

## IR and XANES spectroscopic studies of humic acids reacting with Cr(III) and Cr(VI)

Atsuyuki Ohta<sup>1,\*</sup>, Hiroyuki Kagi<sup>2</sup>, Hiroshi Tsuno<sup>3</sup>, Masaharu Nomura<sup>4</sup>,  
Takashi Okai<sup>1</sup> and Norio Yanagisawa<sup>5</sup>

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**Abstract:** To elucidate processes of Cr(VI) reduction by humic acids in soils, humic acids reacting with Cr(VI) were characterized using IR and X-ray absorption near edge structure (XANES) spectroscopy. It is expected that oxidation of humic acid by Cr(VI) gives rise to the formation of aldehyde, ketone, and carboxyl species. However, no significant increase of IR-bands assignable to these functional groups has been reported. Instead, IR absorption spectra of humic acid oxidized by Cr(VI) show similar features to those of humic acid reacting with Cr(III). Consequently, the types and proportions of functional groups of HA substances did not differ significantly among experimental conditions. The IR spectra of humic acid reacting with Cr(III) and Cr(VI) show increased intensity of IR bands at 3400 cm<sup>-1</sup>, 1608 cm<sup>-1</sup>, and 1384 cm<sup>-1</sup>, with decreased intensity of peaks at 1707 cm<sup>-1</sup> and 1236–1250 cm<sup>-1</sup>. Those changes suggest the existence of bonding structures of two kinds: hydrated Cr forming an outer-sphere complex with humic acid, and Cr forming an inner-sphere complex with the carboxylate ligand of humic acid.

The Cr-K edge XANES spectra of humic acid reacting with Cr(VI) suggest that Cr(III), reduced from Cr(VI), binds with humic acid. No systematic difference of XANES spectra was found with increased amounts of Cr(VI) in experimental solutions. These features are consistent with IR absorption spectra. The fractions of two kinds of binding forms suggested by IR spectra were determined from linear combination fitting using XANES spectra of reference compounds: 50% hydrated Cr(III) adsorbed onto HA electrostatically and the remainder of Cr(III) binding to carboxylic acid of HA. However, with increasing pH of experimental solutions, some Cr precipitates as Cr(OH)<sub>3</sub>·nH<sub>2</sub>O in the solid phase. The pH level or Cr concentration must be reduced to prevent production of a Cr(OH)<sub>3</sub>·nH<sub>2</sub>O precipitate.

**Keywords:** hexavalent chrome, humic acid, FT-IR, XANES, oxidation state, speciation analysis

### 1. Introduction

Cr(VI), with high oxidizing capability, causes skin inflammation and tumors in humans and is linked with carcinogenesis. In stark contrast, Cr(III) is an essential element for living organisms and is both less toxic and less soluble than Cr(VI). The reduction–oxidation process of Cr in natural water and soil environments has therefore been of great scientific interest. Especially, the reduction of Cr(VI) by organic materials in soil environments, such as humic acid (HA) and fulvic

acid (FA), is important for alleviating environmental problems because the pollutant Cr(VI) can be readily reduced to Cr(III) in field systems (Kožuh *et al.*, 2000; Wittbrodt and Palmer, 1996). Studies of reduction of Cr(VI) in soils have mainly targeted their reduction kinetics and have particularly addressed the presence of Cr(VI) (Kožuh *et al.*, 2000; Wittbrodt and Palmer, 1995, 1997). However, little information is available in relation to the chemical state of Cr after Cr(VI) is reacted with soil. Fukushima *et al.* (1995) compared IR spectra of the HA and Cr(III)-HA complex. They con-

<sup>1</sup>AIST, Geological Survey of Japan, Institute of Geology and Geoinformation

<sup>2</sup>Geochemical Research Center, Graduate School of Science, The University of Tokyo, Tokyo 113-0033, Japan

<sup>3</sup>Faculty of Education and Human Sciences, Yokohama National University, Kanagawa, 240-8501, Japan

<sup>4</sup>Photon Factory, Institute of Materials Structure Science, KEK, Ibaraki 305-0801, Japan

<sup>5</sup>AIST, Geological Survey of Japan, Institute for Geo-Resources and Environment

\* Corresponding author: A. OHTA, Central 7, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8567, Japan. E-mail: a.ohta@aist.go.jp

cluded that Cr(III) binds with carboxyl groups of HA. Nevertheless, it remains unclear how Cr(VI) influences the complex formation of Cr(III/VI) and HA. Tokunaga *et al.* (2003), Tsuno *et al.* (2006) and Kappen *et al.* (2008) applied X-ray absorption near edge structure (XANES) spectroscopy to observe differences of Cr speciation in Cr(VI)-contaminated soils. They also specifically examined detection of the presence or absence of Cr(VI) because soil systems are too complex for speciation studies of Cr. The complex formation of HA oxidized by Cr(VI) and Cr(III) might differ from that of undamaged HA and Cr(III). In addition, Cr(III) that is reduced from Cr(VI) might form oxide and hydroxide precipitates without complexation with HA. To provide answers to these questions, we examine the changes of functional group of HA oxidized by Cr(VI) using IR absorption spectroscopy and elucidate the speciation of Cr(VI) reduced by HA using XANES spectroscopy.

## 2. Materials and experimental methods

### 2.1 Experiments

Two kinds of HA, purchased respectively from Wako Pure Chemical Industries Ltd. and Aldrich Chemical Co. Inc., were selected for use as reducing agents. The Wako HA had been extracted from peat soils in Hokkaido (Fukushima *et al.*, 1995), but the place of extraction of Aldrich HA, originally in Na-salt form, was unknown.

Humic acid reactants with Cr(VI) and Cr(III) were examined using FT-IR spectroscopy. First, 250 mg of Wako HA was dissolved in 500 ml MilliQ (MQ) water for measuring IR absorption spectra. An aliquot of 50 ml of Wako HA stock solution (0.5 mg/ml) was placed in a 200 ml glass conical flask. The  $K_2Cr_2O_7$  and  $Cr(NO_3)_3 \cdot 9H_2O$  were used, respectively, as reactants for Cr(VI) and Cr(III). Solutions of 2.5 ml and 25 ml of 0.5 mg/ml Cr(VI), 120 mg of  $K_2Cr_2O_7$  reagent, and 10 ml of 1 mg/ml Cr(III) nitrate solution were also placed in the vessels. A 0.17 mg/ml HA solution without Cr(III/VI) was also prepared as a blank. After the pH in experimental solution was adjusted at pH=2 using  $H_2SO_4$  and NaOH, solutions were diluted to 150 ml using MQ water.

For the measurement of XANES spectra, 50 mg of Wako HA and Aldrich HA were dissolved respectively in 500 ml MQ water with 5 ml of 1 mol/l NaOH. Then 50 ml of HA stock solutions (0.1 mg/ml) was placed in a 60 ml PFA vessel; 2.5 ml of 0.5 mg/ml, 5 mg/ml and 50 mg/ml Cr(VI) solutions and 2.5 ml of 10 mg/ml of Cr(III) solution were also added to the PFA vessels. The pH in the experimental solution was adjusted to pH=2 for Cr(VI) experimental systems to accelerate Cr(VI) reduction using  $H_2SO_4$  and NaOH. The pH of Cr(III) experimental systems was adjusted to 4, 6, and 8 to achieve adsorption efficiency. Solutions were di-

luted to 55 ml using MQ water. The 0.1 mg/ml humic acid solutions without Cr(III/VI) were also prepared as a blank.

Reactant vessels were covered with aluminum foil to shield light-transmittance. The reactant vessels were shaken at 40 rpm using a turn-overturn mechanical shaker during 15 days for measurement of IR spectra and during 7 days for XANES analysis. After the reaction, a few drops of 2 mol/l  $H_2SO_4$  were added to the experimental solution to precipitate HA. Cr(III) was not dissolved from HA in this process because Cr-HA bonding is expected to exhibit substitution inertness (Ohashi *et al.*, 2005). A few minutes later, the solution was centrifuged at 3,000 rpm for 15 min. The precipitate was filtered using a 0.1  $\mu m$  PTFE membrane filter and dried under vacuum at room temperature. The sample materials were placed on a filter and were kept in a refrigerator before IR and XANES measurements.

### 2.2 Determination of Cr(VI) concentration in solution

A spectrophotometer (Model 6C; HIRAMA Rika Kenkyujo Ltd.) with 1 cm glass-flowing-cell was used for determining Cr(VI) concentration in solution. The Cr(VI) concentration was determined from absorbance at 540 nm derived from Cr(VI)-diphenylcarbazide complex. Table 1 shows the Cr(VI) concentrations remaining in solution and the respective initial concentrations. We confirmed that the Cr(III) was not oxidized to Cr(VI) by humic acids in the experimental condition at pH=2–8.

### 2.3 IR absorption spectra of Wako HA reacted with chromium

A Fourier transform infrared spectrometer (Magna 550; Nicolet Biomedical Inc.) with a DTGS detector was used for the measurement of IR absorption spectra. The resolution was 4  $cm^{-1}$ ; the scan number was 64. The KBr pellet method was adopted for spectral measurements. Pellets were prepared from approximately 1 mg of HA scratched from a membrane filter and 200 mg KBr.

### 2.4 XANES spectra of K-edge chromium reacted with Wako HA and Aldrich HA

The Cr K-edge XANES spectra were recorded in fluorescence mode at the BL-12C of the Photon Factory in the Institute of Material Structure Science, High Energy Accelerator Research Organization. A Si(111) double-crystal monochromator was used to produce a monochromatic X-ray beam. The monochromator was calibrated at the sharp pre-edge peak of Cr(VI) at 5,989 eV using  $K_2Cr_2O_7$  powder in the transmission mode. Fluorescence X-rays (Cr  $K\alpha$ : 5.4 keV) were measured using a 19 element pure-Ge solid-state detector (No-

Table 1 Reduction rate of Cr(VI) with Humic substances

Humic substances for FT-IR analysis				
Sample no.	Wako HA	Cr concentration	pH	Cr(VI) reduction rate
1	0.17 mg/ml	-	2.0	n.d.*
2	0.17 mg/ml	Cr(III): 67 µg/ml	2.0	n.d.*
3	0.17 mg/ml	Cr(VI): 8.3 µg/ml	2.0	21%
4	0.17 mg/ml	Cr(VI): 83 µg/ml	2.0	8%
5	0.17 mg/ml	Cr(VI): 800 µg/ml	2.0	7%
Humic substances for XANES analysis				
Sample no.	Wako HA	Cr concentration	pH	Cr(VI) reduction rate
1	0.09 mg/ml	Cr(VI): 2.3 µg/ml	2.0	100%
2	0.09 mg/ml	Cr(VI): 23 µg/ml	2.0	30%
3	0.09 mg/ml	Cr(VI): 230 µg/ml	2.0	15%
4	0.09 mg/ml	Cr(III): 45 µg/ml	4.0	n.d.*
5	0.09 mg/ml	Cr(III): 45 µg/ml	6.0	n.d.*
6	0.09 mg/ml	Cr(III): 45 µg/ml	8.0	n.d.*
Sample no.	Aldrich HA	Cr concentration	pH	Cr(VI) reduction rate
1	0.09 mg/ml	Cr(VI): 2.3 µg/ml	2.0	100%
2	0.09 mg/ml	Cr(VI): 23 µg/ml	2.0	100%
3	0.09 mg/ml	Cr(VI): 230 µg/ml	2.0	31%
4	0.09 mg/ml	Cr(III): 45 µg/ml	4.0	n.d.*
5	0.09 mg/ml	Cr(III): 45 µg/ml	6.0	n.d.*
6	0.09 mg/ml	Cr(III): 45 µg/ml	8.0	n.d.*

n.d.\* : not determined

mura, 1998). Detuning was performed by reducing the incident flux to 70 %. The XANES spectra of all samples were measured under atmospheric pressure and at room temperature. Interference in Cr K-edge XANES spectra resulting from the blank in a PTFE membrane filter and HA not reacting with Cr(III) and Cr(VI) was negligible. For comparison, chromium compounds of several kinds ( $K_2Cr_2O_7$ ,  $Cr_2O_3$ ,  $Cr(NO_3)_3 \cdot 9H_2O$ ,  $Cr(OH)_3 \cdot nH_2O$ , and  $Cr(CH_3COO)_3$ ) were also measured in fluorescence mode.

### 3. Results and Discussion

#### 3.1 FT-IR spectra of Wako HA reacted with Cr(III/VI)

Figure 1 presents IR absorption spectra of Wako HA reacted with and without Cr(III/VI) in the region of 4000–400  $cm^{-1}$ . The broad peak at 3400  $cm^{-1}$  and the band at 2920  $cm^{-1}$  are assigned respectively to H-bonded O–H stretch and aliphatic C–H stretching (Senesi *et al.*, 1986; Stevenson, 1994). Four prominent IR bands

are found in Wako HA in the 1800–1200  $cm^{-1}$  region, where COOH stretch,  $COO^-$  asymmetric, and symmetric stretch bands are clearly visible. The absorption at 1707  $cm^{-1}$  is caused by C=O stretching of COOH groups; the peak at 1608  $cm^{-1}$  is attributed to C=C vibrations of aromatic rings and/or carboxylate  $COO^-$  asymmetric stretching; 1384  $cm^{-1}$  is explained by OH deformation, C–O stretching of phenolic OH, CH deformation of  $CH_2$  and  $CH_3$  groups and carboxylate  $COO^-$  symmetric stretching); the band at 1236–1250  $cm^{-1}$  is assigned for carboxylic C–O stretching or C–O–H deformation (Fukushima *et al.*, 1995; Stevenson, 1994). Absorption at 1107  $cm^{-1}$  is attributable to OH deformation or C–O stretching of phenolic and alcoholic OH groups (Senesi *et al.*, 1986). The band at 1035  $cm^{-1}$  is attributed to C–O stretching of polysaccharides (Senesi *et al.*, 1986).

Matsubara and Nakayama (1992) and Shinozuka *et al.* (2002) reported that HA oxidation by permanganic acid potassium ( $KMnO_4$ ), ozone, and hydrogen perox-

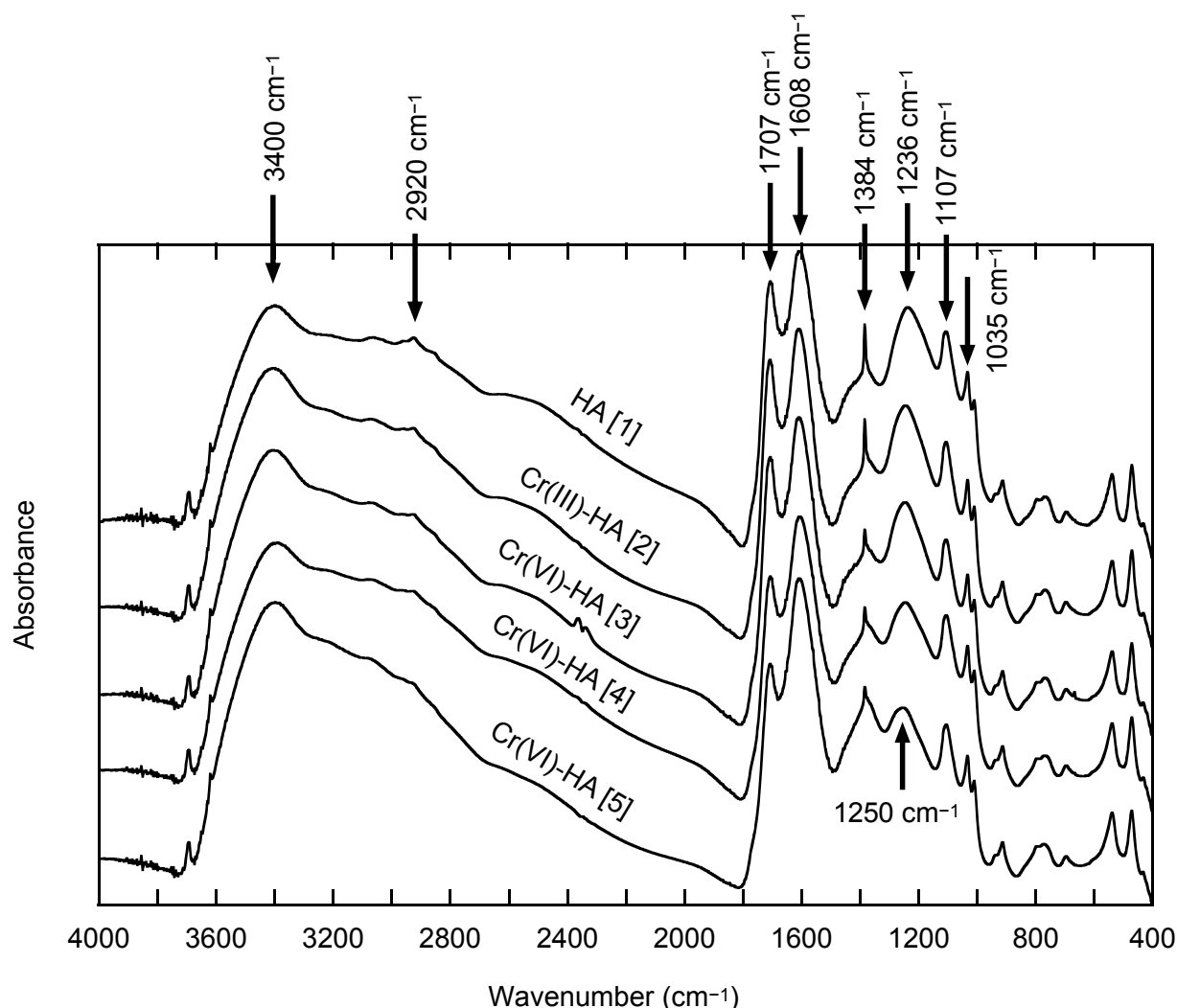


Fig. 1 IR absorption spectra of Wako HA reacted with and without Cr(III/VI). For all spectra, the relative percentage of transmittance is shown against the wavenumber (reciprocal centimeters). Numbers in brackets are sample numbers presented in Table 1. Spectra are shifted upward and downward for clarity.

ide ( $\text{H}_2\text{O}_2$ ) gives rise to formation of aldehyde, ketone, and carboxyl species and to dissociations of aliphatic species and C=C bonding of aromatic species. These reactions strengthen the IR bands at  $2920\text{ cm}^{-1}$  (aliphatic C–H stretching),  $1720\text{ cm}^{-1}$  (ketone and carboxyl species), and  $1400\text{ cm}^{-1}$  (OH deformation of phenolic OH) and weaken the IR band at  $1600\text{ cm}^{-1}$  (C=C vibrations of aromatic rings) (Shinozuka *et al.*, 2002). Figure 2 portrays the relation of absorption ratios of  $1707\text{ cm}^{-1}/1608\text{ cm}^{-1}$ , and  $1707\text{ cm}^{-1}/3400\text{ cm}^{-1}$  and  $1608\text{ cm}^{-1}/3400\text{ cm}^{-1}$  to concentrations of Cr(IV) reduced by HA in experimental solutions. The  $1707\text{ cm}^{-1}/1608\text{ cm}^{-1}$  and  $1707\text{ cm}^{-1}/3400\text{ cm}^{-1}$  ratios should increase and the  $1608\text{ cm}^{-1}/3400\text{ cm}^{-1}$  ratio should decrease concomitantly with increasingly reduced Cr(IV) because the IR band at  $3400\text{ cm}^{-1}$  is irrelevant to a reduction–oxidation reaction. Actually, all ratios decrease concomitantly with increasingly reduced Cr(IV) (Fig. 2). The result

is inconsistent with the fact that a considerable amount of Cr(VI) was reduced (Table 1). A likely explanation is that the Cr(VI) oxidized low-molecular-weight HAs thoroughly to  $\text{H}_2\text{O}$  and  $\text{CO}_2$  because Cr(VI) ( $\text{K}_2\text{Cr}_2\text{O}_7$ ) is highly oxidative. Alternatively, Cr(VI) concentration might be too low to produce notable changes in the IR spectra of HA.

Figure 1 shows that the IR bands of  $3400\text{ cm}^{-1}$  and  $1608\text{ cm}^{-1}$  became slightly intense and that the band at  $1384\text{ cm}^{-1}$  broadened and increased its intensity with increasing initial Cr(VI) concentrations in experimental solutions. The peak at  $1707\text{ cm}^{-1}$  became weak and the band at  $1236\text{ cm}^{-1}$  shifted to  $1250\text{ cm}^{-1}$ . Its intensity became weaker with increased Cr(VI) concentration. These changes of IR spectra are consistent with the changes caused by HA–Cr(III) complex formation (Fukushima *et al.*, 1995). Fukushima *et al.* (1995) explained that the inner-sphere complex formation of

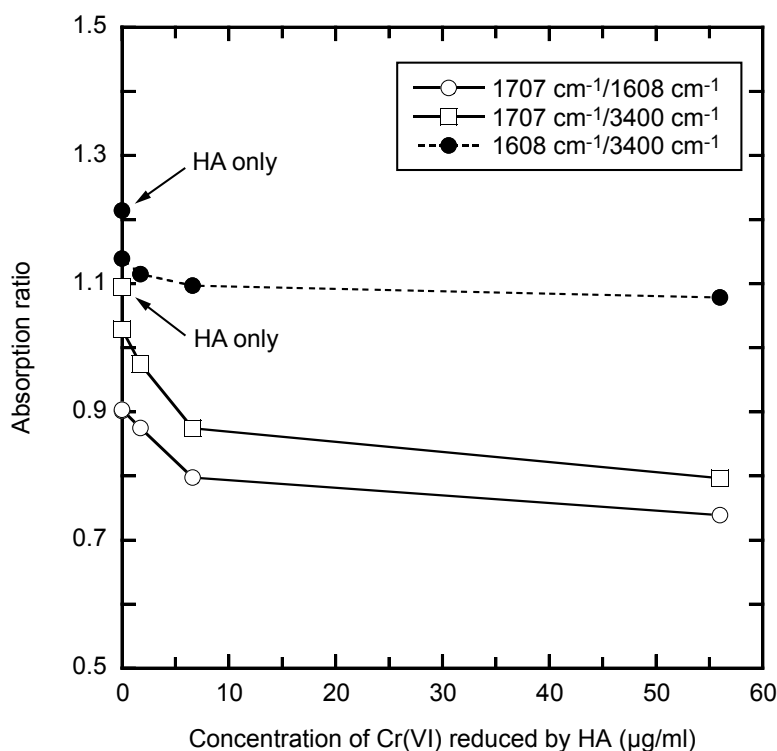


Fig. 2 Relation of IR absorption ratios of  $1707\text{ cm}^{-1}/1608\text{ cm}^{-1}$ , and  $1707\text{ cm}^{-1}/3400\text{ cm}^{-1}$  and  $1608\text{ cm}^{-1}/3400\text{ cm}^{-1}$  to concentrations of Cr(IV) reduced by HA in experimental solutions.

Cr(III) and  $\text{-COO}^-$  strengthens the band at  $1608\text{ cm}^{-1}$  and broadens the band at  $1384\text{ cm}^{-1}$ ; weakened two peaks at  $1707\text{ cm}^{-1}$  and  $1230\text{ cm}^{-1}$  are explained by the dissociation of  $\text{-COOH}$ , resulting in the increase of  $\text{-COO}^-$  species. In contrast, the increased intensity of IR band at  $3400\text{ cm}^{-1}$  might result from precipitation of Cr hydroxide. However, the experimental pH (2.0) was too low for the formation of Cr hydroxide (e.g., Richard and Bourg, 1991). Moreover, Figure 1 shows no intense IR band at  $540\text{ cm}^{-1}$  that results from the Cr-O lattice vibration of Cr hydroxide (Amonette and Rai, 1990). Senesi *et al.* (1986) assigned the strong absorption at  $3410\text{ cm}^{-1}$  for Cu absorbed on HA samples as outer-sphere complex formation. That inference was supported also by their ESR data. Therefore, the increased intensity of IR band at  $3400\text{ cm}^{-1}$  is explained by the presence of hydrated Cr forming an outer-sphere complex with HA. Nevertheless, it is difficult to determine the fraction of two kinds of binding forms using the IR spectra. The problem is discussed in the following section.

### 3.2 XANES spectra of K-edge Cr(III/VI) reacted with humic acid

Figure 3 portrays Cr K-edge XANES spectra of several chromium compounds, HA reacting with Cr(VI) and Cr(III). The XANES spectra of  $\text{K}_2\text{Cr}_2\text{O}_7$  have

a sharp pre-edge peak at 5988 eV and a broad peak around 6030 eV. The main peaks of  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and  $\text{Cr}(\text{OH})_3 \cdot n\text{H}_2\text{O}$  were assigned at 6003 eV. The  $\text{Cr}_2\text{O}_3$  and  $\text{Cr}(\text{CH}_3\text{COOH})_3$  are also trivalent Cr compounds. The former has duplicate peaks at 6002 eV and 6006 eV. The latter has a broad peak at 6007 eV, which features differ from those of XANES spectra of  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and  $\text{Cr}(\text{OH})_3 \cdot n\text{H}_2\text{O}$ . Because XANES spectra are sensitive not only to valence states but also to chemical species, they are useful for fingerprint analysis.

Figure 3 also presents Cr XANES spectra of reactant HA. No sharp pre-edge peak characteristic of Cr(VI) (5988 eV) was found in any HA sample. Moreover, the Cr XANES spectra show no considerable differences with increased amounts of initial Cr(VI) in the experimental solutions. Instead, they resemble XANES spectra of HA reacting with Cr(III). Results suggest that only Cr(III) that had been reduced from Cr(VI) by HA is bound to HA, although unreacted Cr(VI) apparently remained in some experimental solutions after the experiment (Table 1). Moreover, no evidence indicates that Cr XANES spectra differ between the reactant HA of two kinds. Results suggest that types and proportions of functional groups that bind Cr(III) might be similar.

IR spectra suggest that Cr forms the inner-sphere complex with a carboxylate ligand of HA and the

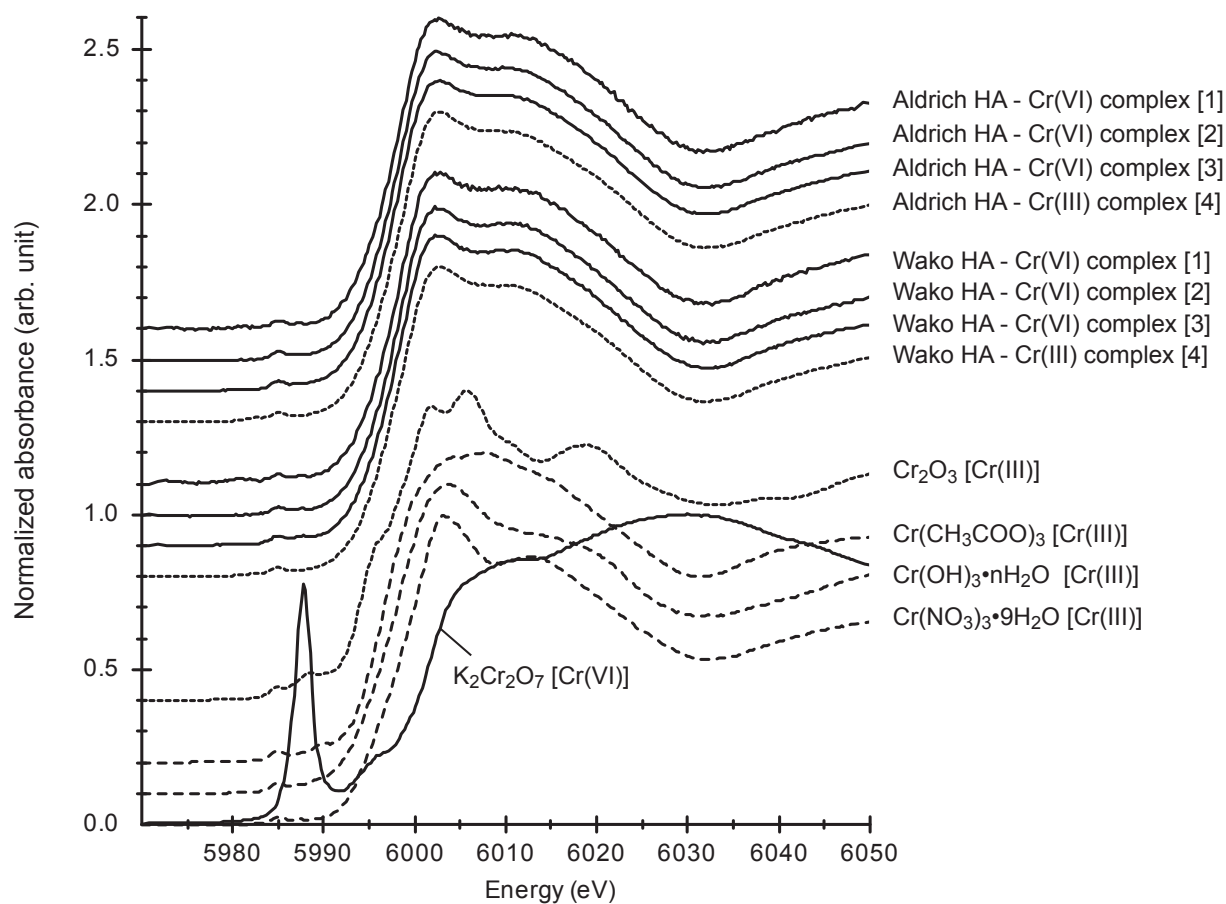


Fig. 3 Cr K-edge XANES spectra of several reference materials, Wako HA and Aldrich HA reacting with Cr(III/VI). Numbers in brackets correspond to the sample numbers presented in Table 1. Spectra are shifted upward and downward for clarity.

outer-sphere complex with HA. The fraction of two kinds binding forms is determined from the linear combination fits using  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and  $\text{Cr}(\text{CH}_3\text{COO})_3$  as end members. A standard material,  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  has high ion binding property and its XANES spectra is useful as a model of pseudo-outer-sphere complexes of Cr(III) and HA. Chromium acetate is substituted for Cr-carboxylate binding, although HA contains both aromatic and aliphatic carboxylic acids. Figure 4 shows the linear combination fitting results of 0.09 mg/ml Wako and Aldrich HA reacting with 23  $\mu\text{g}/\text{ml}$  Cr(VI), which suggests that the contribution of outer-sphere and inner-sphere complexes is about half-and-half for each HA sample. Similar fitting results were obtained for Wako and Aldrich HA reacting with 2.3  $\mu\text{g}/\text{ml}$  Cr(VI) and 230  $\mu\text{g}/\text{ml}$  Cr(VI).

Figure 5 shows XANES spectra of Wako HA reacted with Cr(III) at pH = 4, 6, and 8 and  $\text{Cr}(\text{OH})_3 \cdot n\text{H}_2\text{O}$ . The main peak shifts slightly to the higher energy side (see small allows in Fig. 5) and the absorbance in the region of 6008–6018 eV becomes weak with the increase of pH. The XANES features of HA reacted with Cr(III) at pH= 8 and  $\text{Cr}(\text{OH})_3 \cdot n\text{H}_2\text{O}$  resemble one

another. The same result was found in the Aldrich HA experimental system. It is possible that a part of Cr in solid phase exists as  $\text{Cr}(\text{OH})_3 \cdot n\text{H}_2\text{O}$  because trivalent chromium ion is hydrolyzed even in low pH conditions and precipitates as Cr hydroxide (e.g., Richard and Bourg, 1991). Actually, Kappen *et al.* (2008) reported that  $\text{Cr}(\text{OH})_3$  precipitates in the reduction process of Cr(VI) in soils at experimental pH of 4–6, although they were not formed in our Cr(VI) reduction experiments at low pH.

The fraction of  $\text{Cr}(\text{OH})_3 \cdot n\text{H}_2\text{O}$  in HA substances can be determined from linear combination fits using HA reacted with 23  $\mu\text{g}/\text{ml}$  Cr(VI) at pH=2 (sample no. 2 in Table 1) and  $\text{Cr}(\text{OH})_3 \cdot n\text{H}_2\text{O}$  as end members. Figure 6 suggests that the concentration of  $\text{Cr}(\text{OH})_3 \cdot n\text{H}_2\text{O}$  in the solid phase increases with increased pH values: 12 % at pH=4, 30 % at pH=6 and 50 % at pH=8. Similar fitting results were obtained for Aldrich HA experimental systems: the percentages of  $\text{Cr}(\text{OH})_3 \cdot n\text{H}_2\text{O}$  in the solid phase were, respectively, 7 % at pH=4, 31% at pH=6 and 46 % at pH=8. These observations are consistent with values reported by Kappen *et al.* (2008). The experimental method we used here should be improved

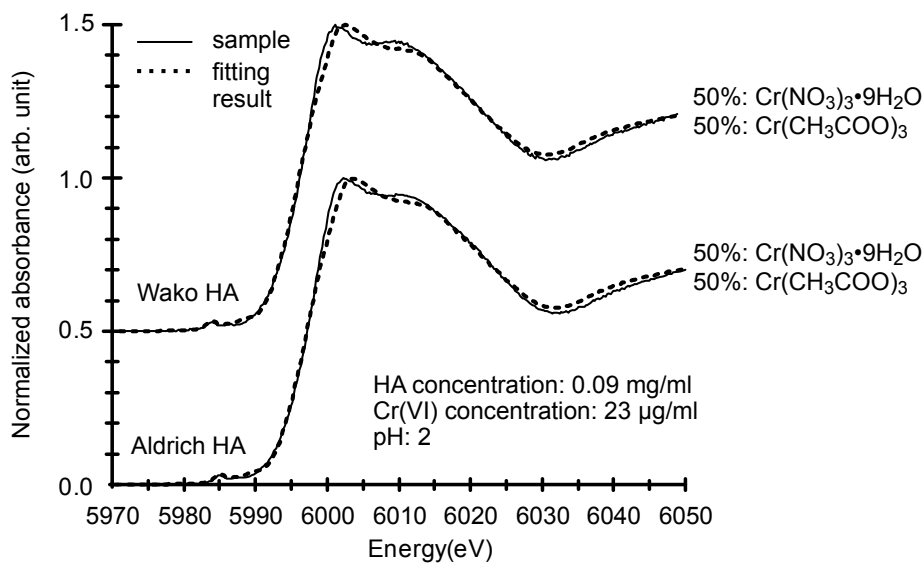


Fig. 4 Linear combination fitting results (dotted lines) of XANES spectra of Wako HA and Aldrich HA reacted with 23 µg/ml Cr(VI) (solid lines) using  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and  $\text{Cr}(\text{CH}_3\text{COO})_3$  as endmembers. Proportions of the endmember spectra to the linear combination fit are indicated for each sample. Spectra are shifted upward and downward for clarity.

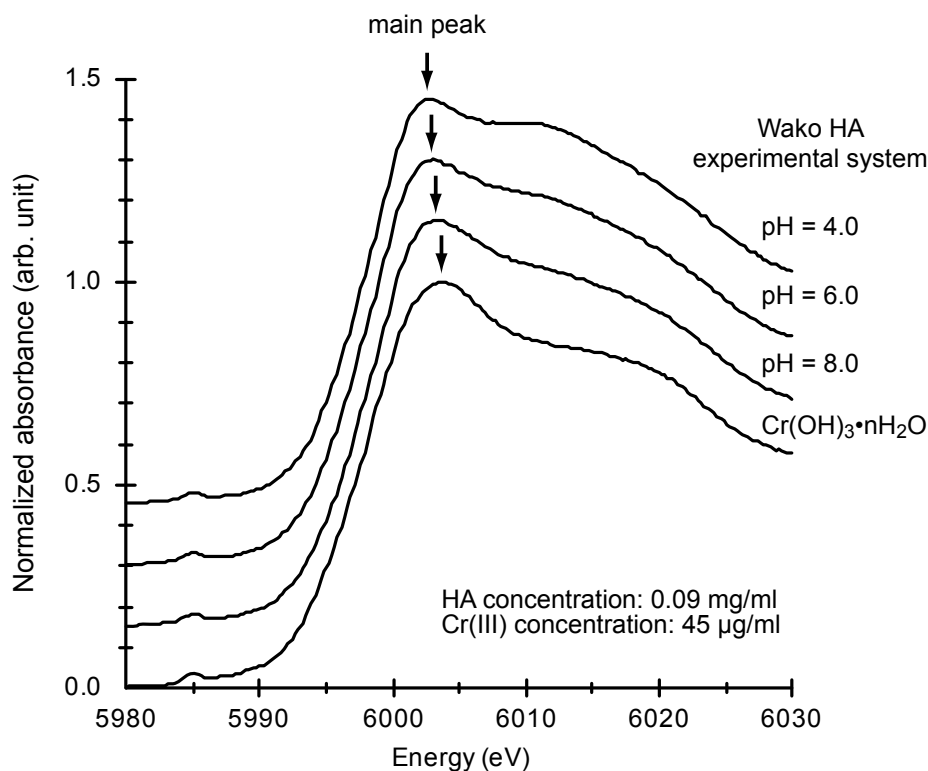


Fig. 5 Comparison of the Cr K-edge XANES spectra of Wako HA reacted with Cr(III) in various pH conditions; the spectra of  $\text{Cr}(\text{OH})_3 \cdot n\text{H}_2\text{O}$  are included for reference. Spectra are shifted upward and downward for clarity.

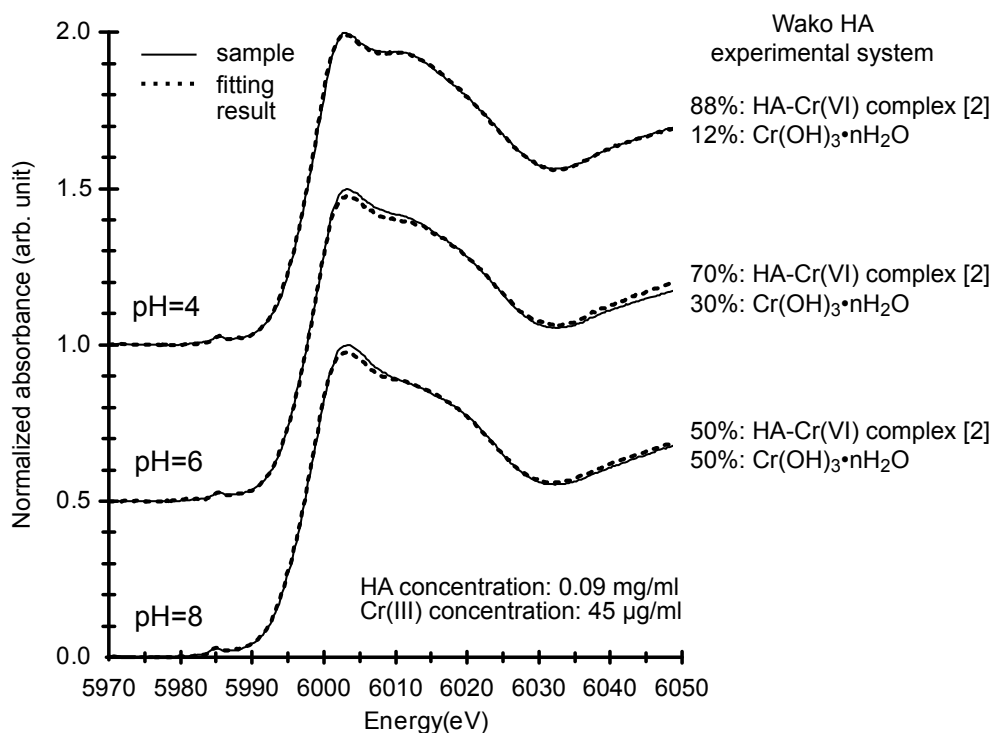


Fig. 6 Linear combination fitting results (dotted lines) of XANES spectra of Wako HA reacted with Cr(III) in various pH conditions (solid lines) using Wako HA reacting with 23  $\mu\text{g/ml}$  Cr(VI) at pH=2 (sample no. 3 in Table 1) and  $\text{Cr(OH)}_3 \cdot n\text{H}_2\text{O}$  as endmembers. Proportions of the endmember spectra to the linear combination fit are indicated for each sample. Spectra are shifted upward and downward for clarity.

to obtain Cr(III)-HA complex without the associated  $\text{Cr(OH)}_3$  precipitate. The reducing pH level (about pH=2) or dilution of Cr concentration is expected to be effective for the purpose.

#### 4. Summary

Properties of humic acid substances and speciation of Cr in the reduction process of Cr(VI) by humic acids were examined, respectively, using IR and XANES spectroscopic methods. Although it was expected that the oxidation process of humic acid by Cr(VI) produce aldehyde, ketone, and carboxyl species, no significant difference was found in IR spectra. XANES spectra revealed that Cr(III) reduced from Cr(VI) binds with HA. The IR spectra of HA reacting with Cr(VI) and Cr(III) suggest the presence of an inner-sphere complex and outer-sphere complex of Cr(III) and HA. The proportions of binding forms of the two types are estimated as one-to-one from XANES spectra. However, with increasing pH,  $\text{Cr(OH)}_3 \cdot n\text{H}_2\text{O}$  precipitation associated with HA-Cr complexes is not negligible.

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## 六価クロムおよび三価クロムと反応したフミン酸に対する IR および XANES 分光学的研究

太田充恒・鍵 裕之・津野 宏・野村昌治・岡井貴司・柳澤教雄

### 要 旨

土壌中の腐植物質による六価クロムの還元反応をよりよく理解するために、フミン酸を六価及び三価クロムと反応させ、それらを赤外分光法および X 線吸収端近傍構造 (XANES) を用いて特性解析を行った。六価クロムによって酸化されることで、腐植酸中のアルデヒド基、ケトン基、カルボキシル基が増加することが期待される。しかし、これらの官能基に該当する赤外吸収スペクトルバンドに有意な強度の増加は認められなかった。六価クロムによって酸化された腐植酸の赤外吸収スペクトルは、三価クロムと反応させた腐植酸のスペクトルに類似していた。つまり、今回の実験条件下では、酸化還元反応の前でクロムの結合に関与する官能基の種類または量に大きな変化がない事を示している。六価・三価クロムと反応させた腐植酸の赤外吸収スペクトルには、 $3,400\text{ cm}^{-1}$ 、 $1,608\text{ cm}^{-1}$ 、 $1,384\text{ cm}^{-1}$ の吸収強度が増加し、 $1,707\text{ cm}^{-1}$ や $1,236\text{--}1,250\text{ cm}^{-1}$ の吸収強度が減少する傾向が認められた。これらの特徴から、クロムは2つの異なる結合形態を持っていると考えられる。すなわち、水和したクロムが腐植酸に外圏錯体として結合しているものと、腐植酸のカルボキシル基と内圏錯体として存在しているものである。

次に、クロムの K 吸収端 XANES スペクトルを測定したところ、六価から三価に還元されたクロムが腐植酸と結合することが明らかになった。実験溶液中の六価クロム濃度の変化の違いによる XANES スペクトルの変化は認められなかった。これらの結果は赤外スペクトルの特徴と一致する。赤外スペクトルによって示唆された2種類の結合形態の割合は、XANES スペクトルを用いることで定量的に見積もることができ、水和したクロムイオンが静電的に腐植酸に吸着した割合が50%、腐植酸中のカルボキシル基と結合したクロムの割合が50%であった。しかし、実験溶液中の pH が高くなるにつれ、一部のクロムが水酸化物として沈殿することも明らかになった。そのため、水酸化クロムの沈殿を避けるためには、pH をより低くする、クロムの濃度を下げるなど注意が必要である。

