One-Pot Speciation Method for Cr(Ⅲ) and Cr(Ⅵ) with APCD/DIBK Extraction System Based on Difference in Rate of Complex Formation

Yoshiro Honma

Department of Chemistry, College of Science, Rikkyo (St. Paul's) University,
3-34-1 Nishi-Ikebukuro, Toshima-ku, Tokyo 171-8501

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A simple speciation of chromium oxidation states based only on the difference in reaction rates of Cr(Ⅲ) and of Cr(Ⅵ) has been developed. This speciation, which was carried out in an ammonium 1-pyrrolidinecarbodithioate (APCD)/diisobutyl ketone (DIBK) extraction system, required no sample splitting. At the first extraction, Cr(Ⅵ) was extracted into a DIBK phase, and Cr(Ⅲ) remaining in the sample was extracted secondly after replacement of the phase by fresh DIBK. Inert Cr(Ⅲ) was extracted directly without the oxidation process. The concentration of chromium in the extract was measured by AAS. In the first extraction, 0.4–0.5% of Cr(Ⅲ) was extracted and 0.2% of Cr(Ⅵ) was carried over to the second extraction. Using artificial seawater, the detection limit (3σ) and the relative standard deviation ($n = 5$, at 100 μg/L) were 10 μg/L and ca. 4% (concentration factor = 2). Interferences of heavy metal ions were examined; 5-fold cation group (Mn^{2+}, Fe^{3+}, Ni^{2+}, Cu^{2+} and Zn^{2+}) and 1-fold anion group (VO_3^-, $Mo_7O_{24}^{6-}$ and WO_4^{2-}) exhibited negative errors of 5 and 10% in Cr(Ⅲ) determination respectively. Validity of the method was checked with the standard reference material JAC-0032 (river water); total chromium was determined as 11.0 μg/L (certified value is 10.1 ± 0.2 μg/L).

Recently, speciation techniques have gained great interest in environmental analysis. Chromium exists in environmental water samples mainly as Cr(Ⅲ) and/or Cr(Ⅵ). Although Cr(Ⅲ) is essential for normal metabolism of mammals,[1–3] Cr(Ⅵ) is considerably toxic to mammals.[4–6] Thus, the speciation of chromium is one of the most important subjects in environmental analysis.

In principle, there are two possibilities for the speciation of Cr(Ⅲ) and Cr(Ⅵ) existing in aqueous solutions by such as atomic absorption spectroscopy (AAS), inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and inductively coupled plasma-mass spectroscopy (ICP-MS). One is complexing and extracting selectively both Cr(Ⅲ) and Cr(Ⅵ) before instrumental analysis, the other is analyzing one of the two species and the total chromium and then calculating the concentration of another species by subtraction. The former method (direct speciation process) is superior to the latter in sample consumption. Since the latter requires sample division, it may be said that the sample consumption in the latter method is doubled. However, the latter was exclusively applied to the speciation of Cr(Ⅲ) and Cr(Ⅵ) because it is difficult to find a suitable chelating agent for the former method.

The dithiocarbamate-chelating agents have the possibility of being one of the suitable regents for the direct speciation process. It is known that some kinds of dithiocarbamate ions form chelate complexes with both Cr(Ⅲ) and Cr(Ⅵ),[7–10] and that the complexation behavior of the two chromium species is considerably different. In contrast with reactive Cr(Ⅵ), Cr(Ⅲ) does not quantitatively form the dithiocarbamato complex under the reaction conditions applied to the dithiocarbamato complex formations of the other metal ions because of the inertness of Cr(Ⅲ) in ligand exchange.[11] These properties of the dithiocarbamate ions indicate that the reagents have the potential to be chelating agents for chromium speciation using the direct speciation process. In spite of this potential, the chelating agents were not used in the direct speciation process of chromium. A major cause of this is the inertness of Cr(Ⅲ). It is difficult to chelate Cr(Ⅲ) quantitatively. Therefore, only the reactions between Cr(Ⅵ) and dithiocarbamate ions have been used in most of the chromium speciation methods based on the dithiocarbamato complex formation.[12–15] Sample solutions were divided into two portions, one of the two was directly used for the determination of Cr(Ⅵ) and the other was used for the determination of total chromium after oxidation of Cr(Ⅲ).

In this situation, some investigators developed the speciation methods into procedures that required no oxidation process. Bergmann et al. heated sample solutions with ammonium 1-pyrrolidinecarbodithioate (APCD)[16] and Subramanian used a large excess of APCD[17,18] in order to quantitatively form the dithiocarbamato complex from Cr(Ⅲ). Their speciation methods utilizing the complex formations from both Cr(Ⅲ) and Cr(Ⅵ) have merit in that the addition of an oxidizing agent is not required. However, these methods also consisted of the determinations of Cr(Ⅵ) and of the total chromium, and still required the same sample division as the conventional speciation methods containing the oxidation process, because Cr(Ⅵ) formed the dithiocarbamato complex in their methods simultaneously with Cr(Ⅲ) under the reaction conditions for the complex formation with Cr(Ⅲ).

The speciation studies utilizing dithiocarbamate formation from Cr(Ⅲ) indicated that the complexation with Cr(Ⅲ) is slower than that of Cr(Ⅵ).[17,18] If reactive Cr(Ⅵ) quantitatively forms the dithiocarbamato complex before a measurable

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amount of the complex is formed with Cr(Ⅲ), and then if the remaining Cr(Ⅲ) quantitatively forms the complex within a practical reaction time without any change in the reaction conditions, the speciation of Cr(Ⅵ) and Cr(Ⅲ) can be carried out sequentially from one sample solution. This conceptual speciation method, which requires neither the sample division nor the oxidation process, is superior to the methods described above in terms of simplicity.

The objects of this study are to find suitable analytical conditions for the conceptual direct speciation method and to apply the method to practical analyses. This study has been carried out using an APCD/diisobutyl ketone (DIBK) extraction system. The stability of APCD in aqueous solution is higher than that of the generally used sodium diethyldithiocarbamate, especially under acidic conditions,[19] and the mutual solubility between DIBK and aqueous solutions is very low.[20,21] It has been clearly indicated that the combination of the two chemicals has great advantages in the determination of metal ions with the chelate extraction-AAS analyses.[21–24]

Experimental

Apparatus. An HM-30S glass electrode pH meter (TOA, Tokyo, Japan) was used for pH measurement. An SR-IIw vertical reciprocating shaker (TAITEC, Saitama, Japan) was used in the extraction process. Concentration of chromium was determined with an AA-782 atomic absorption spectrometer (Nippon Jarrell-Ash, Kyoto, Japan). The AAS measurement was carried out at 357.9 nm with a fuel-rich air-C_2H_2 flame (0.8–5.0 L/min for DIBK phase or 1.4–5.0 L/min for aqueous phase). A hollow cathode lamp was operated at 7.0 mA. All the experiments were carried out at room temperature 21 ± 1 °C.

Reagents and Samples. All chemicals used were analytical-reagent grade or better. Doubly distilled water was used throughout. The chelating agent solution was prepared daily by dissolving an APCD (Wako Pure Chemical Industries, Ltd., Osaka, Japan) in water. Including DIBK (Wako Pure Chemical Industries, Ltd., Osaka, Japan), all chemicals were used without further purification. Atomic absorption standard solutions of Cr(Ⅲ) and Cr(Ⅵ) (Aldrich Chemical Co. Inc., Milwaukee WI) were used as stock solutions. A solution of tris(1-pyrrolidinecarbodithioato)chromium(Ⅲ)[25] in DIBK was used as the standard solution to make calibration curves for AAS measurements. A river-water standard reference material (JAC-0032) was supplied from the Japan Society for Analytical Chemistry, and an effluent obtained from an automotive factory and artificial seawater[26] were used to evaluate the abilities of the proposed speciation method.

Optimization of Extraction Conditions. To determine the optimal extraction conditions for the speciation of chromium, the initial pH of the chromium solution, concentration of APCD, and extraction time were examined. A 2.5 mL of Cr(Ⅲ) (7.7×10^{-5} or 7.7×10^{-4} mol/L) or Cr(Ⅵ) solution (7.7×10^{-5} mol/L) was placed in an Erlenmeyer flask. A 20 mL of diluted hydrochloric acid was added to the flask and the acidity of the chromium solution was adjusted to pH 1–6. In the cases of initial pH 5 or above, the mixture was allowed to stand for 18 h or more under nitrogen gas atmosphere in order to establish the species of Cr(Ⅲ). A 10 mL of DIBK and 2.5 mL of APCD solution (0.08–0.8 mol/L) were added to the chromium solution and the mixture was shaken (1–180 min). After the shaking, the contents of the flask were poured on a Whatman 1PS phase separator (Whatman Int. Ltd., Maidstone, England) in order to separate the two layers. The organic layer passed through the separator and the aqueous layer remained on the separator. The organic layer separated was aspirated into the flame of AAS.

Procedure for Speciation of Cr(Ⅲ) and Cr(Ⅵ). A 20 mL of a mixed solution of Cr(Ⅲ) and Cr(Ⅵ) or of sample solution was placed in an Erlenmeyer flask. As a salting-out agent, 1–5% (w/v) of sodium chloride was dissolved in the solution. Acidity of the contents of the flask was adjusted to pH 1.9–2.1 with diluted hydrochloric acid (0.1 mol/L). A 2.5 mL of APCD solution (0.40 mol/L) was added to the flask. As the first extraction process for determination of Cr(Ⅵ), the mixture was shaken for 5 min immediately after the APCD addition. The organic layer of the contents was separated after the shaking from the aqueous layer with a 1PS phase separator, and the aqueous layer remaining on the separator was restored to the flask. A 10 mL of fresh DIBK was placed in the flask containing the separated aqueous layer and shaking was resumed. This second extraction process for the extraction of Cr(Ⅲ) was stopped 90 min after the addition of APCD solution. As in the first extraction step, the second organic layer was separated from the aqueous layer with a new 1PS separator. Concentrations of chromium in the two organic layers separated were determined with AAS.

Effect of Coexistent Heavy Metal Ions. The interference from coexisting heavy metal ions in the determination of Cr(Ⅲ) and Cr(Ⅵ) was examined using eight kinds of heavy metal ions. The matrix metal ions were divided into two groups. One of the groups consisted of Mn^{2+}, Fe^{3+}, Ni^{2+}, Cu^{2+} and Zn^{2+} and the other consisted of V^{5+}, Mo^{6+} and W^{6+}. The matrix ions of the former group were introduced as nitrate and those of the latter were introduced as NH_4VO_3, $(NH_4)_6Mo_7O_{24}$ and Na_2WO_4. All the matrix elements in each group were prepared in the same molar concentration. The solution of the matrix groups was added to the chromium solution before the pH adjustment and the processes for determination of chromium were carried out in the same manner as described above.

Results and Discussion

Optimization of Extraction Conditions. In order to put the concept proposed for chromium speciation into practice, the following two requirements must be met. First, both Cr(Ⅵ) and Cr(Ⅲ) in aqueous solution are quantitatively extracted under the same extraction conditions except for the reaction time. Secondly, reactive Cr(Ⅵ) is quantitatively extracted before inert Cr(Ⅲ). To find out the reaction conditions filling the above two requirements, the extraction behavior of Cr(Ⅲ) and of Cr(Ⅵ) in the APCD/DIBK system were surveyed. Extractions of Cr(Ⅵ) and of Cr(Ⅲ) were carried out individually in an initial pH range of 1–6 with several shaking periods (concentration of APCD is 0.08 mol/L in the aqueous phase). Based on the results of the extractions, time-extractability curves were plotted for each initial pH condition. From the time-extractability curves, the extraction times required for 95% extraction were read. The readings were plotted in Fig. 1 with initial pH values on the horizontal axis.

Hexavalent and trivalent chromium were extracted quantitatively at pH 1–6 and 2–6, respectively (Fig. 1). The quantitative extraction of inert Cr(Ⅲ) was achieved without the complicated oxidation process for Cr(Ⅲ) by addition of a large excess of APCD. Although the two chromium species require

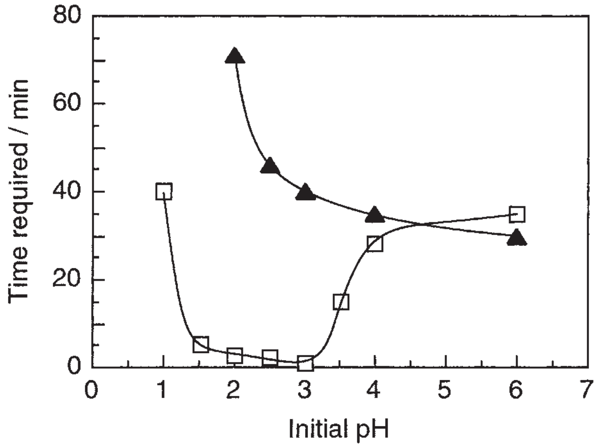

Fig. 1. Shaking time required for 95% extraction as a function of initial pH. ▲: Cr(III), □: Cr(VI). Concentrations of Cr(III) and of Cr(VI) were 7.7 × 10^{-6} mol/L. Concentration of APCD was 0.04 mol/L.

Table 1. Extractability of Cr(III) at Shaking Period Required for Quantitative Extraction of Cr(VI)

Initial pH	Concentration of APCD/mol L^{-1}		
	4.0 × 10^{-2}	6.0 × 10^{-2}	8.0 × 10^{-2}
	Extraction/%		
2.0	1 (5.0)	2 (4.5)	2 (4.0)
2.5	2 (3.0)	3 (2.0)	4 (2.0)
3.0	4 (2.0)	5 (1.5)	5 (1.0)

Extraction was carried out in the absence of Cr(VI). Concentration of Cr(III) was 7.7 × 10^{-5} mol/L in aqueous phase. Shaking times (min) were written in parentheses.

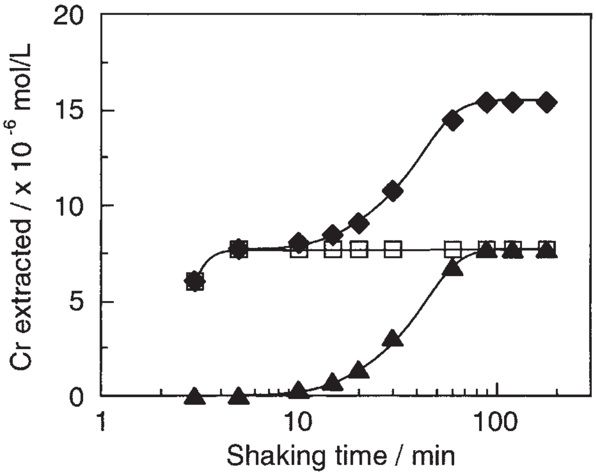

Fig. 2. Time profiles for the extraction of Cr(III), Cr(VI), and Cr(III) + Cr(VI). ▲: Cr(III), □: Cr(VI), ◆: mixture of Cr(III) and Cr(VI). Concentrations of Cr(III) and of Cr(VI) were 7.7 × 10^{-6} mol/L. Concentration of APCD was 0.04 mol/L. Initial pH of chromium solution was 2.0.

practically the same shaking times for 95% extraction above the initial pH 4, the time requirements of the two species differ considerably at the initial pH range 2–3 (Fig. 1). For example, at pH 3 Cr(VI) and Cr(III) require 1 min and 40 min, respectively. These facts indicated that the possibility of the proposed speciation method lay around the initial pH 2–3.

The optimum extraction conditions for the proposed method were examined at an initial pH range 1.5–3.5. Another parameter examined in the optimization was the concentration of APCD (8 × 10^{-3}–8 × 10^{-2} mol/L in total aqueous solution). Trivalent chromium (7.7 × 10^{-5} mol/L) and hexavalent chromium (7.7 × 10^{-6} mol/L) were extracted individually under nine condition sets: combinations of three initial pH values and three APCD concentrations. For all the condition sets time-extractability curves of Cr(VI) and of Cr(III) were drawn. A shaking time required for the quantitative extraction of Cr(VI) (>99%) was read off from the time-extractability curve of Cr(VI) obtained under a specific condition set, and then the extractability of Cr(III) at the shaking time was estimated from the curve of Cr(III) obtained under the same condition set. The estimated extractabilities of Cr(III) were listed in Table 1 with the minimum shaking times required for quantitative extraction of Cr(VI). The results indicate that lower APCD concentration tends to give a lower extractability of Cr(III). In the case of at or below 2 × 10^{-2} mol/L or lower of APCD, however, Cr(III) could not be extracted quantitatively within 180 min of shaking. On the other hand, shaking times required for quantitative extraction of Cr(VI) at initial pH 2 are longer than those required at higher pH conditions, but the extractabilities of Cr(III) at pH 2 are lower than those at higher pH conditions. Since it is desirable in this method that Cr(III) is not extracted in the first extraction process, extraction conditions for the proposed method were chosen as following: the initial pH of chromium solution is 1.9–2.1, concentration of APCD in total aqueous solution is 0.04 mol/L, and shaking times for Cr(VI) and for Cr(III) are 5 and 90 min, respectively. At the initial pH range, Cr(VI) will be extracted as the oxygen including complex bis(1-pyrrolidinecarbodithioato)[1-pyrrolidinecarbothio-(thioperoxoato)]chromium(III) rather than as tris(1-pyrrolidinecarbodithioato)chromium(III).[25]

One-Pot Speciation Method. In order to check the function of the proposed method, the extraction behavior of a mixture of Cr(VI) and Cr(III) was examined under the conditions chosen above with the individual extraction behaviors of the two species. In this examination, the extractions of the mixture were carried out without phase separation for speciation: only total concentrations of Cr(VI) and Cr(III) were measured at several shaking times. Results are shown in Fig. 2.

The resulting extraction curves of Cr(VI) and of Cr(III) indicate the following. Although Cr(VI) was extracted quantitatively at 5 min after the addition of APCD, Cr(III) was not extracted significantly at this point. Trivalent chromium was extracted quantitatively after more than 90 min of shaking, and the extractability of Cr(VI) does not drop even after 100 min of shaking. The extractabilities of Cr(VI) after 5 min of shaking and of Cr(III) after 90 min of shaking were verified by the determination of chromium remaining in the aqueous phase. Both of the extractabilities were 99% or more. On the other hand, the extraction curve obtained from the mixture of Cr(III) and Cr(VI) closely matched in with a sum of the curves obtained from the individual extractions of the two species. These facts prove that the proposed method is applicable to speciation of chromium in aqueous samples. Calibration curves were made for determinations of Cr(Ⅵ) and of Cr(Ⅲ) over the chromium concentration range 5×10^{-6}–5×10^{-5} mol/L (5 points). Both of the curves showed good linearity ($R \geq 0.995$) and the ratio of the slopes of the two curves was 1.00. This precise agreement between the slopes makes it possible to carry out this speciation method with one calibration line regardless of the composition of the two species in samples.

The last of the important matters in the substantiation of the proposed method is emulsification of the two phases. Because APCD is used in high concentration for the dithiocarbamate formation from Cr(Ⅲ), vigorous shaking of the two phases caused some emulsification. Although 1PS phase separator passed the DIBK phase exclusively, the aqueous phase left on the 1PS included droplets of DIBK and that lingered in the phase over 1–2 min. The formation of the droplets protracted the separation process and unexpected extraction of Cr(Ⅲ) may occur within the first separation process. Furthermore, the emulsification may cause carry-over of Cr(Ⅵ) into the second extraction step for extraction of Cr(Ⅲ), because the droplets including some extracted Cr(Ⅵ).

Therefore, the degree of the extraction of Cr(Ⅲ) in the first extraction step and of the carry-over of Cr(Ⅵ) into the second extraction step were determined with and without the salting-out technique. Sodium chloride was dissolved as a salting-out agent in 22.5 mL of acidified chromium solution (8.6×10^{-5} mol/L) in various concentrations (1–5% (w/v)) before the APCD addition. More than 2% sodium chloride prevented the emulsification completely and reduced the standing time for the phase separation from 1.5–2.0 min to 0.5 min. The salting-out agent did not cause any interference in the extraction or in the AAS measurement. Consequently, the application of the salting-out technique suppressed the extractabilities of Cr(Ⅲ) in the first extraction from 1.0–1.8% to 0.4–0.5% and the carry-over of Cr(Ⅵ) from 0.5–0.7% to lower than 0.2%. The clear phase separation brings one more improvement to this method. In the absence of the salting-out agent, it is difficult to fully recover the DIBK phase in a 5:1 or above sample to DIBK volume ratio due to the emulsification. This technique made it possible to apply 20:1 of the volume ratio in this speciation method. In the following sample analyses, 3% (w/v) of sodium chloride was added to samples, except in the analysis of artificial seawater.

Interference of Coexisting Metal Ions. The interference of coexisting heavy metal ions with the speciation was examined with eight transition metal ions. Five common transition element ions (Mn^{2+}, Fe^{3+}, Ni^{2+}, Cu^{2+} and Zn^{2+}), which form dithiocarbamato complexes, were chosen as ions existing universally in environmental samples. The oxoanions of three elements (V^{5+}, Mo^{6+} and W^{6+}) were selected as analogues of Cr^{6+}. The ions were grouped into five cations and three oxoanions. Each group contained the elements in same concentration. The groups were added individually into a mixed solution of Cr(Ⅲ) and Cr(Ⅵ) and speciation was carried out according to the analytical procedures described above with the salting-out technique.

The results of the examination are shown in Table 2. Measurable concentrations of Cr(Ⅲ) and Cr(Ⅵ) were not taken by the addition of the matrices. The addition of the cation group did not interfere in the speciation up to 3-fold. In the determination of Cr(Ⅲ), a 5-fold addition of the cation group decreased the measurement value by 5%. However, the addition of the oxoanion group interfered with the determination of Cr(Ⅲ) (ca. −10%), even at the low addition of 1-fold. Although the causes of the interference observed in the case of the cation group have not become clear, one possibility is pointed out for the latter case. In the experiments of the oxoanion group, some pale yellow insoluble substance was observed after 90 min of shaking. The yellow substance was not observed after 5 min of shaking. These facts indicated that one or more anions in the group formed an insoluble substance, and that Cr(Ⅲ) was incorporated into the substance. It seems that the extraction of Cr(Ⅵ) progressed completely free from the interference, because the complexation of Cr(Ⅵ) finished prior to that of the other oxoanions.

Table 2. Effect of Coexisting Metal Ions on Speciation of Chromium

Matrix elements	Concentration ratio to chromium	Recovery/%	
		Cr(Ⅲ)	Cr(Ⅵ)
none	—	99.0	101
Mn^{2+}, Fe^{3+}, Ni^{2+}, Cu^{2+} and Zn^{2+}	1	100	101
	2	100	102
	3	100	101
	5	95.0	100
V^{5+}, Mo^{6+} and W^{6+}	1	89.5	101

Concentrations of Cr(Ⅲ) and of Cr(Ⅵ) were 7.7×10^{-6} mol/L in aqueous phase. All matrix elements in each group were in same concentrations.

Recovery Test with Artificial Seawater. Since the substances coexisting with chromium in real samples frequently cause redox reactions between Cr(Ⅲ) and Cr(Ⅵ), there is no certified reference material for the speciation of Cr(Ⅲ) and Cr(Ⅵ). Therefore, recovery experiments were carried out using artificial seawater. Results are given in Table 3.

When chromium was not added to the artificial seawater, both Cr(Ⅲ) and Cr(Ⅵ) were not detected. Most of the added Cr(Ⅲ) and Cr(Ⅵ) (50 or 500 µg/L) was fully recovered within 4% and 1% deviation respectively. All the recovery data for Cr(Ⅲ) are lower than the data for Cr(Ⅵ), although all the recoveries in total are nearly 100%. These facts indicate that Cr(Ⅲ) in the artificial seawater was slightly extracted in the first extraction step with Cr(Ⅵ); it is thought from the found values that about 1% of Cr(Ⅲ) in samples was extracted with Cr(Ⅵ). Although a relatively large recovery error (8%) occurred in the recovery of Cr(Ⅵ) at a Cr(Ⅲ) to Cr(Ⅵ) concentration ratio of 10:1, the total recovery obtained under this condition is almost 100% (99.8%). Thus, the cause of the error is also attributable to the extraction of Cr(Ⅲ) in the first extraction step. On the other hand, recovery errors observed at the Cr(Ⅲ) to Cr(Ⅵ) ratio 1:10 are −3.4% for Cr(Ⅲ) and 1% for Cr(Ⅵ); both of the errors are smaller than a half of the above 8% of error. These data are a demonstration of the facts described in the above section: the carry-over of Cr(Ⅵ) into the second extraction step is one-half or less of the extractability of Cr(Ⅲ)

Table 3. Recovery of Cr(III) and Cr(VI) from Artificial Seawater

No.	Species	Concentration/μg L^{-1}		Recovery/%
		Added	Found	
1	Cr(III)	0	N.D.	—
	Cr(VI)	0	N.D.	—
	Total	0	—	—
2	Cr(III)	50	48.9	97.8
	Cr(VI)	50	50.4	101
	Total	100	99.3[a)]	99.3[b)]
3	Cr(III)	500	492	98.2
	Cr(VI)	500	506	101
	Total	1000	998[a)]	99.8[b)]
4	Cr(III)	50	48.3	96.6
	Cr(VI)	500	503	101
	Total	550	551.3[a)]	100[b)]
5	Cr(III)	500	495	99.0
	Cr(VI)	50	54.1	108
	Total	550	549.1[a)]	99.8[b)]

All data were average of 3 times of measurements. a) Sum of the found concentrations of Cr(III) and Cr(VI). b) Calculated as "Total Cr found/Total Cr added."

Table 4. Analysis of Water Samples

	Concentration/μg L^{-1}		
	Cr(III)	Cr(VI)	Total chromium
Industrial effluent	210	52	262 (257)[a)]
JAC-0032 (River water)	11.0	N.D.	11.0 (10.1 ± 0.2)[b)]

All data were average of 3 times of measurements. a) Determined by ICP-MS. b) Certified value.

in the first extraction step. Trivalent chromium to hexavalent chromium concentration ratios higher than 10:1 perhaps raise the recovery error of Cr(VI) to 10% or more, although samples in concentration ratios lower than 1:10 may be analyzed accurately.

The speciation results of the artificial seawater indicated that concentrations of 50 μg/L (9.6×10^{-7} mol/L) or more of Cr(III) and of Cr(VI) in aqueous samples were determined satisfactorily by the proposed one-pot speciation method. The constituents of the artificial seawater did not interfere with the chromium speciation. The detection limit (3σ) was estimated as 10 μg/L (1.9×10^{-7} mol/L) in sample solution and the RSD ($n = 5$) at 100 μg/L (1.9×10^{-6} mol/L) was 4.1% for Cr(III) and 3.6% for Cr(VI) (sample to DIBK volume ratio = 2:1).

Application of One-Pot Speciation Method in Water Analysis. The proposed method has been applied with the salting-out technique for the analyses of two samples. One is an industrial effluent obtained from an automotive factory and the other is a standard reference material (SRM) JAC-0032 (river-water). Results are shown in Table 4.

The industrial effluent contained ca. 2 mg/L of zinc and ca. 1 mg/L of iron as major coexisting elements. Because there are no certified values for the effluent sample, total chromium concentration in the effluent was directly determined with ICP-MS for comparison. The total concentration of chromium determined by the proposed method (262 μg/L) agreed closely with the data obtained from the ICP-MS measurement (257 μg/L). Although there is the possibility as described above, that a sample in a high Cr(III) to Cr(VI) concentration ratio, more than 10:1, can give a large recovery error in the determination of Cr(VI), the effluent sample does not fit this condition. It seems that the results are reliable.

Because the concentration of total chromium in the SRM is at the 10 μg/L level, it is impossible to determine the concentrations in the standard sample to DIBK volume ratio (2:1). As described above, 10 μg/L corresponds to the detection limit in the volume ratio 2:1. Therefore, a higher volume ratio of sample solution to DIBK (20:1) was applied for the determination of the SRM. The total concentration of chromium determined for the SRM JAC-0032 agreed well with the certified value. Since the concentrations of Cr(III) and of Cr(VI) are not certified, reliabilities of the data obtained for the individual species could not be evaluated. However, the good agreement in the total concentration of chromium demonstrated that the proposed method acts effectively. In most of the analytical methods for metal elements based on dithiocarbamate extraction-AAS measurement, sample to organic solvent volume ratios are usually 2:1–10:1.[15–17,27,28] The achievement of the speciation in a high volume ratio such as 20:1 is attributed to the low mutual solubility between DIBK and water.[20]

Except for chromatographic methods, there are few speciation methods which require no sample splitting. The one-pot speciation method substantiated here is the first of such speciation methods. One of the samples divided contains only half the amount of the species compared with the whole sample; the proposed method does not throw the analyte in sample away. Lan et al. designed a speciation method, which did not require sample splitting, utilizing dithiocarbamate formation from Cr(VI).[11] In their method, the Cr(III) in a sample was coprecipitated not as chromium(III) dithiocarbamate, but as a gel-form chromium(III) hydroxide with bis(1-pyrrolidinecarbodithioato)lead(II) at pH 9.0. It is of no matter to the neutron activation analysis used in their method that Cr(VI) and Cr(III) form different types of compounds in a speciation method. Considering the use of the measurement techniques such as AAS or ICP-AES, however, it is favorable that the two species form the same type of compounds, which have the same solubilities in a certain solvent. In contrast with most chromium speciation methods based on the dithiocarbamate formation, the proposed one-pot method requires neither an oxidizing agent, such as potassium permanganate[15] and cerium(IV) sulfate,[12] nor reconditioning of the sample solution in the middle of the procedure. These features simplify the proposed method and remove the risk of contamination from the agents.

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