 10^{-3}$  M Cr(III) solution ( $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  added to DDDW) were used in place of the 5 ml of stock  $^{51}\text{Cr}$  solution. One of these was not heated. Another was heated only for about one hour. A third was heated for about two hours. The other three were heated exactly as the  $^{51}\text{Cr(VI)}$  tracers. After heating, all solutions, including the tracers, were air-cooled to room temperature. All of the solutions not containing  $^{51}\text{Cr}$  were diluted to 100 ml with DDDW, and analyzed for relative Cr(VI) content using a Hitachi-Perkin-Elmer Model UV-VIS spectrophotometer. A Cr(VI) standard was not used because the original Cr(III) concentration was not known accurately (see previous section). The results are shown in Figure 1. An absorbance of 0.400 was recorded for the solution heated for two hours at  $97^\circ\text{C}$ . When heating was continued for an additional 14 hours, the absorbance increased to only 0.404. It was concluded, therefore, that the tracers used for sample storage and for extraction experiments were in the +6 state. No tests were conducted to confirm that the excess hydrogen peroxide was completely decomposed by the conditions of  $\text{pH} > 12$  and heating at  $97^\circ\text{C}$  for approximately 16 hours. However, after the  $^{51}\text{Cr(VI)}$  tracer was added to the sea water sample, any reduction of Cr(VI) caused by the  $\text{H}_2\text{O}_2$  (upon addition of the hydrochloric acid) would affect the tracer as well, and would not invalidate the results. The possibility of excess



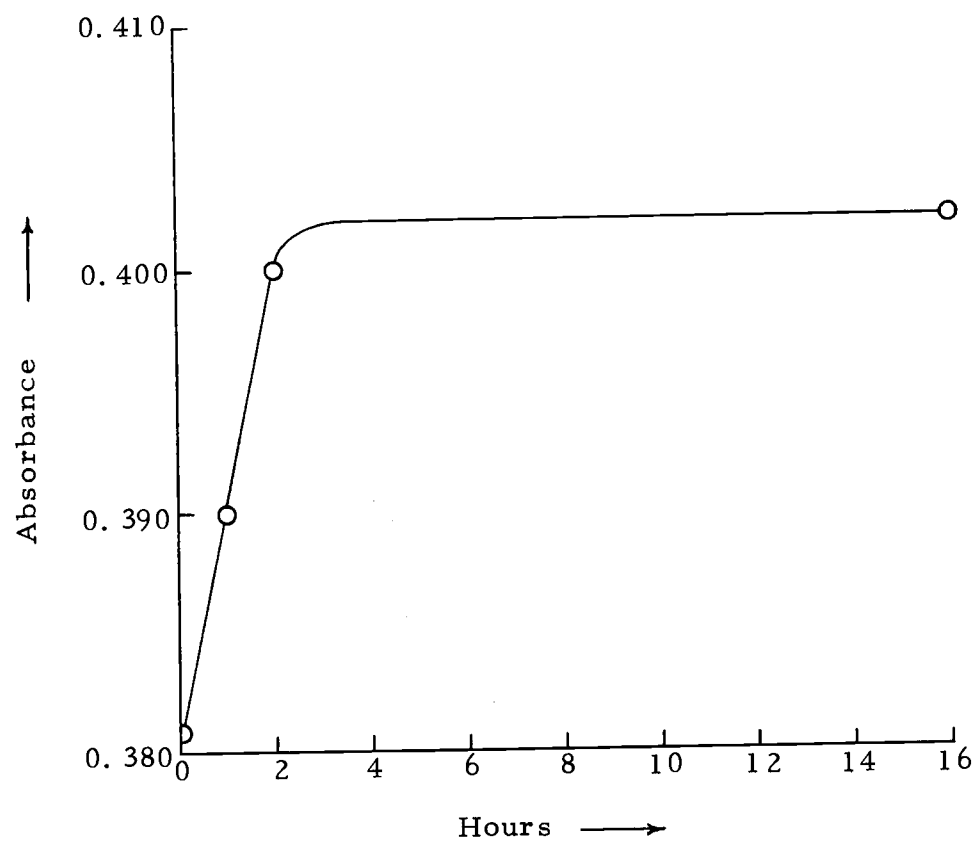


Figure 1. Oxidation of Cr(III) to Cr(VI) by  $\text{H}_2\text{O}_2$  as a function of time (at  $97^\circ\text{C}$  and pH 12).

peroxide oxidizing Cr(III) present in the sea water (at pH ~ 8.1 and at a temperature ranging from about 5° C to room temperature), remains open.

### Sample Storage

The results of the sample storage experiments were not conclusive. The activity of the  $^{51}\text{Cr(VI)}$  tracer, added to 10-1 aliquots of filtered (through a 0.45- $\mu$  membrane filter) and unfiltered sea water from station NH-10, was not great enough to provide counting statistics better than about 10.5% (at the 90% confidence level). Although eight samples were taken from each aliquot over a period of eight days, only samples removed at 0, 1, 3 and 7 hours from the unfiltered aliquot, and samples removed at 0, 1 and 3 hours from the filtered aliquot were actually counted. Within the limits so established, storage in the polyethylene containers had no effect on the added  $^{51}\text{Cr(VI)}$  tracer, and, by inference, on the Cr(VI) content of the sea water.

### Data Treatment for Sea Water Samples, Standards and Blanks

Extraction efficiencies were obtained by comparing the activities of the ketone extracts to the activity of an identical volume of aqueous solution containing the same amount of tracer as added to the samples, standards and blanks during the extraction process. Triplicates were

made of the extraction reference, and a weighted mean<sup>2</sup> and its associated standard deviation calculated for comparison purposes. Duplicates were made of all samples, standards and blanks. After the evaporation procedure, all ketone extracts were counted once again to determine the effect of a change in counting geometry. A third set of counts was made after neutron activation of the evaporated ketone extracts. When corrected for background, and referenced to a single

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<sup>2</sup>When counting replicate samples, for which the degree of precision is not the same (examples include sample replicates having low activity levels, and repeated counting measurements of a fairly rapidly decaying sample), the best value is obtained by favoring those individual determinations having the least associated error (Harley, 1967).

The weighting factor,  $w_i$ , which minimizes the variance,  $\sigma_i^2$ , in the final result is:

$$(12) \quad w_i = \frac{1}{\sigma_i^2}$$

The weighted mean,  $\bar{x}$ , of the individual determinations,  $x_i$ , is calculated as:

$$(13) \quad \bar{x} = \frac{\sum w_i x_i}{\sum w_i}$$

The standard deviation of the weighted mean,  $\sigma_{\bar{x}}$ , is:

$$(14) \quad \sigma_{\bar{x}} = \left[ \frac{1}{\sum w_i} \right]^{1/2}$$

This weighting method was used to treat data for replicates of samples, standards and blanks.

time (decay correction), the three counts for each sample, standard and blank were used, as outlined below, to obtain values for Cr(VI) and Cr(T) in the sea water samples.

R = reference activity	1 = first count (corrected for background); for extraction efficiency
X = sample activity	2 = second count (corrected for background); for geometry change
S = standard activity	3 = third count (after neutron activation, corrected for background); for sample yield
T = empty counting tube activity	

The ratio of the chromium content of the sample (which also includes the chromium content of the standard) to that of the standard (which contained the equivalent of 0.800  $\mu\text{g/l}$ ) is:

$$(15) \quad \frac{\left[ \frac{R_1}{X_1} \cdot \frac{X_1}{X_2} \cdot \frac{(X_3 - X_2 - T_3)}{1} \right]}{\left[ \frac{R_1}{S_1} \cdot \frac{S_1}{S_2} \cdot \frac{(S_3 - S_2 - T_s)}{1} \right]} = \frac{X_3 - X_2 - T_3}{X_2} \cdot \frac{S_2}{(S_3 - S_2 - T_s)}$$

When simplifying the ratio of the sample plus standard to the standard, the reference count and the extraction efficiency counts are cancelled. However, these counts were made (1) to determine what the actual extraction efficiencies were, and (2) to determine the total chromium content of the counting tubes. In the latter case, the ratio of the chromium content of the counting tube to that of the standards (which contained 1.400  $\mu\text{g}$ ) is:

$$(16) \quad T_3 / \left[ \frac{R_1}{S_1} \cdot \frac{S_1}{S_2} \cdot \frac{(S_3 - S_2 - T_3)}{1} \right] = \frac{T_3}{R_1} \cdot \frac{S_2}{(S_3 - S_2 - T_3)}$$

After activation, gamma spectra for samples, standards and empty tubes were treated by the method of Covell (1959), outlined in Appendix A, to determine that portion of the spectra due to  $^{51}\text{Cr}$  activity. From the activity of the sample and standard were subtracted the activity of the empty counting tube and the activity of the tracer (in this case also treated by the method of Covell (1959)). Duplicate determinations of the  $^{51}\text{Cr}$  activity of the standard, and of the empty counting tube were made. Weighted means and their standard deviations were calculated and used for all computations involving the samples and blanks.

#### Cr Content of the Counting Tubes and MIBK

Within the bounds of one standard deviation (due to counting errors only), there is no difference between the weighted means for the duplicate determination of the activity of the empty counting tube and of the counting tube containing evaporated MIBK. Therefore, the assumption that there is no chromium contamination in MIBK stored over 2 M HCl is warranted, at least within the precision of the counting. All four of the activity values were then treated as replicates, and were used to calculate a weighted mean for the empty tube activity.

This weighted mean was used to correct the gross activity of the samples and blanks after neutron activation, and correction for background. Employing Equation (16), the chromium content of the empty counting tubes was ascertained to be  $0.338 \pm 0.057 \mu\text{g}$ .

### Extraction Efficiencies

The efficiencies of Cr(VI) extraction ranged from 60% to 80%, with two exceptions. One, 18%, was the result of a time delay during the extraction procedure which allowed the cooled sample and cooled reagents to come nearly to room temperature. The studies of Weinhardt and Hixson (1951) on the effect of temperature on the distribution coefficient between the ketone and aqueous phases, show that such a change in extraction efficiency could be due solely to the warming of the sample and reagents prior to the actual extraction. The other, 39%, was the result of using a smaller volume of MIBK during the extraction procedure than normally used. This exception is also adequately explained by the studies of Weinhardt and Hixson (1951). They found an apparent decrease in the distribution coefficient when the ratio of the volume of the aqueous phase to the volume of the ketone phase increased, due, probably, to the miscibility of MIBK in the acidic aqueous phase (Pilloton, 1958).

In contrast, the efficiencies of the Cr(T) extractions ranged from 6.0% to 80%. When the data are examined in historical sequence, they

fall into two groups. The first six Cr(T) samples treated have extraction efficiencies which ranged from 6.0% to 11%. The last five Cr(T) samples and blanks treated have extraction efficiencies which ranged from 64% to 80%. The dividing line between the two groups of samples coincides with a change in the brand of concentrated hydrochloric acid used to make the sea water 2 M in HCl. The brand change was from B & A to Dupont. Since any chromium contamination present in the concentrated HCl would be in the +3 state, little or no effect on the final results was expected from this slight modification of the chromium extraction procedure.

A possible explanation of the low Cr(T) extraction efficiencies when B & A acid was used, and the high Cr(T) extraction efficiencies when Dupont acid was used is that the B & A acid contained impurities which reduced some of the Cr(VI) to non-extractable Cr(III). Since this effect was seen in the Cr(T) extractions but not in the Cr(VI) extractions when using B & A acid, it appears that the Cu(II) present in the Cr(T) extractions catalyzed the otherwise kinetically slow reduction of the Cr(VI) (also expressed as a kinetically slow oxidation of the impurities by Cr(VI)). Such kinetically slow oxidations by Cr(VI) are well documented for both organic (Stewart, 1964) and inorganic materials (Haight, Rose and Preen, 1968).

### Causes of the Complex Spectra after Neutron Activation

The reason for the poor precision of the Cr(VI) and Cr(T) values for the sea water samples and blanks lies, primarily, in the large counting error associated with the subtraction of the apparent Compton continua (see Appendix A) from the spectra after neutron activation. The relatively small  $^{51}\text{Cr}$  photopeaks were superimposed on the large Compton continua caused by photopeaks of higher energy. The primary long-lived interferants (relative to the half-life of 27.8 days for  $^{51}\text{Cr}$ ) with appropriate photopeak energies appear to be  $^{124}\text{Sb}$  (half-life, 60.9 days),  $^{60}\text{Co}$  (half-life, 5.24 years),  $^{59}\text{Fe}$  (half-life, 45.1 days),  $^{65}\text{Zn}$  (half-life, 245 days) and  $^{46}\text{Sc}$  (half-life, 83.9 days). The primary short-lived interferant appears to be  $^{82}\text{Br}$  (half-life, 35.9 hours).

Data printouts of the zero to 2.50 MeV region were made only for the few samples which were counted for 400 minutes (those with low extraction efficiencies). Printouts of the spectra for the other samples, standards and blanks included only the region from 0.160 MeV to 0.400 MeV. Therefore, it is not possible to determine whether the interferants were from the counting tubes, from the reagents, or from the sea water itself. It should be noted, however, that Co, Zn, Sb(III, V) and Fe(III) are extracted from aqueous hydrochloric acid solution by methyl isobutyl ketone (Doll and Specker, 1958; Goto and Kakita, 1959).



Concentration and Oxidation State of Chromium in Sea Water Off Oregon

Cr(VI) and Cr(T) analyses of filtered and unfiltered surface sea water samples and blanks from stations NH-5 and NH-10, located five and ten nautical miles, respectively, off the Oregon coast, are given in Table 7. Duplicate analyses were made of all samples, standards and blanks. However, due to poor extraction efficiencies (discussed previously) and, therefore, poor counting statistics, four samples gave results which were not interpretable, and are not included in Table 7 (positions marked with asterisks). Within the limits of one standard deviation, based solely on counting statistics, there is no difference between the Cr(VI) and Cr(T) contents of the filtered and unfiltered samples from stations NH-5 and NH-10. Also, within these same limits, there is no difference between the Cr(VI) and Cr(T) contents of the singly-filtered samples from the two stations, of the filtration blanks (from station NH-10, filtered three times) or of the reagent blanks (from station NH-10, treated with twice the amount of reagents normally used during the oxidation procedure). If the compounding of counting errors had not caused such large standard deviations for all chromium values, differences attributable to the following might have been seen:

1. Filtration blank. Robertson (1968) determined that a Millipore membrane filter contains 17.6 ppm chromium.

Table 7. Results of chromium analyses of individual sea water samples and blanks.

Station	Soluble Cr (filtered) ( $\mu\text{g/l}$ )		Soluble Cr plus particulate Cr (unfiltered) ( $\mu\text{g/l}$ )	
	Cr(VI)	Cr(T)	Cr(VI)	Cr(T)
NH-5	.569 $\pm$ .403	*	.430 $\pm$ .640	*
Weighted mean and standard deviation	<u>.208 <math>\pm</math> .218</u>	<u>.597 <math>\pm</math> 1.20</u>	<u>.221 <math>\pm</math> .283</u>	<u>.526 <math>\pm</math> .372</u>
	.290 $\pm$ .192	.597 $\pm$ 1.20	.256 $\pm$ .259	.526 $\pm$ .372
NH-10	.318 $\pm$ .300	*	.126 $\pm$ .259	.555 $\pm$ 1.65
Weighted mean and standard deviation	<u>.248 <math>\pm</math> .269</u>	<u>*</u>	<u>.099 <math>\pm</math> .235</u>	<u>.075 <math>\pm</math> .217</u>
	.279 $\pm$ .200	*	.111 $\pm$ .174	.083 $\pm$ .215
Reagent blank (NH-10, with twice amount of reagents for oxidation)		.242 $\pm$ .256 <u>.443 <math>\pm</math> .337</u>		
Weighted mean and standard deviation		.316 $\pm$ .204		
Filtration blank (NH-10, filtered three times)	.032 $\pm$ .194 <u>.118 <math>\pm</math> .213</u>	.310 $\pm$ .269 <u>.126 <math>\pm</math> .208</u>		
Weighted mean and standard deviation	.077 $\pm$ .150	.194 $\pm$ .165		
Overall weighted mean and standard deviation	.189 $\pm$ .102	.246 $\pm$ .127	.156 $\pm$ .144	.194 $\pm$ .186

Error limits are one standard deviation, based solely on counting errors.

\* = data were uninterpretable, due to poor extraction efficiencies.

Assuming this value to be applicable for the Gelman GM-6 membrane filters used in these experiments (no data for the chromium content of these filters is known), then as much as 0.295  $\mu\text{g Cr/l}$  could have been introduced to the filtered samples from the filter alone.

2. Reagent blank. The label on the bottle of reagent grade  $\text{K}_2\text{S}_2\text{O}_8$ , used as an oxidant, indicated a maximum limit of heavy metals (exclusive of Fe and Mn) of 5 ppm. Since 2 ml of a 0.175 M solution were used during the oxidation procedure, a maximum of 0.3  $\mu\text{g Cr(T)/l}$  could have been introduced if all the impurity were chromium.

Since the Cr(VI) and Cr(T) contents of the filtered and unfiltered samples and blanks cannot be distinguished at the 68% confidence level, all samples were treated as replicates. A weighted mean and its standard deviation for the Cr(VI) and Cr(T) concentrations were computed. They are listed in Table 7 and presented graphically in Figure 2. These results, and the constraints:

$$[ \text{Cr(VI)}_s + \text{Cr(VI)}_p \geq \text{Cr(VI)}_s ] \text{ and } [ \text{Cr(T)}_s + \text{Cr(T)}_p \geq \text{Cr(T)}_s ] ,$$

where  $s$  represents that chromium in soluble form, and  $p$  represents that chromium in particulate form, lead to the following tabulated conclusions as to the chromium content of surface sea water off Oregon (Table 8):

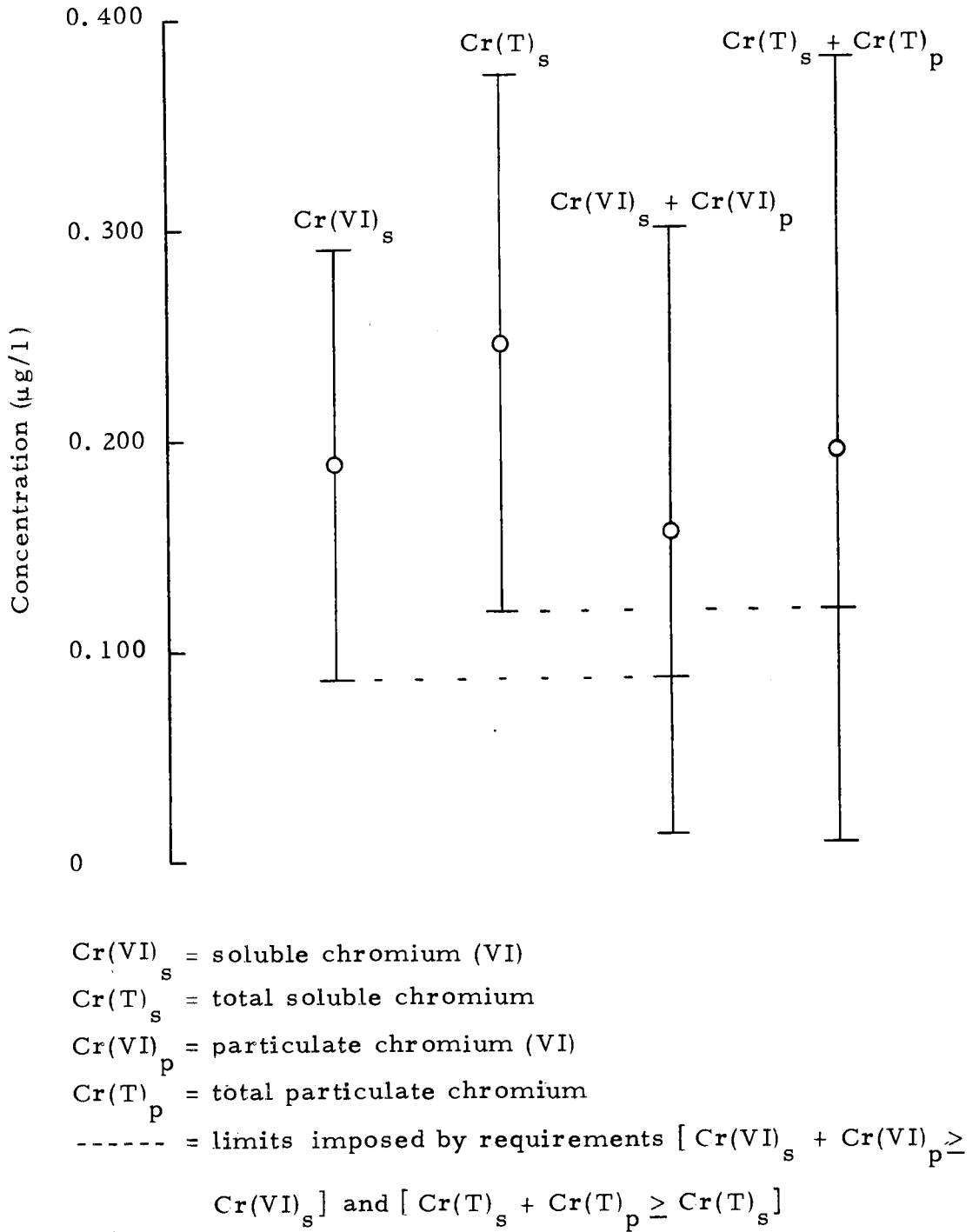


Figure 2. Concentration and oxidation state of chromium in surface sea water off Oregon.

Table 8. Concentration and oxidation state of chromium in surface sea water off Oregon.

Species	Presence confirmed	Presence disproved	Minimum possible concentration ( $\mu\text{g/l}$ )	Maximum possible concentration ( $\mu\text{g/l}$ )
$\text{Cr(T)}_s$	yes	--	0.119	0.373
$\text{Cr(VI)}_s$	yes	--	0.087	0.291
$\text{Cr(III)}_s$	no	no	0.000	0.286
$\text{Cr(T)}_p$	no	no	0.000	0.261
$\text{Cr(VI)}_p$	no	no	0.000	0.213
$\text{Cr(III)}_p$	no	no	0.000	0.261

s = soluble

p = particulate, the difference between the unfiltered and filtered samples

The presence of soluble Cr(III), particulate Cr(III) or particulate Cr(VI) can neither be confirmed nor disproved. This may result from: (1) the poor precision of the data, or (2) the inability of the analytical method to detect Cr(VI) or Cr(T) associated with particulate matter. Because of the rather drastic oxidation procedure used, however, the former reason seems more likely.

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## APPENDICES

## APPENDIX A

An Outline of the Method Used to Analyze Gamma Spectra

In a complex gamma-ray spectrum of a sample containing a number of radionuclides, the total area of a photopeak in question ( $R$ ) is considered to be that area above the Compton continuum resulting from higher-energy photopeaks (Figure 3). Techniques are available for determining  $R$  (Choy and Schmitt, 1965). However, when making all calculations by hand, it is much easier to determine some fraction ( $N$ ) of the total photopeak area and to use  $N$  for comparison with standards. Such a method is valid if  $N$  remains a constant fraction of  $R$  as  $R$  varies from sample to sample.

The method used to analyze gamma spectra is an adaptation and slight modification of the method of Covell (1959) for determining  $N$ . In the photopeak region, the peak channel ( $n_0$ ) containing the greatest number of counts is selected. An equal number of channels ( $n$ ) on either side of  $n_0$  is then chosen. The counts in each of the  $2n + 1$  channels are summed. From this sum or area ( $P$ ) is subtracted the total number of counts in the trapezoid ( $Q$ ) (cross-hatched area in Figure 4). The remaining area ( $N$ ) is directly proportional to the area of the pure photopeak, and can be compared to similarly determined areas for standards and other samples.

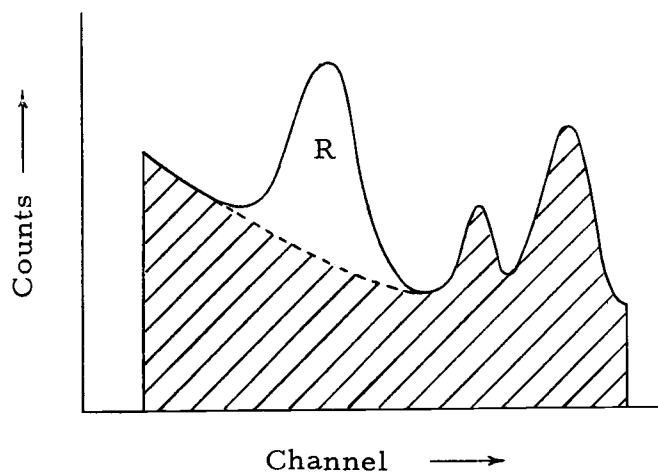


Figure 3. A photopeak superimposed on a Compton continuum from higher-energy photopeaks.

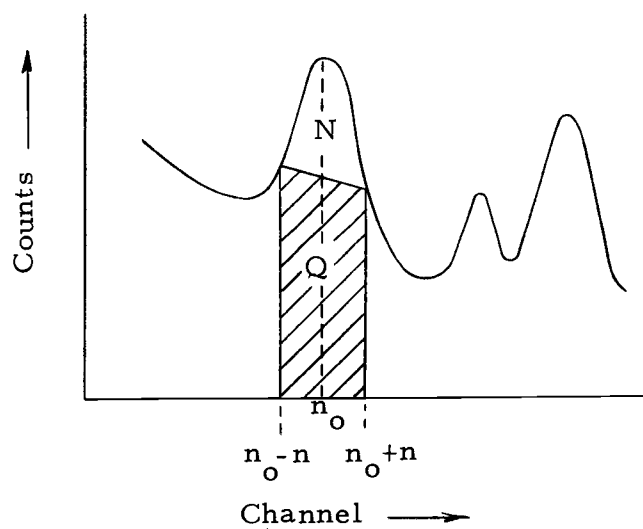


Figure 4. Determining a representative fraction of a photopeak.



The overall counting error in computing  $N$  results from the combined errors associated with the determination of the area  $P$ , the area  $Q$ , and the background area  $B$  in the same  $2n + 1$  channels. If a background of equal counting time is considered, the standard deviation for  $N$  can be calculated from the equation

$$(17) \quad \sigma = \sqrt{P + B + \frac{(2n + 1)^2}{4} (X_{n_0 - n} + X_{n_0 + n} + X'_{n_0 - n} X'_{n_0 + n})}$$

where  $X$  is the number of counts in the designated channel for the gross sample or standard spectrum, and  $X'$  is the number of counts in the designated channel for the background spectrum. It is the third term, that associated with the determination of the area of the trapezoid, that was controlling in these experiments, and which was responsible for the large standard deviations obtained. Suggested ways of improving the error associated with counting are included in Appendix B.

## APPENDIX B

Possible Ways of Improving the Experimental Procedures

The exact concentration of soluble Cr(VI), and the presence or absence of soluble Cr(III), particulate Cr(VI) and particulate Cr(III) could not be determined because of the poor precision of analytical data. To obtain more precise values using the same general experimental procedure, improvements, particularly in the evaluation of the activity of the samples, standards and blanks after neutron activation (see Appendix A), are necessary.

The  $^{51}\text{Cr}$  photopeaks of the activated MIBK extracts were superimposed on large Compton continua caused by other radionuclides. Consequently, the error in the residual peak-area determination was comparable to the area itself. The error could be substantially reduced by:

1. Chemical separation of the chromium from the other interfering radionuclides. If the interfering radionuclides are from the sea water or reagents, precipitation of the lead chromate after activation and prior to counting would alleviate the problem. The ketone extracts (and the counting tubes) could be placed in a muffle furnace, the residue taken up in solution, and the lead chromate precipitation carried out. Alternatively, the ketone extract, prior to

activation, could be back-extracted with dilute NaOH to remove the Cr(VI) and, perhaps, the other interfering elements. This aqueous solution could then be activated without the prior evaporation step. After activation, the chromium could be precipitated as lead chromate.

2. Modification of the activation and subsequent counting procedures. Increasing the activation period from three hours to 24 hours, and counting the activated samples for 400 minutes instead of 20 minutes (only these samples having low extraction efficiencies were counted for 400 minutes) would improve counting precision by a factor of more than 12.

A mistake was made in having the concentration of the standards approximate the concentration of the samples. The counting errors for the standards were, therefore, comparable to those for the samples. The use of more concentrated standards would overcome this problem.

Table 9 summarizes some of the ways that could be used to improve the precision of the final data, without resorting to radiochemical separation procedures. In combination, these methods could improve the precision of the data by a factor of 25 or more. In other words, the standard deviations could be reduced from about 100% to about 4%.

Table 9. Ways to improve the precision of extraction and counting data.

Method	Approximate improvement of precision
Use twice the amount of water sample.	$\sqrt{2}$
Increase the concentration of the standard,	$\sqrt{2}$
Activate samples for 24 hours instead of three hours.	$\sqrt{8}$
Count samples for 400 minutes instead of 20 minutes.	$\sqrt{20}$
Total (product)	25