

X-ray Fluorescence Analysis of Cr⁶⁺ Component in Mixtures of Cr₂O₃ and K₂CrO₄

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X-ray fluorescence analysis using Cr K_α spectra was applied to the determination of the mixing ratio of Cr⁶⁺ to (Cr⁶⁺ + Cr³⁺) in several mixtures of K₂CrO₄ and Cr₂O₃. Because the powder of K₂CrO₄ contained large particles that were more than 50 μm in diameter, it was ground between a pestle and a mortar for about 8 h. The coarse particles still remaining were removed by using a sieve with 325-mesh (44 μm) in order to reduce the difference in absorption effects between emissions from Cr⁶⁺ and those from Cr³⁺. The mixing ratio, K₂CrO₄/(K₂CrO₄ + Cr₂O₃), of the five mixtures investigated is 0.50, 0.40, 0.20, 0.10, and 0.05 in weight, respectively. Each spectrum obtained was analyzed by decomposing it into two reference spectra, those of the two pure materials, K₂CrO₄ and Cr₂O₃, with a constant background. The results for the mixtures containing K₂CrO₄ of more than 20 wt% are that the relative deviation from the true value is less than ~5%. On the other hand, when the content of K₂CrO₄ decreases to less than 10 wt%, the relative deviation gets so large as 20 – 25%. The error coming from a peak separation of spectrum involved in our results were estimated by applying our method to five sets of data for each mixture computationally generated, taking into account the uncertainty in total counts of real measurements.

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Introduction

XRF (X-ray fluorescence analysis) is one of the well-known techniques frequently used in an elemental analysis. If the resolution of the spectrometer is as high as several tenths of eV (more attainable with a wavelength dispersive method than with an energy dispersive method), it is also applicable to a chemical state analysis since the X-ray emission spectra are often affected by the chemical environment of the investigated atom. Despite this applicability, it is not so widely used in chemical state analysis as other relevant techniques such as XPS (X-ray photoelectron spectroscopy) and XANES (X-ray absorption near edge structure), probably because the chemical shift in an X-ray emission spectrum is usually smaller than those in the others. However, XRF often gives us satisfying results of the quantitative component analysis for the system containing more than one kind of chemical states. The application of XRF method to the Cr⁶⁺ component analysis in the mixtures of K₂CrO₄ and Cr₂O₃ shall be presented in this work.

A quantitative analysis of hexavalent chromium has been of great importance because it is highly toxic. Because trivalent

chromium is also stable, it is necessary to take the Cr⁶⁺ component out from all chromium atoms. Most investigations on its analysis is performed by dissolving the substance into solution.^{1,2} During that process the reduction of hexavalent chromium and/or the oxidation of trivalent chromium can make the precise analysis difficult. In addition, the chemical reactions between the reagent used for the detection and other ions contained in the substance are also a nuisance. In the method we shall present in this article, it is not necessary to worry about these problems because no change is made to the sample. The most important problem which greatly affects the results is the difference in absorption of the fluorescence from hexavalent atoms and from trivalent atoms. For overcoming this problem the particle size of K₂CrO₄ should be reduced to less than about 10 μm in order to make the absorption in the particle containing the emitting atom sufficiently small. Once this problem was resolved, the XRF method turned out to be useful for Cr⁶⁺ component analysis.

Experimental

Reagents and chemicals

K₂CrO₄ (Nacalai Tesque Inc., 98.5%) and Cr₂O₃ (Mitsui Chemicals Co. Ltd., 99.9%) were used to make the mixtures

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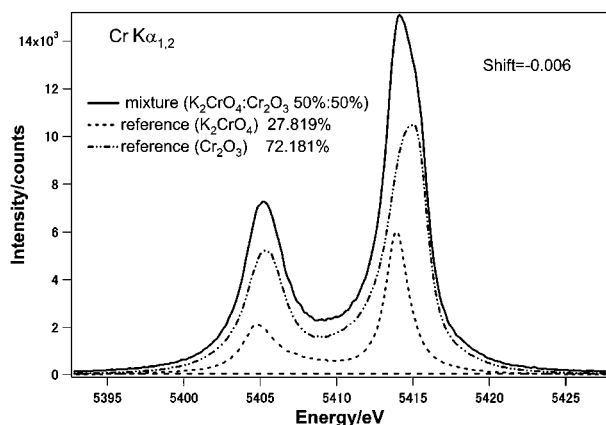


Fig. 1 Cr $K\alpha_{1,2}$ emission spectrum of a mixture of K_2CrO_4 (50 wt%) and Cr_2O_3 (50 wt%).

investigated. They were also used for the reference samples of pure materials. Because the powder of K_2CrO_4 contained particles as large as 50 – 200 μm in diameter, it was ground between a pestle and a mortar for about 8 h. The coarse particles still remaining were removed by using a sieve with 325-mesh (44 μm) in order to reduce the difference in absorption effect between emissions from Cr^{6+} and those from Cr^{3+} .

SEM observation shows us that most of the particles of K_2CrO_4 have diameters of 1 – 3 μm , although some particles are as large as 5 – 10 μm in diameter. As for Cr_2O_3 , the size of the particles is of the order of sub-microns. Now we assume that the particle sizes of K_2CrO_4 and Cr_2O_3 are 2 and 0.5 μm in diameter, respectively, and that the average distance the emitted X-ray propagates in the particle which contains the emitting atom is equal to the radius of the particle. With these assumptions, the effect of the difference in absorption between emissions from Cr^{6+} and those from Cr^{3+} is not so much that the ratio of the transmission of Cr $K\alpha$ radiation from Cr^{6+} to that from Cr^{3+} is closer to 1 than 0.978 (0.944/0.965). Here 0.944 and 0.965 are the transmission of Cr $K\alpha$ radiation through a slab (1 μm thickness) of K_2CrO_4 and Cr_2O_3 , respectively. The powder of K_2CrO_4 obtained was mixed with the powder of Cr_2O_3 in accordance with the mixing ratio of each sample. Finally the powder was pressed into a pellet of 10 mm in diameter.

Apparatus and procedure

Cr $K\alpha_{1,2}$ spectra of five mixtures and two reference compounds were measured using a high resolution double-crystal X-ray fluorescence spectrometer (RIGAKU System3580EKI). The details of the spectrometer were described in another article.³ The analyzing crystals used in our experiment were Si(220) and the detector was a sealed proportional counter (with Xe gas inside). A tungsten X-ray tube was operated at 40, 70 mA. The scanning range was 71.75 – 72.30 degrees in 2θ with a step of 0.001 degrees (approximately 0.06 – 0.07 eV). The estimated resolving power of this spectrometer under this condition is about 0.25 eV. The chamber was evacuated to less than 10 Pa in order to avoid the absorption by the air. It took us about 5 h to obtain each spectrum.

Results and Discussion

Savitzky-Golay nine-point quartic smoothing was applied to

Table 1 Result of mixing ratio analyses of mixtures of K_2CrO_4 and Cr_2O_3

Mixing ratio, weight %		Mixing ratio, atomic %		Shift/eV	Result, atomic %	
K_2CrO_4	Cr_2O_3	Cr^{6+}	Cr^{3+}		Cr^{6+}	Cr^{3+}
50.0	50.0	28.1	71.9	-0.006	27.8	72.2
40.0	60.0	20.7	79.3	-0.006	20.9	79.1
20.0	80.0	8.9	91.1	0.001	8.5	91.5
10.0	90.0	4.2	95.8	0.004	3.2	96.8
5.0	95.0	2.0	98.0	-0.001	1.6	98.4

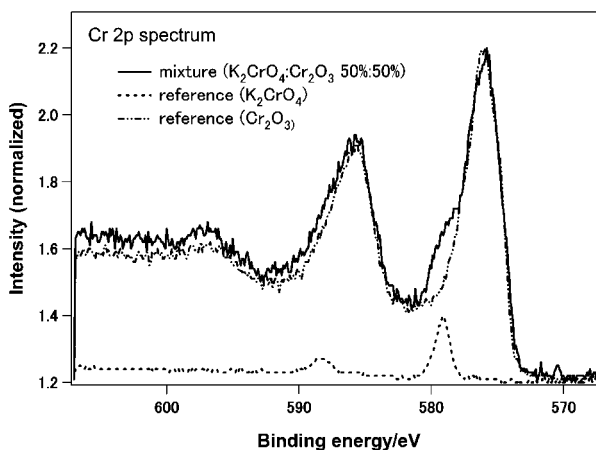


Fig. 2 Cr 2p XPS spectrum of a mixture of K_2CrO_4 (50 wt%) and Cr_2O_3 (50 wt%).

each measured spectrum and each reference spectrum. After being smoothed, each measured spectrum was analyzed by decomposing them into the two reference spectra and a constant background (Fig. 1). In order to get the correct value for mixing ratio of $Cr^{6+}/(Cr^{6+} + Cr^{3+})$, we normalized the two reference spectra in advance after the removal of their backgrounds. A shift in energy is allowed for the mixtures' spectra (not for the reference spectra) because a shift of less than 0.0002 or 0.0003 degree in 2θ can be observed even for the same samples due to the limit of reproducibility of the goniometer. This shift corresponds to only 0.01 – 0.02 eV for our condition ($2\theta = 72.00$ degree). The results are shown in Table 1. The results for the mixtures containing of K_2CrO_4 more than 20 wt% show a relative deviation from the true value of less than ~5%. On the other hand, when the content of K_2CrO_4 decreases to less than 10 wt%, the relative deviation gets as large as 20 – 25%.

We also measured Cr 2p XPS spectrum of each mixture and made the same kind of analysis as we have done using XRF. One of the Cr 2p XPS spectra ($K_2CrO_4:Cr_2O_3 = 50:50$) is shown in Fig. 2. The result of the analysis is that the mixing ratio ($Cr^{6+}/(Cr^{6+} + Cr^{3+})$) of each mixture is consistently about 0.1 for all mixtures. The reason for this may be that because the powder of Cr_2O_3 covers the surface of the sample, which means some inhomogeneity in the surface. This idea is strongly supported by the fact that all mixtures have the same color as that of Cr_2O_3 . The inhomogeneity indicated here may lead to underestimation of the mixing ratio ($Cr^{6+}/(Cr^{6+} + Cr^{3+})$).

In order to make an estimate of errors related to the peak separation of a spectrum involved in the present results,

Table 2 Estimation of errors involved in our method using five sets of computationally generated data

Mixing ratio, atomic %		Result, atomic %
Cr ⁶⁺	Cr ³⁺	Cr ⁶⁺
95.0	5.0	95.2 ± 0.4
90.0	10.0	90.4 ± 0.5
70.0	30.0	69.9 ± 0.2
50.0	50.0	50.2 ± 0.7
30.0	70.0	30.0 ± 0.8
10.0	90.0	10.3 ± 0.4
5.0	95.0	5.1 ± 0.2

our method was applied to five computationally generated sets of data (count level of the data is roughly equal to the one of the measured spectra) for seven mixtures having a ratio, $Cr^{6+}/(Cr^{6+} + Cr^{3+})$, of 0.95, 0.9, 0.7, 0.5, 0.3, 0.1, and 0.05, respectively. The results are shown in Table 2. Errors estimated by this procedure are not as large as 10%. The maximum relative error in Table 2 occurs when we determine the Cr³⁺ component of a mixture containing Cr⁶⁺ of 95 at%, the relative error is ~8.3% (0.4/4.8). Based on the error estimation, we may say that results of our quantitative analysis involve a relative error of ~10% at maximum if the ratio of the minor component is more than 5 at%.

The error estimated above does not include any errors originating from a particle size effect, from a change of the chemical state induced by X-ray radiation and/or by grinding and mixing compounds, and/or from some inhomogeneity of the sample. As for a particle size effect, we made it sufficiently small by grinding the K₂CrO₄ particles. But the possibility of change in a chemical state was not investigated. It was not likely that change in a chemical state occurred to a great extent in the present work since the ratio $Cr^{6+}/(Cr^{6+} + Cr^{3+})$ obtained was not far from the true value. However, that does not mean we do not have to be careful about the reduction of Cr⁶⁺ to Cr³⁺. Actually we have experienced the reduction of Cr⁶⁺ to Cr³⁺ when we measured, using synchrotron radiation, Cr K_α spectra of mixtures of K₂CrO₄ and Cr₂O₃ embedded in soil. Some chemical substances in soil may be induced by X-ray radiation to reduce Cr⁶⁺ to Cr³⁺. It is important to repeat measurements to see if any reduction occurs.

Conclusions

The mixing ratio of Cr⁶⁺ to (Cr⁶⁺/Cr³⁺) in mixtures of K₂CrO₄ and Cr₂O₃ was determined by analyzing a Cr K_α spectrum measured using a double crystal spectrometer. Our results show that, if the minority is larger than ~10%, the mixing ratio can be estimated with the accuracy of 10% or better. The most important problem which causes large error is the difference of the absorption effect between the emission from Cr⁶⁺ and that from Cr³⁺. The difference can be reduced to the negligible extent when the particle is ground to several microns.

For practical use, several problems remain to be solved. Although the particle-size problem was solved by grinding the particles in the present work, it would be cumbersome if grinding process had to be performed on all samples to be investigated. The development of the correction method for the analysis is highly desired because one of the advantages of XRF is its non-destructiveness. Low intensity of the fluorescence due to the double-crystal reflections and the possibility of the X-ray inducing reduction are other problems.

The X-ray fluorescence method is often used only as a screening analysis (an elemental analysis). However, it would be much more convenient if it becomes possible to make a further XRF analysis (chemical state analysis) with a slight modification of the spectrometric system. The analysis described above seems very applicable and we hope it will come into use in the near future.

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