

Spectrophotometric Determination of Chromium (III) and Chromium (VI) in Sea Water

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Fundamental conditions for the state analysis of chromium in sea, lake, and river water were studied, and procedures for the particle fractionation and the separation of chromium (III) from chromium (VI) were recommended.

Some sea, lake, and river water samples were analyzed, and 0.01–0.27 $\mu\text{g Cr (III)/l}$ and 0.04–0.47 $\mu\text{g Cr (VI)/l}$ were obtained. In open sea chromium (VI) was predominant.

INTRODUCTION

For the determination of chromium in natural water, various methods, such as spectrophotometric method,¹⁾ spectroscopic method,²⁾ catalytic method,³⁾ chemiluminescence method,⁴⁾ atomic absorption,^{5,6)} and neutron activation method⁷⁾ have been recommended. In natural water, chromium seems to exist as trivalent species or hexavalent species, and therefore, in order to reveal the oxidation state, these two species must be separated from each other by adequate procedure. Chuceas and Riley reported that the most part of chromium in sea water was trivalent,⁸⁾ while Fukai^{9,10)} and Yamamoto¹¹⁾ suggested that hexavalent chromium was predominant. However, there is a few study on the valency state of chromium in natural water. The present authors attended the fact that chromium (III) was quantitatively coprecipitated with aluminum hydroxide at pH 8–9, but chromium (VI) remained in filtrate, and in this investigation, coprecipitation with aluminium hydroxide was applied for the separation of the two species. Chromium (VI) in filtrate was reduced with hydroxylamine and was coprecipitated with aluminium hydroxide again. Chromium in both fractions was then determined by diphenylcarbazide method. Procedure for the determination of total chromium in suspended matter was also proposed. By the procedures recommended, the oxidation state of chromium in natural water can be elucidated.

REAGENTS AND APPARATUS

Reagents: Chromium (III) standard solution (1 mg Cr^{3+}/ml): 0.7696 g of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was dissolved with 2N-sulfuric acid and diluted to 100 ml.

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Chromium (VI) standard solution (1 mg Cr^{6+} /ml): 0.2829 g of well-dried $\text{K}_2\text{Cr}_2\text{O}_7$ was dissolved and diluted to 100 ml with 2N- H_2SO_4 . These two solutions were adequately diluted before use.

Chromium-51 solution: 1 mCi of $\text{Na}_2^{51}\text{CrO}_4$ (95.9 mCi/mg Cr, 0.9% NaCl solution), purchased from Japan At. Energy Res. Inst., was diluted to 25 ml with water to make a stock solution. $^{51}\text{Cr}(\text{III})$ and $^{51}\text{Cr}(\text{VI})$ were prepared by treating the stock solution with hydrogen peroxide in acidic and alkaline media, respectively. Activity concentration of the solution thus prepared was about 1 $\mu\text{Ci}/\text{ml}$.

Aluminium solution (1 mg Al^{3+} /ml): 1.6802 g of $\text{Al}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$ was dissolved in 100 ml of 2N- H_2SO_4 .

Diphenylcarbazide solution (0.25%): 0.25 g of sym-diphenylcarbazide (DPC) was dissolved in 100 ml of acetone. The solution was prepared fresh daily.

Potassium permanganate solution (0.01 M): 0.158 g of KMnO_4 was dissolved in 100 ml of 1N- H_2SO_4 . The solution was filtered through a glass filter each time for using.

Sodium fluoride solution (0.5 M): 2.1 g of NaF was dissolved in 100 ml of water and stored in a polyethylene vessel.

Sodium azide solution (4%): 1 g of NaN_3 was dissolved in 25 ml of water. The solution was prepared fresh daily.

Hydroxylamine solution (2%): 2 g of $\text{NH}_2\text{OH} \cdot \text{HCl}$, recrystallized from aqueous solution, was dissolved in 100 ml of water.

Cupferron solution (5%): 2.5 g of cupferron was dissolved in 50 ml of water. The solution was prepared fresh daily.

Potassium hydrogen sulfate: KHSO_4 was heated in a platinum dish, powdered in a mortar, and stored in a desiccator.

Apparatus: Absorption measurements were made with a Hitachi spectrophotometer, model 139 with 5 cm long cells. Radioactivity was obtained with an Aloka auto well gamma system and a Kobe Kogyo well type scintillation probe PS-300[$1\frac{3}{4}'' \times 2''$ NaI (TI)] and scaler 5A-230.

EXPERIMENTAL AND RESULTS

1. Determination of Chromium with Diphenylcarbazide

For the determination of chromium, spectrophotometric method with diphenylcarbazide (DPC) was adopted. Chromium (VI) reacts with DPC to form reddish violet complex. The reaction is selective for chromium and very sensitive. One tenth to five microgram of chromium could be determined with an error less than $\pm 2\%$. Procedure was as follows: To a sample solution containing 0.1–5 μg of chromium, add 1 ml of 1N- H_2SO_4 and 0.5 ml of 0.01 M- KMnO_4 solution, and warm the solution in boiling water for 40 min. to oxidize chromium (III) to chromium (VI). Cool, add a few drop of 4%- NaN_3 solution, and warm again at 60°C for 3 min. to reduce excess KMnO_4 . Cool in ice water, add 2 ml of 0.25%-DPC solution, and make up the solution to 25 ml. After standing for 20 min, measure the absorbance at 540 nm against the reagent blank, using 5 cm cell.

Molar extinction coefficient of $\text{Cr}(\text{VI})$ -DPC complex is affected by the purity and the amount of the reagent. Under the condition described above, it was estimated to be 34400

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Table I. Masking of Ferric Iron with Sodium Fluoride

Cr(VI) taken (μg)	Fe(III) added (μg)	0.5 M-NaF added (ml)	Cr found (μg)
2.0	50	0.5	2.0 ₀
2.0	100	0.5	1.8 ₉
2.0	500	0.5	2.0 ₄
2.0	50	1.0	1.9 ₉
2.0	100	1.0	2.0 ₀
2.0	500	1.0	1.9 ₂

at 540 nm, which was in good agreement with 34000, the value already reported.¹²⁾

Vanadium (V) [reddish brown complex] and iron (III) [yellowish brown complex] give large positive error and copper [colorless] cause negative error, but color of vanadium complex rapidly diminish, and therefore, vanadium does not interfere after 20 min. standing and copper does not after 40 min. standing. In natural water, considering the content of these metals, the interfering element is only iron (III), and small amount of iron can be masked by addition of NaF, as shown in Table I. When sample contain relatively large amount of iron, such as suspended matter or sediment, iron (III) and other interfering metal ions are removed by the extraction with cupferron-chloroform.

Figure 1 shows the extraction behaviors of chromium (III), chromium (VI), and iron (III). Iron (III) is quantitatively extracted from 0.23–6N H_2SO_4 solution, but chromium (III) is not. Chromium (VI) is extracted to some extent, but in the presence of hydroxyl-

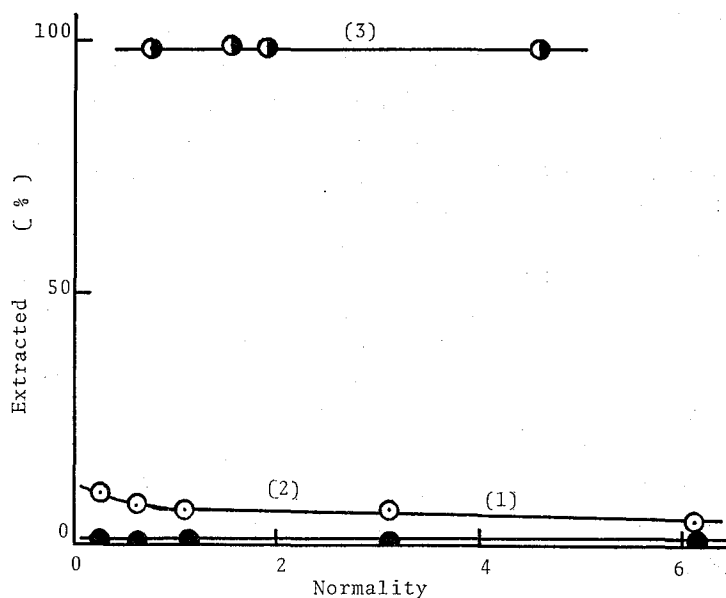


Fig. 1. Effect of concentration of sulfuric acid on extraction of chromium and ferric cupferates.

(1): $^{51}\text{Cr(III)}/40\text{ ml}$ (2): $^{51}\text{Cr(VI)}/40\text{ ml}$

(3): $^{59}\text{Fe(III)}/40\text{ ml}$

5% cupferron solution 1 ml, CHCl_3 20 ml, shaking for 1 min.

Table II. Recovery of Chromium by Cupferron Extraction Method

Cr(III) taken (μg)	Diverse ions (μg)	Cr found (μg)	Recovery (%)
0.5		0.5 ₁	102.0
1.0		1.0 ₂	102.0
1.5		1.5 ₀	100.0
2.0		2.0 ₂	101.0
0.5	Fe(III) 100		
	Cu(II) 50	0.5 ₀	100.0
	V(V) 20		
2.0	Fe(III) 1000		
	Cu(II) 50	1.9 ₉	99.5
	V(V) 20		
2.0	Co(II) 500		
	Zn(II) 500	1.9 ₄	97.0
	V(V) 50		
	* Cr(VI) 1	0.9 ₄	94.0
	* Cr(VI) 1	0.9 ₇	97.0

* Chromium (VI) was reduced to chromium (III) with hydroxylamine.

amine, it is reduced to chromium (III). Table II shows that cupferron extraction can be applied as predetermination procedure for chromium in samples containing large amount of interfering metals.

2. Separation and Concentration of Chromium (III) and Chromium (VI)

Because the content of chromium in sea and river water is very low, the concentration is necessary before the determination. For the concentration of chromium from water sample, coprecipitation,^{1,9,10,11,13} ion exchange,^{5,14} or solvent extraction^{15,16} were recommended. Fukai and Vas proposed the coprecipitation with ferric hydroxide. They determined chromium (III) with one half part of a sample and determined total chromium with the other half part of same sample by reducing chromium (VI) to chromium (III) with sodium sulfite before the coprecipitation with ferric hydroxide.¹⁰ Present authors attended the difference in coprecipitation behaviors of chromium (III) and chromium (VI) with ferric hydroxide and aluminium hydroxide, and sought available procedure for the separation and concentration of chromium. Coprecipitation of chromium (III) and chromium (VI) is influenced by pH value, the amount of carrier and the kind of salts present. Therefore, the control of these factor leads to be effective separation of two species of chromium.

(1) Coprecipitation of chromium with aluminium hydroxide and ferric hydroxide

Coprecipitation behaviors of chromium (III) and chromium (VI) with aluminium hydroxide and ferric hydroxide were studied using radioactive tracers.

A) Coprecipitation of chromium from perchlorate solution

To 150 ml of water, 10 ml of 2M- NaClO_4 solution and $^{51}\text{Cr(III)}$ or $^{51}\text{Cr(VI)}$, which

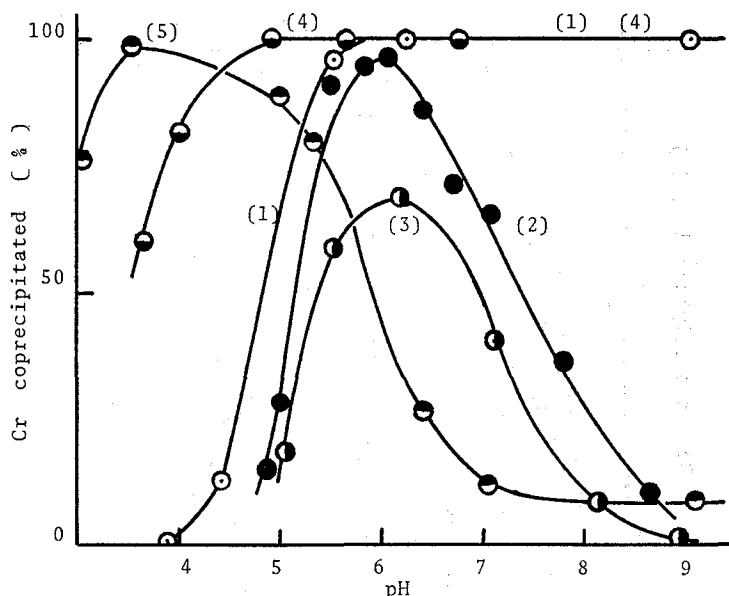


Fig. 2. Effect of pH on coprecipitation of chromium in perchlorate solution with aluminium and ferric hydroxide.

(1): 1.9×10^{-5} M-Cr(III), 1.9×10^{-3} M-Al(III)

(2): 1.0×10^{-5} M-Cr(VI), 1.2×10^{-3} M-Al(III)

(3): 1.0×10^{-5} M-Cr(VI), 3.2×10^{-4} M-Al(III)

(4): 1.0×10^{-5} M-Cr(III), 7.5×10^{-4} M-Fe(III)

(5): 1.0×10^{-5} M-Cr(VI), 7.5×10^{-4} M-Fe(III)

Ionic Strength: 0.1(NaClO₄)

contains appropriate amount of chromium (III) or chromium (VI), are added. After adjusting pH 2 with HClO₄, definite amount of Al(ClO₄)₃ or Fe(ClO₄)₃ is added, and the solution is diluted to 200 ml with water. Two milliliters of the solution is pipetted out as a standard for radioactive measurements. The remainder is adjust to a desired pH with NaOH solution and allowed to stand overnight. The solution is filtered through a 0.45 μ Millipore filter and 2 ml of the filtrate is pipetted out, and the radioactivity is measured.

Coprecipitation behaviors of chromium (III) and chromium (VI) are shown in Fig. 2. From 0.1 M perchlorate salt solution, chromium (III) is quantitatively coprecipitated above pH 6 with aluminium hydroxide, and above pH 5 with ferric hydroxide, respectively. Amount of carrier is not important. Coprecipitation of chromium (VI) with aluminium hydroxide begins at pH 4, showing a maximum near pH 6, and then decreases. In this case, coprecipitation depends upon the amount of carrier: Maximum value is 95.5% with 1.2×10^{-3} M carrier and 67.7% with 3.2×10^{-4} M carrier. Above pH 9, however, chromium (VI) remains almost completely in the filtrate. With ferric hydroxide, coprecipitation of chromium (VI) is found to be about 10% in higher pH range such as pH 9, and therefore the separation of chromium (III) from chromium (VI) is incomplete.

B) Coprecipitation of chromium from various salt solutions

Figure 3 shows coprecipitation behavior of chromium from various salt solutions.

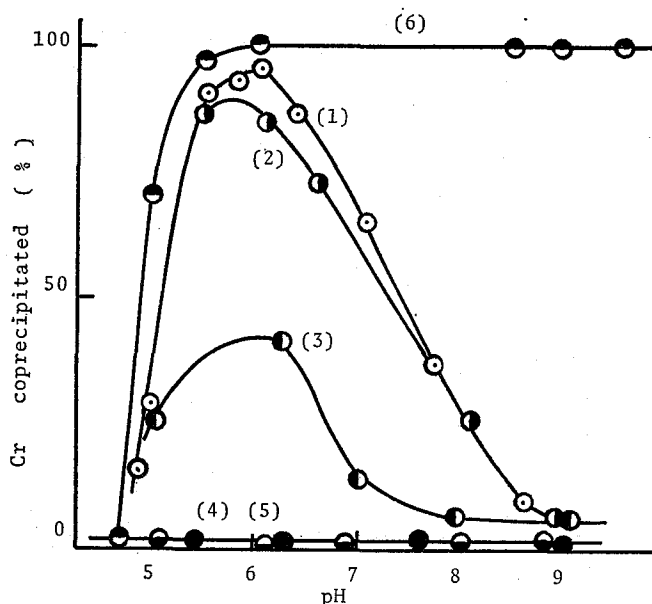


Fig. 3. Effect of diverse salt on coprecipitation of chromium with aluminium hydroxide.

- (1): 0.1 M- NaClO_4 (2): 0.1 M- NaNO_3
 (3): 0.1 M- NaCl (4): 0.1 M- Na_2SO_4
 (5): 0.01 M- Na_3PO_4
 (1)-(5): 1.0×10^{-5} M-Cr(VI)
 (6): 0.1 M- Na_2SO_4 , 1.9×10^{-5} M-Cr(III)

The figure indicates that coprecipitation of chromium (VI) is affected by the kind of anion present. Phosphate and sulfate ions lower the coprecipitation: In the presence of 10^{-3} – 10^{-2} M of these anions, chromium (VI) is not coprecipitated at any pH. Coprecipitation of chromium (III), however, is not influenced by anion, and almost complete above pH 6.

C) Coprecipitation of chromium from sea water

Sulfate contents in sea water and river water are about 2.68 g/kg and 11.2 mg/kg, respectively. Phosphate content is generally lower than sulfate, although it strongly depends upon the environmental conditions. As described above, sulfate and phosphate give favorable effect on the coprecipitation-separation of chromium (III) from chromium (VI). Therefore, it is more desirable that carrier is added as sulfate and sulfuric acid is used instead of perchloric acid.

Figure 4 shows the coprecipitation behaviors of chromium (III) and chromium (VI) from sea water (Cl: 18.3‰, collected from offshore of Shirahama, Wakayama prefecture). The concentration of chromium (III) or chromium (VI) is 10^{-8} M and the concentration of carrier is 5.4×10^{-5} M for ferric ion or 3.7×10^{-4} M for aluminium ion.

Chromium (III) is quantitatively coprecipitated above pH 5.2 with both ferric hydroxide and aluminium hydroxide, but coprecipitation of chromium (VI) with aluminium hydroxide is less than 2% over all pH region, and accordingly, chromium (III) can be completely separated from chromium (VI). Coprecipitation of chromium (VI) with ferric

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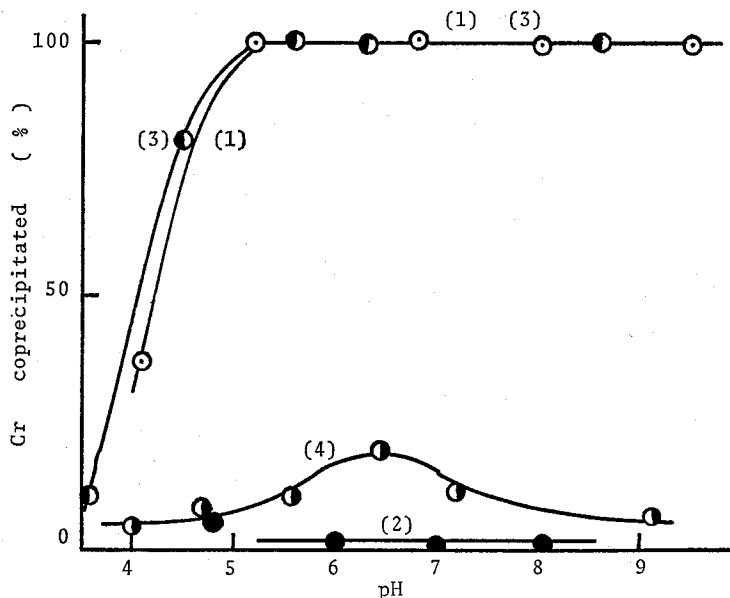


Fig. 4. Coprecipitation of chromium in sea water with aluminium and ferric hydroxide.

(1): 10^{-8} M-Cr(III), 3.7×10^{-4} M-Al(III)

(2): 10^{-8} M-Cr(VI), 3.7×10^{-4} M-Al(III)

(3): 10^{-8} M-Cr(III), 5.4×10^{-5} M-Fe(III)

(4): 10^{-8} M-Cr(VI), 5.4×10^{-5} M-Fe(III)

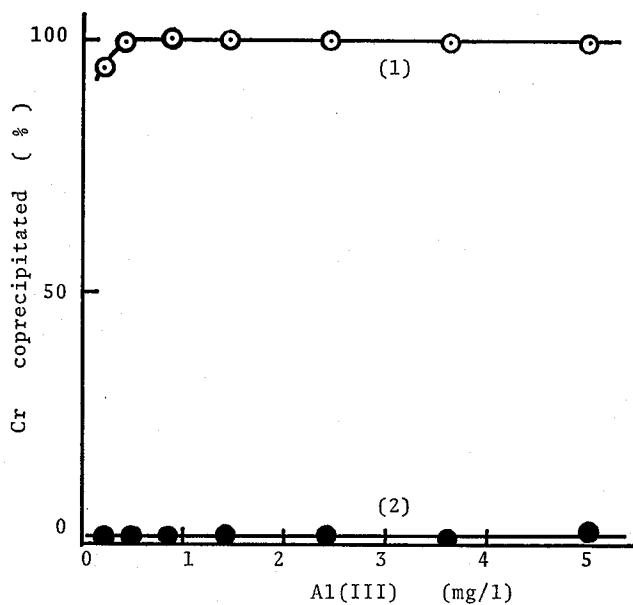


Fig. 5. Effect of amount of aluminium ion on coprecipitation of chromium in sea water.

(1): 0.7×10^{-8} M-Cr(III), (2): 0.7×10^{-8} M-Cr(VI)

pH: 8.2 ± 0.2

hydroxide is somewhat higher than in the case of aluminium hydroxide, and reach more than 10% in the pH range from 5.5–7.5.

Figure 5 indicates that the amount of aluminium required to the separation of chromium (III) from chromium (VI) is 0.2–5 mg per one liter of sea water. The similar results are obtained in the case of river water.

3. Determination of Chromium (III) and Chromium (VI) in Sea and River Water

(1) Change in oxidation state of chromium in water samples

Chromium (III) ion in natural water sample, in analogy with other micro amount of metal ions, is easily coprecipitated with scavenger such as ferric or aluminium hydroxide and then rapidly adsorbed onto the wall of polyethylene bottle or glass vessel, and at the same time, the valency change also may occur on storage. The behavior of chromium on storage was studied.

Table III. Determination of Chromium in Spiked Water Sample

Sample taken (l)	Al(III) added (mg)	Cr added (μ g)		Cr found (μ g)		Recovery (%)
		(III)	(VI)	(III)	(VI)	
distilled water	0.1	3	2.0	1.9 ₅		97.5
	0.1	3	2.0	1.9 ₉		99.5
	0.1	3 (+Fe ³⁺ 100 μ g)	2.0	1.9 ₇		98.5
	0.1	3 (+Fe ³⁺ 100 μ g)	2.0	1.9 ₃		96.5
	0.3	1	1.0	1.0 ₂		102.0
	0.3	1	2.0	1.9 ₉		99.5
	0.3	10	0.3		0.0 ₁ *	
	0.3	10	1.5		0.0 ₅ *	
	0.3	10	2.0		0.0 ₅ *	
	0.3	2	2.0		1.9 ₄	97.0
	0.3	2	2.0		1.9 ₃	96.5
sea water Uragami Bay (A)	1	10	2.0	1.9 ₁		95.2
	1	10	2.0	1.8 ₉		94.5
	1	10	2.0		1.8 ₉	94.5
	1	10	2.0		1.9 ₃	96.5
sea water Uragami Bay (B)	3	10		0.0 ₈	0.00	
	3	10	0.2	0.2 ₈		100.0
	3	10	0.5	0.5 ₆		96.0
	3	10	0.5	1.0	0.6 ₀	104.0, 94.0
sea water offshore Shirahama	3**	10		0.4 ₃	0.6 ₀	
	3***	10		0.3 ₈	0.6 ₃	
	3***	10		1.0 ₈ ****		
	3***	10	0.5	1.0	0.8 ₆	96.0, 99.0

* hydroxylamine was not added

** stored for 2 days

*** stored for 71 days (frozen)

**** hydroxylamine was added

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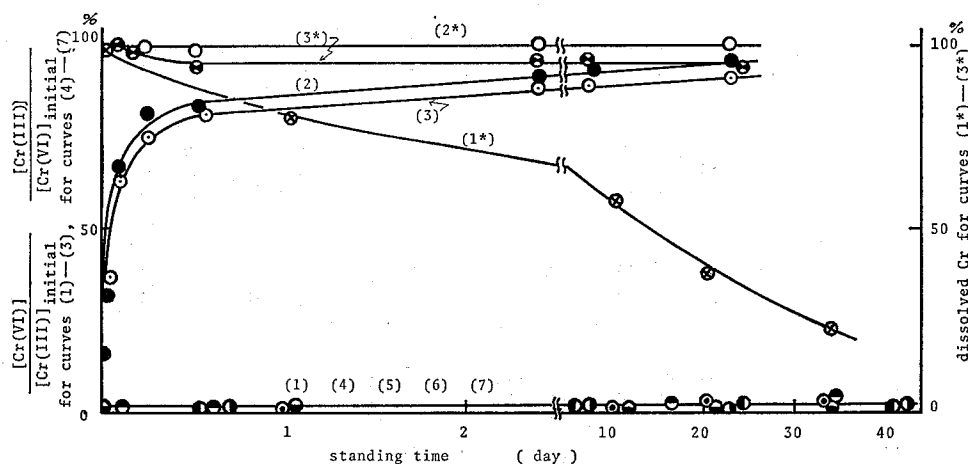


Fig. 6. Effect of storage on oxidation state of chromium in water.

- (1), (1*): Cr(III), distilled water, pH 6.5-7 (2), (2*): Cr(III), sea water
 (3), (3*): Cr(III), sea water, humic acid 5 ppm (4): Cr(VI), distilled water
 (5): Cr(VI), sea water (6): Cr(VI), sea water, humic acid 5 ppm
 (7): Cr(VI), river water
 Chromium concentration: 1.98×10^{-8} M

Figure 6 shows the change in the concentration and the oxidation state of chromium added to distilled water or sea water on storage. In distilled water, at pH 6.5-7, neither chromium (III) nor chromium (VI) show any valency change for 40 days at least (curve 1 and 4), although dissolved chromium (III) quickly loses by adsorption on the wall (curve 1*). Chromium (VI) added to sea water and river water also does not show the valency change (curve 5, 6, and 7), whereas chromium (III) in sea water is very rapidly oxidized to chromium (VI) (curve 2 and 3).

In any case, for the state analysis of chromium, immediately after sampling, suspended matter is filtered and the separation of chromium (III) from chromium (VI) must be carried out as soon as possible. If water samples could be frozen, the sample can be stored over relatively long period without the valency change, as shown in Table III.

(2) Determination of chromium (III) and chromium (VI) in sea and river water

From the results obtained above, a procedure for the determination of chromium (III) and chromium (VI) in sea and river water was established as follows.

After the collection, water sample is filtered through a membrane filter (MFHA 0.45 μ) to remove suspended matter as rapid as possible. To 3 l of filtered sample, 10 mg of Al^{3+} (as sulfate) is added, the and pH of the solution is controlled to 8-9 with NH_3 water. After standing overnight, hydroxide precipitate is filtered with a membrane filter (MFSC 8 μ) [chromium (III) fraction]. To the filtrate, 10 ml of conc. HCl and 30 ml of 2% $NH_2OH \cdot HCl$ solution are added to reduce chromium (VI) to chromium (III). To the solution, 10 ml of Al^{3+} is added and the hydroxide is allowed to precipitate in the similar manner as for chromium (III) fraction [chromium (VI) fraction]. Each precipitate is dissolved with 2N- H_2SO_4 , and after 20 ml of conc. HNO_3 and 1 ml of H_2O_2 are added, the solution is heated to almost dryness. If sample contains large amounts of organic

Table IV. Trivalent and Hexavalent Chromium in Sea Water, Lake Water, and River Water

Sample		Depth (m)	pH	Cl (‰)	D.O (ml/l)	Dissolved (μg/l)					Suspended (μg/l)			
						Cr(III)	Cr(VI)	Cr(III)+ Cr(VI)	(VI) (III)+(VI) (%)	Fe	Al	Cr	Fe	Al
Osaka Bay	St. I	0	8.2	16.3	4.82	0.16	0.32	0.48	66.7	144	3.2	0.99	97.7	144.5
	St. I	12	8.1	17.8	2.91	0.27	0.21	0.49	42.9	160	16.5	0.30	102.8	247.6
	St. II	0	8.1	15.8	4.71	0.10	0.39	0.49	79.6	150	5.3	1.26	108.0	185.5
Uragami Bay		0	8.1	16.19	6.93	0.01	0.33	0.34	97.1	13.3	16.5	0.42	27.1	20.3
		15	8.2	18.85	10.08	0.02	0.40	0.42	95.3	6.7	17.6	—	—	5.2
		25	8.1	19.13	9.97	0.03	0.47	0.50	94.0	11.1	15.2	0.41	42.3	5.2
34°52' N 151°55' E		20	8.2	*34.5	5.27	0.03	0.18	0.21	85.7	0.84	0.40	0.004	0	2.90
		98	8.1	*34.6	4.56	0.01	0.17	0.18	94.5	0	1.74	0.03	0	0.67
Lake Biwa	St. I	0	6.90	**5.0		0.09	0.19	0.28	67.9			0.11	128.7	75.2
	St. II	0	6.95	**5.3		0.12	0.15	0.27	55.6			0.12	43.6	75.5
Yodo River	St. I		7.42	**5.2		0.11	0.04	0.15	26.7			0.25	738.5	295.4
	St. II		7.35	**5.0		0.10	0.08	0.18	44.4			0.31	3203.9	1281.6

* Salinity

** mg/l

substances, the heating with HNO_3 and H_2O_2 to dryness is repeated until organic substances are completely decomposed. The residue is dissolved with 1 ml of $2\text{N-H}_2\text{SO}_4$ and 10 ml of water, and then chromium is determined according to the procedure described in 1.

Table III presents the analytical results obtained from some spiked samples which were prepared by adding a definite amount of chromium (III) or chromium (VI) to distilled water or sea water. Recovery of chromium (III) and chromium (VI) is $97.6 \pm 2.6\%$, and the relative error of the repeated experiments on the same sample is $\pm 1.7\%$.

(3) Determination of chromium in suspended matter

For the determination of chromium in suspended matter, which contains relatively large amounts of iron, following two procedures were recommended.

A. Suspended matter and membrane filter is ashed in a platinum crucible at low temperature. To the ash, 1 ml of $2\text{N-H}_2\text{SO}_4$ and 5 ml of HF are added and it is heated to remove silica. After drying, the residue is fused with 1 g of KHSO_4 , and the melt is dissolved with 20–30 ml of $2\text{N-H}_2\text{SO}_4$. The solution is transferred to a separatory funnel, 3 ml of 5% cupferron aqueous solution is added, and iron and other interfering ions are extracted by shaking with 20 ml of chloroform. The aqueous phase is transferred to a beaker, evaporated, and after organic matter is decomposed with HNO_3 and H_2O_2 , chromium is determined.

B. Suspended matter on filter is dipped in 20–30 ml of $2\text{-}6\text{N-H}_2\text{SO}_4$ for 20 min., and then the H_2SO_4 solution is sucked. The filtrate is treated by the cupferron extraction and chromium is determined [acid soluble chromium fraction]. The residue and filter is transferred to a platinum crucible, and treated by the same procedure as **A** [acid insoluble chromium fraction].

(4) On chromium contents in sea and river water and in suspended particles.

Analytical results of water samples collected from Osaka Bay, Uragami Bay, North Pacific Ocean, Lake Biwa, and Yodo River are summarized in Table IV. Contents of dissolved chromium (III) and chromium (VI) are $0.01\text{--}0.27 \mu\text{g/l}$ and $0.04\text{--}0.47 \mu\text{g/l}$, respectively, and the fraction of chromium (VI) in total dissolved chromium appreciably varies from 26.7 to 97.1% and the fraction tends to increase from coastal to open sea, in general. Suspended chromium shows high value in coastal sea or in bay and very low value in oceanic sea.

Detailed results on the distribution of chromium (III) and (VI), and the geochemical consideration will be described in further paper.

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