DETERMINATION OF IRON SPECIES IN ENVIRONMENTAL SAMPLES BY MÖSSBAUER SPECTROSCOPY

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Abstract - The iron species in environmental particulate matter have been characterized and determined by ^{57}Fe Mössbauer spectroscopy. The urban particulate matters collected in Tokyo contain three kinds of iron components in different chemical states; high-spin Fe^{3+} , high-spin Fe^{2+} and magnetic hyperfine-splitting components. The high-spin Fe^{2+} component is an indicator of the particulate emission from soils and minerals, while the magnetic hyperfine-splitting component is an indicator of the particulate generation by human activities.

Key words particulate matter, iron species, Mössbauer spectroscopy

A knowledge of the chemical states of elements has been shown to play an important role in the estimation of the emission sources of particulate matter. In particular, Mössbauer spectroscopy is well known to be a powerful means to probe the chemical states of iron in environmental samples[1-2]. In the previous work the ^{57}Fe Mössbauer spectra of urban particulate matter were measured and compared with those of standard reference material[3]. Mössbauer spectroscopy also revealed that the constituents of airborne particles depend on their particle size[4]. The high-spin Fe^{2+} component is characteristic of the coarse particulate group, while the magnetic hyperfine-splitting component is typical of the fine particulate group. Recently it has been suggested that the ratio of the high-spin Fe^{2+} component to the high-spin Fe^{3+} component is an indicator of anthropogenic contribution to particulate matter[5]. In spite of much interest in Mössbauer spectroscopic characterization of environmental samples, only few papers have dealt with the quantitative analysis of iron species in particulate matter[6]. The relative abundance of the iron species in environmental samples is easily calculated from the relative intensity of the Mössbauer absorption spectra, if all the recoil-free fractions of the iron species are the same in the spectral samples. However the determination of iron species in different chemical states has been very difficult because the Debye-Waller factor of Mössbauer atoms varies with the chemical states of iron species in the measuring samples. In the present study we have focused on the determination of the quantity of iron species in urban particulate matter.

EXPERIMENTAL

All chemicals were of reagent grade and used without further purification. Iron(II) ammonium sulfate $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$, iron(III) ammonium sulfate $\text{Fe}_2(\text{SO}_4)_3(\text{NH}_4)_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$ and iron(III) oxide Fe_2O_3 were purchased from Wako Pure Chemical Industries, Ltd. Standard Reference Materials were obtained from National Bureau of Standards[4]. The samples of particulate matter were collected on the filter of air samplers or air conditioners for a certain period of April 1987 to March 1991. The sampling sites were located in the urban

area of Tokyo. Mössbauer spectra were measured against a 370 MBq ^{57}Co source in Rh (The Radiochemical Centre, Amersham, England) with a Wissel MA-250 constant-acceleration transducer coupled with a Norland 5500 multichannel analyzer. The absorbance temperature was kept at 77 or 293 K, while the ^{57}Co source was maintained at room temperature. The Doppler velocity was calibrated with iron foil and the isomer shift was referred to the centroid of six absorption lines of iron foil kept at 293 K. The Mössbauer spectra obtained were fitted to Lorentzian curves using an iterative least-square fitting computer program.

RESULTS AND DISCUSSION

Typical Mössbauer spectra of particulate matters collected in the urban area (UR-1) and at the subway station (SUB-1) are presented in Fig. 1 and 2. The absorption lines of the Mössbauer spectra were assigned by comparing their spectral parameters, i.e., isomer shift (δ), quadrupole splitting (ΔE_Q) and magnetic hyperfine splitting (H) with those reported in the previous papers[3-4]. Both of the particulate matters collected in Tokyo were shown to contain mainly three kinds of iron components in different chemical states: high-spin Fe^{3+} , high-spin Fe^{2+} and magnetic hyperfine components. The possible assignments are given

Fig. 1 Mössbauer spectrum of UR-1 at 77 K.

Fig. 2 Mössbauer spectrum of SUB-1 at 293 K.

at the top of each Mössbauer spectrum in Fig. 1 and 2. The Mössbauer parameters obtained are summarized in Table 1. An intense quadrupole-splitting doublet assigned to the high-spin Fe^{3+} component was obtained for all the environmental particulate matter collected in the urban area in Tokyo. The line width at the half height was relatively large because they contain many kinds of paramagnetic components. On the other hand, a weak quadrupole-splitting doublet assignable to the high-spin Fe^{2+} component is useful as an indicator of the emission sources of soils and minerals. A few sets of sextets were also observed and assigned to metallic iron, $\alpha\text{-Fe}_2\text{O}_3$, Fe_3O_4 , etc. It is noteworthy that the particulate samples collected at the subway station contain metallic iron generated by the abrasion of wheels and rails. The magnetic hyperfine-splitting components are associated with the emission sources such as combustion of coal and oil, steel industries, motor vehicles, etc. Therefore, these components are an indicator of particulate generation by human activities.

The above observations agreed with the results reported in the previous papers[3-4]. This indicates that the particulate samples collected this time are suitable for a study on the quantitative analysis of iron species by ^{57}Fe Mössbauer spectroscopy. The high-spin Fe^{3+}

Table 1 Mössbauer parameters obtained for urban particulate matter

Sample	Component	δ (mm s ⁻¹)	ΔE_Q (mm s ⁻¹)	H (T)	Peak area (%)
UR-1 (293 K)	Fe ²⁺	1.01	2.67	-	14
	Fe ³⁺	0.38	0.68	-	48
	Fe ₂ O ₃	0.40	0.17	50.7	38
	(77 K) Fe ²⁺	1.27	2.80	-	18
	Fe ³⁺	0.44	0.70	-	34
	Fe ₂ O ₃	0.49	-0.05	51.5	48
SUB-1 (293 K)	Fe ²⁺	1.03	2.50	-	41
	Fe ³⁺	0.33	0.64	-	40
	Fe(metal)	0	0	33.1	19
	(77 K) Fe ²⁺	1.34	2.43	-	20
	Fe ³⁺	0.39	0.69	-	35
	Fe ₂ O ₃	0.42	-0.18	50.7	20
	Fe(metal)	0.04	0	33.4	25

component, i.e., the major constituent of urban particulate matter consists of iron(III) hydroxides, ultrafine particles of iron(III) oxides, clays, etc., while the high-spin Fe²⁺ component is constituted of soils, minerals, etc. Both of high-spin Fe³⁺ and Fe²⁺ components are a mixture of different kinds of iron compounds, although the magnetic components are unambiguously identified as metallic iron, hematite or magnetite in most cases. This makes it difficult to find a reference material suitable for construction of calibration graphs for determining the high-spin Fe²⁺ and Fe³⁺ components. Here FeSO₄(NH₄)₂SO₄ · 6H₂O and Fe₂(SO₄)₃(NH₄)₂SO₄ · 24H₂O were chosen as a reference material for the high-spin Fe²⁺ component and the high-spin Fe³⁺ component, respectively. The advantages of these compounds are that they are available commercially in high purity and have large molecular weight good for their weighing. The serious disadvantage is that the Debye-Waller factor of these reference materials is not always the same as those of the high-spin Fe³⁺ or Fe²⁺ components. Despite of this disadvantage, a series of calibration graphs were constructed by plotting the absorbance of the ⁵⁷Fe Mössbauer absorption lines against the amount of iron ions in the reference material. The absorbance of the ⁵⁷Fe Mössbauer resonance lines was taken at a Doppler velocity where the absorption line gives a maximal absorption on the spectrum. Fortunately, the slopes of the calibration lines were almost the same in FeSO₄(NH₄)₂SO₄ · 6H₂O and Fe₂(SO₄)₃(NH₄)₂SO₄ · 24H₂O. This suggests that the recoil-free fraction or the Debye-Waller factor is much the same in both compounds. The calibration plots of the ⁵⁷Fe Mössbauer spectral absorbance against the amount of iron ions were also constructed for metallic iron, α -Fe₂O₃ and Fe₃O₄. If necessary, the slope of the calibration graphs was corrected by using the analytical data on the other iron content determined by the other destructive analytical methods such as atomic absorption spectrophotometry. The coefficient of variation (n = 5) ranged from 1.42 to 3.85 % at 1.0 mg of iron in the reference material. The detection limits of iron species were estimated to be 17 to 50 μ g from the standard deviation of the absorbance on the calibration graphs.

The typical narrow Mössbauer spectra measured for the urban particulate matter collected in Tokyo are presented in Fig. 3. These narrow spectra were used mainly for the determination of the high-spin Fe³⁺ and high-spin Fe²⁺ component. The ⁵⁷Fe Mössbauer spectra of two kinds of particulate matters (UR-2 and UR-3) were measured under the same conditions as those for the calibration graphs. The content of iron species in these samples was calculated after a proper correction to the Debye-Waller factors. The analytical results

Fig. 3 Typical narrow Mössbauer spectra of urban particulate matter at 293 K.

obtained are listed in Table 2, where the measurements were repeated at least three times and the average values are presented. It is very interesting to compare these analytical results with those estimated from the absorption peak area on the Mössbauer spectra, although the absorption area shown in Table 1 corresponds to the relative abundance of iron species in the samples.

Table 2 Analytical results on iron species in urban particulate matter

Sample	High-spin Fe^{3+} (wt. %) ^{a)}	High-spin Fe^{2+} (wt. %)	Magnetic component (wt. %)	Total (%)
UR-2	1.52 (40.8) ^{b)}	0.35 (9.38)	1.86 (49.9)	3.73
UR-3	1.37 (53.5)	0.30 (11.7)	0.89 (34.8)	2.56

a) Weight percent as iron. b) Relative abundance in percentage.

It is very important from the viewpoint of source estimation of environmental particulate matters to determine the quantity of the three major components: high-spin Fe^{3+} , high-spin Fe^{2+} and magnetic hyperfine components. The absorbance of the resonance Mössbauer atoms reflects the amount of iron species in particulate matter better than the relative absorption area. The Debye-Waller factor of iron species in different chemical states should be taken into consideration in the determination of iron in environmental samples.

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