

## 琉球大学学術リポジトリ

How does pH affect extraction behavior of Cr(III) and Cr(VI)? -True effect of pH on chromium dithiocarbamate extraction systems-

メタデータ	言語: 出版者: 琉球大学理学部 公開日: 2008-03-27 キーワード (Ja): キーワード (En): Solvent extraction, chromium, dithiocarbamate, diisobutyl ketone, pH dependence 作成者: Honma, Yoshiro, Murakami, Masahiko, Takada, Takeo, Kuniyoshi, Masayuki, 国吉, 正之 メールアドレス: 所属:
URL	<a href="http://hdl.handle.net/20.500.12000/5377">http://hdl.handle.net/20.500.12000/5377</a>

# How does pH affect extraction behavior of Cr(III) and Cr(VI)?

## – True effect of pH on chromium dithiocarbamate extraction systems –

Yoshiro Honma,<sup>a</sup> Masahiko Murakami,<sup>a</sup>  
Takeo Takada,<sup>a</sup> and Masayuki Kuniyoshi<sup>b,\*</sup>

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

<sup>b</sup> Department of Chemistry, Biology and Marine Science, University of the Ryukyus,  
Nishihara-cho, Okinawa, 903-213, Japan

### Abstract

The effect of pH of aqueous phase on the extraction of Cr(III) and Cr(VI) in ammonium 1-pyrrolidinedicarbodithioate/diisobutyl ketone (APCD/DIBK) extraction system was studied. In order to avoid side effects such as masking, all of the experiments were carried out in the absence of buffer agent. As first step, manners of pH change that caused from addition of the chelating agent was examined in detail. Then, based on the results of the examination, effect of pH on the chromium extraction was discussed extensively. Both pH conditions before and after APCD addition affected the extraction behavior of chromium. By considering the change of pH in aqueous solution, it was clear that a root of the effect of pH on the extraction of both Cr(III) and Cr(VI) consists in the change of the species of chromium in aqueous phase. In APCD/DIBK extraction system, species that extracted effectively were  $\text{Cr}(\text{H}_2\text{O})_5(\text{OH})^{2+}$  and  $\text{HCrO}_4^-$ . The results of the examination of the pH change caused by chelating agent also clarified a cause of difference in the extractability of two carbodithioate chelating agents; APCD and sodium diethylcarbodithioate (NaDDTC).

Key word: *Solvent extraction, chromium, dithiocarbamate, diisobutyl ketone, pH dependence*

### INTRODUCTION

Dithiocarbamate complex formation has been used on chromium determination combined with several analytical methods such as solvent extraction<sup>[1,2,3,4,5,6,7,8,9,10,11,12]</sup>, sorbent extraction<sup>[13]</sup>, coprecipitation<sup>[11]</sup>, liquid chromatography<sup>[15,16]</sup> and gas chromatography<sup>[17]</sup>. Because the solvent extraction is simple and requires no special equipment, many

applications based on dithiocarbamate formation-solvent extraction have been proposed for the analysis of fresh water<sup>[9,12]</sup>, seawater<sup>[3,4,12]</sup> and sludge<sup>[7]</sup>. An ammonium 1-pyrrolidinedicarbodithioate/methyl isobutyl ketone (APCD/MIBK) extraction system has been adopted for the determination of chromium in water sample by the U. S. Environmental Protection Agency (EPA)<sup>[18]</sup>.

The aims of the above literatures are establishment of determination method or of differentiation procedure for chromium, there is no study that focus on the extraction behavior of chromium itself. Therefore, there is no unified view even about the pH range over which chromium can be extracted quantitatively. For example, in some literatures Cr(VI) can be extracted quantitatively (i.e. > 90 %) over the pH range 1-4<sup>[4]</sup> and in other literature it was extracted in 50 % or less over the pH range 1-2<sup>[2]</sup>. Although these results are obtained under similar conditions in concentration of APCD and in shaking time, these results considerably differ in extractability over the pH range 1-2. Also in higher pH region, difference in extraction behavior exists among literatures; some report that Cr(VI) is extracted with APCD in only 10 % or less at pH 6<sup>[5,4]</sup>, others report that more than 80 % of Cr(VI) can be extracted at pH 6<sup>[6,8]</sup>. On the other hand, the extraction behavior of Cr(III) is much less known than that of Cr(VI). Because the extractability of Cr(III) is low, it is difficult to extract Cr(III) quantitatively. Hence, in order to determine Cr(III), Cr(III) is usually oxidized to Cr(VI) before extraction step<sup>[4,10,12]</sup>. Only a few investigators succeeded in quantitative extraction of Cr(III) without the pre-oxidation by addition of large amount of chelating agent<sup>[5,11]</sup>. There is few information about the extraction behavior of Cr(III).

In the chelate extractions, pH is one of the most important factor which affect on extractability. Because the difference between the extractability of Cr(III) and of Cr(VI) has been utilized for differentiation of chromium<sup>[4,5,10,12]</sup>, elucidation of the effect of pH on the chromium extraction is necessary both for improvement in reliability and for development of the differentiation methods.

From the nature of monobasic acid of the dithiocarbamic acid<sup>[19]</sup>, it is predicted that the addition of the dithiocarbamate chelating agents change the pH of aqueous phase. Indeed the addition of APCD caused pH change<sup>[18]</sup>. Not only pH itself directly affects on chelation, but the pH change has potential for change the species of chromium. Both Cr(III) and Cr(VI) are able to exist as various species and the distribution of the species is dependent on pH<sup>[20]</sup>. From the above, the following is suggested; in order to exactly elucidate the effect of pH on the extraction of chromium, it is necessary to experiment and to discuss with care in the pH change and in the chromium species change accompanying the pH change. However, in most studies the effect of pH on the extraction was discussed only with the initial pH of the aqueous phase, without consideration of the pH change. Thus we studied with care in the pH change, in order to elucidate true effect of pH on the extraction.

Most ideal solution for the elucidation of *true* effect of pH is to completely suppress

the pH change using a buffer agent without any side reactions. However, since large amount of a chelating agent is required to extract Cr(III)<sup>(5,11)</sup>, it is supposed that the buffers can not suppress the change of pH effectively. Moreover, use of a buffer involves a risk that the buffer agent reacts with chromium, because most of the buffer agents have some complexation ability. For instance, some studies show that the extractability of Cr(III) decrease with increase in concentration of the buffers<sup>(5,11)</sup>. This fact suggests that the added buffer agents (i.e. phthalate, phosphate, citrate) act also as masking agents for Cr(III). Because the insufficient buffer capacity and the possibility of the side reaction shade the *true* effect of pH on the extraction, it is desirable to do experiments in the absence of the buffers. Hence we elucidated the *true* effect of pH on the extraction of chromium with following two steps. First, the pH change caused from addition of a chelating agent was examined in detail. Then *true* pH effect on the chromium extraction was evaluated based on the results of the examination, on the results of extraction and on the nature of chromium species.

An APCD/DIBK extraction system was chosen for this study. In order to elucidate the effect of pH, there is need to choose a extraction system which realize experiments over the wide pH range. We already demonstrated that the APCD and DIBK suit to extract some metals from highly acidic solution<sup>(21,22,23,24)</sup>. A stability of APCD under acidic conditions and a low mutual solubility of DIBK especially under acidic conditions made it possible to carry out the extraction over the wide pH range.

## EXPERIMENTAL

### Apparatus

An HM-30S glass electrode pH meter (TOA, Tokyo, Japan) was used for measurement of pH. An SR-IIw vertical reciprocating shaker (TAITEC, Saitama, Japan) was used in extraction process. An AA-782 atomic absorption spectrometer (Nippon Jarrell-Ash, Kyoto, Japan) was used for the measurement of chromium concentration.

### Reagents

All chemicals used were of analytical-reagent grade or better. Doubly distilled water was used throughout. Commercial Cr(III) and Cr(VI) atomic absorption standard solutions (Aldrich Chemical Co. Inc., Milwaukee WI) were used as stock solutions. A working solution was prepared daily by appropriate dilution of the stock solution. Solutions of chelating agents were prepared daily by dissolving a APCD or NaDDTC (Wako Pure Chemical Industries, Ltd., Osaka, Japan) in water. The solutions of the chelating agents were filtered and stored in cold place. A 0.39 mol/L of potassium hydrogen phthalate buffer solution was prepared by dissolving 40 g of the compound (Wako Pure Chemical Industries, Ltd., Osaka, Japan) and 4 g of sodium hydroxide in 500 mL of water.

Including DIBK (Wako Pure Chemical Industries, Ltd., Osaka, Japan), all chemicals were used without further purification.

### **Evaluation of buffer capacity of phthalate solution**

The concentration and volume of phthalate buffer and APCD solution were set at similar conditions of the reported study<sup>(1)</sup>. A 3.0 mL of phthalate buffer (pH 4.9) and 25 mL of water, or only 28 mL of water was placed into a flask. The pH of the solution was adjusted to 2-8.5 with nitric acid or sodium hydroxide and then 0.6 or 3.0 mL of APCD solution (0.61 mol/L) was added to the solution. The pH of the mixture was measured 1 min after the addition of APCD.

### **Observation of pH change caused from addition of APCD or of NaDDTC**

Appropriate concentration of hydrochloric acid or sodium hydroxide solutions (22.5 mL) was placed into a 50 mL Erlenmeyer flask. The pH of the solution was measured (pH -0.5-13). A 2.5 mL of the 0.80 mol/L APCD solution (pH 6.6-6.9) was added to the flask. After addition of the APCD, pH of the mixture was measured at appropriate time interval. The measurements were repeatedly carried out until the pH change would be negligibly small.

### **Extraction and AAS measurement**

A 20 mL of hydrochloric acid or sodium hydroxide solution was placed into 50 mL Erlenmeyer flask. A 2.5 mL of 4.0  $\mu\text{g/mL}$  Cr(III) or Cr(VI) solution was added to the solution and then pH value of the mixture was measured. Only for extraction of Cr(III), the mixture was allow to stand for over 18 hours. During the standing time, the Cr(III) solution was placed under  $\text{N}_2$  gas atmosphere to prevent the pH decrease caused from the dissolution of atmospheric  $\text{CO}_2$ , especially under the basic conditions. Just before the addition of DIBK and of APCD, the pH of the solution was measured again and the measured pH value was recorded as "initial pH". A 10 mL of DIBK and 2.5 mL of 0.80 mol/L APCD solutions were added to the flask. Then the mixture was shaken vigorously over an appropriate period. Phase separation was carried out with a Whatman 1PS phase separator, then the chromium concentration in the organic phase was determined with the flame AAS. If necessary, chromium concentration in the aqueous phase was also measured. Except below the initial pH 1, the aqueous phase caused emulsification with DIBK, thus the aqueous phase was centrifuged before the AAS measurement. An  $\text{C}_2\text{H}_2$ -Air flame was used in fuel-rich condition (0.8-5.0 L/min for DIBK phase and 1.4-5.0 L/min for aqueous phase) for the AAS measurement. A hollow cathode lamp was operated at 7.0 mA and a resonance line at 357.9 nm was used for the measurement.

## RESULTS AND DISCUSSION

### pH change of buffered solution by addition of APCD

It is known that the addition of APCD causes pH change in aqueous phase<sup>[16]</sup>. Because the pH change during extraction process makes it difficult to elucidate the effect of pH on the extraction, the buffer agents are used in most solvent extraction studies to suppress the pH change. Also in APCD/MIBK system, Subramanian used phthalate buffer to maintain pH<sup>[11]</sup>. However, because the addition of large amount of the dithiocarbamates is required to quantitatively extract Cr(III)<sup>[6,11]</sup>, it seems to be difficult to effectively suppress the pH change with buffer agent. Thus, to check the ability of the buffers, effect of APCD addition on pH of buffered solution was examined in detail. Phthalate was chosen as buffer agent to compare with the results of Subramanian's study<sup>[11]</sup>. It is also a reason for selection of the buffer agent that inhibition of phthalate for the Cr(III) extraction is relatively weak than that of some other buffers (e.g. phosphate, citric acid)<sup>[5]</sup>.

**Table 1.** pH change with addition of APCD and effect of buffer agent on the pH change

	Initial pH			
	1.96	2.97	5.12	8.48
With phthalate buffer				
Vol. of APCD sol. 0.6 mL	2.31	3.24	5.10	7.55
3.0 mL	3.79	4.17	5.07	7.22
Without buffer				
Vol. of APCD sol. 3.0 mL	4.02	4.85	6.60	6.86

Concentration of the added APCD solution was 0.61 mol/L.

The results are shown in Table 1. In the absence of the phthalate buffer, the addition of APCD caused remarkable pH change in the solution over the initial pH range 2-8.5. On the other hand, the pH of the buffered solution was not altered at the initial pH 5. However, in spite of the existence of the buffer, pH was considerably altered except at the initial pH 5. While the phthalate buffer (pH 4.9) fully acted around initial pH 5, it could not effectively suppress the pH change at below the initial pH 3 and at above pH 8. Subramanian reported that the addition of APCD altered only by 0.1-0.2 at pH values below 2.5, even in the absence of buffer<sup>[11]</sup>. However, our results indicates that the addition of 0.6 and 3.0 mL of APCD (0.61 mol/L) increased the pH more than 0.3 and 1.8 respectively at the initial pH 2, even though the buffer existed (Table 1). Although use of higher concentration of phthalate and of lower concentration of APCD may suppress the pH change more effectively, the former ( $\geq 0.039$  mol/L phthalate in total solution)

completely inhibits the extraction of Cr(III) and the latter ( $= < 0.061$  mol/L APCD in total solution) results in incomplete extraction of Cr(III)<sup>(11)</sup>. Our results indicate that the capacity of the phthalate buffer is insufficient to suppress the pH change caused from the addition of APCD, in the chromium extraction system. Rather than to use the buffer which have insufficient capacity, not to use any buffer is simple and clear. Indeed, most of the buffer agents has some complexation ability, and some buffer agents including the phthalate inhibit the extraction of Cr(III)<sup>(5,11)</sup>. The disuse of the buffer agents is desirable to elucidate the *true* effect of pH on the chromium extraction.

### Observation of pH change caused from addition of APCD and of NaDDTC

In the absence of buffer agent, the pH change caused from the addition of APCD has been studied in detail, as the following. The pH of an aqueous solution was adjusted to desired value, and APCD solution was added to the solution. Then the pH of the mixture was measured repeatedly at appropriate time interval.

The results are shown in Fig. 1; results at 1 min and at 2 h after APCD addition are indicated. The dashed line corresponds to the case when the pH values are not changed with the addition of APCD. Thus, the vertical distance from the dashed line to each data point means the magnitude of the pH change caused from the APCD addition. Below the initial pH 1, the pH change was not observed. Over the initial pH range 1.5-6.7, pH of the solution was increased significantly. On the contrary, the decrease in pH was observed over the initial pH range 6.7-12. At the initial pH 13, the pH of the solution was altered

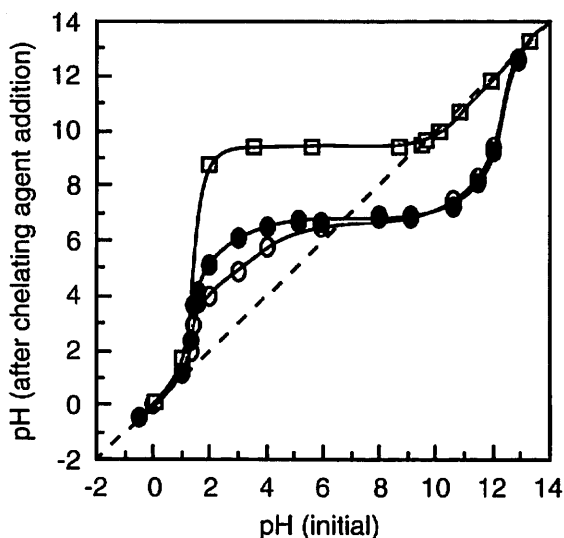


Fig. 1. Effect of chelating agent addition on pH: ○, 1 min after APCD addition; ●, 2 h after APCD addition; □, 1 min after NaDDTC addition.

in little. The two set of the results (i.e. after 1 min and after 2 h) markedly differ only over the initial pH range 1-5. This fact indicates that the pH change caused from the APCD addition almost finished within 1 min after the APCD addition except the initial pH range 1-5. Whereas in the initial pH 1-5, the increase in pH partly progressed within 1 min and then it slowly progressed for about 2 hours. A flat part of the curves over the initial pH range 4-10 means that the added APCD made the pH of aqueous solutions into practically same values, even the initial pH were much different; the APCD acted also as a buffer agent. This fact is important for the following elucidation of the *true* effect of pH on the chromium extraction.

The explanations for the mechanisms of the observed pH change were discussed based on the manner of the pH change and on the nature of APCD. The cause of the pH increase under the acidic conditions can be explained with the protonation of pcd<sup>-</sup> ion and subsequent decomposition of the resulted Hpcd. The results of the study on acidic character of dithiocarbamic acid<sup>[19]</sup> predict that the added pcd<sup>-</sup> ion protonates immediately after mixing of the acidic solution and the APCD solution. Then the protonated pcd<sup>-</sup> (i.e. Hpcd) decomposes relatively slowly into pyrrolidine and carbon disulfide; the reported half-life of decomposition of pcd<sup>-</sup> is 30-90 min<sup>[25]</sup>. The resultant pyrrolidine causes further protonation. Thus, protons in the acidic solution are consumed in two steps (i.e. protonation of pcd<sup>-</sup> and of pyrrolidine). It seems that the two steps of the consumption of protons resulted in the fast pH increase (i.e. within 1 min) and the slow one (i.e. over 2 h) observed over the initial pH range 1-5 (Fig. 1).

On the other hand, cause of the pH decrease observed under the basic conditions can be explained with neutralization with ammonium ion brought from dissociation of APCD. To confirm the effects of the counter ions of the dithiocarbamate agents on the pH change, same experiments were carried out with NaDDTC. The results are shown in Fig. 1 with the results of APCD addition. The addition of NaDDTC caused the pH increase similarly to the addition of APCD over the initial pH range 1-9.5, however, the NaDDTC addition did not cause the pH decrease. Because pKa values for Hpcd (3.29) and for Hdtc (3.38) are nearly same<sup>[26]</sup>, the difference in the natures of anions (i.e. pcd<sup>-</sup> and dtc<sup>-</sup>) is not the cause of the difference in the manner of the pH change. It seems that the difference in the manner of the pH change arise from the difference in the natures of the cations of the two chelating agents. Though the sodium ion is not appreciably hydrolyzed in water, the ammonium ion is considerably hydrolyzed. Thus it can be concluded that the cause of the pH decrease observed in the APCD system is the neutralization of hydroxide ion with ammonium ion.

#### **True effect of pH on extraction behavior of Cr(VI)**

As described above the addition of APCD causes the considerable pH change over the wide initial pH range. Thus, in order to elucidate the *true* effect of pH on the chromium



extraction, the extraction behavior must to be considered based not only on the initial pH values of the chromium solutions but also on the pH values after the APCD addition. However, it is quite difficult to continuously measure the aqueous phase pH which dynamically changes during the extraction process. Then instead of the continuous measurement of the actual pH, the following process has been applied for the elucidation. The expected pH values at the end of the shaking periods were estimated from Fig. 1 and from similar data obtained at various standing times; the estimated pH values were obtained in the absence of DIBK. Then, based on both the initial pH values and the pH values expected at end of shaking periods, the *true* effect of pH on the chromium extraction has been elucidated.

Extraction of Cr(VI) was carried out over the initial pH range -0.5-12, at the several shaking times. To consider both the effect of the initial pH and of the pH after the APCD addition, the data of the percent extraction is plotted into Fig. 2-a with the initial pH on the horizontal axis, and into Fig. 2-b with the estimated pH.

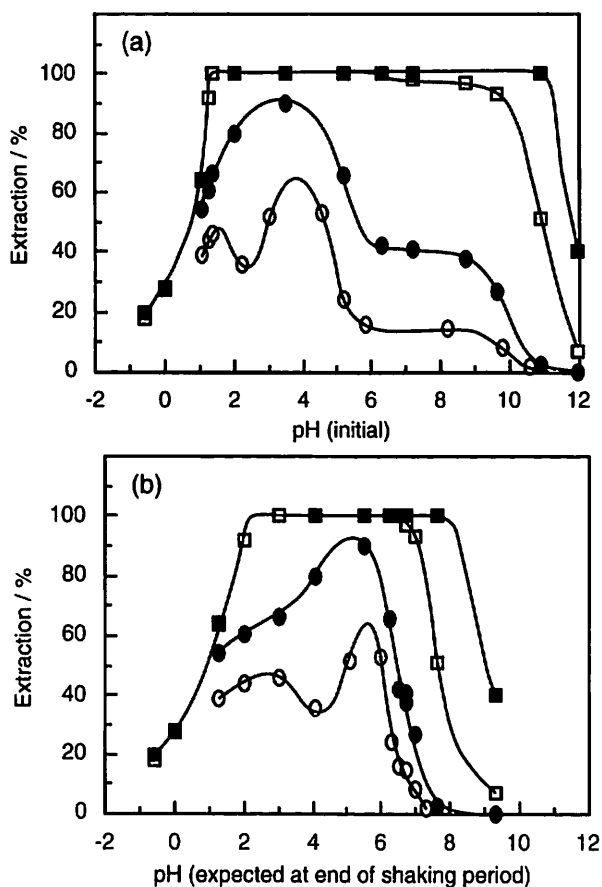


Fig. 2. Effect of pH on the extraction of Cr(VI). Horizontal axis: (a), initial pH; (b), pH after the APCD addition. Shaking time: ○, 1 min; ●, 3 min; □, 3 h; ■, 27 h.

With 1 min and 3 min of shaking periods, Cr(VI) shows highest extractability at the initial pH about 3.5 (Fig. 2-a). The extraction curves obtained with 1 and 3 min decrease above the initial pH 4 and form a plateau over the pH range 6-8.5, then above the pH 11 Cr(VI) is not extracted. These characters of the curves obtained in the short shaking periods resemble the results of the similar extraction studies, below the pH 8<sup>8, 11, 12</sup>; on the other hand there is little literature about the extractability of Cr(VI) above the initial pH 8. Even above the initial pH 10, the extraction proceeded steadily in time though the progress of the extraction was fairly slow. Quantitative extraction is achieved with 5 min of shaking period in the initial pH 3-4, and the pH range in which Cr(VI) can be quantitatively extracted extends with shaking time; the range is 1.4-9 with 3 h and 1.4-11 with 27 h. Under highly acidic conditions such as below the pH 0, Cr(VI) could be extracted, even though in partially. It is known that Cr(VI) is extracted from high concentrate HCl solutions to the oxygen-including solvent such as the ketones without any chelating agent<sup>27</sup>. Our results of the experiments in the absence of APCD also indicated that Cr(VI) is extracted in more than 10 % within 3 min of shaking period at pH 0 or below, however, the long shaking periods such as 3 h resulted in the complete lack in the extractability (< 1 %). Thus it is thought that the partial extraction of Cr(VI) below the pH 0 (Fig. 2-a) were brought by the existence of APCD. Cr(VI) was extracted all over the studied pH range -0.5-12.

These are noted that the plateaus are formed over the initial pH range 6-8.5 and the plateau is observed even with long shaking period such as 3 h. The existence of plateaus suggests that the extractability of Cr(VI) is not affected with the initial pH, in the initial pH 6-8.5; it is thought that the extractability is affected with the pH after APCD addition rather than with the initial pH. Then, the extractability around the initial pH 6-8.5 has been discussed with Fig. 2-b in which the extraction data are plotted with the pH expected at the end of shaking period horizontally. The data that were obtained over the initial pH 4-10 exist over the expected pH range 6-7 in Fig. 2-b, and the plateaus observed in the initial pH 6-8.5 (Fig. 2-a) are missing in Fig. 2-b. This complete disappearance of the plateaus indicates that the plateaus are caused from the pH change with APCD addition (Fig. 1); it is thought that the extractability of Cr(VI) above the initial pH 3.5 mainly depends on the pH after APCD addition.

The extractability with short shaking periods such as 1 or 3 min, significantly changes over the pH range 6-7.5 (Fig. 2-b). The cause of the extractability change around pH 7 is attributable to the alternation of the species between  $\text{HCrO}_4^-$  and  $\text{CrO}_4^{2-}$ . Because the pKa value for the reaction of  $\text{HCrO}_4^- \rightarrow \text{CrO}_4^{2-} + \text{H}^+$  is 6-7<sup>28</sup>, the distribution of concentration between the two species significantly changes around pH 6-7;  $\text{HCrO}_4^-$  and  $\text{CrO}_4^{2-}$  dominantly exist below pH 6 and above pH 7 respectively. The existence of  $\text{Cr}_2\text{O}_7^{2-}$  is negligibly low under such low Cr(VI) concentration. Since the product of the complexation between Cr(VI) and dithiocarbamate ion is not a complex of Cr(VI) but two

kind of Cr(III) complexes<sup>[29]</sup>, thus the extraction process in APCD/DIBK system also includes reduction of Cr(VI) into Cr(III). Because the standard reduction potential for the reaction of  $\text{HCrO}_4^- + 7\text{H}^+ + 3\text{e}^- \rightarrow \text{Cr}^{3+} + 4\text{H}_2\text{O}$  is 1.195 V and that for the reaction of  $\text{CrO}_4^{2-} + 4\text{H}_2\text{O} + 3\text{e}^- \rightarrow \text{Cr}(\text{OH})_3 + 5\text{OH}^-$  is -0.13 V<sup>[28]</sup>,  $\text{HCrO}_4^-$  is easily reduced to Cr(III) than  $\text{CrO}_4^{2-}$ . Based on the pKa value for  $\text{HCrO}_4^-$  and on the difference in the reduction potentials for  $\text{HCrO}_4^-$  and  $\text{CrO}_4^{2-}$ , it can be concluded that Cr(VI) is extracted relatively fast at below pH 7 in which reactive  $\text{HCrO}_4^-$  dominantly and Cr(VI) is not extracted with short shaking periods at above pH 7 in which Cr(VI) mainly exists as inert  $\text{CrO}_4^{2-}$ . Unlike our result, Thomas et al.<sup>[3]</sup> concluded that extraction efficiency of Cr(VI) is apparently not determined by the protonation of chromate, based on the fact that change of the extractability appears around initial pH 4. The discrepancy between Thomas's conclusion and our conclusion is due to that their discussion bases on only the initial pH values without the consideration for the increase of pH caused from APCD. The species of Cr(VI) apparently determine the extraction behavior of Cr(VI). Slow progress of the extraction at pH 8 and above, seems to be caused from the reaction between pcd and  $\text{HCrO}_4^-$  which exist in extremely low concentration or and predominant  $\text{CrO}_4^{2-}$  which have low oxidizing ability.

Tsuchiya et al. reported that APCD and NaDDTC exhibit same extractability for Cr(VI) under low pH conditions (pH < 3), but at higher pH region APCD shows higher extractability than NaDDTC<sup>[6]</sup>. Fig. 1 indicates that, the addition of NaDDTC increases the pH values more than that of APCD above initial pH 1, and APCD and NaDDTC make flat part on the curves at pH 6.7 and 9.4. Thus, under same conditions the addition of NaDDTC give higher pH values than that of APCD, and the addition of NaDDTC easily derive the pH values into more than 8 in which  $\text{CrO}_4^{2-}$  dominantly exists. These our results indicates that the difference in the extractability Cr(VI) between APCD and NaDDTC<sup>[6]</sup> was caused from the difference in the ability of pH change between the two reagents.

There is no persuasive explanation for the formation of the valley at pH 4 on the curve obtained with 1 min shaking (Fig. 2-b). Because pH increased more than 2 in pH unit immediately after the APCD addition at below the initial pH 4 (Fig. 1), the extraction data that exist below pH 6 in Fig. 2-b were obtained during the drastic pH change. The rapid pH change certainly complicate the clarification for the cause of the valley, however, two possibilities can be pointed out as the cause; the effects of change in species of dithiocarbamate ion and of Cr(VI) ion. Because the pKa for pyrrolidine carbodithioate ion is 3.29<sup>[30]</sup>, dominant species change between pcd and Hpcd at pH about 3. Thus, there is possibility that reactivity between Cr(VI) and chelating agent drastically change at pH about 3. On the other hand, Finston et al. reported that Cr(VI) exist as hydronium complex ion below pH 2<sup>[30]</sup>. Since the three data that form the peak at pH 2.5 in Fig. 2-b are obtained below the initial pH 2 (Fig. 2-a), there is possibility that the hydronium species give the left peak around pH 3.5 in fig. 2-b.

As described above, the extraction behavior of Cr(VI) was mainly dominated by the pH which was changed with the dithiocarbamate chelating agent. Although the pH after the addition of the dithiocarbamate is not a directly adjustable factor on the contrary to the initial pH, it is highly important for the extraction of Cr(VI). Thus, in order to quantitatively extract Cr(VI) in analytical use, the initial pH of sample solution must be adjusted by considering the pH change with addition of chelating agent. Fig. 2-b indicates that Cr(VI) can be quantitatively extracted at the pH range 3-8, however, at above pH 7 long shaking period more than 3 h is required for the quantitative extraction. Thus, to practically use the extraction of Cr(VI) for determination, it is recommended that the pH become 3-6 after the addition of chelating agent. Under the extraction conditions used in this paper, in order to satisfy the recommended pH condition, it is required that the initial pH of chromium solution is adjusted to 1.4-4 (Fig. 1). When different extraction conditions are applied to determination of chromium, initial pH of a sample must be adjusted to another suitable value, because degree of the alternation of pH depends on many factors (i.e. initial pH, volume of sample and amount of chelating agent).

### Extraction of Cr(III)

#### *Effect of standing time of Cr(III) solution after pH adjustment on extraction of Cr(III)*

The species of Cr(III) in aqueous solution change with the pH and the rate of the ligand exchange of Cr(III) is relatively slow<sup>(20)</sup>. Thus it was supposed that the Cr(III) solution should be allowed to stand for a while after the pH adjustment in order to equilibrate the species of Cr(III) before the addition of APCD. Because the object of this paper is the elucidation of *true* effect of pH on the chromium extraction, the data of extractability which are obtained in non-equilibrium state is not suitable for this study. If the extractability of Cr(III) change with the standing time, it will be decided that the equilibrium of the Cr(III) species is still not established. Then, to determine the time required for the pre-equilibrate, the effect of the standing time after pH adjustment on the extractability of Cr(III) was examined.

The results are shown in Fig. 3. Although all the data in Fig. 3 were obtained with 30 min of shaking period, three curves obviously differ the initial pH above 5. For instance at the initial pH 7, Cr(III) was extracted in about 50 % after 1 min of the standing time, however, it was extracted in only 20 % after 2.25 h of the standing time. This fact suggests that the species of Cr(III) did not equilibrate within 2.25 h after the pH adjustment, above the initial pH 5. However, more than 18 hours of the standing time did not cause further change in the extractability; the species of Cr(III) equilibrated within 18 hours after the adjustment. Some investigators report that Cr(III) could be extracted partially even under basic conditions<sup>[9,10,11,12]</sup>. These partial extraction indicated that the extraction process were started without pre-equilibrium of Cr(III) species. In order to

evaluate the *true* effect of pH on the extraction, we applied 18 hours of equilibration time for subsequent extraction of Cr(III).

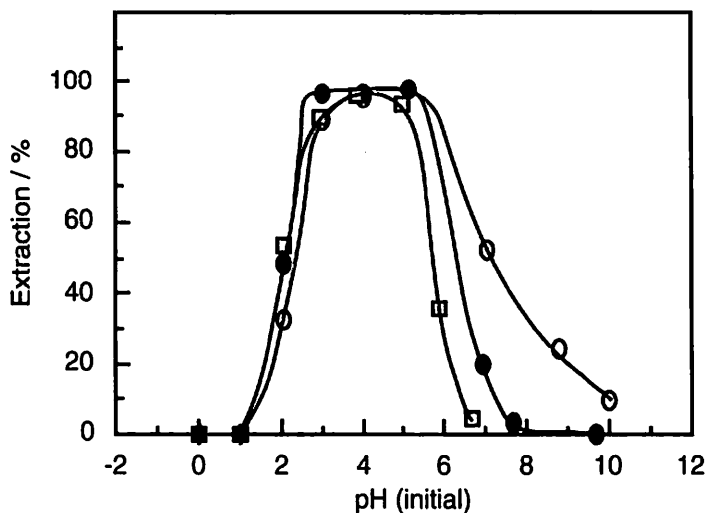


Fig. 3. Effect of the standing time after pH adjustment on the Cr(III) extraction. Standing time: ○, 1 min; ●, 2.25 h; □, 18 h.

#### *True effect of pH on extraction behavior of Cr(III)*

The extraction of Cr(III) was carried out over the initial pH range 0-11.4, at the several shaking times. The results are plotted in Fig. 4-a with the initial pH on the horizontal axis and in Fig. 4-b with the estimated pH, with same manner for the case of Cr(VI).

With 10 min of shaking, Cr(III) was extracted in more than 60 % in the initial pH 4-5, however, quantitative extraction was not achieved all over the initial pH range 0-11.4 (Fig. 4-a). Cr(III) could be quantitatively extracted with 30 min or above. The lower limit of the pH range in which the Cr(III) was extracted quantitatively was lowered with elongation of the shaking period; the quantitative extraction was observed over the pH range of 4-5 with 30 min, of 3-5 with 60 min and of 2-5 with 2 h. Further lowering of the lower pH limit was not observed with more than 3 h of shaking period and Cr(III) was not extracted completely below the initial pH 1 even with 3 h of shaking. In contrast to the lower pH limit of quantitative extraction, the upper limit (i.e. initial pH 5) did not extend toward higher pH region with the elongation of shaking period.

It is known that the pKa value for the reaction  $\text{Cr}^{3+} + \text{H}_2\text{O} \rightarrow \text{Cr}(\text{OH})^{2+} + \text{H}^+$  is 3.8-4.4<sup>[28]</sup>, thus the distribution of concentration between  $\text{Cr}^{3+}$  and  $\text{Cr}(\text{OH})^{2+}$  is significantly changed with the pH change, at around pH 4. Furthermore, it was reported that the ligand exchange of  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$  is very slow and that of  $\text{Cr}(\text{H}_2\text{O})_5(\text{OH})^{2+}$  is relatively fast<sup>[28]</sup>. These facts suggest that  $\text{Cr}(\text{H}_2\text{O})_5(\text{OH})^{2+}$  reacts faster with pcd than  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$  and the existence of  $\text{Cr}(\text{H}_2\text{O})_5(\text{OH})^{2+}$  makes the total rate of Cr(III) extraction fast at above pH 4. Indeed,

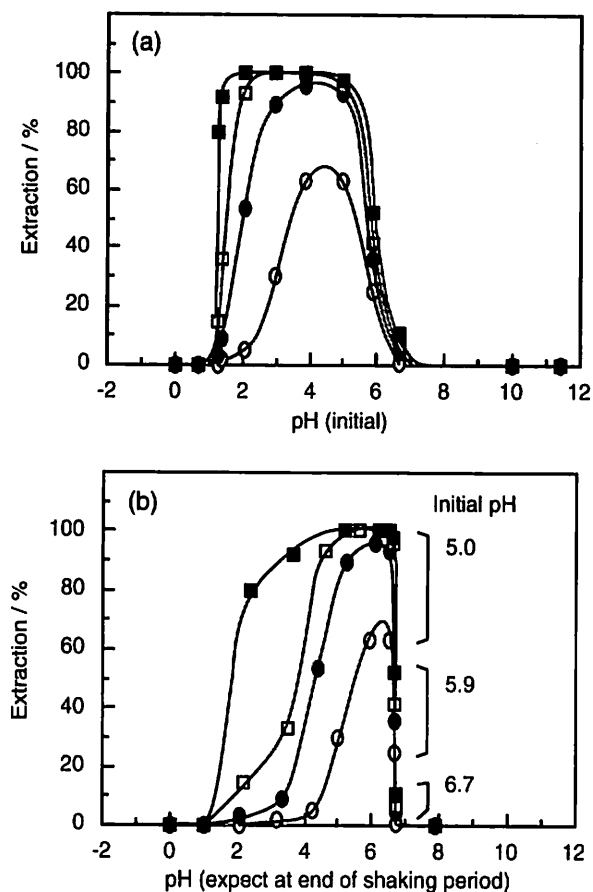


Fig. 4. Effect of pH on the extraction of Cr(III). Horizontal axis: (a), initial pH; (b), pH after the APCD addition. Shaking time: ○, 10 min; ●, 30 min; □, 60 min; ■, 2 h.

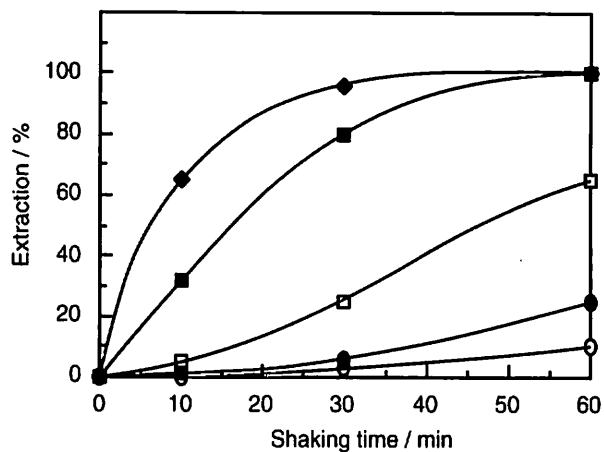


Fig. 5. Effect of shaking time on the extraction of Cr(III). pH: ○, 2; ●, 3; □, 4; ■, 5; ◆, 6.

Fig. 4-b indicates that the predicted change in the extraction rate around pH 4; the extraction curves which obtained with short shaking periods such as 10 or 30 min indicates that the extractability of Cr(III) changes in the pH 3-5. Then, to examine the effect of the pH after the APCD addition on the extraction rate, extractability data were plotted with shaking time (Fig. 5). The extractability data at the particular pH values (i.e. 2, 3, ..., 6) were read out from the curves in Fig. 4-b, and the read data were plotted as a function of shaking time in Fig. 5. The lower pH results in the lower extractability at all shaking time. It is indicated that the rate of extraction is significantly change around pH 4. For instance with 30 min of shaking, Cr(III) is extracted in less than 10 % at pH 2 and 3, on the other hand, more than 80 % of Cr(III) is extracted at pH 5 and 6. Such change in the rate of extraction around pH 4 suggests that Cr(III) is extracted relatively fast when pH increases to more than about 4 after APCD addition. Thus we concluded that the extractability of Cr(III) below the initial pH 4 is mainly dependent on the pH after the APCD addition.

As opposed to below the initial pH 4, the extraction behavior of Cr(III) observed over the initial pH range 5-8 (Fig. 4-a) was mainly dependent on the initial pH. In Fig. 4-a, the upper limit of the initial pH of quantitative extraction is not changed with shaking time, differ from the lower limit. The extractability decreased above the initial pH 5 with any shaking time, then Cr(III) was not extracted completely even with 3 h of shaking over the initial pH range 8-11.4.

It was reported that the solubility of  $\text{Cr(OH)}_3$  drastically decrease from pH 4 to pH 7, and Cr(III) ion mainly exists as  $\text{Cr(OH)}_3$  above pH 7 and as  $\text{Cr(OH)}^{2+}$  below pH 4<sup>[52]</sup>. To obtain the evidence for the reported change between the species, we carried out microscopic observation of the Cr(III) solution around the initial pH 7. As the results of the observation, formation of insoluble particle that was about 1  $\mu\text{m}$  in diameter was observed in the initial pH above 7 and the amount of the particle slowly increased with the standing time. The formation of the particle indicated that insoluble species of Cr(III) was formed around pH 7. Generation of the insoluble species and the slow increase in amount of the species fully correspond with the extraction behavior of Cr(III); Cr(III) was extracted hardly at initial pH 7 after pre-equilibration (Fig. 4-a) and the extractability decreases with the standing time at initial pH 7 (Fig. 3). From the above, the extraction behavior of Cr(III) above the initial pH 4 could be explained by the following. The  $\text{Cr}^{3+}$  which was supplied from stock solution (pH 0.5) changed into  $\text{Cr(OH)}^{2+}$  and further changed slowly into  $\text{Cr(OH)}_3$ , after the pH adjustment. If the adjusted pH value is about 4, chromium will exist mainly as  $\text{Cr(OH)}^{2+}$ , and if the value is about 7, chromium will exist mainly as  $\text{Cr(OH)}_3$ . Because the reactive  $\text{Cr(OH)}^{2+}$  chelated relatively fast, Cr(III) was extracted steadily around initial pH 4. On the other hand, Cr(III) was hardly extracted around initial pH 7, because  $\text{Cr(OH)}_3$  was inert in substitution. In brief, extractability of Cr(III) above initial pH 4 was mainly dominated by the initial pH rather than by the pH

after APCD addition.

The domination of the extractability by the initial pH is also evidenced by Fig. 4-b. Because added APCD alters the pH of solutions to 6.7 in the initial pH 5-10 (Fig. 1), all the percent extraction data obtained in the initial pH range 5-10 exist at the estimated pH 6.7 in Fig. 4-b. The data at the estimated pH 6.7 is clustered with three groups of the data, which is obtained at the same initial pH (Fig. 4-b). If the extractability of Cr(III) is mainly dominated by the pH after APCD addition, the data at pH 6.7 will be clustered with each shaking time.

From the above elucidation for the *true* effect of pH on the Cr(III) extraction, following notice for application of the extraction of Cr(III) was given. In order to quantitatively extract Cr(III), pH of sample solution must be adjusted lower than 5 before chelating agent addition and pH must become higher than 5 after the chelating agent addition. To satisfy the later, initial pH value must be adjusted more than 2 under our extraction condition, however, degree of the pH alternation which caused from chelating agent depends on many factors as described in the Cr(VI) section. Thus, when different extraction conditions are applied to determination of Cr(III), it is necessary to previously check the manner of the pH alternation under the candidate extraction conditions and then to decide initial pH value.

## CONCLUSION

In order to elucidate the *true* effect of pH on the extraction of chromium with dithiocarbamate, pH change caused from addition of dithiocarbamate has been observed in detail and then the extraction behavior of Cr(III) and of Cr(VI) in APCD/DIBK system has been discussed by considering the observed pH change.

The addition of the examined two dithiocarbamates (i.e. APCD and NaDDTC) significantly changed the pH of chromium solution over the wide initial pH range. Cause of the pH increase observed in low initial pH region was attributed to protonation of the dithiocarbamate ion and to protonation of amine, which is derived from decomposition of the protonated dithiocarbamate. Cause of the pH decrease observed only in case of the addition of APCD was attributed to neutralization with ammonium ion.

The *true* effect of pH on the extraction was discussed with consideration for change in species of Cr(III) and Cr(VI) with the pH change caused from chelating agent addition, and the discussion gave the following conclusions. The extractability of Cr(VI) is mainly dominated by the pH after the addition of APCD. When Cr(VI) dominantly exist as  $\text{HCrO}_4^-$  after the addition; pH is lower than 7, Cr(VI) is extracted faster than under condition that Cr(VI) exist as  $\text{CrO}_4^{2-}$  (i.e. pH > 7). The extractability of Cr(III) is dominated by the pH after the addition of dithiocarbamate when the initial pH value of Cr(III) solution is lower than 5, on the contrary, when the initial pH is higher than 5 the



extractability is dominated by the initial pH of chromium solution rather than by the pH after the addition. When  $\text{Cr}(\text{OH})_2^+$  dominantly exist after pH adjustment, Cr(III) is extracted relatively fast. When Cr(III) solution is adjusted to pH 5 or above, Cr(III) forms insoluble particle of  $\text{Cr}(\text{OH})_3$  or analogous which is hardly extracted.

The discrepancies among the previous studies in the extraction behaviors of chromium with the dithiocarbamates can be explained with the results of this study. Most of the discrepancies are arisen from that the extraction behavior was discussed without consideration of the pH change which, caused from addition of chelating agent. The cause of some discrepancies about extraction behavior of Cr(III) seems to be difference in standing time before chelating agent addition after pH adjustment, among previous literatures.

The results of this study not only explain the discrepancies about extraction behavior but also become fundamental information about the dithiocarbamate extraction system for chromium speciation. Although many kind of dithiocarbamates have been used to chromium speciation, conditions (e.g. pH of sample, amount of chelating agent) which used in all of the previous speciation methods have been determined based only on trial and error. Our results of this study become effective help for the determination of the conditions for such speciation. A novel speciation technique for chromium, which requires no sample splitting is being developed based on the results of this study.

## REFERENCES

1. Mansell RE, Emmel HW (1965) *Atom Abs News* 4: 365-366
2. Midgett MR, Fishman MJ (1967) *Atom Abs News* 6: 128-131
3. Gilbert TR, Clay AM (1973) *Anal Chim Acta* 67: 289-295
4. Osaki S, Osaki T, Shibata S, Takashima Y (1976) *Bunseki Kagaku* 25: 358-362
5. Bergmann H, Hardt K (1979) *Fresenius Z Anal Chem* 297: 381-383
6. Shigematsu T, Kudo K (1980) *J Radioanal Chem* 59: 63-73
7. Takahashi N, Ogawa Y, Ogasawara M, Kurokochi K, Takahashi K (1982) *Bunseki Kagaku* 31: T91-T94
8. Tsuchiya H, Hasegawa N, Shima S (1985) *Analyst* 110: 1347-1349
9. Sugiyama M, Fujino O, Kihara S, Matsui M (1986) *Anal Chim Acta* 181: 159-168
10. Wai CM, Tsay LM, Yu JC (1987) *Mikrochim Acta [Wien]* II: 73-78
11. Subramanian KS (1988) *Anal Chem* 60: 11-15
12. Shimizu T, Suzuki A, Nitta A, Shijo Y (1991) *Nippon Kagaku Kaishi* 380-385
13. Miyazaki A, Barnes RM (1981) *Anal Chem* 53: 364-366
14. Lan CR, Tseng CL, Yang MH (1991) *Analyst* 116: 35-38
15. Schwedt G (1979) *Fresenius Z Anal Chem* 295: 382-387
16. Andrieu CM, Broekaert JAC (1993) *Fresenius J Anal Chem* 346: 653-658

17. Schaller H, Neeb R (1987) *Fresenius Z Anal Chem* 327: 170-174
18. EPA-600/4-79-020 (1979) *Method for Chemical Analysis of Water and Wastes*
19. Joris SJ, Aspila KI, Chakrabarti CL (1969) *Anal Chem* 41: 1441-1445
20. Cotton FA, Wilkinson G (1988) *Advanced Inorganic Chemistry*, 5th edn. Wiley-Interscience, New York
21. Masahiko M, Takada T (1985) *Talanta* 32: 513-516
22. Masahiko M, Takada T (1990) *Talanta* 37: 229-232
23. Masahiko M, Takada T (1991) *Talanta* 38: 1129-1135
24. Masahiko M, Takada T (1992) *Talanta* 39: 1293-1298
25. Aspila KI, Sastri VS, Chakrabarti CL (1969) *Talanta* 16: 1099-1104
26. Scharfe RR, Sastri VS, Chakrabarti CL (1973) *Anal Chem* 45: 413-415
27. Katz SA, McNabb WM, Hazel JF (1962) *Anal Chim Acta* 27: 405-415
28. Sillen LG, Martell AE (1964) *Stability Constants of Metal-Ion Complexes*, 2nd edn. The Chemical Society London
29. Hope M, Martin RL, Taylor D, White AH (1977) *JCS Chem Comm* 99-100
30. Finston HL, Lychtman AC (1982) *A New View of Current Acid-Base Theories*. Wiley-Interscience, New York
31. Lewis J, Wilkins RG (1960) *Modern Coordination Chemistry - Principles and Methods*. Interscience Publishers New York
32. Rai D, Sass BM, Moore DA (1987) *Inorg Chem* 26: 345-349