

Development of Forensic Identification Method with
X-Ray Absorption Fine Structure Analysis

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Acknowledgement

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Chapter 1 Introduction

1.1 The present state of criminality in Japan

In Japan, the number of crimes increased from 1980 to 2002, surpassing 2,850,000 cases in 2002. After 2003, the number decreased, reaching 1,210,000 in 2014, which was the same as between 1960 and 1980.¹ Trends in confirmed and cleared criminal cases are presented in Fig. 1.1.¹ The number of serious cases (such as murder) tended to decrease during this time, with a peak of 24,000 cases in 2005 and only 14,000 cases in 2014. However, new types of fraud (such as bank transfer fraud) are increasing. In 2014, the economic damage of the 13,000 cases of bank transfer fraud that occurred during this year reached 57 billion yen. The modus operandi of such crimes, where the roles of the criminals systematically are divided into calling and cash receiving etc., has become more sophisticated.

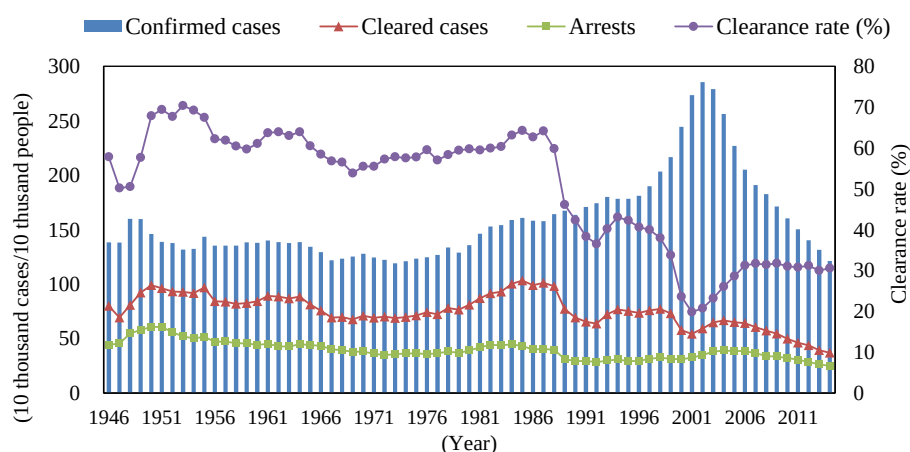


Fig 1.1 Trends in confirmed and cleared criminal cases.

Arrests for crimes involving pharmaceuticals numbered more than 13,000 in 2014, and are still at a high level. Some 11,000 arrests were connected to stimulant drugs and some 1800 related to cannabis, representing a large proportion of illicit drug cases and indicating that drugs are smuggled extensively into Japan from abroad. Recently, in addition to these drugs, “dangerous drugs” have also been abused. The dangerous drugs have similar chemical structures and pharmacological properties to controlled substances. However, they are made to look harmless by disguising them as herbs, aromatic oils, and bath salts.

In 2014, the number of arrests for negligent driving resulting in injury and death reached 55,000.² Recently, the proportion of arrests for fatal hit-and-run accidents has persistently been >90%, which is the result of quick and sophisticated initial investigations. When investigating a traffic accident, it is important to determine the cause of the accident using objective evidence and a scientific approach. On the other hand, domestic situation of traffic accidents remains severe. In Japan, a law regarding the crime of dangerous

driving causing death or injury was established in 2001; however, this law was rarely applied because of the precise conditions under which it holds. The law was subsequently revised to ensure that it could be applied more extensively. In this situation, it is desirable to determine the cause of an accident using sophisticated and advanced forensic sciences.

Recently, the number of arrests for waste offense tends to decrease; the number was 6,400 in 2015. Half of the arrests were due to illegal dumping. Regulation of the Waste Disposal Law is applicable to corporations as well as individuals. In 2015, 369 corporations were arrested for violation of the law. Police strive for early detection and clearance in cooperation with the environmental administrative department.

1.2 Forensic science

Attenuation of the local community network can make criminal investigations difficult, where such investigations must evolve to match the sophistication of organized crime. The installation of a lay judge system has made the presentation of objective evidence more critical. Identification of evidence is conducted within forensic science laboratory in prefectural police headquarter.

In the laboratory, a wide variety of analysis, such as DNA type, drug, image, handwriting, polygraph test etc. are conducted for investigation. Forensic science combines five fields: chemistry, biology, physics, graphology, and psychology. Of these, both analytical chemistry and pharmacy are used in evidence identification. A wide range of samples are subjected to identification procedures, including stimulants, narcotics, alcohol, drugs, oil, car paint, glass, fibers, plastic, and industrial waste, which presents an

Table 1.1 Analytical method used in forensic science.

object	analytical method			
glass	Reflux Index	SEM-EDS ^{*2}	ICP-MS(AES) ^{*3}	XRF ^{*4}
plastic	FT-IR [*]	SEM-EDS ^{*2}	Py-GC-MS ^{*5}	
fibers	FT-IR [*]	SEM-EDS ^{*2}		
car paint	FT-IR [*]	SEM-EDS ^{*2}		
oil	GC/MS ^{*6}			
drugs	FT-IR [*]	GC/MS ^{*6}	LC-MS-MS ^{*7}	
alcohol	GC/MS ^{*6}			
Industrial waste	GC/MS ^{*6}	XRF ^{*4}	ICP-MS(AES) ^{*3}	AAS ^{*8}

* Fourier transform infrared spectroscopy

*2 Scanning electron microscopy/energy dispersive spectroscopy

*3 Inductively coupled plasma mass spectrometry (atomic emission spectroscopy)

*4 X-ray fluorescence

*5 Pyrolysis Gas chromatography mass spectrometry

*6 Gas chromatography mass spectrometry

*7 Liquid chromatography tandem mass spectrometry

*8 Atomic absorption spectroscopy

analytical challenge. Analytical methods used for forensic science are summarized in Table 1.1. Certain materials are frequently analyzed within forensic analysis, including the presence or absence of fuel oil within fire residues, or comparison of car paint. However, it is necessary to consider the analytical scheme carefully within specific cases that requires analysis with no experience. For instance, adequate consideration may be needed for crime related to industrial waste, or illegal dumping case. In the Waste Disposal Law, it is stipulated that a waste discharging company is responsible for the waste disposal. However, some discharging companies commission the waste disposal to a disposal company who does not process properly, to avoid costs. As a result, inappropriate disposal, like illegal dumping, may be caused by disposal companies. In Teshima Island case, more than 500,000 tons of industrial waste were dumped illegally by an industrial waste disposal company³. In Japan, the number of illegal dumping decreased from 1998 (1,200 cases), and was below 170 cases in 2014 (Fig. 1.2).⁴ Because the origin of illegally dumped waste is complicated, it is difficult to select an appropriate analysis method. Therefore, it is necessary to pay attention to analysis in illegal dumping case. Within Mie Prefecture, extensive industrial waste crime “Ferosilt Problem”, including hexavalent chromium compounds contained within recycled products occurred.⁵ In the case, the products were manufactured from industrial byproducts or waste, and subsequently sold as a soil improvement agent. A great deal of expertise was necessary to identify the source of contamination because it was necessary to determine the mechanism of formation of hexavalent chromium.

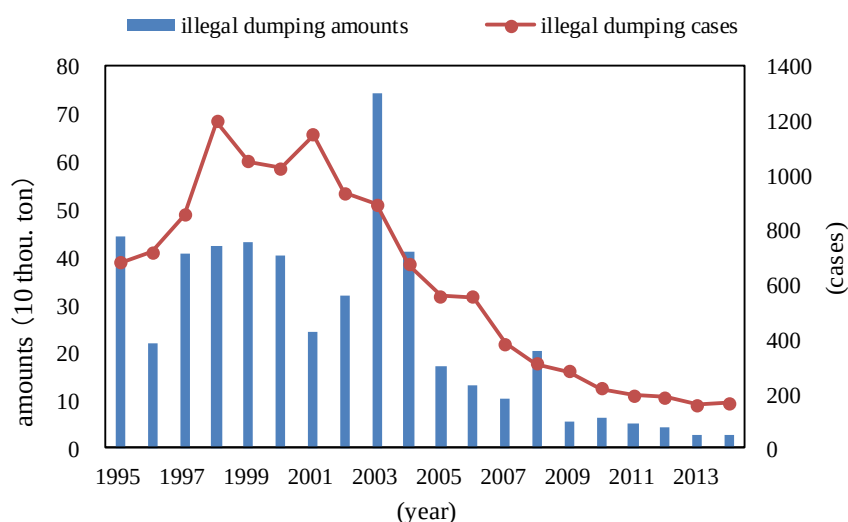


Fig 1.2 Trends in illegal dumping amounts and cases.

1.3 Background and aims of this study

Identification begins with a request from the investigation organization. A typical request is for a substance to be identified; for example, whether a sample powder is stimulant or not, or whether a sample

liquid is fuel oil or not. Additionally, comparison among samples is sometimes requested; for example, whether a sample collected from the scene was derived from a suspect's vehicle.

The results of analysis are presented using specific expressions, such as “I admit/presume that A is B” or “I consider that A can be B.” The more obscure the analytical results, the more negative the tone of the response. To identify drugs, the Science Working Group for the Analysis of Seized Drugs (SWGDRUG) recommends identification using two or more stand-alone methods. The more methods conducted, the greater the scientific validity of the results. However, the choice of analytical method is limited by time, economics, and the amount of sample.

Although two or more analytical methods should be used for identification, sample loss should be minimized. Generally, samples collected from a crime scene are so minute that it is preferable to analyze them in a non-destructive way. It is often impossible to analyze a sample without some degradation. However, methods that needs very little sample, or are non-disruptive, are ideal.

1.3.1 X-ray absorption fine structure

This study examines forensic identification using X-ray absorption fine structure (XAFS) analysis. XAFS is an analytical method that allows analysis of minute quantities of samples in non-destructive way. In XAFS, X-ray is irradiated on a substance and an absorption spectrum is measured. As the energy of X-ray increases, the absorption coefficient drastically increases at the energy corresponding to binding energy of inner shell electron; this edge structure is called absorption edge (Fig. 1.3). XAFS spectra is divided into two areas. The sharp absorption near the absorption edge is called X-ray Absorption Near Edge Structure (XANES). XANES is observed from the absorption edge to 50 eV. The XANES structure appears by X-ray exciting photoelectrons into the unoccupied orbits without escaping the binding potential of absorbed atom. XANES spectra, which is sensitive to changes in atomic arrangement and potential, has information on

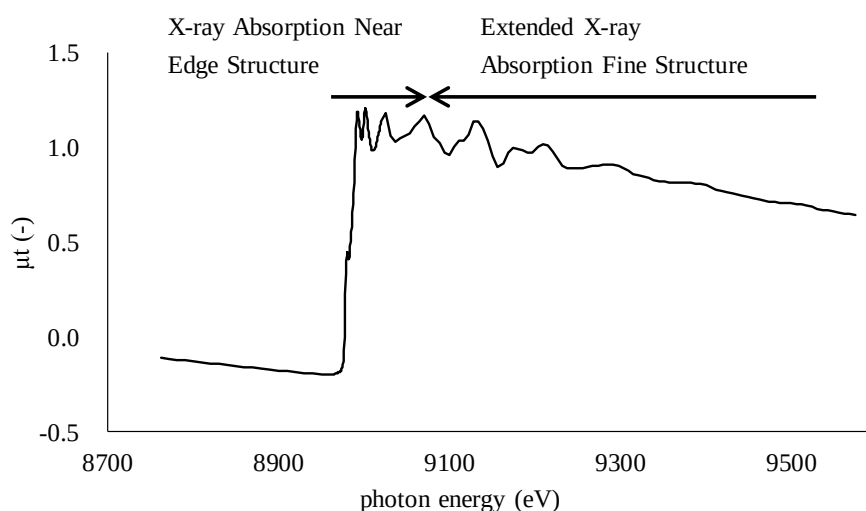


Fig 1.3 Copper K edge XAFS spectra.

valence and local structure of the absorbed atom. On the other hands, a wavy structure appears in the high energy region. This structure is Extended X-ray Absorption Fine Structure (EXAFS). When X-ray with sufficient energy to excite orbital electrons such as K shell of target atom are irradiated, photoelectrons are emitted as spherical waves. EXAFS is observed due to interference between the spherical waves emitted directly from absorbed atom and waves scattered by surrounding atoms. By comparing the edge structure obtained from unknown sample with ones of known samples, information about local environment around the targeted atom can be obtained, such as chemical state, including valence, atomic bond distance, and coordination number. In addition, the method is applicable to non-crystalline substances, unlike X-ray diffraction. Therefore, XAFS analysis has great potential for forensic chemical identification. This method, which has not been extensively used within forensic sciences, could be a potential option to improve the scientific validity of forensic chemical analysis.

1.3.2 Analysis for XAFS data

As a first step of XANES analysis, it is necessary to remove absorption of other elements and other shell electrons in addition to target shell electron in the measured X-ray absorption spectrum. The procedure of these removal is as follows. An area with lower energy than the absorption edge is selected and represented by an appropriate formula (background formula). This formula is extrapolated to the high energy region. The absorption spectrum is subtracted with this formula. The spectra are normalized by setting the height 1 at the point of about 50 – 100 eV after the absorption edge in order to treat the spectra quantitatively. The XANES spectra of reference materials were compared with those of fly ash to identify major species. It was assumed that the spectra of unknown species were expressed by the synthesized spectra of known reference species (Fig. 1.4). Based on the formula (1) below, convergence calculation is conducted so that the difference between the sample and the synthesized spectra was minimized.

$$\text{Residual value } R = \frac{\sum(\text{XAFS}_{\text{measd}} - \text{XAFS}_{\text{calcd}})^2}{\sum(\text{XAFS}_{\text{measd}})^2} \quad (1)$$

Thus, the major species in fly ash was identified and quantified using the linear combination fit (LCF) technique, in which spectra of known reference species were fitted to the spectrum of the unknown sample.

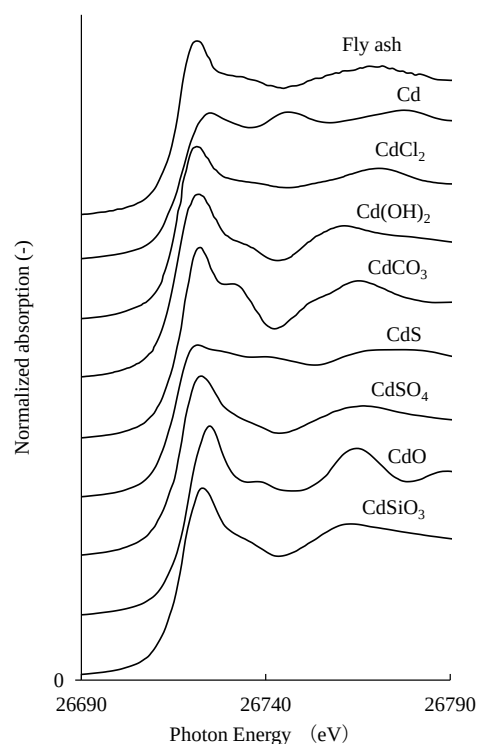


Fig 1.4 Cd K edge XANES spectra of sample and reference materials

That is, the ratio (mol %) of the chemical states can be known.

Analysis for EXAFS is performed as follows. Background corresponding to the target element and the first coordination atom is inserted, to obtain EXAFS spectra (Fig. 1.5). The obtained spectrum can be analyzed by the LCF technique similar to XANES spectrum. Alternatively, the EXAFS spectrum is Fourier transformed, and the peak derived from the first coordination atom is subjected to inverse

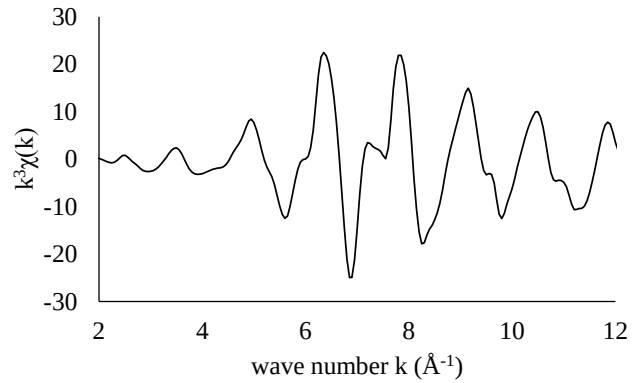


Fig. 1.5 k^3 -weighted EXAFS spectra of metal copper.

Fourier transformation (Fig. 1.6). Based on the EXAFS equation (2) below, curve-fitting to the inverse Fourier transform is performed, to compute the atomic distance (R), coordination number (N), and Debye-Waller factor (σ^2) (FEFF simulation).

$$\chi(k) = N/kR^2 \sum f(k) \exp(-2\sigma^2 k^2) \exp(-2R/\lambda) \sin(2kR + \Phi) \quad (2)$$

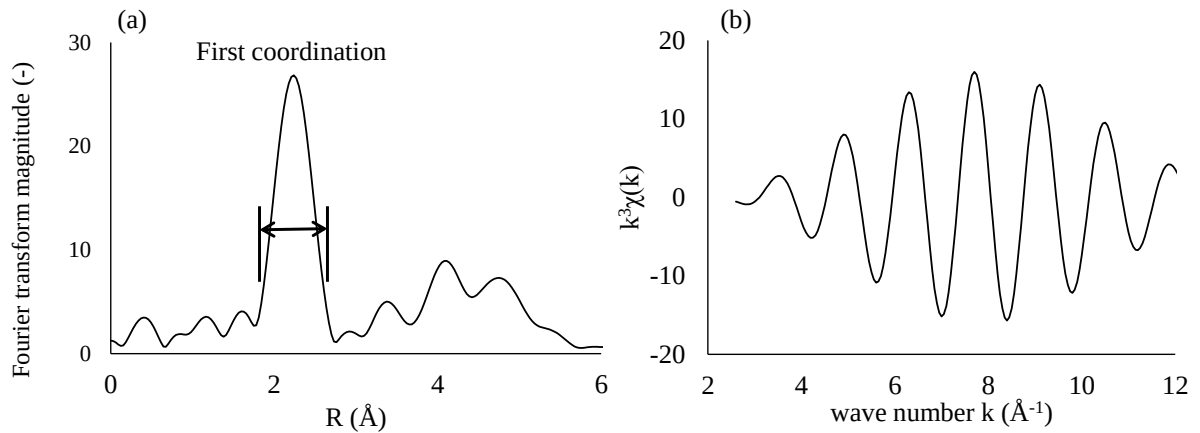


Fig. 1.6 (a) Fourier transform of metal copper EXAFS spectra. (b) Inverse Fourier transformation of the peak derived from the first coordination atom in Fourier transform.

1.3.3 Aims of this thesis

In this study, glass and rubber from common industrial products, as well as fly ash from industrial waste were measured as analytical samples. I attempted to obtain more detailed results by XAFS in addition to conventional analysis techniques presented in Table 1.1. In this study, fly ash was targeted especially for lead and cadmium, which are used industrially for many products. In case of illegal waste dumping, these heavy metals may elute.³ It is difficult to estimate the health risk posed by heavy metals contained in fly ash, which will be reused within concrete aggregates in the future. It is thus necessary to use methods such as

XAFS to estimate the health risk of the metals contained in fly ash. This study examined appropriate identification schemes for such industrial products and industrial waste by combining XAFS with the conventional analysis method. Thus, in the identification scheme, it became possible to obtain detailed information which is not currently available. The advancement of forensic analysis is expected to contribute to police investigation.

1.4 Applying synchrotron radiation analysis in forensic science

The SPring-8, synchrotron radiation facility, was established in the 1990s in Japan. This facility is extensively used within science and industry. In forensic sciences, it has been used to analyze minute samples that would be difficult to analyze within general laboratories. This section presents examples when forensic science synchrotron radiation X-ray fluorescence (SR-XRF) was applied in forensic analysis.

1.4.1 Discrimination of sheet glass by SR-XRF

Previously, Suzuki et al. discriminated sheet glass samples using refractive index (RI) and SR-XRF.⁶ Analytical methods such as inductively coupled plasma mass spectrometry (ICP-MS) have also been used to discriminate glass fragments, which has potential for forensic glass analysis. However, the sample is destroyed during this method, in contrast to SR-XRF and RI. For this study, eleven glass samples were collected from three glass manufacturers. Glass samples were broken with a hammer, and four pieces were chosen for each sample for measurement by RI and SR-XRF.

It was reported that variation of RI within a sheet of glass was < 0.0002 .^{7,8} Therefore, a pair of sheet glass samples are distinguishable when their RI differs by > 0.0002 , and are indistinguishable when the difference in RI is ≤ 0.0002 . Of the 66 pairs within the 11 samples, 54 were distinguishable, whereas 12 were indistinguishable.

Three different fragments were used from each sample for SR-XRF measurement, where six elements (Ca, Fe, Sr, Zr, Ba, and Ce) were measured. Cluster analysis was conducted using intensity ratios ($\text{Ca } K_{\alpha}/\text{Fe } K_{\alpha}$, $\text{Sr } K_{\alpha}/\text{Ba } K_{\alpha}$, $\text{Zr } K_{\alpha}/\text{Fe } K_{\alpha}$, $\text{Ce } K_{\alpha}/\text{Ba } K_{\alpha}$) as variances. Of the 528 pairs within the 33 samples, 515 pairs were discriminated correctly. This is much better than discrimination using only RI. Pairs that were indistinguishable by RI could be discriminated by comparing its SR-XRF spectrum. SR-XRF analysis is thus superior to RI in terms of precision.

1.4.2 Analysis of arsenic compound in a micro-scale sample using SR-XRF

A case of curry poisoning that occurred in Japan in 1998 is one of the most famous cases involving forensic science as reported in the Japanese media.^{9,10} In this case, samples (arsenic compound) collected at

the scene was compared to samples from the suspect, as requested by the prosecution. This was the first case in which synchrotron radiation was utilized in forensic science. Samples consisted of arsenic compounds from: 1) a drum can in related person A's home, 2) a milk can in A's home, 3) a white can in A's home, 4) a plastic container in A's home, 5) a milk can in related person B's home, 6) a plastic container in the suspect's home, 7) a paper cup discovered at the scene, and 8) the curry pot itself. Of these, samples from 6) and 8) was present in trace amounts, which was barely verified under a microscope and difficult to analyze by ICP-MS, which is often used in normal laboratories. Scientists attempted analysis by SR-XRF. Arsenic compound is obtained by refining minerals, and sold as rat poison, which is a kind of industrial products. To discriminate among industrial products, the species and concentration of trace elements can be compared. It is important to know detailed information regarding the derivation of the sample, including possible manufacturing contamination. Moreover, it is necessary to choose the elements for measurement carefully based on previous studies. In this case, the elements As, Sb, Sn, Bi, and Mo were chosen for discrimination because As, Sb, and Bi are congeners, and Sn and Mo are mixed as foreign impurity into arsenic compound during manufacture. In the case of the contaminated curry, arsenic samples could be discriminated using intensity ratios of Sb, Sn, and Bi, and the detection (or not) of Mo. It was concluded that all the samples had the same origin, where samples were also checked by analyzing products from China, South Korea, and Mexico.

Afterwards, regarding this discrimination, doubts were indicated by a third party; that is about the scientific reasonability of the element species used as discrimination indicators.^{11,12} Since this approach was unprecedented, such indication might be made. Thus, it is necessary to thoroughly examine and provide scientific supporting data for unprecedented analysis.

1.4.3 Key points in identifying industrial products

Because industrial products are mass-produced, it is necessary to consider how accurately an industrial sample can be identified. In Chapter 1.4.2, the origin of arsenic compound is an important point for identification, including the country of origin, the place of production (mine), the product lot, and the time of manufacture. During analysis, it is necessary to clarify the level of accuracy required for identification. When this accuracy is not known, we cannot judge the value of identification, even if a result of "the same" is derived from analysis.

In this study, the identification of industrial products, including the qualitative analysis of samples, selection of control samples, and examination of different identification methods are considered. Qualitative analysis takes time and care to accomplish, depending on the type and variety of samples. Additionally, a method of identification should have a high discrimination capability, while consuming as little sample as possible. However, it takes a lot of time to confirm the discrimination ability of a method. During analysis,

it is not always possible to examine the method with sufficient rigor due to deadlines related to the legal process. For such reason, it is important to study identification methods across a wide range of specimens in advance.

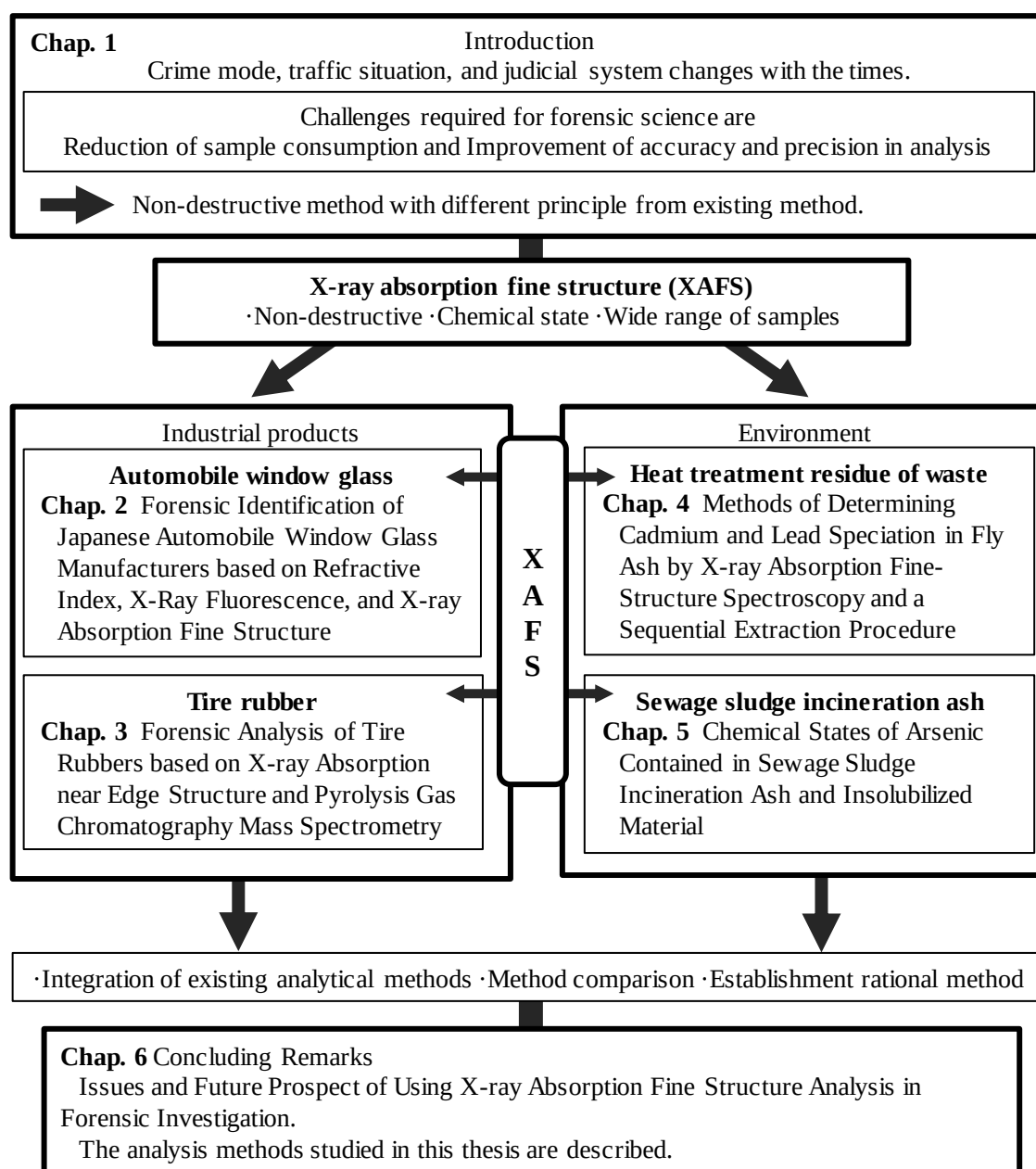


Fig 1.7 The framework of this thesis.

1.5 Thesis framework

In this study, analytical method for forensic science was sophisticated in order to solve incidents and accidents involving complicated industrial products and waste. Automobile window glass and tire rubber

which are industrial products, and waste heat treatment residue and sewage sludge incineration ash which are industrial waste are used as analytical samples. Since glass and rubber are common industrial products, they are often subject to forensic analysis. The sophistication of their analytical method is highly demanded in forensic science. On the other hand, with respect to industrial waste, there are cases where specific samples of industrial waste are handled, and the inappropriate handling and treatment has a risk of becoming a criminal case. Therefore, it is needed to sophisticate the analytical method. Regarding lead, cadmium, and arsenic contained in industrial waste, there are examples where they were eluted from illegally dumped waste³, and they are the matters that can be a focus in the criminal investigation because of their toxicity to the living body. Environmental analysis and forensic analysis have common characteristics of (1) trace amount of sample, (2) sample of complex matrix, (3) highly sensitive and highly accurate analysis, and the needs for these analyses are similar. Therefore, it is possible to utilize each other's knowledge, and to advance the entire technique of analysis. The combination of conventional analysis method and XAFS, which is not applicable in the field of forensic science, advanced sophistication of the analysis method. More detailed information was obtained by XAFS in addition to information by conventional techniques.

The framework of this study is presented in Fig. 1.7. This thesis is composed of 6 chapters:

In chapter 1, the present state of crime and forensic science in Japan is explored, and the background and aim of this study are described.

In chapter 2, automobile window glass manufacturers are identified based on refractive index, XRF, and XAFS analyses.

In chapter 3, eleven tires are analyzed using XANES and pyrolysis gas chromatography mass spectrometry in order to discriminate between various tire rubbers.

In chapter 4, fly ash is analyzed for the speciation of cadmium and lead using sequential extraction, pH-dependent leaching test, XAFS, and chemical equilibrium modeling.

In chapter 5, the chemical states of arsenic contained in sewage sludge incineration ash and insolubilized materials are analyzed.

In chapter 6, all of the findings in this study are summarized. Analysis protocols for glass, tire rubber, and chemical state of heavy metals contained in ash is described on the basis of the above results.

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Chapter 2 Forensic Identification of Japanese Automobile Window Glass Manufacturers based on Refractive Index, X-Ray Fluorescence, and X-ray Absorption Fine Structure

2.1 Introduction

Fragments of window glass after a traffic accident are important evidence in the case of hit-and-run traffic incidents. In general, the forensic analysis of glass is performed using elemental analysis and refractive index (RI). A variety of methods for elemental analysis, such as X-ray fluorescence spectrometry (XRF),¹⁻⁴ inductively coupled plasma atomic emission spectrometry (ICP-AES),³ inductively coupled plasma mass spectrometry (ICP-MS),^{5,6} and synchrotron XRF,⁷ have been reported. An oil immersion method for determining RI has also been reported.^{8,9} However, it is difficult to use glass fragments from an accident site alone to identify a suspect vehicle. Analyses of the glass's elemental content and RI are used to compare glass fragments; however, another method is needed for concrete identification of the suspected vehicle. Therefore, X-ray absorption fine structure (XAFS) analysis was challenged as a method of analyzing glass.¹⁰⁻¹⁹ Glass manufacturers use different manufacturing conditions, resulting in diverse glass chemical states and elemental composition. Accordingly, the chemical states of elements in glass can represent the manufacturing conditions and, ultimately, the manufacturer. Cerium is often added during the manufacturing of automobile window glass to protect against ultraviolet rays. The chemical states of cerium in automobile window glass can be affected by temperature and reductive atmosphere during manufacturing, resulting in different chemical states. Accordingly, the chemical states of cerium in glass can represent the manufacturing conditions and, ultimately, the manufacturer. These chemical states of cerium can be determined using XAFS.

As described in this chapter, automobile window glass was collected from three major glass manufacturers for a year; these manufacturers supply almost all of the glass used for automobiles manufactured in Japan. Because small amounts of glass fragments are typically present after traffic accidents, it is important to perform analysis using non-destructive techniques. Additionally, an analytical conclusion should be drawn from multilateral results using uncorrelated techniques. I analyzed samples using non-destructive analysis methods including RI, XRF, and XAFS. The scheme of identifying manufacturers was based on each analysis individually, and the results in combination; I then attempted to identify the glass manufacturer based on the analytical results.

2.2 Experimental

2.2.1 Samples

Three manufacturers provided a total of 75 samples of sheet glass: manufacturer A (sample a01–a18), manufacturer B (b01–b22), and manufacturer C (c01–c35) (Table 2.1). Information regarding whether cerium had been added to the samples was also obtained. Groups containing cerium included groups A1 (sample a01–a09) and B1 (sample b01–b16). Sample groups without cerium included groups A2 (sample a10–a18) and B2 (sample b17–b22). Samples from

Table 2.1 Sample glasses collected for the

Manu- facturers	Samples	group	Addition of Ce	Date
A	a01 - a04	A1	✓	Jun. - Jul. 2010
	a05 - a09			Sept. - Oct. 2010
	a10, a11			Apr. and May 2010
	a12, a13	A2		Aug. 2010
	a14, a15			Nov. and Dec. 2010
	a16 - a18			Jan. - Feb. 2011
B	b01 - b07	B1	✓	Jun. - Aug. 2010
	b08 - b13			Feb. - Mar. 2011
	b14 - b16			Dec. 2011
	b17 - b20	B2		Apr. - Jun. 2010
	b21			Dec. 2010
	b22			Jan. 2011
C	c01 - c12	C		Apr. - Jun. 2010
	c13 - c23			Sept. - Dec. 2010
	c24 - c35			Feb. - Apr. 2011

manufacturer C that did not contain cerium included samples c01–c35. Glass produced by these 3 manufacturers were used for almost all automobiles manufactured in Japan.

2.2.2 RI

The RI values of samples were measured using the oil-immersion method with an automated RI system GRIM3 (Foster & Freeman, UK).²⁰ Five independent fragments were used from each sample, and each fragment was measured at four edges. The measurements were conducted under conditions as previously described.²⁰

2.2.3 XRF

Component concentrations in samples were determined using XRF (RIX3001, Rigaku, Japan) using the fundamental parameter method. Measurement holes were set to 25 mm. Two measurements were performed per sample, and the average value was reported. The concentration of each element was calculated as oxides, including Na₂O, MgO, Al₂O₃, SiO₂, K₂O, CaO, Fe₂O₃, and CeO₂.

2.2.4 XAFS

XAFS analysis was performed for 25 samples from groups A1 and B1 (a01–a09 and b01–b16). Samples were cut and the X-ray transmission path length (1.4–2.0 cm) was adjusted to a suitable absorption. When preparing reference materials (Ce₂(CO₃)₃ and CeO₂), reagents were mixed with boron nitride (BN), such that the S/N ratio of the spectrum was optimized. The resultant pellets were then stored in sealed

polyethylene bags.

XAFS measurements were performed on beam lines 01B1 and 14B2 of SPring-8 (Hyogo, Japan). Spectra were recorded under atmospheric conditions in transmission mode using an ionization chamber and a Si (311) monochromator, inserting mirror (1.2 mrad). The energy steps were set to 5 eV (40,140–40,410 eV), 0.5 eV (40,410–40,500 eV), and 2 eV (40,500–41,090 eV). Data were analyzed using a REX2000 (Rigaku Co., Ltd., Japan).²¹ An EXAFS simulation was performed using the FEFF 8.20 code,²² based on the crystal structure parameters of hexagonal Ce₂O₃.²³ Peaks derived from the first coordination shell were analyzed by curve-fitting to compute the atomic distance (R), coordination number (N), and Debye-Waller factor (σ^2).

2.2.5 Cluster analysis

Hierarchical cluster analysis was conducted using the results of RI, XRF and XAFS. Cluster analysis was conducted using OriginPro 9.0 (OriginLab Corp., USA). The Euclidean distances between points were then calculated, and the distances between clusters were computed using Ward's method.

2.3 Results

2.3.1 RI analysis

Sample RI values are shown in Fig. 2.1. Of the 75 samples, the greatest variation in RI values from one sample was 0.00021 (SD = 0.00005). These results were comparable to those in previous studies.^{3,8} I observed differences between groups A1 and A2 in the case of manufacturer A, indicating that the difference was observed

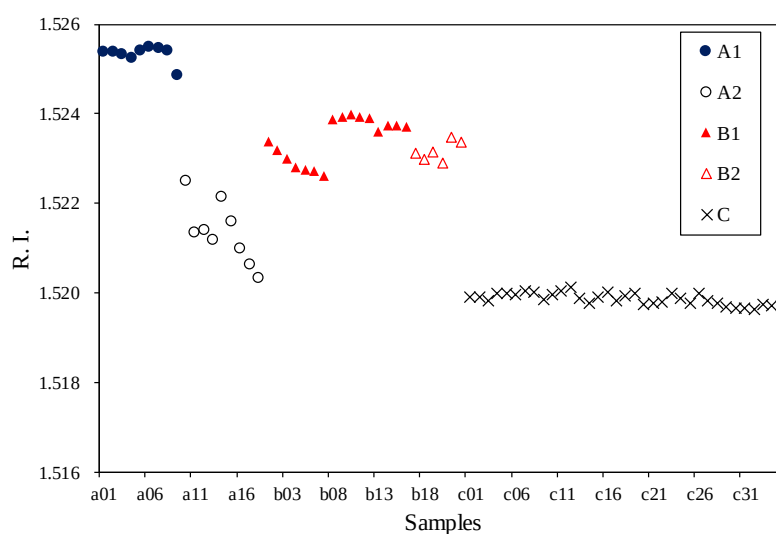


Fig. 2.1 Results of the Refractive Index (RI) analysis for samples.

with or without cerium. RI values of samples in group A1 (with cerium) were higher than those in A2 (without cerium), where the difference between groups A1 and A2 was at least 0.0024. The RI values of samples a01–a08 in group A1 were similar (except for sample a09), where the variation was < 0.0002. However, RI values of group A2 were more widely distributed than those of A1, where the variation of A2 was within 0.0022. Secondly, there was no difference between groups B1 and B2 for manufacturer B (unlike

manufacturer A) whether cerium was added to the samples or not. Group B1 showed differences based on manufacturing time (Table 2.1). The RI values of samples b01–b07 (1.5226–1.5234) were lower than those of other B1 samples (1.5236–1.5240). However, the RI values of samples b08–b13 and b14–b16 (which differed by manufacturing times) were within the same range. Finally, the variation of RI values of 35 samples from manufacturer C (which did not have cerium) was less than 0.0005. Although the samples from manufacturer C had three manufacturing times (Table 2.1), they showed little difference based on manufacturing time (unlike manufacturer B). An RI value of 0.0002 is considered to be a standard for discriminating glass, based on a study by Koons.³ However, this difference may be less than 0.0002 even if glass fragments originate from different manufacturers, as was the case between manufacturers A and B.

Samples from manufacturers A and B were indistinguishable, as manufacturer B fell within the distribution of groups A1 and A2. As discussed previously, the samples from manufacturer C fell within the same range regardless of the manufacturing time, unlike manufacturers A and B. However, because samples a17 and a18 were similar to group C, group C could not always be distinguished.

Cluster analysis using RI values to classify samples statistically gave three clusters¹²: clusters X_{A1} [a01–a09], X_1 [a10, a14, and b01–b22], and X_2 [a11–a13, a15–a18, and c01–c35]. This could be expanded to five clusters when cerium was considered: clusters X_{A1} [a01–a09], X_3 [a11–a13, a15, and a16], X_4 [a10, a14, b02–b07, and b17–b20], X_5 [b01, b08–b16, b21, and b22], and X_6 [a17, a18, and c01–c35]. Samples from group A1 belong to cluster X_{A1} , and samples from group C, a17, and a18 belong to cluster X_6 . For clusters X_3 , X_4 , and X_5 , samples were not classified based on the manufacturer or the sample group.

2.3.2 Component analysis using XRF

XRF analysis showed that glass was composed of SiO_2 (66–68%), Na_2O (13–14%), CaO (10–12%), and Al_2O_3 (2%). Fig. 2.2a and 2.2b show XRF results for groups A1, A2, B1, B2, and C. There were natural differences regarding cerium addition. Samples were thus classified into groups A1 and B1 (which contained cerium), and groups A2, B2, and C, whose cerium concentrations were below the limit of quantitation. The average CeO_2 concentration of group A1 was 1.9% (SD = 0.05), where the concentration for B1 was 0.6% (SD = 0.06). Overall, there were differences in CeO_2 concentrations for manufacturers A and B. Furthermore, there were differences in concentrations of MgO , Al_2O_3 , K_2O , and CaO between A1 and B1. The concentrations of MgO , Al_2O_3 , K_2O , CaO , and Fe_2O_3 in A1 were 4.2% (SD = 0.11), 1.7% (SD = 0.03), 0.8% (SD = 0.04), 10.0% (SD = 0.18), and 0.7% (SD = 0.04), respectively. The concentrations of MgO , Al_2O_3 , K_2O , CaO , and Fe_2O_3 in B1 were 3.4% (SD = 0.09), 1.8% (SD = 0.03), 1.0% (SD = 0.02), 10.8% (SD = 0.18), and 0.9% (SD = 0.14), respectively.

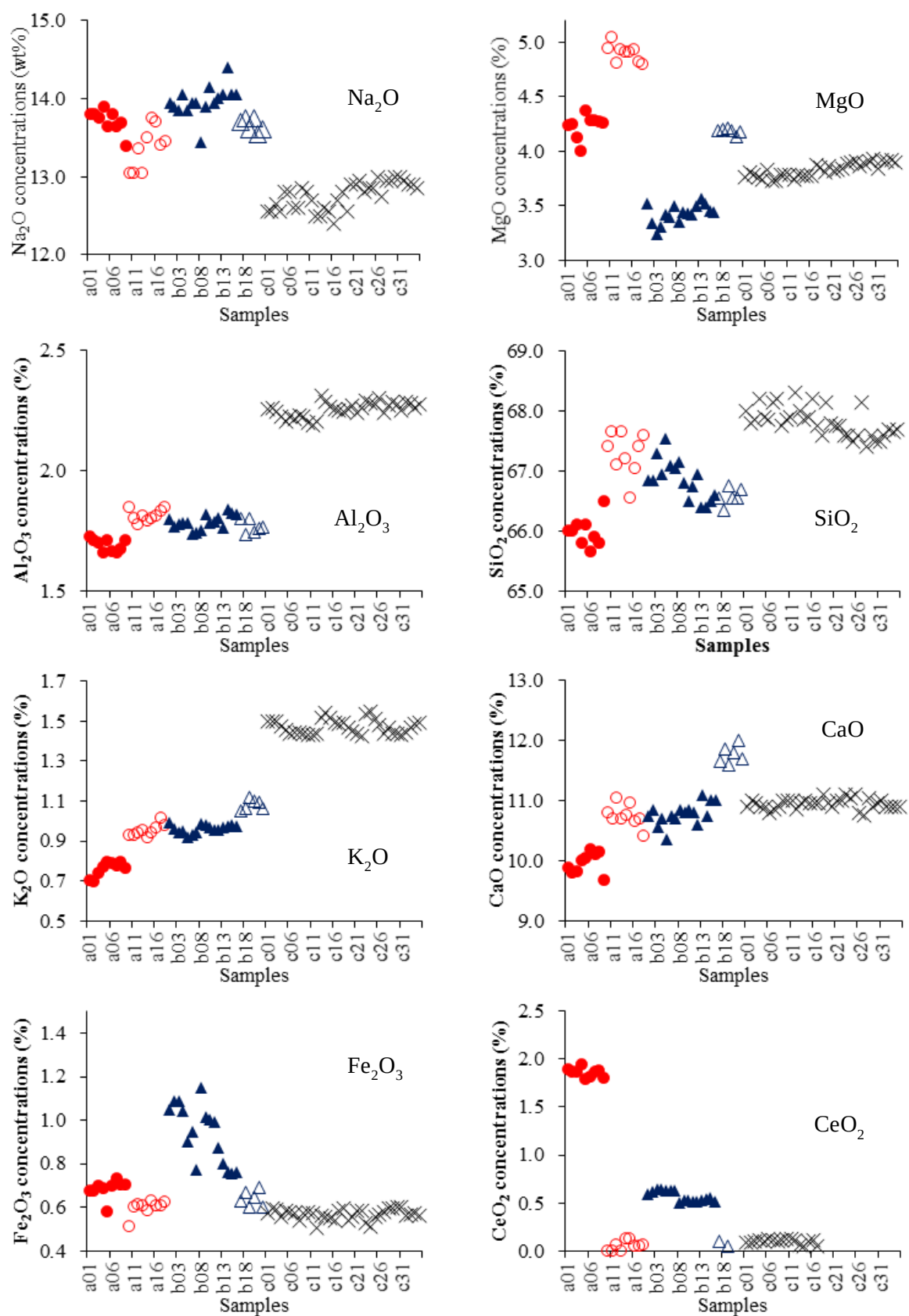


Fig. 2.2a The results of XRF analysis for samples. The CeO₂ concentrations of sample a10, a11, a13, b18, b20 – b22 and c18 – c35 are under limit of quantitation (0.04 %).

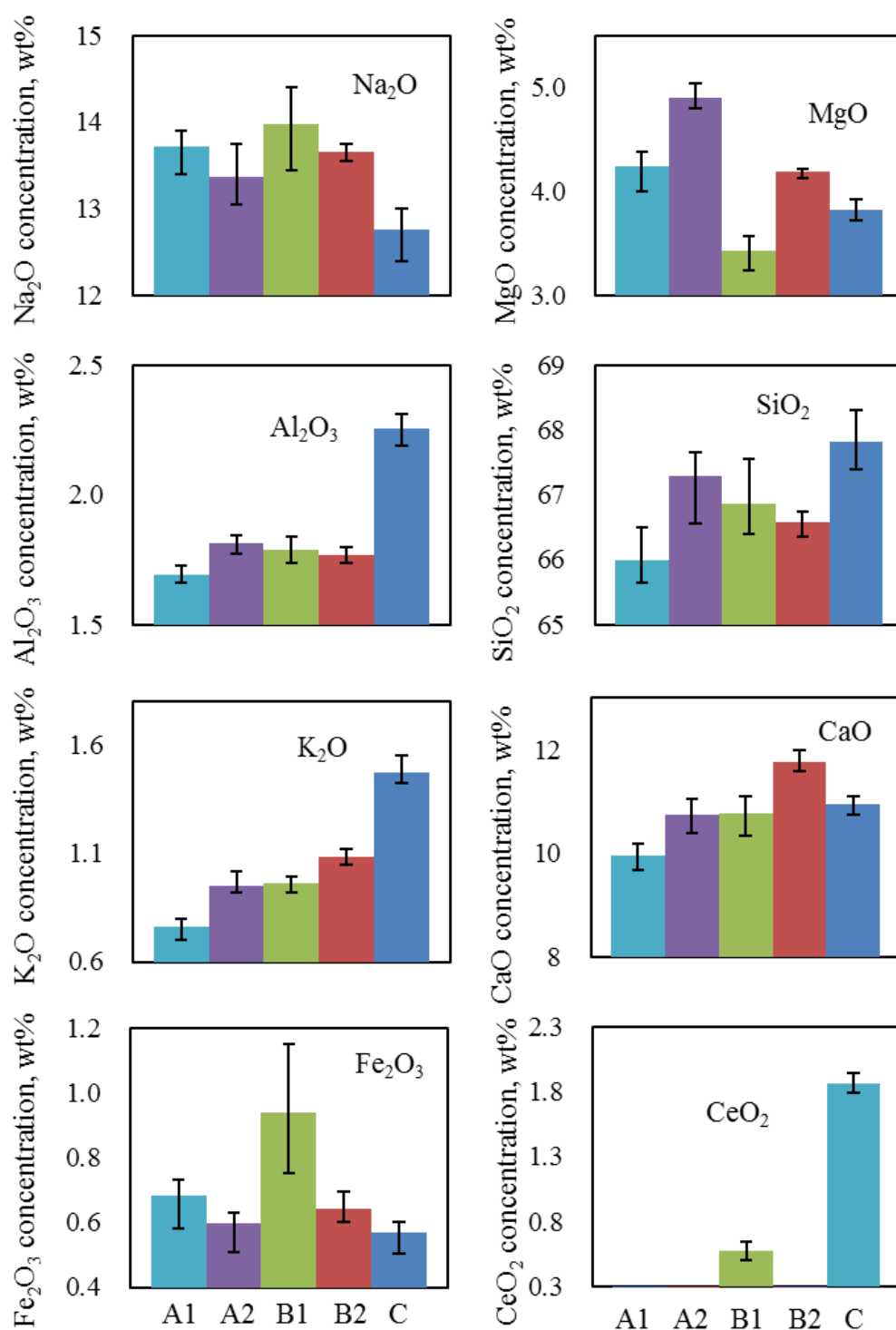


Fig. 2.2b Results of XRF analysis for each group. The CeO₂ concentrations of group A2, B2 and C are under limit of quantitation (0.2 %). The bars represent the maximum and minimum values of each groups.

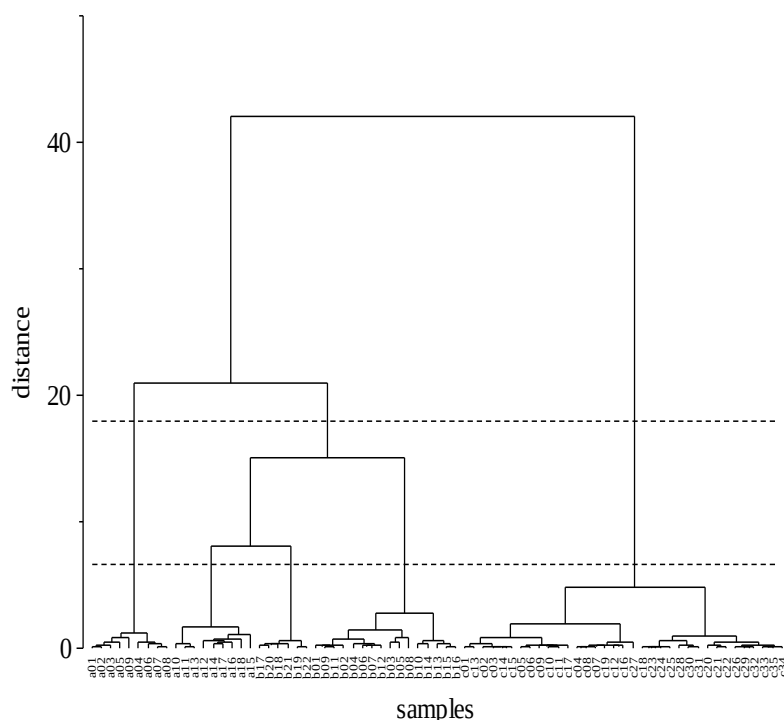


Fig. 2.3 Dendrogram based on the result of XRF analysis.

Fe_2O_3 concentrations in B1 were distributed more widely than for other elements (with a relative SD of 14.5%). In addition, differences in manufacturing time were not large, based on XRF results compared to RI.

Groups A2, B2, and C, which did not have cerium addition, showed differences in MgO and K_2O . The concentrations of MgO and K_2O in group A2 were, respectively, 4.9% (SD 0.08) and 1.0% (SD 0.03); those in group B2 were, respectively, 4.2% (SD 0.03) and 1.1% (SD 0.03); and those in group C were, respectively, 3.8% (SD 0.06) and 1.5% (SD 0.04). Although there was no or little difference between A2 and B2 for Al_2O_3 , the levels did differ from group C. The concentrations of Al_2O_3 were 1.8% (SD 0.02), 1.8% (SD 0.03), and 2.3% (SD 0.03) in groups A2, B2, and C, respectively.

Based on XRF results, groups A1 and B1 (which had cerium) could be distinguished from groups A2, B2, and C (which did not have cerium). Group A1 could thus be distinguished from group B1 based on the cerium concentration.

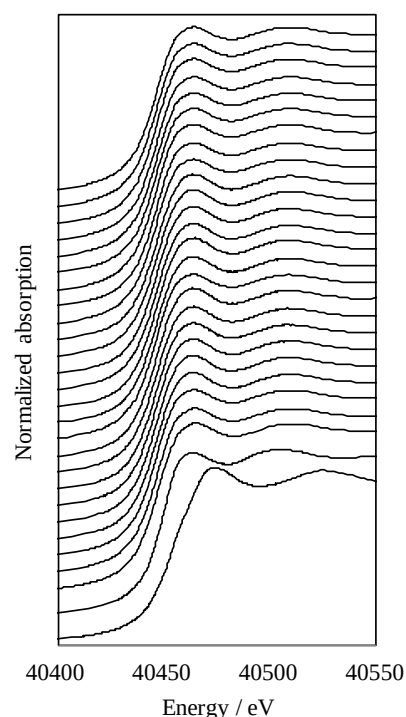


Fig. 2.4. Cerium K edge XANES spectra of reference materials and glass samples. From the top, the spectra of samples a01 - a09, b01 - b16 and reference materials $\text{Ce}_2(\text{CO}_3)_3$ and CeO_2 are shown.

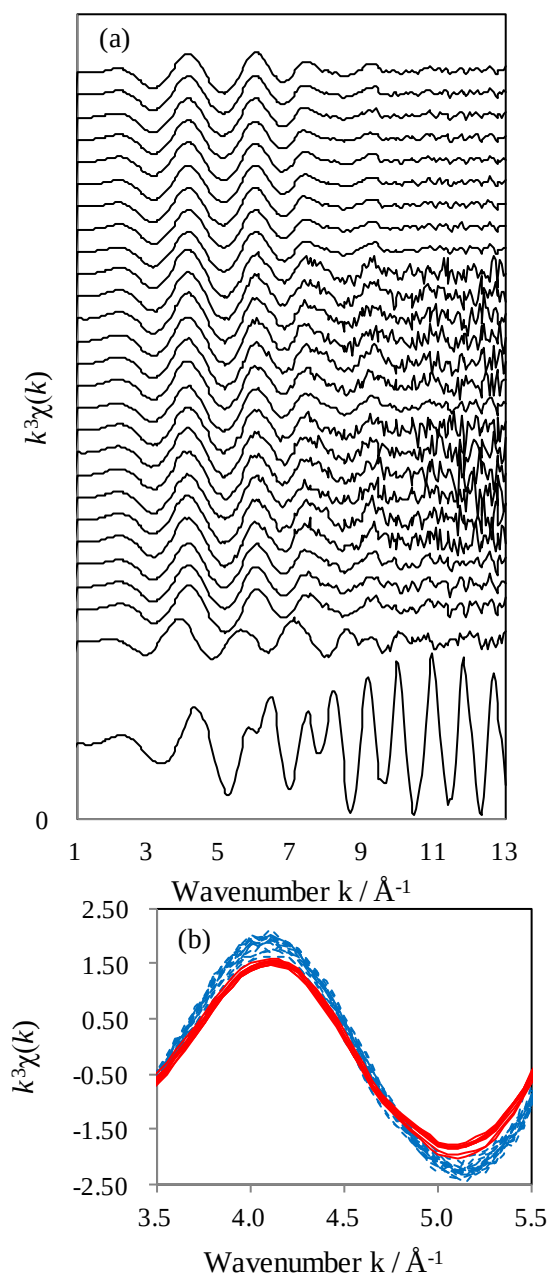


Figure 2.5 k^3 -Weighted Cerium K edge EXAFS spectra. (a) From the top the data of samples a01-a09, b01-b16 and reference materials $\text{Ce}_2(\text{CO}_3)_3$ and CeO_2 are shown. (b) Samples data around maximum and minimum values are shown in range from 3.0 to 6.0 $\text{\AA}^{-1}$. Solid red lines show manufacture A and dashed blue lines show manufacture B.

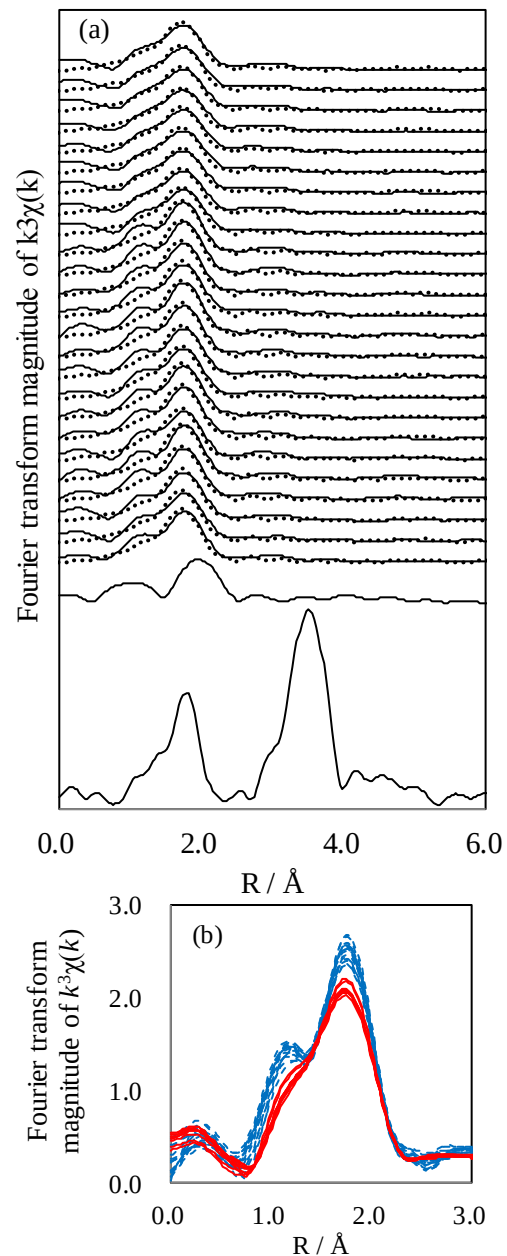


Figure 2.6 Fourier transforms of Cerium K edge EXAFS spectra. (a) From the top the data of samples a01-a09, b01-b16 and reference materials $\text{Ce}_2(\text{CO}_3)_3$ and CeO_2 are shown (solid lines). Dashed lines overlapped on solid lines show simulation spectra. (b) Samples data around maximum values are shown. The solid lines are manufacture A and dashed lines are manufacture B.

Additionally, groups A2, B2, and C could be distinguished from each other using concentrations of MgO, Al₂O₃, and K₂O.

Cluster analysis of XRF data (concentrations of Na₂O, MgO, Al₂O₃, SiO₂, K₂O, CaO, Fe₂O₃, and CeO₂) resulted in three clusters (Fig. 2.3):¹² clusters Y_{A1} [a01–a09], Y_X [a10–a18 and b01–b22], and Y_C [c01–c35]. The CeO₂ concentration was set to 0 when cerium concentrations were below the limit of quantitation. This could be expanded to five clusters based on XRF data (with or without cerium addition): clusters Y_{A1} [a01–a09], Y_{A2} [a10–a18], Y_{B1} [b01–b16], Y_{B2} [b17–b22], and Y_C [c01–c35]. The resultant clusters (Y_{A1}, Y_{A2}, Y_{B1}, Y_{B2}, and Y_C) corresponded to groups A1, A2, B1, B2, and C, respectively. In other words, the samples could be classified by manufacturer (when cerium was present) based on XRF analysis.

2.3.3 Chemical states of cerium based on XAFS

The XANES spectra of glass samples and reference materials are shown in Fig. 2.4. Every spectrum was similar in shape, with absorption edges of 40,447 eV. The cerium in the samples was determined to be trivalent by comparing the sample spectra with Ce₂(CO₃)₃ and CeO₂ reference materials.

Cerium K-edge EXAFS spectra $k^3\chi(k)$ from samples and reference materials are shown in Fig. 2.5 (backgrounds were calculated using a Victoreen law). All sample spectra were clear, with oscillations up to 10 Å⁻¹ (Fig. 2.5a). Although their periods were similar, the amplitude differed between manufacturers (Fig. 2.5b). The maximal (4.1 Å⁻¹) and minimal (5.1 Å⁻¹) values of manufacturer A were 1.5 to 1.6 and –1.9 to –1.8, respectively. The maximal and minimal values of manufacturer B were 1.6 to 2.1 and –2.5 to –2.2, respectively.

Figure 2.6 shows Fourier transforms of $k^3\chi(k)$ of the Ce K-edge. Fourier transforms were performed within a k range of 1.7 to 9.5 Å⁻¹ using a Hanning window (dk : 0.05 Å⁻¹). Every sample spectrum had a

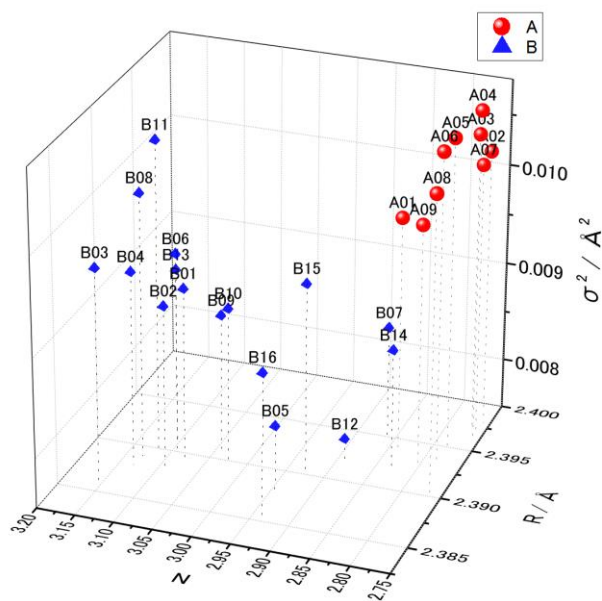


Figure 2.7 Results of the structural analysis of the first coordination shell at the Ce K edge. Sphere symbols show manufacture A and tetrahedrons show manufacture B.

peak of around 1.8 Å, which was derived from the first coordination shell (Fig. 2.6a). Peak intensity differed between manufacturers A and B, ranging from 2.01 to 2.22 (A) and 2.35 to 2.67 (B), respectively (Fig. 2.6b). Based on these peak intensities, the average and SD for manufacturer A were 2.09 ± 0.059 , and 2.50 ± 0.083 for manufacturer B. The intensities of manufacturers A and B differed more than two times their respective standard deviation. Therefore, the sample manufacturer can be identified based on peak intensity. We then performed FEFF simulations on peaks derived from the first coordination shell in the range of 0.89–2.24 Å using the back *k*-space fitting method, which was used to compute *R*, *N*, and σ^2 (Fig. 2.7). Figure 2.7 shows that the samples of manufacturer B were more widely distributed than those of manufacturer A.

Cluster analysis of FEFF simulation results (*R*, *N*, and σ^2) resulted in two clusters¹²: clusters *Z*_{A1} [a01–a09, b05, b07, b12, and b14–b16] and *Z*_{B1} [all others]. This could be further expanded to three clusters: cluster *Z*_{A2} [a02–a09], *Z*_{B2} [b01–b04, b06, b08–b11, and b13], and *Z*_X [a01, b05, b07, b12, and b14–b16]. Thus, although samples within cluster *Z*_X could not be classified based on manufacturer (7 out of 25 samples), the samples from clusters *Z*_{A2} and *Z*_{B2} (18 out of 25 samples) could be classified based on manufacturer. Cluster analysis of these results along with the RI values mentioned above thus gave the same results as using XAFS alone.

2.4 Discussion

Cluster analysis of XRF results classified samples into five cerium-related groups that correspond to each sample's manufacturer. Although samples from group A1 were distinguished in cluster analysis using RI, the other samples could not be classified. Based on XAFS results, the amplitude of EXAFS spectra and the intensities of the Fourier transforms differed between groups A1 and B1. Based on cluster analysis for curve fitting from FEFF simulations, 18 of 25 samples could be classified according to manufacturer. Differences observed in XAFS characteristics between manufacturers are likely due to differences in manufacturing conditions and elemental composition. The reduction atmosphere and temperature may affect chemical state, as described by Farges.²⁴ Additionally, chemical states may change depending on the elemental composition, as shown in a previous study by Song.²⁵ Therefore, the same product manufactured under similar conditions results in the same chemical state; different products from different manufactures may result in different chemical states. We used samples that were 2.0 cm in size, which would be much larger than most samples present at the scene of an accident. In the future, minute samples should be used within fluorescence mode XAFS measurements. The differences between cluster analysis results of RI, XRF, and XAFS are considered below. XRF provides the ability to obtain information based on eight variables (chemical compounds). More information can be obtained using XRF than the other methods. Moreover, even if samples with different manufacturing times are analyzed using XRF, data falls within

the determinate range, unlike other methods. Consequently, cluster analysis using XRF results enabled accurate classification into corresponding groups.

Important information was also obtained using RI and XAFS. Samples with different manufacturing times showed dissimilarities in RI; this was not true for all samples. XAFS results indicate that the amplitude of the EXAFS spectra and the intensities of Fourier transforms differed between manufacturers, where the cerium chemical state differed between manufacturers. Therefore, the chemical state of other elements should be measured in the future. Furthermore, it is important to collect automobile window glass over a longer period of time to create a comprehensive analytical database. Additionally, manufacturing conditions can affect analytical results, as shown for the RI data. Although the results of XRF in this study were similar regardless of manufacturing time, changes in chemical composition affect the elemental concentrations.

Although it is clear that certain methods are more effective for classification, it is important to use multiple techniques. An analytical conclusion should be drawn from multilateral results obtained using uncorrelated techniques. However, XRF is the first choice to identify automobile window glass manufacturers. RI and XAFS have different measurement principles than XRF, and can thus complement XRF results. This allows us to draw conclusions from multidirectional analysis. Although CeO_2 concentrations in this study differed among manufacturers, RI and XAFS should be performed in addition to XRF because the concentration of CeO_2 (which is an additive compound) may vary. As mentioned, it is assumed that XAFS results are affected by manufacturing conditions and the elemental composition. Even if cerium concentrations in glass made by manufacturers A and B are similar, the XAFS results may differ because of coexistent elements. Additionally, even if the concentrations of compounds in glass made by manufacturers A and B are similar, manufacturing conditions may affect XAFS results. Based on my experience, it is quite unlikely that the concentration of compounds would be similar between different manufacturers, which agrees with the XRF results.

In the manufacturer identification scheme proposed in this study, XRF and RI are the first step; both may be conducted relatively easily in the laboratory. When samples contain cerium, the concentration of CeO_2 allows us to distinguish between groups A1 and B1. Without cerium, groups A2, B2, and C can be distinguished based on the concentrations of MgO , Al_2O_3 , and K_2O . Secondly, the results of RI can be used to distinguish between samples of manufacturer A or B, or of manufacturer C. Finally, for samples with cerium, groups A1 and B1 can be distinguished based on the EXAFS spectra amplitude and the Fourier transform intensity. This protocol can thus be used for identification by glass manufacturer.

2.5 Conclusions

As described in this chapter, samples were collected from three major glass manufacturers for one

year; these manufacturers supply almost all of the automobile window glass in Japan. These samples were examined multilaterally by three analytical methods (RI, XRF, and XAFS).

A total of 75 samples in this study could be classified into corresponding groups using XRF. Additionally, I observed differences among the manufacturers based on RI and XAFS. Based on the results of this study, XRF (which is the most powerful approach) should be the first choice. RI and XAFS can be used in addition to XRF, as they have a different measurement principle than XRF.

This study showed that the glass manufacturer could be identified on the basis of RI, XRF, and XAFS analysis. The identification of glass manufacturer makes it possible to search for the possible model of a suspect vehicle, and to obtain other valuable information for traffic accident investigations.

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Chapter 3 Forensic Analysis of Tire Rubbers based on X-ray Absorption near Edge Structure and Pyrolysis Gas Chromatography Mass Spectrometry

3.1 Introduction

Tire rubber collected from clothes or road surfaces after a traffic accident represents important evidence when the vehicles involved in the accident are absent, e.g., in hit-and-run incidents. Discrimination between the remaining rubber and the tire rubber of vehicles involved in accidents is important to identify the suspected vehicle. However, rubber smeared on clothes or the road is commonly present only in trace amounts. Additionally, analyzing tire rubber with Fourier transform-infrared (FT-IR) microscopy, which is commonly used to analyze trace materials, is difficult because tire rubber is nontransparent due to the presence of carbon black. Generally, trace tire rubber is analyzed using pyrolysis-gas chromatography^{1,2} or pyrolysis-gas chromatography mass spectrometry (Py-GC/MS).³ Rubber used for automobile tires is composed of styrene-butadiene copolymer, 1,3-butadiene (BD) and isoprene (IP). Rubber can be discriminated using Py-GC/MS via a quantitative comparison of the pyrolysis products typical of each rubber. However, discriminating different samples of the same product is not possible for Py-GC/MS. Even when analyzing different products, discrimination is poor when the main component is the same. Therefore, another analytical method is needed to increase the accuracy of rubber identification.

Generally, rubber is vulcanized with sulfur-based additives to improve its durability. Analyzing the chemical state of sulfur found in rubber (monosulfide, disulfide or polysulfide bonds) is difficult. X-ray absorption near-edge structural (XANES) analysis has been used to determine the chemical states of elements in materials.^{4,5} XANES analysis for sulfur chemical states was reported,^{6–12} as well as for sulfur included in the rubber.^{13,14} The chemical state of sulfur changes when rubber degrades over time or with use. As a result, variability exists among the sulfur chemical states included in each tire because the chemical state changes from the time of purchase to the time of disposal depending on the environment the tire has been exposed to or the history of usage. Therefore, the tire rubber may be discriminated based on the chemical states of sulfur.

This chapter discusses such tire rubber discrimination using Py-GC/MS and sulfur chemical state analyses. Discrimination of tires of the same brand (i.e., by a single manufacturer) is also discussed.

3.2 Experimental

3.2.1 Sample

Eleven tires from five manufacturers were collected shortly after removal from cars (tires *a–k*); their properties are listed in Table 3.1. The group consisted of three Bridgestone tire brands and one brand from

each of the other manufacturers. For tires *a–i*, the surfaces were shaved off from the center line of the tire tread every 90° in the rotational direction (e.g., samples *a1–a4* of tire *a*); four points were thus shaved off in total. For tire *j*, the surfaces of both side lines were shaved off every 180° in the rotational direction (samples *j2-1, j2-2, j3-1 and j3-2*) and from along the center line (samples *j1-1 to j1-4*), giving eight samples in total. For tire *k*, the surfaces of both side lines were shaved off (samples *k2-1 and k3-1*) and from along the center line (samples *k1-1 to k1-4*), giving six samples in total. The shaved samples were examined by XANES.

Table 3.1 Sample tires collected for the experiment.

Tire	Manufacturer	Brand	Number	width/rim-diameter	Date of manufacture
a	BRIDGESTONE	SNEAKER	4	195/15	14/09
b			4	205/16	28/08
c			4	195/15	31/08
d			4	195/15	38/10
e			4	175/13	36/12
f		DURAVIS	4	165/14	16/11
g	TOYO	POTENZA	4	225/17	39/09
h		PROXES	4	215/16	36/06
i		GT3	4	185/15	51/09
j		SP31	8	175/15	27/09
k		ECOS	6	215/16	10/13

(mm/inch) (week/year)

3.2.2 Pyrolysis-gas chromatography mass spectrometry

The sample tire rubbers listed in Table 3.1 were first analyzed by Py-GC/MS. Samples (about $0.5 \times 0.5 \text{ mm}^2$) included the tire surfaces. Four pieces from one location per tire were analyzed. Additionally, to confirm the variation in a single tire, six pieces from the six locations noted above for tire *k* were analyzed (*k1-1 to k1-4, k2-1 and k3-1*). The Py-GC/MS instrument consisted of a GC-MS unit (QP2010 Plus; Shimadzu, Japan) and a pyrolysis apparatus (JPS-700; Japan Analytical Industry, Japan). The analysis

Table 3.2 Analysis conditions of Py-GC/MS.

Pyrolizer	JPS-700 (Japan Analytical Indutry)	
	pyro-foil	F 590 (Japan Analytical Industry)
	needle	300°C
	oven	300°C
	pyrolysis time	5 sec
GC/MS	QP2010 plus (Shimadzu)	
	column	VF-5ms (30 m, 0.25 mm, 0.25 μm , Agilent technologies)
	oven	50°C (5min) - 5°C min^{-1} - 300°C(5 min)
	split ratio	1:100
	carrier gas	He, 1.0 mL min^{-1}
	m/z	10-450
	mode	SCAN mode

conditions are listed in Table 3.2.¹⁵ The peak area value of each detected component of the pyrogram was determined. Details of the identification method are described below.

3.2.3 XANES

XANES measurements were performed on the 27SU beamline at SPring-8 (Hyogo, Japan). The samples and reference materials were placed on an aluminum holder using conductive double-stick tape, so that the beam was irradiated on the original surface of the sample. The energy steps were set to 0.1 eV (2,455-2,500 eV), and 1 eV (2,500-2,520 eV). Spectra were recorded in fluorescence mode with an Si(111) double-crystal monochromator and silicon drift detector under vacuum conditions. The data obtained were analyzed using REX2000 software (Rigaku, Japan).¹⁶

3.3 Results and discussion

3.3.1 Identification based on Py-GC/MS

The thermal decomposition products characteristic of rubber, such as BD, IP, styrene (ST), vinyl-cyclohexene and dipentene were detected by Py-GC/MS analysis. Figure 3.1 shows the pyrograms of samples *a* and *k*. The ratios of the peaks derived from each pyrolysis differed between samples, which indicated that the sample compositions were different. The ratios of the BD, IP and ST pyrolysis monomers were used to identify the samples. The ratios of the area of the IP and ST peaks to that of the BD peak for each sample, i.e., IP/BD and ST/BD, were calculated and used as an

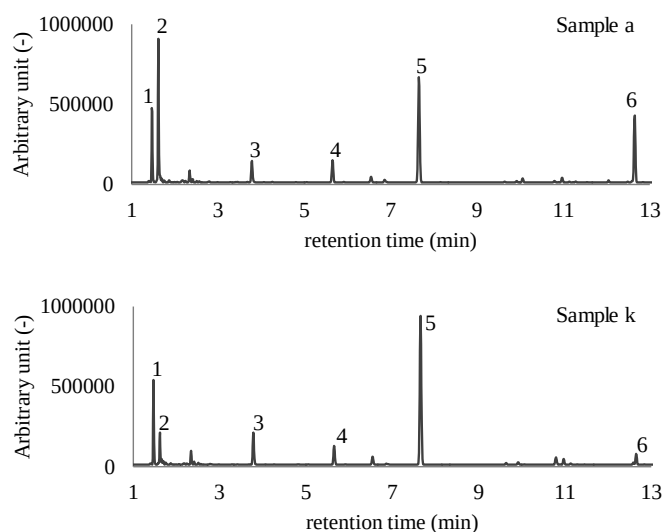


Figure 3.1 The pyrograms of sample *a* and *k*.

1: 1,3-butadiene, 2: isoprene, 3: toluene, 4: vinyl-cyclohexene, 5: styrene, 6: dipentene.

index for identification. The following average results were obtained for the sample *k* tire ($n = 6$). The mean IP/BD value was 0.30 with a standard deviation (SD) of 0.033 and a coefficient of variation of 10.9%. The

mean ST/BD value was 3.45 with a SD of 0.208 and a coefficient of variation of 6.0%. The variation in the composition analysis result for one tire had a maximum of 11%. Additionally, these data were confirmed to be a normal distribution by the Shapiro-Wilk method (OriginPro 9.0, OriginLab Corp., USA: p value = 0.62

in IP/BD, p value = 0.68 in ST/BD).

Figure 3.2 shows the Py-GC/MS results, where the SD is indicated by the error bars. Sample *j* with a high

IP/BD, and sample *f* with a low IP/BD and ST/BD, were clearly different from the other samples. The IP/BD ratio of the other samples ranged from 0.31 to 2.75 while the ST/BD ratio ranged from 2.46 to 4.13; some results were within three times the SDs of each other. Samples *a–e*, which were from the same brand of one manufacturer, had different IP/BD and ST/BD values. Notably, sample *e*, which was smaller than the others

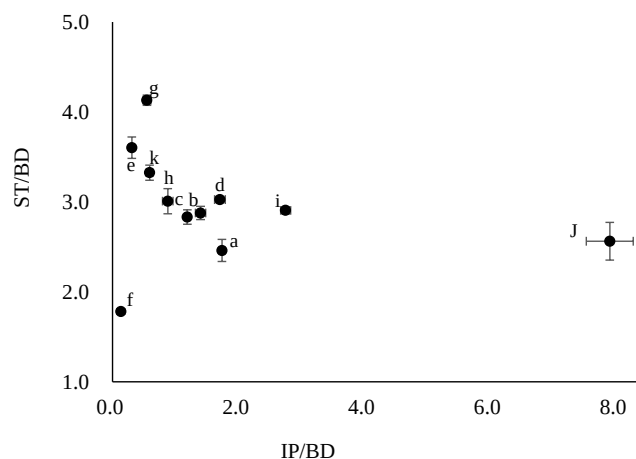


Figure 3.2 The results of Py-GC/MS analysis. Error bars represent standard deviation of each sample.

Table 3.3 Results of t-tests for a)IP/BD and b)ST/BD are shown. The shaded cells mean unequal variance at a significant level of 5%.

a)											
	a	b	c	d	e	f	g	h	i	j	k
a		18.0	42.7	15.6	38.3	0.1	30.9	17.4	17.9	0.3	43.2
b			13.9	45.8	26.4	0.0	33.2	48.9	49.7	1.6	14.2
c				11.9	31.6	0.1	24.9	13.4	13.8	0.2	49.5
d					23.2	0.0	29.6	46.9	46.1	1.9	12.1
e						0.0	42.0	25.5	26.2	0.5	32.0
f							0.0	0.0	0.0	0.0	0.1
g								32.3	33.0	0.7	25.3
h									49.2	1.7	13.6
i										1.6	14.0
j											0.2
k											
b)											
	a	b	c	d	e	f	g	h	i	j	k
a		21.4	25.3	3.0	27.8	2.4	12.1	42.0	4.8	20.1	47.6
b			44.8	11.2	41.7	9.1	34.1	16.3	16.7	6.0	23.1
c				9.2	46.9	7.4	29.5	19.5	13.8	7.5	27.1
d					8.1	44.6	20.0	2.1	39.2	0.7	3.3
e						6.5	27.0	21.6	12.4	8.4	29.7
f							16.6	1.7	34.1	0.5	2.6
g								8.9	28.2	3.0	13.2
h									3.4	25.9	39.7
i										1.1	5.3
j											18.5
k											

(Table 3.1), had a smaller IP/BD. This smaller value was attributed to less IP rubber, which is used typically in tires of heavy-load vehicles, such as trucks.

The samples were analyzed by f- and t-tests performed with Excel 2016 software (Microsoft Corp., USA). The IP/BD and ST/BD ratios were used as indices of each sample. The f-test was done prior to the t-test and the results are shown in Table 3.3. Concerning the IP/BD ratio, samples *f* and *j* were unequally distributed with the other samples at the 5% significance level. For the ST/BD ratio, samples *d*, *f* and *i* with sample *a*, samples *d*, *f* and *i* with sample *h*, samples *d*, *f*, *g* and *i* with sample *j*, and samples *d* and *f* with sample *k* were unevenly distributed at the 5% significance level. The t-test was then carried out. For the ST/BD ratio, among the 55 combinations, 53 pairs differed at the 5% significance level, while 45 pairs had different IP/BD ratios (Table 3.4). The IP/BD and ST/BD results together were sufficient to identify all of the samples used in this study.

Table 3.4 Results of t-tests for a)IP/BD and b)ST/BD are shown. The shaded cells mean less than a significant level of 5%.

a)

	a	b	c	d	e	f	g	h	i	j	k
a		0.0	0.0	52.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0
b			0.3	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0
c				0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
d					0.0	0.0	0.0	0.0	0.0	0.0	0.0
e						0.0	34.4	0.1	0.0	0.0	0.0
f							0.1	0.0	0.0	0.0	0.3
g								0.1	0.0	0.0	0.1
h									0.0	0.0	0.0
i										0.0	0.0
j											0.0
k											

b)

	a	b	c	d	e	f	g	h	i	j	k
a		0.1	0.2	0.0	0.0	0.1	0.0	0.1	0.0	43.6	0.0
b			45.3	1.1	0.0	0.0	0.0	14.6	51.5	5.2	0.0
c				0.4	0.0	0.0	0.0	7.2	15.5	7.7	0.0
d					0.0	0.0	0.0	82.1	0.4	2.0	0.1
e						0.0	0.0	0.3	0.0	0.3	1.0
f							0.0	0.0	0.0	0.5	0.0
g								0.0	0.0	0.0	0.1
h									20.6	1.6	0.1
i										4.5	0.1
j											0.0
k											

3.3.2 Identification based on XANES

Figure 3.3-1 to -3 shows the XANES spectra of the samples and reference materials. The spectra of each tire were similar, which suggested that the spectra of the tread surface rubber were not dependent on the rotation and cross direction of the tire.

The spectra of all of the samples displayed peaks at ca. 2,471.5 (peak 1) and 2,480.5 eV (peak 2). Comparison with the spectra of the reference materials identified these peaks as being due to R–S–R' (sulfide) and SO_4^{2-} (sulfate) structures, respectively. The shapes and heights of the peaks differed among the tires. For example, the heights of peak 2 of tire *a* were relatively low compared with that of tire *j*. Additionally, although tires *a* to *e* were of the same brand (i.e., produced by the same manufacturer; Table 3.1), their spectra were different.

The peak height ratios were calculated by subtracting the intensity at 2,520 eV (defined as unity) from the measured peak intensity, as follows:

$$[\text{peak 1}']/[\text{peak 2}'] = ([\text{peak 1}] - 1)/([\text{peak 2}] - 1)$$

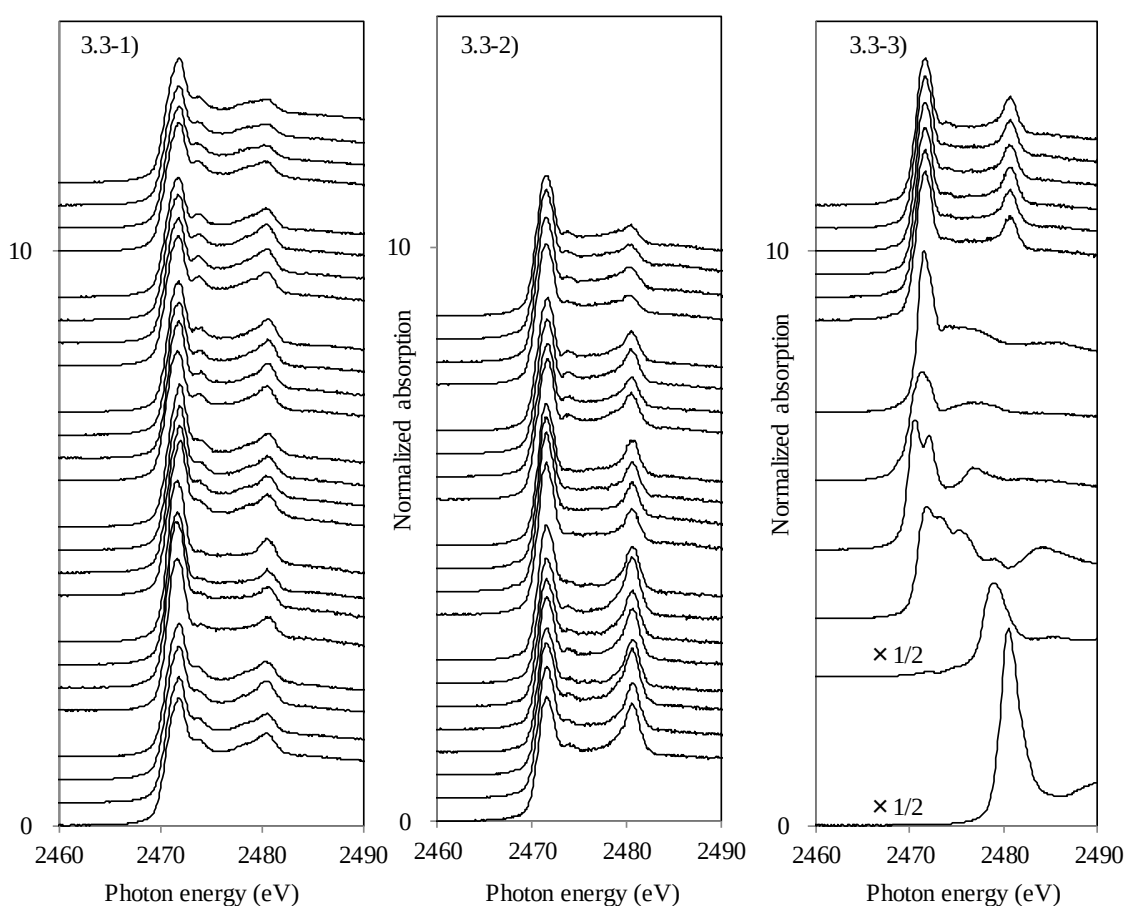


Figure 3.3-1~3.3-3 Sulfur K edge XANES spectra of samples and reference materials. 3.3-1) From the top the spectra of samples *a1~a4*, *b1~b4*, *c1~c4*, *d1~d4*, *e1~e4* and *f1~f4* are shown. 3.3-2) From the top the spectra of samples *g1~g4*, *h1~h4*, *i1~i4* and *j1~j3-2* are shown. 3.3-3) From the top the spectra of samples *k1~k3-1* and reference materials (methionine, Cysteine, Cystine, ZnS, Cystic acid and ZnSO_4) are shown.

The ratios ranged from 1.2 to 2.5 (Figure 3.4 and Table 3.5). Previous research¹³ established that the R-S-R content of rubber decreased, while the SO_4^{-2} peak intensity increased, when evaluated using the heat aging test (160°C). This indicated that the sulfur was oxidized as aging progressed. Because the ratios represent the sample degradation state, samples having low ratios should thus be both more oxidized and more degraded. However, comparing these results with those in Table 3.1 indicates that the older samples were not more oxidized. It is speculated that traveling distances and speed affect the chemical states of sulfur in addition to the period of usage, although additional studies would be needed to confirm this. The relative standard deviations (RSDs) of each tire were within 6%, excluding tire *j* (11%), which was twice the size of the other tires. The lowest RSD was 3% for tire *a*. For tire *j*, peak 2 was more intense than peak 1 compared with the other tires, which suggested that the surface of tire *j* was more oxidized and its oxidation state was not uniform. These data were confirmed to be a normal distribution by the Shapiro-Wilk method (OriginPro 9.0, OriginLab Corp., USA: p value = 0.96 in tire *j*).

The tires were then discriminated according to the means and SDs of the peak height ratios ([peak 1']/[peak 2']). The mean values ± 3 SD of the ratios of tire *a* were different from those of tires *b*, *h*, *i*, *j* and *k*,

although the mean values $\pm$ SD overlapped in the case of tire *a* with tires *e* and *g*. Although tires *a*–*c* were of the same brand from the same manufacturer (Table 3.1), the mean values ± 3 SD of the ratios for tire *a* and *b* were different, and tires *a* and *c* had mean values ± 2 SD that were distinguishable.

A t-test was done to discriminate the peak height ratios of the tires (Table 3.6). F-tests for variance in the ratios indicated that every set was homoscedastic ($P > 0.05$). The t-test established that 43 of 55

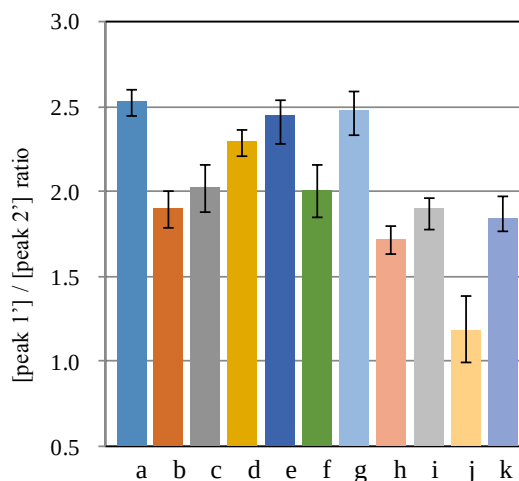


Figure 3.4 [peak 1']/[peak 2'] ratios of each tire are shown. The bars represent the maximum and minimum values of each.

Table 3.5 [peak 1']/[peak 2'] ratios of each tire are shown.

Tire	peak 1/peak 2 ^a	RSD ^b (%)	n ^c
a	2.54 $\pm$ 0.07	2.9	4
b	1.90 $\pm$ 0.11	5.7	4
c	2.02 $\pm$ 0.12	5.7	4
d	2.30 $\pm$ 0.07	3.0	4
e	2.45 $\pm$ 0.12	4.7	4
f	2.01 $\pm$ 0.12	6.2	4
g	2.48 $\pm$ 0.11	4.3	4
h	1.72 $\pm$ 0.08	4.9	4
i	1.90 $\pm$ 0.08	4.4	4
j	1.19 $\pm$ 0.13	10.6	8
k	1.84 $\pm$ 0.07	3.9	6

a. Mean values $\pm$ standard deviation.

b. Relative standard deviation.

c. Number of sample.

combinations were different at the 5% significance level. Additionally, 7 of 10 combinations in tires *a–e* differed at the 5% significance level. Tire *b* could not be distinguished from tires *c*, *f*, *i* and *k*, i.e., nearly half of the samples.

Py-GC/MS distinguished all 55 pairs of the 11 samples used in this study, while XANES could discriminate only 43 pairs. This difference was attributed to the different information gleaned by the different techniques. For the Py-GC/MS method, three types of monomers were analyzed and two variables were obtained from them. The XANES technique, however, obtained only one variable from two peaks.

Table 3.6 Results of t-tests for [peak 1']/[peak 2'] ratio (%) of each tire are shown. The shaded cells mean less than a significant level of 5%.

	a	b	c	d	e	f	g	h	i	j	k
a		0.0	0.0	0.3	25.6	0.0	40.1	0.0	0.0	0.0	0.0
b			17.1	0.1	0.0	24.3	0.0	3.7	99.5	0.0	34.5
c				0.7	0.2	85.2	0.1	0.5	13.4	0.0	1.6
d					6.5	0.6	3.1	0.0	0.0	0.0	0.0
e						0.2	74.2	0.0	0.0	0.0	0.0
f							0.1	0.9	20.3	0.0	2.9
g								0.0	0.0	0.0	0.0
h									2.2	0.0	3.5
i										0.0	28.9
j											0.0
k											

3.4 Conclusion

Py-GC/MS analysis confirmed that commercial tire rubbers can be distinguished by the ratio of their pyrolysis monomers. Differences in composition, even for the same brand of the same manufacturer, were attributed to tire size differences.

Sulfur XANES analysis revealed that the peak shapes and heights differed among the tire samples. Some sets of tires could be distinguished by the ratio of their mean peak height ratios ± 3 SD. The tire rubbers could thus be discriminated by this analytical technique.

Statistical t-testing of the Py-GC/MS results showed that the 55 pairs differed at the 5% significance level. However, t-testing of the XANES data distinguished only 43 of the 55 combinations at the 5% significance level. The Py-GC/MS technique was thus considered to be superior. Nevertheless, because XANES analysis is a non-destructive method, it should be the first choice for forensic analysis and Py-GC/MS should be used only when samples cannot be distinguished by XANES. XANES analysis is clearly an effective option. When Py-GC/MS yields similar results for a given product (e.g., two distinct samples from tire *a* in this study), XANES analysis may be able to distinguish them statistically.

The XANES technique evaluated two oxidation states of the sulfur contained in rubber as indicators. However, XANES could also be used to identify other chemical species and thereby allow improved

identification of samples. Additional research is needed to develop suitable standards in this case.

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Chapter 4 Methods of Determining Cadmium and Lead Speciation in Fly Ash by X-ray Absorption Fine-Structure Spectroscopy and a Sequential Extraction Procedure

4.1 Introduction

In Japan, general waste and industrial waste are usually treated by incineration or melting for purposes of public sanitation and volume reduction in landfills. Although organic matter is decomposed in such high-temperature treatments, metal matter transitions into residue, with changes in chemical form. The residue is classified as bottom ash, boiler ash, and fly ash in the case of municipal solid waste incineration. Of these ashes, fly ash, which is collected in exhaust-gas treatment equipment, contains heavy metals, such as lead and cadmium, condensed in the gas-cooling process, and is a kind of industrial waste. Lead and cadmium are hazardous to many living environments; thus, careful attention is required to avoid their release. Actually, incident in which these heavy metals were eluted from illegal dumped industrial waste has occurred. Cases of illegal dumping, like Teshima Island industrial waste case¹, have been investigated by police. Cadmium and lead may leach from industrial waste beyond the legal standard, and are harmful to living body. The elution of an element depends on its chemical form. Therefore, the detailed analytical method of lead and cadmium contained in fly ash is important in forensic science. It is essential to insolubilize fly ash by intermediate processes, such as chemical treatment. The elution behavior of such processed material is estimated by leaching tests. In Japan, the regulatory leaching test is conducted under 6 h shaking with distilled water under conditions of a 50 g/500 mL solid/liquid ratio. When the elution amount meets the regulatory standard, the sample is considered to be “not hazardous”. It is important to understand the chemical state of cadmium and lead to store the treated material safely, because the behavior or mobility of cadmium and lead in the environment depends on its chemical state. Although we should understand the chemical state of lead and cadmium to store the treated material safely over the long term, it is difficult to obtain detailed information on chemical states by a leaching test alone. Additionally, because fly ash is often highly alkaline, due to lime in exhaust gas treatment equipment, other analysis techniques are necessary to estimate long-term behavior before fly ash neutralization.

X-ray diffraction (XRD)^{1,2}, X-ray photoelectron spectroscopy (XPS)³⁻⁵, X-ray absorption fine structure (XAFS) spectroscopy,⁶⁻¹² and a sequential extraction procedure^{1,12-16} have been used to determine the chemical speciation of heavy metals in ash. XRD and XPS have the advantage of being non-destructive methods. However, XRD is generally used to identify crystalline compounds and XPS is a surface analysis method. Thus, it is difficult to determine the chemical

speciation of heavy metals at low concentrations in ash by these methods. XAFS is a more specialized technique. XAFS spectroscopy enables quantitative chemical speciation to be performed in dilute and chemically complex systems. In the sequential extraction procedure, a sample is added to an extraction reagent, and is then shaken, centrifuged, and filtered to obtain an extract solution; this process is performed repeatedly for each fraction. Thus, the sequential extraction procedure can be performed in a general laboratory.¹⁷ The sequential extraction procedure also allows for the analysis of heavy metals present at low concentrations by inductively coupled plasma (ICP) analysis. However, in performing the sequential extraction procedure, it is necessary to take account of the incomplete dissolution of target phases, the removal of non-target species, and the incomplete removal of dissolved metals, due to re-adsorption on the remaining components or due to re-precipitation with the added reagent.¹⁷

In addition to the experimental approach above, we can obtain information on the chemical state by a simulation using chemical equilibrium model calculations. Such simulations have been conducted generally for information on chemical states in the environment and have been applied often to fly ash, as well soil and water.^{3,14-16,18-20}

In this chapter, I present the results of our study on the chemical states of cadmium and lead. The purpose of this research was first to obtain information on the cadmium chemical state in fly ash. Second, the chemical state of lead in fly ash was analyzed, to investigate the quantitative analytical method of lead chemical species. For both cadmium and lead, a sequential extraction procedure and XAFS were performed. Additionally, the chemical states in one kind of fly ash and the residues of the sequential extraction procedure were analyzed with XAFS to research the chemical state changes before and after the extractions. On the basis of the these experimental results, chemical equilibrium model calculations were performed. Additional experiments were carried out according to the properties of cadmium and lead, respectively. For cadmium, the influence of pH on the elution were evaluated by pH-dependent leaching test. On the other hand, for lead, to quantify the various lead species using the sequential extraction procedure, reference materials were fractionated using the procedure. The results of these lead analyses were examined statistically and compared using cluster analysis. Few studies have estimated lead species in fly ash by combining multiple analyses. Herck *et al.*¹⁴ used a sequential extraction procedure and a chemical equilibrium model simulation. Abanades *et al.*¹⁶ used a thermodynamic simulation, a sequential extraction procedure, and X-ray microanalysis. Furthermore, chemical states analysis method by sequential extraction procedure alone was examined.

In this study, samples were collected from Japanese facilities that use general equipment

and processes. Thus, the outcomes of this study can be applied to fly ash generally. Additionally, based on the results obtained from composition analyses, the sequential extraction procedure, and XAFS analysis, the chemical species of cadmium and lead extracted in the sequential extraction procedure were estimated via simulations using a chemical equilibrium model calculation program (Visual MINTEQ).

4.2 Experimental

4.2.1 Samples

Eight kinds of municipal solid waste incineration (MSWI) fly ash and seven kinds of molten fly ash were collected; both MSWI fly ash and molten fly ash are referred to here as “fly ash”. Table 4.1 provides the specifications of the fly ashes investigated. Fly ashes A–F were MSWI fly ash collected from stoker-type incinerators, whereas fly ash G was MSWI fly ash collected from a fluidized bed-type incinerator. The electrostatic precipitator of facility D was separated into anterior (D1) and posterior chambers (D2). Fly ashes H and I were molten fly ashes collected from shaft-type furnace incinerators, fly ashes J and K were molten fly ashes collected from surface melting furnace incinerators, and fly ashes L–N were molten fly ashes collected from plasma-type furnace incinerators. There were significant differences between the flue gas treatment systems; those producing fly ashes A–C and H–N had lime processing, whereas those producing fly ashes E, F, H–J, M, and N had activated carbon processing. For cadmium, fly ashes A–H and J were analyzed, and for lead fly ashes A–C, D1, E and G–N were analyzed.

Table 4.1 Configurations of sample.

Sample	Incinerator	Waste ¹	Dust collector ²	Lime	Activated carbon
A	Stoker fired	MSW	BF	+	
B	Stoker fired	MSW	BF	+	
C	Stoker fired	MSW	BF	+	
D1, D2	Stoker fired	MSW	EP		
E	Stoker fired	MSW	EP		+
F	Stoker fired	MSW	EP		+
G	Fluidized bed	MSW	BF		
H	Shaft furnace direct melting	ASR	BF	+	+
I	Shaft furnace direct melting	BA, FA	BF	+	+
J	Burner melting	ASR	BF	+	+
K	Burner melting	BA	BF	+	
L	Plasma melting	FA	BF	+	
M	Plasma melting	BA	BF	+	+
N	Plasma melting	BA, FA	BF	+	+

*1 MSW: Municipal solid waste, ASR: Automobile shredded residue, BA: Bottom ash, FA: Fly ash

*2 BF: Bag filter, EP: Electric precipitator

4.2.2 Characterization of fly ash

The Cl, O, S, and Si concentrations in fly ash were determined by X-ray fluorescence (XRF; Shimadzu, XRF-1700) spectroscopy using the fundamental parameter method.²¹ Other elements were measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES). To 100 mg of a sample, 5 mL of hydrofluoric acid, 3 mL of nitric acid, and 2 mL of hydrochloric acid were added; samples were subsequently digested with a microwave digestion system (CRM, MARS5, 1240 kPa, 15 min). A saturated boric acid solution (30 mL) was then added to the solution, which was heated with the microwave digestion system (690 kPa, 5 min). The supernatant was filtered with a 0.2- μ m pore membrane filter.²² The filtrate solution was diluted to 100 mL with 1.0 mol L⁻¹ HNO₃. Yttrium was added to all solutions at a constant concentration of 5 mg L⁻¹ as an internal standard. The solution was then measured by ICP-AES (Shimadzu, ICP-8000 or Thermo ELECTRON, IRIS Intrepid). According to a previous study,²² the recovery ratio of the microwave digestion was 92% (certified value of lead concentration was 10,870 mg kg⁻¹), and the relative standard deviation for the measurement ($n = 8$) was 3.0%.

4.2.3 Sequential extraction procedure

Fly ash and known reference materials were fractionated into six fractions, a water-soluble fraction, an ammonium acetate-extractable fraction, an acid-soluble fraction, a reducing-extractable fraction, an oxidizing-extraction fraction, and a residual fraction, by the sequential

Table 4.2 Sequential extraction protocol.

Fraction	Protocol			
	Reagent	L/S /ml g ⁻¹	Shaking /h	Temp. ^a
Fr1 Water soluble	Ion exchange water	10	6	rt
Fr2 Ammonium acetate extractable	1.0 mol l ⁻¹ CH ₃ COONH ₄	10	6	rt
Fr3 Acid soluble	1.0 mol l ⁻¹ CH ₃ COONa (pH5 with CH ₃ COOH)	8	5	rt
Fr4 Reducing extractable	0.2 mol l ⁻¹ NH ₂ OH.HCl (with CH ₃ COOH in 25 vol/vol %)	10	6	85°C
Fr5 Oxidizing extractable	(1) 30% H ₂ O ₂ (pH 2 with HNO ₃)	5	2	85°C
	0.02 mol l ⁻¹ HNO ₃	3		
	(2) 30% H ₂ O ₂ (pH 2 with HNO ₃)	3	3	85°C
	(3) 1.78 mol l ⁻¹ CH ₃ COONH ₄ (with CH ₃ COOH in 25 vol/vol %)	9.66	0.5	rt
Fr6 Residual	0.1 g of sample is added to with HNO ₃ , HCl, HF (3 ml, 2 ml, 5 ml each), and digested by microwave. After digestion, 30 ml of saturated boracic acid is added, and heated by microwave again.			

a. r.t.: room temperature

At the end of each step, sample was centrifuged and filtered. Then residue was dried at 105°C in 12 h, and weighed. Fr5s 3 steps, and sample was cooled to room temperature between 2nd and 3rd step.

extraction procedure.^{1,12,13,16,17,23} Table 4.2 lists the steps involved in the sequential extraction procedure, where these fractions are referred to as Fr1 to Fr6, respectively. As mentioned above, the concentrations of the components in the extract solutions were then measured by ICP-AES.

Fractions from the sequential extraction procedure, which was originally designed for soil, do not necessarily correspond to the physicochemical nature of the chemical species. Thus, reference materials were also fractionated by the sequential extraction procedure as controls. SiO₂ was mixed with 5 wt% lead compounds, and these were used as known reference materials. To prepare the reference materials, Pb, Pb₂O(OH)₂, PbS, PbCO₃, PbCl₂, Pb₃(PO₄)₂, PbHPO₄, chloropyromorphite (Pb₅(PO₄)₃Cl; CP), PbSiO₃, Pb(OAc)₂ (Pb(CH₃COO)₂), PbO, Pb₃O₄, PbO₂, and PbSO₄ were purchased from Soekawa Chemical Co., Ltd. (Tokyo, Japan), Nacalai Tesque Inc. (Kyoto, Japan), and Nichika Inc. (Kyoto, Japan).

4.2.4 XAFS experiments

In preparing reference materials for XAFS experiments, reagents were mixed with boron nitride (BN), such that the *S/N* ratio of the spectrum was optimized; they were formed into pellets, and stored in sealed polyethylene bags. Fly ash was prepared by sealing the powder directly into polyethylene bags. XAFS measurements were carried out on beam line 01B1 of Spring-8 (Hyogo, Japan). Spectra were recorded in the fluorescence mode using a Lytle detector for fly-ash samples and in the transmission mode using an ionization chamber for reference materials with Si (111). The energy steps for cadmium were set to 10 eV (26,400-26,670 eV), 1 eV (26,670-26,780 eV), and 3 eV (26,780-27,300 eV). On the other hand, the energy steps for lead were set to 10 eV (12,780-13,000 eV), 0.5 eV (13,000-13,120 eV), and 2 eV (13,120-13,300 eV).

For cadmium, X-ray absorption near edge structure (XANES) regions of the samples were analyzed. For lead, both the XANES and extended X-ray absorption fine structure (EXAFS) regions of samples were analyzed. The XANES spectra of reference materials were compared with those of fly ash to identify major species. It was assumed that the spectra of unknown species were represented by the synthesized spectra of known reference species. Thus, the major species in fly ash were identified and quantified using the linear combination fit (LCF) technique, in which spectra of known reference species were fitted to the spectrum of an unknown sample.^{2,7-10} The LCF for XANES was conducted using the REX 2000 software (ver. 2.3.3; Rigaku Co., Ltd.). It was assumed that each percentage of the total lead obtained by LCF of the XANES spectrum indicated the mole percentage. In the XANES analysis, 26,716.7 eV was defined as the cadmium K absorption edge (the first inflection point) in cadmium metal foil, and 13,037.7 eV was defined

as the lead L3 absorption edge in lead metal foil.

The EXAFS spectra of reference materials were compared with the spectral shapes of samples, using amplitudes and phases to identify the major species.²⁴ The LCF of EXAFS was conducted using the SixPACK software (ver. 0.68).²⁵ PCA was conducted for 13 kinds of EXAFS spectra from unknown samples, as compared with their XANES spectra. The residual value (R), calculated using Eq. (1), was used to evaluate the LCF for the experimental spectra of both XANES and EXAFS.

$$\text{Residual value } R = \frac{\sum(\text{XAFS}_{\text{measd}} - \text{XAFS}_{\text{calcd}})^2}{\sum(\text{XAFS}_{\text{measd}})^2} \quad (1)$$

For reference materials for cadmium, Cd, CdCl₂, Cd(OH)₂, CdCO₃, CdS, and CdSO₄ were purchased from Nacalai Tesque Inc. (Kyoto, Japan), and CdO and CdSiO₃ were purchased from Soekawa Chemical Co., Ltd. (Tokyo, Japan). Reference materials of lead were the same as those used in the sequential extraction procedure.

Fly ash A was typical of MSWI fly ash in Japan, collected from stoker-type incinerators with a bag filter and lime processing. Because cadmium and lead concentrations in fly ash A were greater than those in B and C, which were also typical fly ash, it should be easier to observe changes in chemical states in A before and after extraction than in B or C. Thus, fly ash A and the sequential extraction residues were used for XAFS samples.

4.2.5 Leaching model

Chemical species within the extract solutions obtained from the sequential extraction procedure were estimated using chemical equilibrium model calculations. Calculations were conducted using the chemical equilibrium model program Visual MINTEQ (ver. 2.61).^{3,20,26} The default values of Visual MINTEQ were used for all parameters, such as the value of log K_{sp} . The input condition details, such as the kind of element, the chemical species, and their concentrations, were based on the results of the sequential extraction procedure and the XANES spectral fitting.

4.2.6. pH-Dependent leaching test

The dissolution behavior of an element is influenced by pH, the solvent, and solid/liquid ratio.²⁷ I estimated the influence of pH on cadmium dissolution, changing the terminal pH of solution. With stirring, acid was titrated with an automatic titrator according to the targeted pH value.

To 5.0 g of sample, 50 mL of ion exchanged water was added. The sample was stirred for 2 h at 600 round per minute with an automatic titrator (Metrohm, Stat Titrino 718), which monitored the pH value. For the titration, 8 mol L⁻¹ HNO₃ was used. The terminal pH value was set to 1.0, 3.0, 5.0, 7.0, and 9.0. Because cadmium did not dissolve in alkaline solutions, the terminal pH value was not set to higher than 10.0: cadmium's log K_{sp} value = -13.644. In the case of samples where the pH was lower than 7.0 with just adding ion-exchanged water, the terminal pH value was not set to 7.0 or 9.0. After stirring, the supernatant was filtered with a 0.2-μm pore

membrane filter. The solution was then measured by ICP-AES as mentioned above.

4.2.7 Cluster analysis

In order to classify the results of lead, cluster analysis was conducted on the results of the sequential extraction procedure and XAFS fitting.²⁸ The origins of the fly ashes were then examined in relation to their classification. The cluster analysis was conducted using commercially available add-on software in Excel (Esumi Co., Ltd., Tokyo, Japan). Euclidean distances between points were calculated and the distances between clusters were computed using Ward's method.

Table 4.3 Chemical composition of sample.

Sample	A	B	C	D1	D2	E	F	G	H	I	J	K	L	M	N	unit
Al	9300	27000	35000	37000	7000	39000	38000	59000	5600	1700	700	N.D.	N.D.	N.D.	N.D.	mg kg ⁻¹
Cd	360	58	180	470	2600	310	220	44	120	210	130	130	480	390	330	
Cr	130	160	120	110	260	440	510	570	150	N.D.	65	N.D.	N.D.	N.D.	N.D.	
Cu	310	540	480	1400	4000	1400	710	5000	7800	2300	16000	2400	1000	920	850	
Fe	9800	9600	8300	10000	4700	6000	5600	18000	18000	2000	13000	900	2500	1800	1500	
Mg	4200	18000	6700	9800	1400	9200	6900	25000	11000	1200	3100	2500	810	600	2300	
Mn	860	450	320	800	190	620	460	3000	910	100	150	N.D.	N.D.	N.D.	N.D.	
P	2500	4700	6600	5600	1900	5300	3400	25000	1600	1200	920	580	760	25000	14000	
Pb	6600	1100	1100	5000	22000	4900	2600	2900	16000	13000	19000	16000	7800	30000	18000	
Ti	580	8700	6700	11000	610	8000	6800	31000	1700	160	260	390	150	110	610	
Zn	14000	9100	6600	24000	78000	21000	11000	9500	74000	35000	49000	53000	38000	130000	89000	
C	30	9.0	N.D.	11	9.4	11.0	9.8	2.8	32.0	N.D.	8.1	N.D.	N.D.	N.D.	N.D.	wt %
Ca	32	19	18	9.8	17	17	14	16	15	8.5	29	29	20	4.9	7.6	
Cl	20	23	25	16	20	15	25	11	4.3	34	28	14	27	23	24	
K	5.1	9.6	11	4.6	9.3	8.1	3.5	9.5	9.9	15	6.5	3.3	8.8	12	11	
Na	3.6	10	6.5	9	11	7	3.8	4.1	6.2	17	5.4	2.9	10	11	12	
O	30	15	18	20	21	21	25	25	14	18	15	40	24	24	23	
S	1.6	2.3	1.6	2.8	6.6	2.7	1.4	1.6	1.4	1.4	0.84	1.7	2	1.4	0.42	
Si	1.7	3.5	6.6	5.5	2.3	2	8.9	10	2.9	0.43	0.43	0.26	1.5	1.3	3.3	

The Cl, O, S, and Si concentrations were determined by XRF spectroscopy. Other elements were measured by ICP-AES.

4.3 Results and discussion

4.3.1 Characterization of and the sequential extraction procedure for fly ash

Table 4.3 lists the compositions of the various fly ash samples studied. They consisted mainly of Ca, Cl, and O. The concentrations of cadmium ranged from 44 to 2,600 mg kg⁻¹ and the concentrations of lead ranged from 1,100 to 30,000 mg kg⁻¹. Although variable, the fly ashes used in this study are typical.^{3,22,28-30} The results of the sequential extraction procedure for fly ash samples and the pH of the extract solutions are shown in Fig. 4.1 for

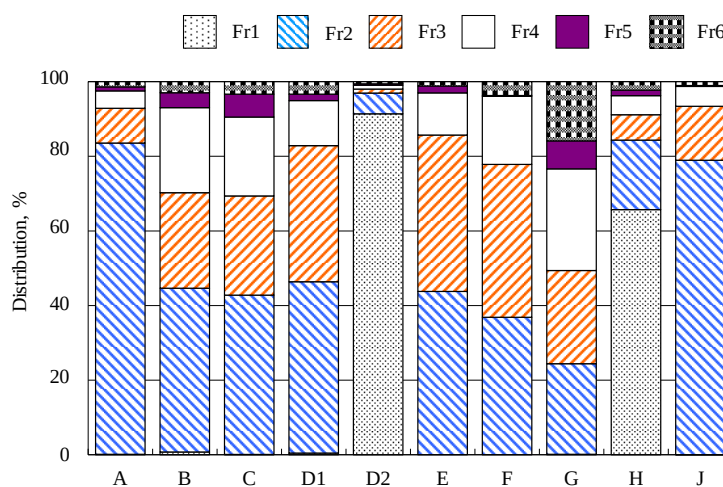


Fig. 4.1 Cadmium distributions of sample by sequential extraction procedure.

cadmium and Fig. 4.2 for lead, respectively. The pH values of extract solutions are shown in Table 4.4. Although the pH of the solvents used in the sequential extraction procedure had been adjusted (as shown in Table 4.2), the pH of the extract solution was greatly influenced by the sample matrix. In particular,

the pH values in Fr1 were greatly affected by the sample matrix; the pH in this fraction ranged from 6.2 to 12.5. In the case of fly ash D2 (pH 6.2) and H (pH 6.2), whose pH values in Fr1 were neutral, Fr1 ratios were 91% and 66%, respectively, and Fr2 ratios were 6% and 19%, respectively. As a result, the sum of Fr1 and Fr2 ratios were 97% and 84%, respectively. However, in the case of the other fly ashes, where the pH values in Fr1 were alkaline (pH: 9.6–12.3), although Fr1 ratios were less than 1%, more than 90% were extracted in Fr2–4. In fly ash G, the sum of Fr5 and Fr6 was 25%, although they were less than 10% in the other samples. Consequently, because at least 25% of cadmium contained in the fly ash was extracted in Fr1 and Fr2, it was found that cadmium existed in chemical states that were easy to elute. A previous study²⁸ of lead in fly ash reported that, in the sequential extraction procedure, Fr4 had the highest fraction ratios, Fr3 or Fr5 had the second-highest fraction ratios, and Fr1 of some samples had ratios in excess of 20%. Our results are consistent with this study.

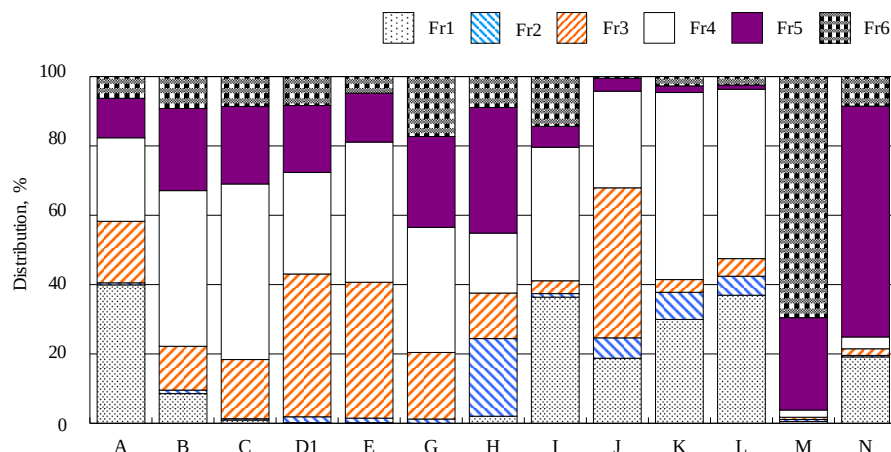


Fig. 4.2 Lead distributions of samples by sequential extraction procedure.

Table 4.4 pH value at each step of the sequential extraction procedure for sample.

	A	B	C	D1	D2	E	F	G	H	I	J	K	L	M	N
Fr1	12.0	12.3	11.8	10.7	6.2	10.4	12.1	9.6	6.2	12.4	11.8	12.3	12.2	10.6	12.5
Fr2	9.6	9.6	9.3	9.0	6.9	9.1	9.1	8.9	7.3	8.9	8.2	10.9	10.4	8	8.5
Fr3	7.0	6.0	6.4	5.8	5.4	5.9	6.3	5.8	6.7	7.5	6.6	7.9	7.6	6.3	6.9
Fr4	3.4	3.6	3.2	3.5	3.5	3.3	3.5	3.1	3.2	3.9	3.5	4.1	4	3.7	3.7
Fr5	2.0	1.5	1.1	1.4	0.5	1.4	0.9	1.3	1.4	0.8	0.6	1.1	1.1	1.8	1.4
Fr6	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

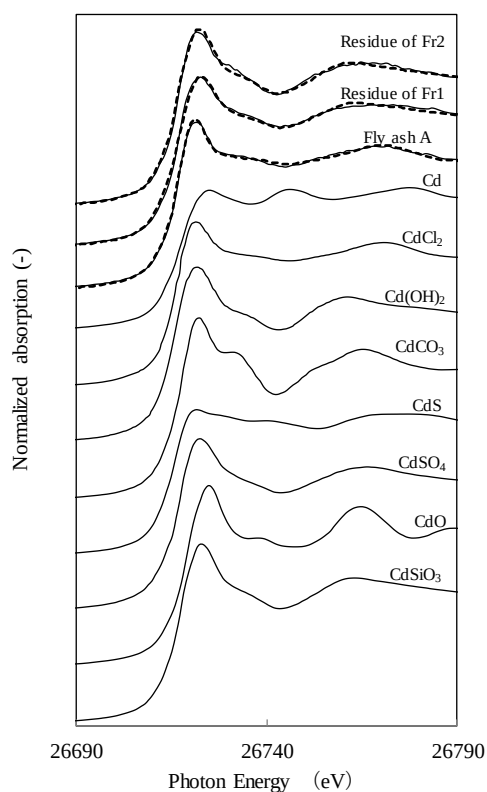


Fig. 4.3 Cd K edge XANES spectra of reference materials and sample (solid lines). Broken lines overlapped on solid lines show simulation spectra.

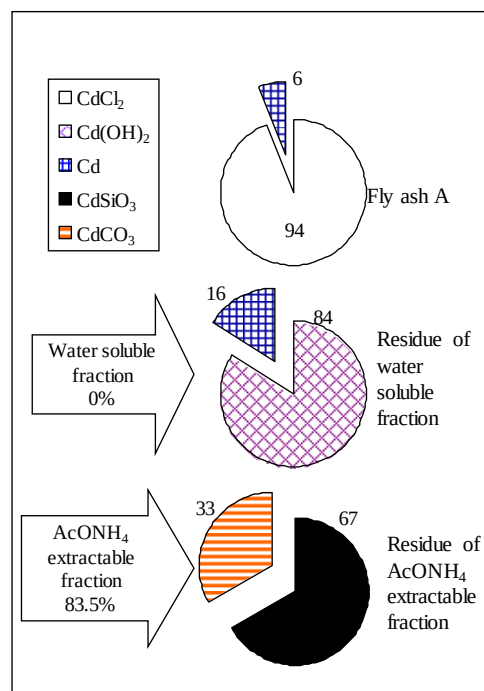


Fig. 4.4 Percentages of the chemical forms relative to total Cd of sample or residue of each fraction (%).

4.3.2 XAFS analysis of fly ash

The cadmium XANES spectra of fly ash and reference materials are shown in Figs. 4.3 and 4.4 and Table 4.5 shows the LCF results. The calculated R values calculated for fly ash A and the residue of Fr2 were 0.012 and 0.016, respectively, indicating satisfactory fits. However, the R value for residue of Fr1 was 0.028, about twice as high. The numbers on the arrows in Fig. 4.4 represent the leaching ratios in the fraction; the ratios in Fr1 and Fr2 were 0.0% and 83.5%, respectively. Consequently, the residue after Fr2 contained 16.5% ($100 - 0 - 83.5 = 16.5$). First, cadmium in fly ash was represented as CdCl_2 94% + Cd 6%. The break line on the solid line of

Table 4.5 Percentages of the chemical forms relative to total Cd of sample or residue of each fraction (%).

	CdCl_2	Cd	Cd(OH)_2	CdCO_3	CdSiO_3	Extraction ratio(%)	R
Fly ash A	94	6				-	0.012
Residue of Fr1		16	84			0.0	0.028
Residue of Fr2				5.4	11	83.5	0.016

the measured spectra shows simulation spectra in Fig. 4.3. According to the thermodynamic equilibrium model calculation for waste incineration by Zhang *et al.*, in the case with chlorine in an incineration system, cadmium existed predominantly as CdCl_2 (g) at 400–100°C and Cd (g) appeared at 800°C or more.¹⁹ Moreover, cadmium existed mainly as Cd (g) above 1,000°C. Generally, the temperature of a stoker incinerator, from where fly ash A was derived, would be expected to be more than 800°C. Accordingly, this report does not conflict with our results, that fly ash A contained CdCl_2 and Cd.

The lead XANES spectra of fly ash and reference materials are shown in Fig. 4.5. In the analysis of lead, to determine statistically the number of reference species, a principal component analysis (PCA) was conducted on XANES spectra from 13 kinds of fly ash.^{7,25,31-34} PCA was conducted with commercially available add-on software in Excel (Esumi Co., Ltd.). PCA of the 13 XANES spectra showed that the first, second, third, and fourth components were responsible for 43, 23, 16, and 9% of the variance, respectively. The cumulative contribution ratio of the four components was 90%, suggesting that there were four or fewer major chemical lead species in the fly ashes.⁷ Regarding the shape of the XANES spectra, the fly ashes were classified roughly into three groups: (1) those with a sharp absorption edge peak around 13,055 eV (fly ashes A, B, I, J, K, and L),

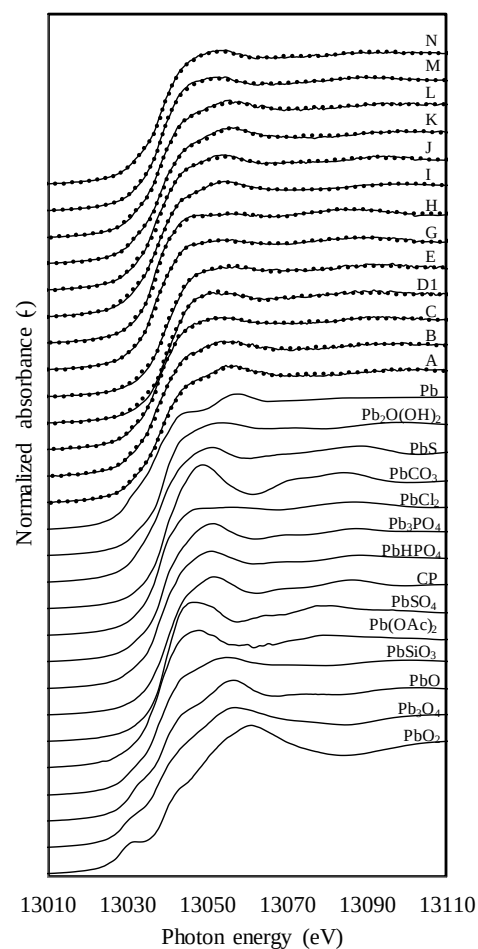


Fig. 4.5 Lead L3 edge XANES spectra of reference materials and sample (solid lines). Broken lines overlapped on solid lines show simulation spectra.

Table 4.6 The results of lead XANES fitting of the samples (%).

Sample	PbSiO ₃	PbCl ₂	PbO	Pb	PbS	Pb ₂ O(OH) ₂	PbCO ₃	R
A	48	17	21	15				0.009
B	48	23	18		10			0.008
C	32	21			14	33		0.006
D1	49	22					29	0.010
E	54	35					11	0.009
G	21	62			17			0.007
H		90		10				0.008
I	88					12		0.007
J		24	27		18	30		0.009
K	52	15	21	12				0.007
L	51	28	10	11				0.008
M		32			25	43		0.007
N	20				36	44		0.006

(2) those with a flat absorption edge peak (fly ashes E, G, and H), and (3) others (fly ashes C, D1, M, and N). Table 4.6 shows the results of the lead XANES fitting of synthesized spectra of known references to those of the fly ashes. The synthesized spectra are shown as a dashed line on the XANES spectra of fly ash in Fig. 4.5. The R values for all samples were ≤ 0.010 , indicating satisfactory fits. Previous studies^{9,11} reported that PbCl_2 or PbO is the predominant form of lead in fly ash when PbSiO_3 was not used as a reference material.

The k^3 -weighted lead EXAFS spectra from both samples and the reference materials are shown in Fig. 4.6. The k^3 -weighted EXAFS spectra of fly ash were smoothed by the Savitzky–Golay method (three smoothing points; one smoothing time). The EXAFS spectra became noisier above $6 \text{ \AA}^{-1}$ for the fly ash samples. PCA showed that for the 13 EXAFS spectra of fly ash in the range of $2\text{--}6 \text{ \AA}^{-1}$; the first, second, third, and fourth components were responsible for 62, 18, 7, and 5% of the variance, respectively. The cumulative contribution ratio of the four components was thus 92%, suggesting that the lead in the fly ash consisted of four or fewer major species, similar to the XANES spectra results. We conducted the LCF of EXAFS in the range of $2\text{--}8 \text{ \AA}^{-1}$. Table 4.7 gives the results of an EXAFS fitting of synthesized spectra of known references to those of the fly ashes. The synthesized spectra are shown as a dashed line on the EXAFS spectra of fly ashes in Fig. 4.6. R values for all samples were in the range of 0.13 to 0.73, indicating poor fits. The result of an EXAFS fitting of most samples indicated CP, PbHPO_4 , and/or $\text{Pb}_3(\text{PO}_4)_2$, which was not reasonable thermodynamically, in view of the formation of fly ash.

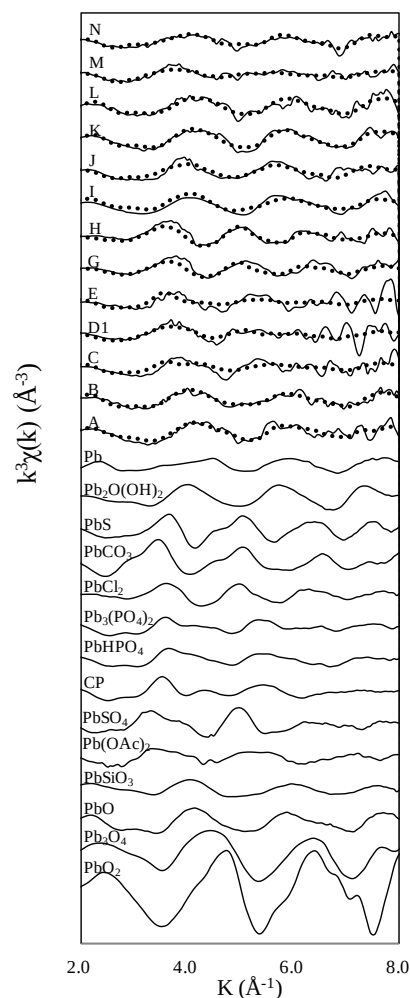


Fig. 4.6 k^3 -weighted lead EXAFS spectra of reference materials and fly ash samples.

Table 4.7 The results of lead EXAFS fitting of samples (%).

Sample	PbO	PbCl ₂	Pb ₂ O(OH) ₂	CP	PbHPO ₄	Pb ₃ (PO ₄) ₂	Pb(OAc) ₂	PbSO ₄	Pb	PbO ₂	PbSiO ₃	PbCO ₃	PbS	Pb ₂ O ₃	R
A	41		33	15						10					0.32
B	64	14			21										0.21
C	33	10		32		25									0.57
D1	12				55			34							0.59
E	15	27		38		19									0.73
G	14	72					14								0.32
H		63				16		21							0.22
I	25				25						50				0.19
J	18		34			32	16								0.27
K	50		20						31						0.13
L	48								52						0.31
M	28	16				21	36								0.32
N	34		40									25			0.25

Although the result of EXAFS of fly ashes D1, J, and M contained CP, PbHPO_4 , and/or $\text{Pb}_3(\text{PO}_4)_2$ at 55, 48, and 57%, respectively, the results of the sequential extraction of those showed that the ratio of Fr5 was 19, 4, and 27%, respectively. There was a noticeable division between them. Additionally, the results of the EXAFS fitting disagreed with previous studies.^{9,30}

4.3.3 XAFS analysis of the sequential extraction procedure residues of fly ash A

XAFS analyses were performed on Fr1, Fr2, and Fr3 residues from fly ash A; these are referred to as residues A1, A2, and A3, respectively. The fractions were compared before and after extraction. Although little cadmium was extracted in Fr1, the XANES spectrum in the residue changed from the original fly ash (Fig. 4.3 and 4.4). Cadmium in A1 was represented as $\text{Cd}(\text{OH})_2$ 84% + Cd 16%; the break line on the solid line of measured spectra shows the simulation spectra in Fig. 4.3. Our research group confirmed that reference material CdCl_2 had leached almost entirely in Fr1 during the sequential extraction procedure.²⁸ However, little was fractionated to Fr1. On the basis of XANES results of A1, it was assumed that CdCl_2 in fly ash A once leached but precipitated again as $\text{Cd}(\text{OH})_2$ due to the highly alkaline conditions. This is also suggested by the fact that the ratios in Fr1 of fly ashes D2 and H were high, which were neutral in Fr1. Because a large part was extracted in Fr2, the chemical states of the residue varied greatly before and after Fr2 extraction; cadmium in A2 was represented as CdSiO_3 67% + CdCO_3 33%.

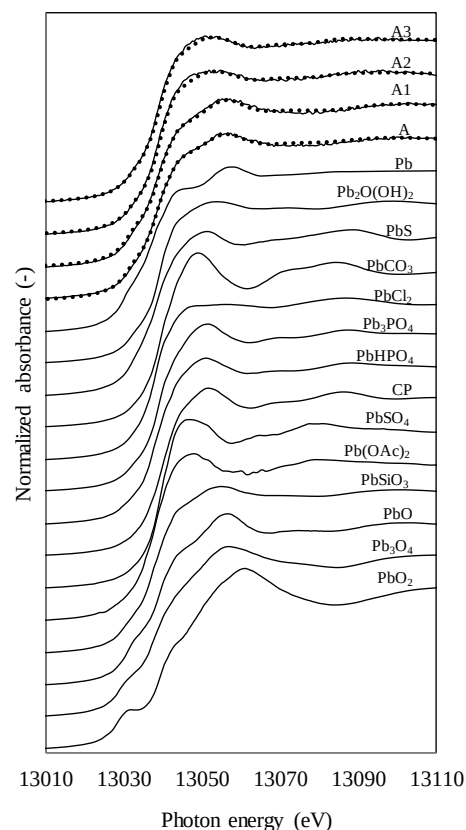


Fig. 4.7 Lead L3 edge XANES spectra of reference materials, sample and residue of sequential extraction procedure (solid lines). Broken lines overlapped on solid lines show simulation spectra.

The lead XANES spectra of fly ash A and the residues of the sequential extraction procedure are shown in Fig. 4.7. As mentioned above, the XANES spectrum of fly ash A was similar to that of PbO or PbSiO₃. A1 was roughly similar to A, but the spectral shape of A1 was more linear in the 13,040–13,054 eV range than that of A. A2 was similar to Pb₂O(OH)₂. The absorption edge peak position of A3 did not differ much from that of A2, but the spectral shape was more distinctive. Table 4.8 gives the results of XANES fittings of synthesized spectra of known references along with the residues of the sequential extraction procedure; the ratios of chemical species when the lead contained in A is normalized to 100% are given in parentheses. For example, 40% was extracted from fly ash A in Fr1, with a total ratio of A1 of 60% (100% – 40% = 60%); thus, the total ratio of chemical species contained in A1 is 60% (60% = 28% + 16% + 9% + 7%). Synthesized spectra are shown in Fig. 4.7 as dashed lines on the XANES spectra of residues obtained from the sequential extraction procedure. The *R* values calculated for all fly ashes were ≤ 0.009, indicating satisfactory fits. These results suggest that most PbCl₂ and a portion of PbO and PbSiO₃, were dissolved in Fr1, and are subsequently partially re-precipitated as hydroxide. Our research group has confirmed that both PbSiO₃ and PbO dissolve under alkaline conditions. The ratio of hydroxide

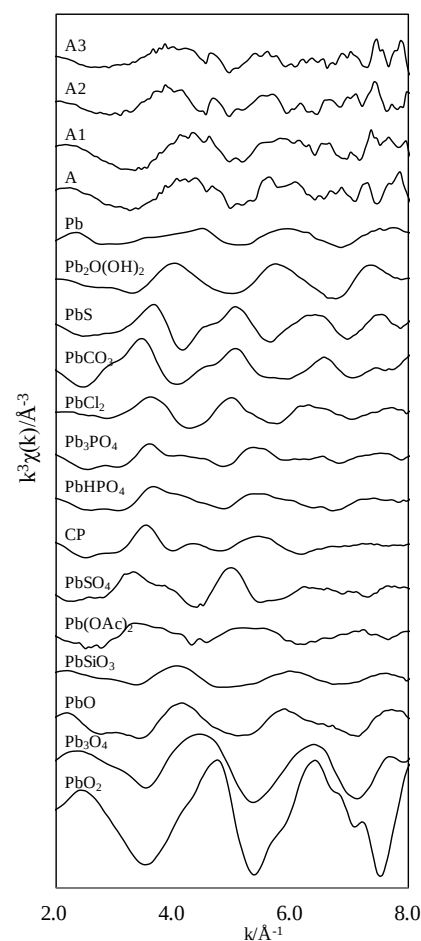


Fig. 4.8 k^3 -weighted lead EXAFS spectra of reference materials, fly ash A and residues of sequential extraction procedure.

Table 4.8 Results of lead XANES fitting of synthesized spectra of known references with residues of the sequential extraction procedure (%).

sample	R	PbSiO ₃	PbCl ₂	PbO	Pb	Pb ₂ O(OH) ₂	CP	PbS
A	0.009	48	17	21	15			
A1	0.009	47 (28)		26 (16)	15 (9)	12 (7)		
A2	0.008					73 (44)		27 (16)
	0.009 *1				15 (9)	58 (35)	27 (16)	
	0.008					58 (24)	8 (3)	34 (14)
A3	0.009 *1				19 (8)	40 (16)	39 (17)	

The value in parenthesis are rate when the lead contained in A is made into 100 %.

*1: Fitting analysis for XANES is carried out without using PbS as reference data.

in A2 was greater than that in A1. This result is not reasonable, given that the product contains PbS, which cannot be generated by re-precipitation. When PbS was excluded from the spectral fitting of A2, CP made up 27% of A2 (16% when the lead level in A was normalized to 100%). When PbS was excluded from a spectral fitting of A3, CP comprised 27% of A3 (17% when the lead level in A was normalized to 100%). In past work,³⁵ which aimed to stabilize heavy metals in MSWI bottom ash using soluble phosphate, XPS revealed that lead in bottom ash formed CP.

Figure 4.8 shows the k^3 -weighted EXAFS spectra of residues obtained from the sequential extraction procedure. Both the XANES spectra and the EXAFS spectra of A1 and A2 changed despite little extraction in the sequential extraction procedure, suggesting that dissolved species re-precipitated in Fr2.

4.3.4 Results of chemical equilibrium model calculations

Chemical states within the extract solutions in the sequential extraction procedure were estimated using chemical equilibrium model calculations. First, the chemical states of cadmium were calculated. Input conditions in Fr1 were based on the experimental results: the elemental concentrations in the extracted solution and XANES LCF results. Because cadmium in fly ash A existed chiefly as CdCl_2 , based on the results of the LCF, 0.32 mmol L^{-1} (36 mg L^{-1}) CdCl_2 was added to the conditions. Under these conditions, it was assumed that chlorine and sulfur, given as sulfate, could be dissolved at least once into solution. Table 4.9 shows the conditions in Fr1. The pH was set as a fixed value, ranging from 0.0 to 14.0 at 0.5 intervals. Oversaturated solutions were allowed to precipitate. Figure 4.9 shows the results of a chemical equilibrium model

Table 4.9 Condition of component concentration in Fr1.

Element	Concentration
Al^{3+}	16 mg L^{-1}
Ca^{2+}	13000 mg L^{-1}
Cd^{2+}	42 mg L^{-1}
Cu^{2+}	27 mg L^{-1}
Fe^{3+}	2.0 mg L^{-1}
K^{+}	110 mg L^{-1}
Mg^{2+}	1.2 mg L^{-1}
Na^{+}	220 mg L^{-1}
PO_4^{3-}	1.3 mg L^{-1}
Pb^{2+}	5.3 mg L^{-1}
Zn^{2+}	1000 mg L^{-1}
SO_4^{2-}	1100 mg L^{-1}
$\text{Cd}(\text{OH})_2$	0.51 mmol L^{-1} ($\text{Cd}:57 \text{ mg L}^{-1}$)

calculation. Cadmium was precipitated predominantly as $\text{Cd}(\text{OH})_2$ within the pH range of 11.5–14.0 and as $\text{Cd}_4(\text{OH})_6\text{SO}_4$ within the range of 10.0–11.0. Within the range of 9.5 and below, CdCl^+ , $\text{CdCl}(\text{aq})$, and Cd^{2+} were present, besides $\text{Cd}_4(\text{OH})_6\text{SO}_4$. Cadmium was totally dissolved at $\text{pH} < 8.5$, appearing in definite proportions of CdCl^+ 49%, $\text{CdCl}(\text{aq})$ 48%, and Cd^{2+} 3%. These

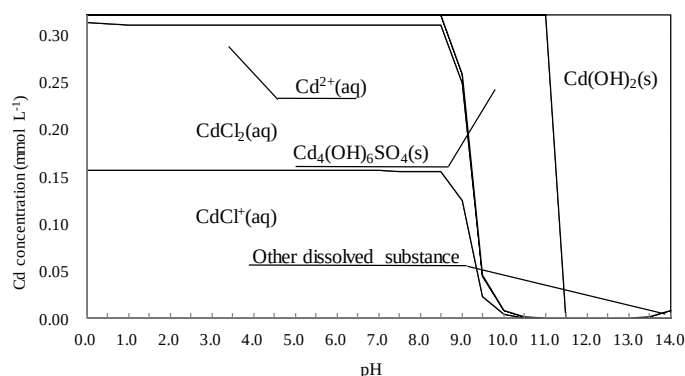


Fig. 4.9 The result of Visual MINTEQ modeling in Fr1.

results agreed with the tendencies of the sequential extraction procedure and the pH-dependent leaching test, which is presented in Fig. 4.13 below. That is, in the calculation results, cadmium precipitated at $\text{pH} \geq 10.0$ and the leaching ratios increased with a reduction in pH value, as with the experimental results. The results of the calculation at pH 12.0 were consistent with the XANES LCF results, that was CdCl_2 dissolved entirely and was then precipitated as $\text{Cd}(\text{OH})_2$.

Input conditions for Fr2 were based on the experimental results, as mentioned above (Table 4.10). The calculations were conducted in two ways. First, the ammonium acetate concentration was changed from 0.0 to 3.0 mol L^{-1} , setting the pH value to 9.6, the condition of Fr2. Second, the pH value was changed from 0.0 to 14.0, setting the ammonium acetate concentration to 1.0 mol L^{-1} , the condition of Fr2. Because cadmium existed as $\text{Cd}(\text{OH})_2$, 0.51 mmol L^{-1} (57 mg L^{-1}) $\text{Cd}(\text{OH})_2$ was added. As above, oversaturated solutions were allowed to precipitate. Figure 4.10 shows the results of the first case, when the pH value was set to 9.6. When the ammonium acetate concentration was 0.0 mol L^{-1} , cadmium existed as a $\text{Cd}_4(\text{OH})_6\text{SO}_4$ precipitate. However, with concentrations $> 0.1 \text{ mol L}^{-1}$, ammine complexes of $\text{Cd}(\text{NH}_3)_4^{2+}$, $\text{Cd}(\text{NH}_3)_3^{2+}$, $\text{Cd}(\text{NH}_3)_2^{2+}$, and CdNH_3^{2+} existed apart from the $\text{Cd}_4(\text{OH})_6\text{SO}_4$ precipitate. At an ammonium acetate concentration of $\geq 0.25 \text{ mol L}^{-1}$, $\text{Cd}_4(\text{OH})_6\text{SO}_4$ disappeared and the

Table 4.10 Condition of component concentration in Fr2.

Element	Concentration
Al^{3+}	16 mg L^{-1}
Ca^{2+}	13000 mg L^{-1}
Cd^{2+}	42 mg L^{-1}
Cu^{2+}	27 mg L^{-1}
Fe^{3+}	2.0 mg L^{-1}
K^+	110 mg L^{-1}
Mg^{2+}	1.2 mg L^{-1}
Na^+	220 mg L^{-1}
PO_4^{3-}	1.3 mg L^{-1}
Pb^{2+}	5.3 mg L^{-1}
Zn^{2+}	1000 mg L^{-1}
SO_4^{2-}	1100 mg L^{-1}
$\text{Cd}(\text{OH})_2$	0.51 mmol L^{-1} ($\text{Cd}:57 \text{ mg L}^{-1}$)

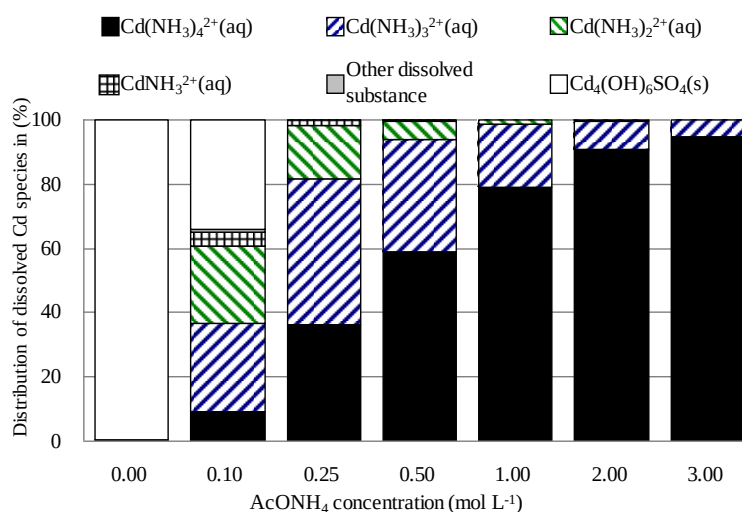


Fig. 4.10 Leaching diagram of Cd in Fr2 (pH9.6).

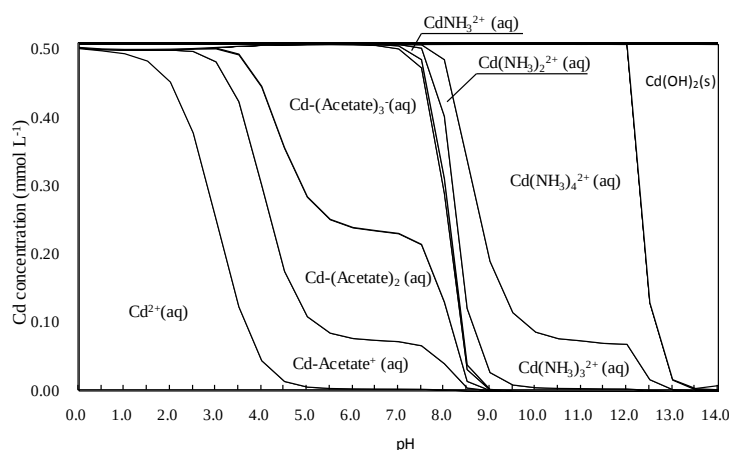


Fig. 4.11 Leaching diagram of Cd in Fr2 (AcONH_4 : 1.0M).

$\text{Cd}(\text{NH}_3)_4^{2+}$ ratio increased with higher ammonium acetate concentrations: 79% at 1.0 mol L^{-1} and 95% at 3.0 mol L^{-1} existed as $\text{Cd}(\text{NH}_3)_4^{2+}$. In the XANES results, although $\text{Cd}(\text{OH})_2$ was the main chemical species in the Fr1 residue, $\text{Cd}(\text{OH})_2$ disappeared in the Fr2 residue; this result agreed with the calculation results, above. Moreover, the acetic acid complex showed a small proportion compared with the ammine complex. Figure 4.11 shows the results of the second case, when the ammonium acetate concentration was set to 1.0 mol L^{-1} . At $\text{pH} \geq 8.0$, cadmium existed as an ammine complex. At $\text{pH} \leq 8.0$, acetic acid complex, or Cd-acetate^+ , $\text{Cd}(\text{acetate})_2(\text{aq})$, and $\text{Cd}(\text{acetate})_3^-$, became predominant. At $\text{pH} \leq 5.0$, the ratio of Cd^{2+} increased with decreasing pH value; cadmium existed almost as Cd^{2+} at pH 0.0. Considering the results of the calculation and the XAFS LCF together, it was found that CdCl_2 contained in fly ash A changed into $\text{Cd}(\text{OH})_2$ in Fr1 and the $\text{Cd}(\text{OH})_2$ dissolved in Fr2, when dissolved cadmium existed predominately as $\text{Cd}(\text{NH}_3)_4^{2+}$.

Table 4.11 Component concentrations input into Visual MINTEQ (mg L^{-1})

Component	Concentration
Al^{3+}	16
Ca^{2+}	13000
Cd^{2+}	42
Cl^-	380
Cu^{2+}	27
Fe^{3+}	2.0
K^+	110
Mg^{2+}	1.2
Na^+	220
Zn^{2+}	1000
SO_4^{2-}	2200
CH_3COO^-	59000
NH_4^+	18000
Pb^{2+}	520
PO_4^{3-}	1200

Next, the chemical states of lead were calculated. The results of the XANES fitting and the sequential extraction of fly ash A suggested that CP was formed by re-precipitation in Fr2. To confirm this, the chemical species in A2 were estimated using a chemical equilibrium model. The input conditions were based on the component concentrations in Fr2. Under these conditions, it was assumed that all phosphorus (P) existed as PO_4^{3-} , and could be dissolved at least once into solution in Fr2. Thus, all of the P contained in the Fr1 residue was used in the calculation (PO_4^{3-} , $1,200 \text{ mg L}^{-1}$). Additionally, all of the PbSiO_3 , PbO , and $\text{Pb}_2\text{O}(\text{OH})_2$ contained in the Fr1 residue was also used to calculate the composition (Pb^{2+} , 520 mg L^{-1}), because it was assumed that these chemical species could precipitate with PO_4^{3-} , based on the results of the XANES fittings of A1 and A2 (Table 4.8). Cl^- and SO_4^{2-} within the extract solution were measured using ion chromatography (IC; DIONEX, ICS-3000). Table 4.11 gives the input conditions. The pH was entered as a fixed value, ranging from 0.0 to 14.0.

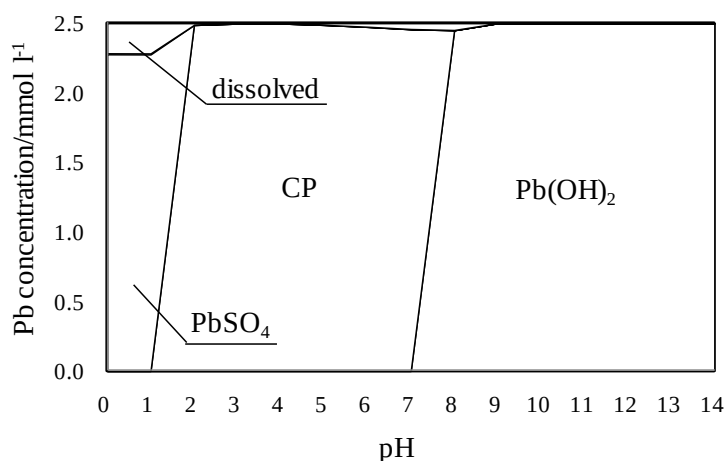


Fig. 4.12 Leaching diagram of Pb in Fr2.

Oversaturated solutions were allowed to precipitate. Figure 4.12 shows the results of a chemical equilibrium model simulation. Within the pH range of 2.0 to 7.0, lead existed primarily as CP, suggesting that it is precipitated as CP at a neutral pH, in agreement with simulations in previous studies.^{14,20} Moreover, CP could show extraction selectivity in Fr5 (This is shown in the Fig. 4.14 below); 11% was extracted in Fr5 in the sequential extraction procedure (Fig. 4.2). A XANES fitting produced a ratio of CP in A3 of 17% (Table 4.8), which did not completely agree with the result of the sequential extraction procedure; however, this makes sense if it is assumed that CP, which was not originally contained in fly ash A, could have formed by re-precipitation.

4.4 Result of pH-dependent leaching test on cadmium in fly ash

In order to confirm the effect of the ammine complex in Fr2, pH-dependent leaching test was carried out. Figure 4.13 shows the results of the pH-dependent leaching test. The leaching ratios were less than 6% at pH 9.0 in all samples. At pH 7.0 or less, the ratios increased with a decrease in pH value. In the range of pH 1.0–5.0, the ratios were nearly flat. There was little difference among the fly ashes with regard to the leaching trend with pH.

In the results of the sequential extraction procedure, the cadmium ratios in Fr2 ranged from 24% to 83%; there were significant differences among the samples. However, in the results of the pH-dependent leaching test, the ratios of all samples were less than 5% at pH 9.0; there was little difference among them. Cadmium might be dissolved in solution via ammine complex formation (such as CdNH_3^{2+} , $\text{Cd}(\text{NH}_3)_2^{2+}$, $\text{Cd}(\text{NH}_3)_3^{2+}$ and $\text{Cd}(\text{NH}_3)_4^{2+}$) with ammonium acetate. Thus, it was assumed that cadmium leached, to some degree, at pH in Fr2. The chemical states in Fr2, such as ammine complexes, are discussed above in 4.3.3 (chemical equilibrium model calculations). Additionally, due to the significant differences among leaching ratios in Fr2, it was assumed that the residues of Fr1 differed in chemical states among the samples.

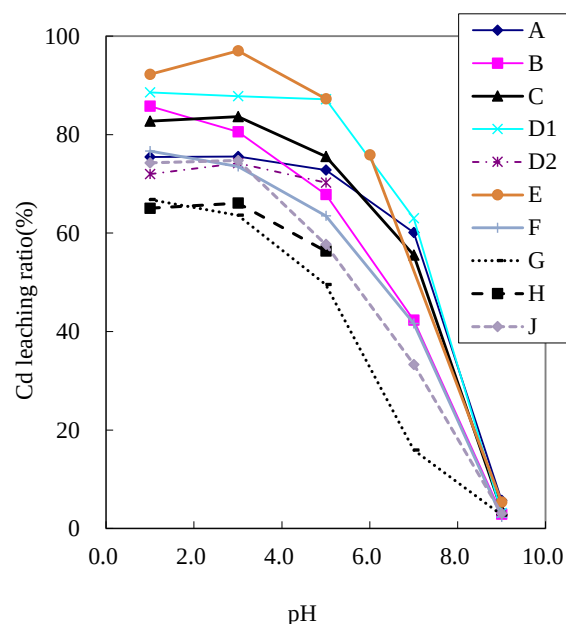


Fig. 4.13 The result of pH dependent test.

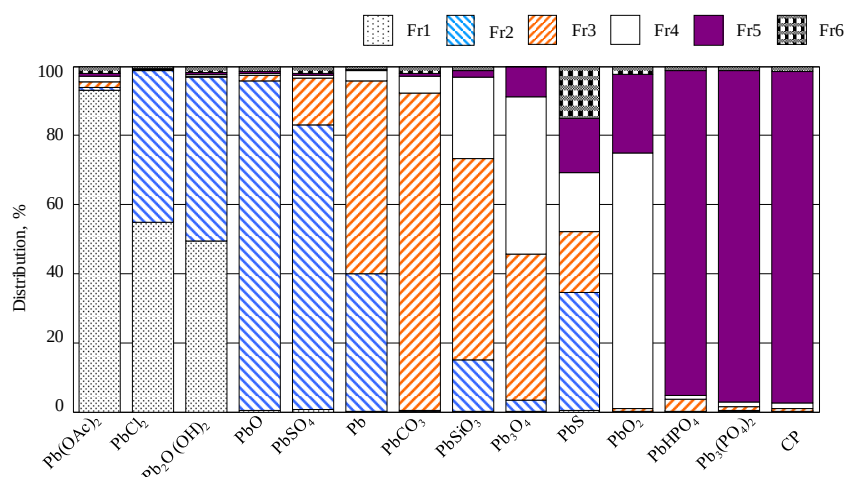


Fig. 4.14 Lead distributions of reference materials by sequential extraction procedure.

Table 4.12 pH value at each step of sequential extraction procedure for reference materials.

	Pb(OAc) ₂	PbCl ₂	Pb ₂ O(OH) ₂	PbO	PbSO ₄	Pb	PbCO ₃	PbSiO ₃	Pb ₃ O ₄	PbS	PbO ₂	PbHPO ₄	Pb ₃ (PO ₄) ₂	CP
Water	6.1	4.9	6.8	10.0	7.0	10.5	6.8	8.3	6.6	7.0	8.3	4.1	4.1	6.9
NH ₄ OAc	7.1	7.1	7.3	8.1	7.1	8.2	7.8	7.7	7.3	7.2	7.1	7.0	6.7	7.8
Acid Soluble	5.0	5.0	5.1	5.1	5.1	5.1	5.3	5.4	5.3	5.1	5.0	5.3	5.3	5.2
Reducible	1.8	1.9	1.9	2.0	1.9	1.9	2.0	2.0	2.3	2.0	2.1	1.9	1.9	1.8
Oxidisable	0.3	0.3	0.3	0.4	0.4	0.3	0.2	0.3	0.5	0.3	0.3	0.2	0.3	0.4
Residual	-	-	-	-	-	-	-	-	-	-	-	-	-	-

4.5 Extraction behavior of lead contained in fly ash

4.5.1 Sequential extraction procedure for the references materials

The results of the sequential extraction procedure for the known lead reference materials and the pH of the extract solutions are shown in Fig. 4.14 and Table 4.12, respectively. More than 90% of all Pb(OAc)₂, PbO, PbHPO₄, Pb₃(PO₄)₂, and CP were extracted in one fraction in the sequential extraction procedures. Thus, these lead species were estimated to have high extraction selectivity in each fraction in the sequential extraction procedure. However, the other lead species was extracted in three or more fractions. For example, as the lead in fly ash was extracted in two fractions, Fr1 and Fr2, it is suggested that there are four or fewer lead species: (Pb(OAc)₂, PbCl₂, Pb₂O(OH)₂, or PbO) (Fig. 4.14). The lead in fly ash was extracted in three or more fractions; none was extracted in one or two fractions, as shown in Fig. 4.2. Consequently, it was difficult to estimate the ratio of the lead species based on the fraction ratios obtained from the sequential extraction procedure.

4.5.2 Influence of phosphorus concentration on lead extraction of Fr5

Based on the high extraction selectivity of CP in Fr5, as well as the possibility that CP formed by re-precipitation, the impact of P concentration on the extraction of Fr5 was estimated. Two points in particular were noted: first, calcium could also form hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$) with PO_4^{3-} , based on the results of the chemical equilibrium model, and, second, what was extracted in Fr6 (after Fr5) did not influence re-precipitation before Fr5. There was a strong correlation (correlation coefficient = 0.86) between the ratio of P to Ca concentrations and the ratio of Fr5 to Fr1–5 (Fig. 4.15).

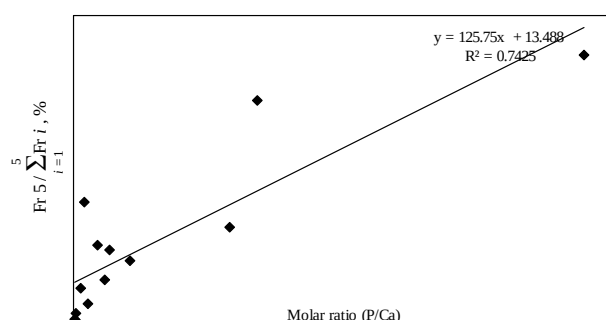


Fig. 4.15 Relation between rate of P to Ca in sample and rate of Fr5 to the sum total from Fr1 to Fr5 obtained from sequential extraction procedure. ($y = 126x + 13$, correlation coefficient $r = 0.86$).

4.5.3 Cluster analysis of the results of lead chemical state analysis

The results of a cluster analysis of lead fraction ratios obtained by the sequential extraction procedure are shown as a dendrogram (Fig. 4.16). Three clusters were obtained: X1 (A, I, K, and L), X2 (B, C, D1, E, G, and J), and X3 (H, M, and N). The relationships between these clusters and the specifications of samples are compared in Table 4.1. Except for fly ash A, the fly ashes in cluster X1 were molten fly ashes, formed from a melting process of bottom ash or fly ash; their Fr1 and Fr4 fraction ratios were high. Except for fly ash J, the fly ashes in cluster X2

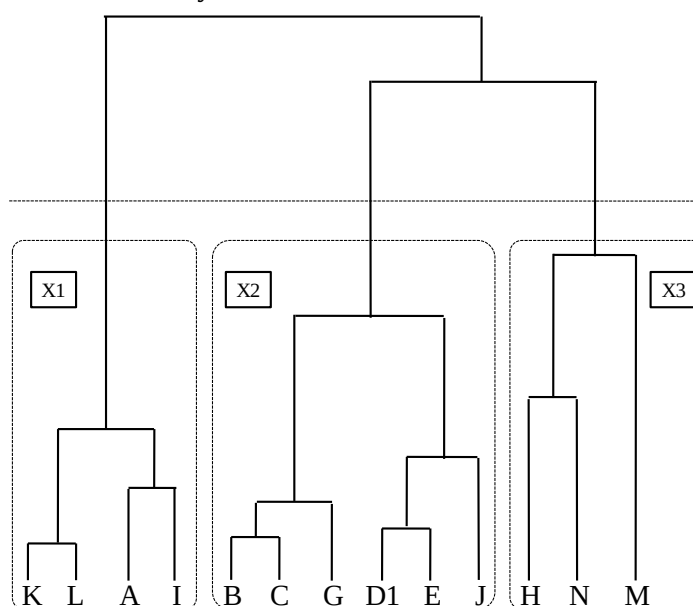


Fig. 4.16 Dendrogram based on the result of lead sequential extraction procedure.

were MSWI fly ashes with high Fr3 and Fr4 fraction ratios. The fly ashes in cluster X3 comprised molten fly ashes with high fraction ratios of Fr5 and Fr6. These results show that fly ashes classified as X1 eluted readily, those classified as X2 were eluted somewhat, and X3 fly ashes were hardly eluted at all. Thus, it was assumed that the results of the sequential extraction procedure were related to the manner in which the different fly ashes were produced. However, while it was expected that differences in the flue gas treatment systems (lime and activated carbon) would influence the results of the sequential extraction procedure, cluster analysis revealed no clear tendency as to the flue gas treatment systems. Table 4.4 along with Fig. 4.16 show that X1 fly ashes had high pH values in Fr1, from 12.0 to 12.4, and, with the exception of B, X2 fly ashes had pH values of 9.6 to 11.8 in Fr1. Thus, it was assumed that the results of the sequential extraction procedure were greatly influenced by the pH.

The results of a cluster analysis of the XANES fitting are shown in a dendrogram (Fig. 4.17). Three clusters were obtained: clusters Y1 (A, B, D1, E, I, K, and L), Y2 (C, J, M, and N), and Y3 (G and H). Y1, Y2, and Y3 consisted primarily of PbSiO_3 , $\text{Pb}_2\text{O}(\text{OH})_2$, and PbCl_2 , respectively. These classifications obtained from the XANES fitting are dissimilar to those obtained from the sequential extraction procedure, and do not appear to be related to the origins of the fly ash. As mentioned previously, it was assumed that the results of the sequential extraction procedure were more influenced by the pH than by the chemical species.

The results of a cluster analysis of the EXAFS fitting are shown in a dendrogram (Fig. 4.18). Two clusters

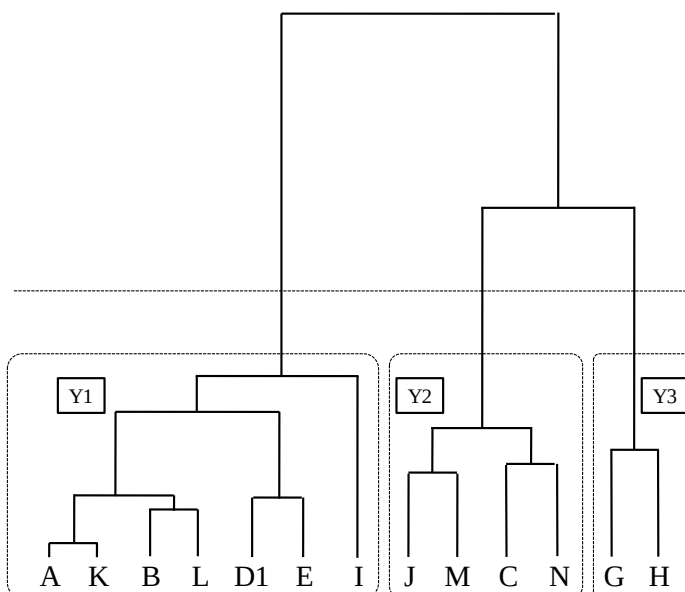


Fig. 4.17 Dendrogram based on the result of lead XANES fitting.

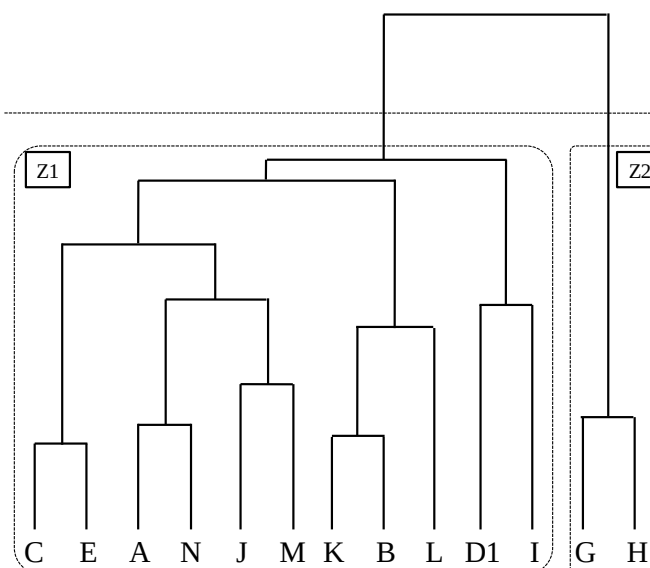


Fig. 4.18 Dendrogram based on the result of lead EXAFS fitting.

were obtained: clusters Z1 (A– E and I–N) and Z2 (G and H). In the classification of EXAFS fitting and XANES fitting, cluster Z2 had the same members as cluster Y3 (fly ashes G and H), and fly ashes belonging to Z1 could not be classified more fully. Thus, it was difficult to examine quantitatively the chemical species using only EXAFS, and the quality of EXAFS spectra should be improved.

4.5.4 Comparison of analysis methods for lead in fly ash

The results of the sequential extraction procedure were more influenced by the pH than by the chemical species of lead. In this procedure, the chemical species of lead in fly ash may be estimated, as described below:

[Fr1] Both PbCl_2 and $\text{Pb}_2\text{O}(\text{OH})_2$ are dissolved. Under highly alkaline conditions, PbSiO_3 , PbO , and a proportion of Pb also dissolve, and re-precipitate, partially as hydroxide. Under slightly alkaline or neutral conditions, most of the dissolved lead re-precipitates as hydroxide.

[Fr2 and Fr3] Pb, $\text{Pb}_2\text{O}(\text{OH})_2$, PbCO_3 , PbO , and a proportion of PbS dissolve. When the ratio of P to Ca contained in the fly ash is high, a proportion of lead re-precipitates as CP.

[Fr4] All residual PbSiO_3 and a proportion of PbS dissolve.

[Fr5] All residual PbS and re-precipitated CP dissolve.

Based on the results of the sequential extraction procedure (Fig. 4.14), a proportion of PbS is assumed to correspond to Fr6, which is not necessarily consistent with the XANES fitting of fly ash M (Table 4.6).

In comparing the three methods (the sequential extraction procedure, XANES analysis, and EXAFS analysis) for lead chemical state analysis, it is difficult to quantify the chemical species using the sequential extraction procedure, due to re-precipitation that occurs because of the fly ash characteristics (*e.g.*, pH and concentrations of P and Ca). Thus, it is difficult to obtain accurate information reflecting the chemical species in fly ash using the sequential extraction procedure alone. However, this method can be used to estimate the mobility potential of lead contained in fly ash. The EXAFS spectra were found to be quite noisy. The shape of the EXAFS spectra could be used to roughly identify the chemical species; however, it was difficult to quantify these species. In using EXAFS analysis to quantify fly ash, the data measurement range maximum was 13,460 eV, because the absorption edge of bromine appears after that of lead, causing interference. Consequently, it is difficult to quantitatively examine lead chemical species using EXAFS, because they exist at trace levels in fly ash. XANES was able to quantify directly the chemical species of lead contained in fly ash, without interference from sample matrices, and was thus the most suitable method.

4.6 Conclusion

In this chapter, the results of our study on the chemical states of heavy metals are presented in which I focused on the means to determine quantitatively cadmium and lead chemical states in fly ashes. The results of the sequential extraction procedure showed two types of cadmium in fly ash depending on whether Fr1 was alkaline or neutral. The major amount was accounted for by Fr2–4 in the former type and by Fr1 in the latter. On the results of the XANES LCF, fly ash and the residue of Fr1 were represented as CdCl_2 94% + Cd 6% and $\text{Cd}(\text{OH})_2$ 84% + Cd 16%, respectively. It is assumed that CdCl_2 in fly ash dissolves and precipitates again as $\text{Cd}(\text{OH})_2$ in Fr1 and the $\text{Cd}(\text{OH})_2$ dissolves in Fr2, if the pH condition of Fr1 is alkaline. However, if the pH condition in Fr1 is neutral, it is presumed that $\text{Cd}(\text{OH})_2$ does not precipitate. Consequently, we may underestimate the hazardousness of cadmium contained in fly ash by the leaching test where the metals are extracted with distilled water, if the fly ash has high basicity. The results of the chemical equilibrium model calculations were consistent with those of the sequential extraction procedure, the pH-dependent leaching test, and the XANES LCF.

Of the three methods (the sequential extraction procedure, XANES analysis, and EXAFS analysis), it was found that the results of the sequential extraction procedure were related to the material process (ash or municipal solid waste) and the processing system, and thus did not reflect the chemical species in fly ash due to the influences of the pH and the sample matrix. It is also difficult to quantify the lead chemical species in fly ash using EXAFS alone. The XANES method enabled the greatest degree of quantification of lead chemical species in fly ash. XANES analysis showed that lead in fly ash is mainly in the form of PbSiO_3 , PbCl_2 , or $\text{Pb}_2\text{O}(\text{OH})_2$. The present study shows that the results of multiple analyses should be examined to improve the accuracy of the final analysis. Additionally, it is important to ascertain whether a computational approach, such as the chemical equilibrium model simulation, is consistent with the analytical approach.

On the basis of XAFS, it was found that cadmium and lead contained in the fly ash were mainly in chemical forms easy to dissolve. In the sequential extraction procedure, depending on the pH, these were not necessarily fractionated into Fr1, or re-precipitated into the forms difficult to dissolve. Considering re-precipitation, it is possible to evaluate chemical forms easy to dissolve, such as CdCl_2 and PbCl_2 , by extraction in Fr1–Fr3. In other words, the sequential extraction procedure is a method to estimate easily eluting chemical state of trace elements in fly ash. However, when extracted in three or more fractions, it is difficult to estimate the chemical status. On the other hand, by XAFS, especially XANES, it was possible to directly and quantitatively analyze the chemical forms. From the above, in order to evaluate the hazardousness of heavy metals, it is not necessarily enough to evaluate by sequential extraction procedure or leaching test

with distilled water, and necessary to directly and quantitatively analyze the chemical state by XAFS in case of illegal dumping of industrial waste. Assuming to testify at trial, analysis by XAFS should be conducted. In evaluating the leachability of the heavy metals, it is effective to compare the results of the sequential extraction procedure and pH dependent leaching test with the results of XAFS.

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Chapter 5 Chemical States of Arsenic Contained in Sewage Sludge Incineration Ash and Insolubilized Material

5.1 Introduction

In Japan, the abundance of sewage sludge is increasing yearly, along with the popularization of swage. In 2014, the generation amount of sewage sludge was 2.34 million t/year by dry weight.¹ In 2010, recycle ratio of the sewage sludge increased to 78%, for the shortage of the final disposal site, and switch to the efficient use. Though the ratio decreased to 55% because of the landfill disposal of the sewage sludge contaminated by radioactive material due to the great east Japan earthquake in 2011, 63% of sludge was recycled in 2014.¹ In 2014, 1.02 million tons of the sludge were recycled as building materials, and 360 thousand tons were recycled for green farmland. It is expected that the sludge will be recycled more than in 2010.

In recycle of sewage sludge incineration ash, the recycled materials must comply with the raw related to applications. When the recycled materials are used for building materials or soil conditioners, the elution and content of hazardous metals must satisfy the environmental quality standards for soil contamination. However, the elution of hazardous metals including arsenic occasionally exceeds the standards. For this reason, the effective utilizations of the recycled materials are prevented. In the environment, arsenic is often included at several to several 10 ppm in the geology. The arsenic groundwater contaminations occur in many regions of the world such as India and Bangladesh.^{2,3} Recently, ashes are treated with chemical agents for harmful metals insolubilization in local municipality. Typical agents for insolubilization are calcium hydroxide and iron sulfate. It is assumed that arsenic forms calcium salts with calcium hydroxide treatment. In past study, it was reported that the ashes treated with calcium hydroxide can meet the environmental standards in the leaching test (Japan environment agency notification No. 46: JLT-46).⁴⁻⁶ However, even if the standards are satisfied in JLT-46 in which pure water adjusted to neutral is used as extraction solvent, effects of acid rain exposure and stability of long-term storage are uncertain. Additionally, it was reported that the treatment with ferrous sulfate can satisfy the standards in JLT-46, but heavy metals eluted with time.⁴ It is important to understand the chemical states of arsenic in order to store the treated material safely, as the behavior or mobility of arsenic in the environment depends on its chemical state. From the above, understanding the arsenic chemical states of insolubilized materials is needed to make efficient use of the sewage sludge incineration ash as resources in future.

Some problems related to recycle items occurred; heavy metals eluted from recycled soil conditioner in Mie prefecture⁷, and recycled steel slag in Gunma prefecture⁸. These cases were investigated by the Police, and developed into social problems. Based on recent recycling circumstances like Law for the Promotion of Utilization of Recyclable Resources, it is expected that such recycled products will be used in the future. Therefore, we should pay attention to elution of heavy metals from such recycled products. In other words, it is

necessary to consider the analysis method of heavy metals contained in the recycled materials. In addition, arsenic compounds, which can cause problems in recycle of sewage sludge, are noted as poisons used in injury cases by police. There are numerous examples of analysis of arsenic, including Wakayama arsenic curry case.^{9,10} From above, more sophisticated forensic analysis methods for arsenic compounds contained in recycled products will be necessary in the future.

As mentioned in chapter 3, X-ray absorption fine structure (XAFS)¹¹⁻¹⁴ spectroscopy have been used to determine the chemical state of heavy metals in ash. Since arsenic has different strength of toxicity depending on the chemical form, it is important to understand chemical state of arsenic contained in samples. XAFS, which can nondestructively analyze chemical state of arsenic contained in complex matrix, is valuable for forensic science. Besides XAFS technique, ion chromatography inductively coupled plasma mass spectrometry (IC-ICP-MS), which is composed of a combination of ion chromatography with inductively coupled plasma mass spectrometry, is available to understand chemical state of trace level arsenic.^{15,16} This technique enables us analyze arsenic on the order of ng/L in fresh water samples and biological samples, that is below the environmental standards.

In this study, I analyzed the chemical states of arsenic in the sewage sludge incineration ash and the insolubilized materials. In particular, I insolubilized the ashes which was collected from sewage sludge incinerators, by chemical agents. As the chemical agents, I used calcium hydroxide and ferrous sulfate.^{17,18} I conducted the leaching test (JLT-46) for the insolubilized ashes. Additionally, the ashes and the insolubilized materials were analyzed by XAFS analysis. The effluents from JLT-46 were analyzed for valence of arsenic by IC-ICP-MS and were simulated using a chemical equilibrium model calculation program (Visual MINTEQ). Finally, I identified the chemical states of the arsenic.

5.2 Experimental

5.2.1 Samples

Four kinds of sewage sludge incineration ash were collected from two treatment lines (incinerator X and Y) at a plant in operation. Fig. 5.1 shows the process flow of each line and sampling points. I collected sample from bug filter at incinerator X (X-BF and X-BF2). The samples collected from the bug filter and the cyclone separator of the incinerator Y are referred to as Y-BF, Y-CY respectively.

The compositions (from carbon to uranium) of the samples were determined by X-ray fluorescence (XRF; Shimadzu, XRF-1800 and Rigaku, PrimusII) spectroscopy using the Fundamental Parameter method. 5 g of samples were pressed into briquette form in 30 ton at 10 sec, and were measured by XRF.

The trace metals were measured by inductively coupled plasma-mass spectrometry (ICP-MS). 5 mL of nitric acid, 3 mL of hydrofluoric acid, and 2 mL of hydrochloric acid were added to 100 mg of sample, which were allowed stand still for 60 min. Samples were subsequently digested with a microwave digestion system (CEM Japan, MARS5, 1.2 MPa, 190 °C). A saturated boric acid solution (18 ml) was then added to the solution, which was heated with the microwave digestion system (690 kPa, 170°C). The supernatant was filtered with a 0.2-μm pore membrane filter. The filtrate solution was diluted to 100 mL with 1.0 mol L⁻¹ HNO₃. The solution was then measured by ICP-MS (Yokogawa Analytical Systems, HP4500 or Thermo Scientific, X Series2 Xt).

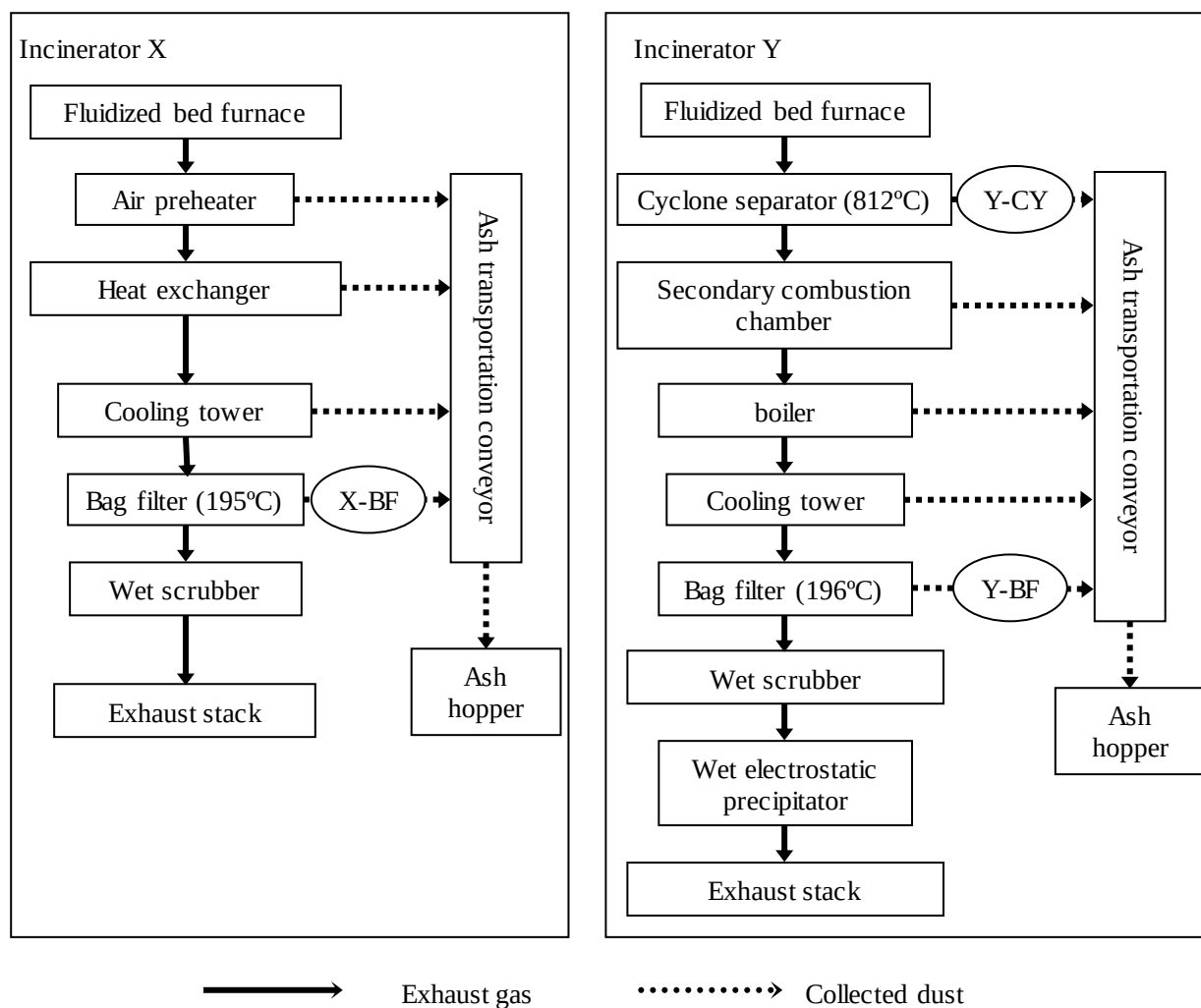


Fig. 5.1 Process flows and sampling points (incinerators X and Y).

5.2.2 Insolubilization treatment

As insolubilization technique, I selected the treatment with the calcium hydroxide and ferrous sulfate, which were conventional and inexpensive. In these, the chemical agents are mixed with the samples, and I do not need to heat the samples.

5.2.2.1 Calcium Hydroxide

I added the calcium hydroxide to the samples to insolubilize the arsenic. In this technique, heavy metals of the samples are insolubilized by being adjusted to an alkalinity with calcium hydroxide. In past study^{17,18}, the insolubilized ashes, which originally exceed the environmental standards in JLT-46, satisfy the standards by the process of calcium hydroxide. Powdered calcium hydroxide (0.5% or 1.0%) was mixed into 20 g of sample with a pestle and mortar for 10 min. Additionally, the samples put in polypropylene bottle were horizontally shaken (200 round/min, 1 h) in shaking apparatus.

5.2.2.2 Ferrous Sulfate

I mixed the ferrous sulfate solution into the samples to insolubilize the arsenic.¹⁹ In this technique, it is expected that arsenic is insolubilized by co-precipitation along with iron hydroxide or adsorption onto iron compounds. In the past study¹⁷, the insolubilized ashes, satisfy the standards by the process of ferrous sulfate as well as calcium hydroxide. The solution (0.3, 1.0 or 5.0% as ferrous sulfate anhydride) was mixed into 20 g of sample with a pestle and mortar for 10 min. Additionally, the samples put in polypropylene bottle were horizontally shaken (200 round/ min, 1 h) in shaking apparatus.

5.2.3 A leaching test JLT-46 (Japan environment agency notification No. 46)

In this study, the arsenic eluting was estimated by JLT-46. The samples must pass through a 2 mm screen in JLT-46. Because more than 2 mm particle does not obviously exist in the samples, sieving operation omitted

To 5 g of samples, 50 mL of the solvent (pure water whose pH is adjusted pH 5.8 to 6.3 with hydrochloric acid) was added. The solution was put in 100 mL polypropylene bottle and shaken (200 round min⁻¹, 6 h) in shaking apparatus. Though sample amount is regulated more than 50 g in the JLT-46, I used 5 g of samples for each experiment because of limit of the samples. After shaking, the solution is allowed to set still for 15 min. The solution was filtered with a 0.2 μm pore membrane filter. The filtrate solution was then measured by ICP-MS.

X-BF2 is analyzed by IC (Shimadzu, HIC-20A SUPER) and IC-ICP-MS (ICP-MS; PerkinElmer, NexION 300D, IC; PerkinElmer, Flexa) for a chemical equilibrium model calculation mentioned below. Table 5.1 shows the analysis conditions of IC-ICP-MS.¹⁵ The lower limit of quantifications of both As(III) and As(V) were 2.0 $\mu\text{g L}^{-1}$.

5.2.4 XAFS experiments

XAFS measurements were performed on beam line 01B1 of SPring-8 (Hyogo, Japan) and beam line 12c of Photon Factory (Ibaraki, Japan).

Spectra were recorded in fluorescence mode using 19 elements solid state detector for samples and in

transmission mode using an ionization chamber for reference materials (As_2O_3 and As_2O_5).^{13,14} The energy steps were set to 5 eV (11,710-11,835 eV), 0.3 eV (11,835-11,930 eV), 2 eV (11,930-12,400 eV).

The XANES regions of samples were analyzed. The major species in samples were identified and quantified (mol %) using the linear combination fit (LCF) technique, in which spectra of known reference species were fitted to the spectrum of the unknown sample. The arsenic XANES range was set range 11,850 to 11,890 eV. I conducted the LCF of XANES using the commercial software REX 2000 ver. 2.5.5 (Rigaku, Japan).

5.2.5 A Chemical equilibrium model calculation

Arsenic chemical species within the solution obtained from the JLT-46 were estimated using a chemical equilibrium model calculation. The calculation was conducted using the chemical equilibrium model program Visual MINTEQ ver. 3.0. The default values of Visual MINTEQ ver. 3.0 were used over all parameters, such as the value of log K_{sp} . Input condition details, such as the kind of element, the chemical species, and their concentrations, were based on results of the composition analysis and IC-ICP-MS analysis. It should be noted that the systems come to the equilibrium in the results obtained by the simulations.

5.3 Results and discussion

5.3.1 Characterization of samples

Table 5.2 shows the results of the composition analysis and JLT-46 of X-BF, Y-BF, and Y-CY. Table 5.3 and Table 5.4 show the results of the composition analysis and JLT-46 of X-BF2, respectively.

Table 5.1 Analytical conditions of IC-ICP-MS.

IC	
Column	Shiseido CAPCELL PAK C18 MG II 4.6 mm id × 250 mm, 5 μm
Guard column	Shiseido CAPCELL PAK C18 MG II 4.0 mm id × 10 mm, 5 μm
Mobile phase	10 mmol L ⁻¹ sodium 1-butansulfonate
	4 mmol L ⁻¹ tetramethylammonium hydroxide
	4 mmol L ⁻¹ malonic acid
	0.5% methanol pH 3.0 adjusted with HNO_3
Mode	Isocratic
Runtime	3.5 min
Flow	1.2 mL min ⁻¹
Column temperature	40 °C
Injection volume	50 μL
ICP-MS	
Rfpower	1600 V
Reaction gas	O_2 (99.999%)
Reaction gas flow	0.6 mL min ⁻¹
RPa	0
RPq	0.5
m/Z	90.9165
Pasma gas flow	18 L min ⁻¹
Nebulizer gas flow	1.04 L min ⁻¹
Auxiliary gas flow	1.2 L min ⁻¹
Axial field voltage	475 V
Dwell time per unit	330 ms

Table 5.2 Chemical compositions and JLT-46 results (X-BF, Y-BF, and Y-CY).

Element	X-BF	Y-BF	Y-CY	Method	Unit
C	3.5	2.3	2.5	XRF	mass%
O	49	49	49		
Na	1.2	1.1	1.1		
Mg	1.4	1.5	1.6		
Al	8.0	7.9	8.2		
Si	10	9.8	10		
P	11	11	12		
S	0.64	1.12	0.10		
K	2.1	2.2	2.2		
Ca	3.7	3.9	4.0		
Ti	0.35	0.37	0.37		
Fe	7.2	7.9	7.8		
Zn	0.66	0.79	0.63		
others	1.1	1.0	1.0		
As	58	82	32	ICP-MS	mg kg ⁻¹
As (JLT-46)	1.4	1.7	0.16	ICP-MS	mg L ⁻¹
pH (JLT-46)	5.4	4.2	6.8	-	-

Table 5.3 Chemical compositions of

X-BF2.			
Element	Concentration	Method	Unit
C	4.8	XRF	mass%
O	49		
Na	0.74		
Mg	2.0		
Al	7.0		
Si	12		
P	10		
S	0.43		
K	1.8		
Ca	3.4		
Ti	0.40		
Fe	7.0		
Zn	0.47		
others	1.0		
V	66	ICP-MS	mg kg ⁻¹
Cr	320		
Mn	1300		
Co	46		
Ni	120		
Cu	860		
As	47		
Se	14		
Sr	330		
Mo	32		
Cd	2.2		
Sn	62		
Sb	10		
Cs	5.3		
W	30		
Pb	130		

Table 5.4 JLT-46 results for X-

BF2 (mg L ⁻¹).		
Element	Concentration	Method
Na	140	ICP-MS
Mg	110	
Al	<2	
K	75	
Ca	19	
Ti	<0.76	
V	0.48	
Cr	<0.0022	
Mn	0.69	
Fe	15	
Co	0.04	
Ni	0.048	
Cu	<0.0056	
Zn	<0.44	
Se	0.24	IC-ICP-MS
Sr	0.19	
Mo	1.4	
Cd	<0.0041	
Sn	<0.018	
Sb	0.0044	
Cs	<0.0012	
W	0.041	
Pb	<0.002	
As(III)	0.013	
As(V)	0.25	
F ⁻	0.64	IC
Cl ⁻	47	
NO ₂ ⁻	<0.75	
Br ⁻	3.7	
NO ₃ ⁻	<1.5	
SO ₄ ²⁻	700	
pH	6.8	-

In Table 5.2, the arsenic content of X-BF and Y-BF, which were collected from bug filter, were 2-2.5 times higher than Y-CY. Additionally, the elution amount of X-BF and Y-BF were 10 times higher than Y-CY. It is considered that because arsenic which exists as gas in 800 °C condensed into ash to be cool down to 200°C, the contents of arsenic from bug filter are higher than that from cyclone separator ash. It is also assumed that the arsenic condensed from gas into ash can elute easily because ratio of elution amount increasing is bigger than that of content increasing.

The XANES spectra of sample and reference materials are shown in Fig. 5.2. Every peak top was 11870-11871 eV and the form of spectra was similar to As₂O₅; that indicated that the arsenic in the samples was predominantly pentavalent. In the past XAFS study for sewage sludge incineration ash²⁰, the arsenic existed as As(V), that agreed with results of this study. There was difference between the peak top energy of X-BF and X-BF2 which were collected at different period; the peak top of X-BF2 was approximately 1 eV lower than that of

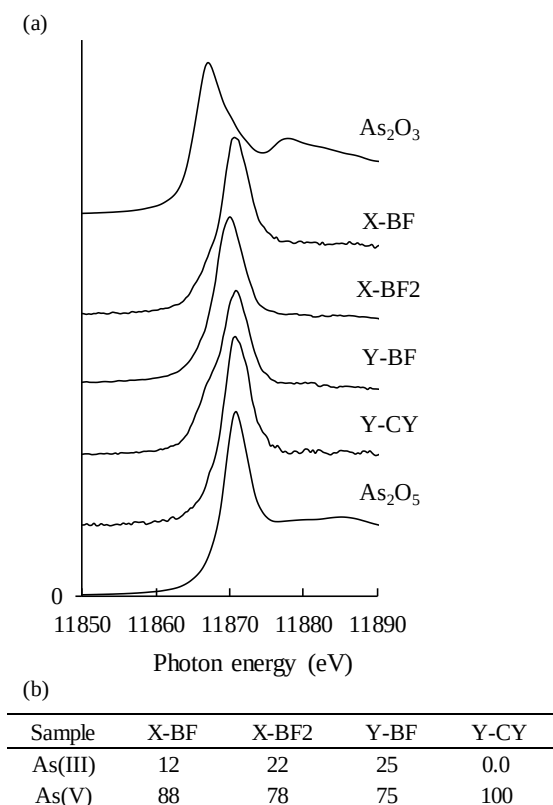


Fig. 5.2 Results of X-ray absorption fine structure spectroscopy (XAFS) analysis. (a) XAFS spectrum of standards and samples. (b) Results of XAFS pattern fitting (%).

X-BF. The spectra of X-BF, X-BF2 and Y-BF had a shoulder on the low energy side, which indicated that a portion of the arsenic was trivalent. In the results of LCF results, actually, As(V) fractions of X-BF, X-BF2, and Y-BF were 88, 78, 75% respectively, though that of Y-CY was 100%. In other words, the ash of the bag filter, which was provided in a rear stage of process contained more As(III) form than that of the cyclone separator, which was provided in a front stage. In the results of X-BF2 IC-ICP-MS, eluting As(V) and As(III) were 0.25mg L⁻¹, 0.013 mg L⁻¹ respectively; 95% of eluting arsenic was As(V).

5.3.2 Insolubilized material

5.3.2.1 Insolubilization with calcium hydroxide

The results of JLT-46 for the insolubilized materials with calcium hydroxide are showed in Fig. 5.3. In Fig. 5.3(b), the relative elution ratios were represented when the elution ratio of original ash was 1, and the ratios were let be 0 under quantitation limit. In the result of X-BF2, the sum of As(III) and As(V), which were measured by IC-ICP-MS, was shown. In Table 5.5, the JLT-46 and the IC-ICP-MS result for the insolubilized material of

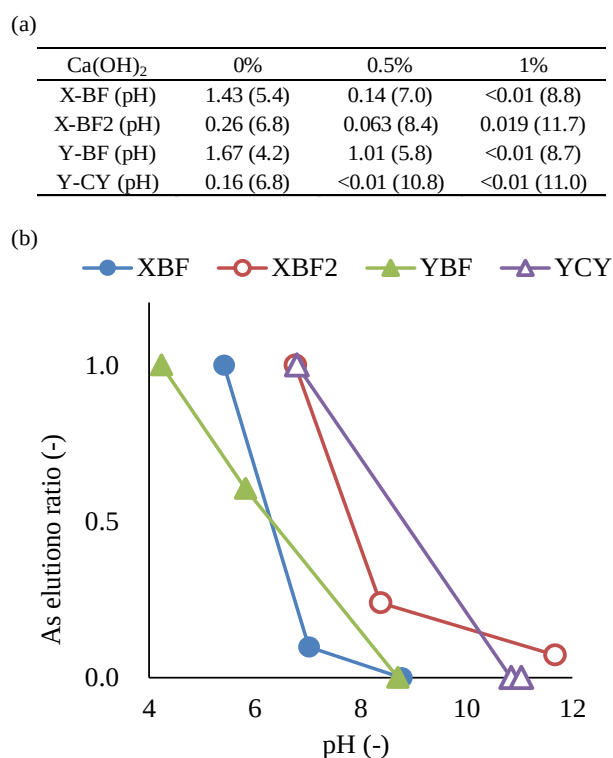


Fig. 5.3 Japan Environment Agency Notification No. 46 (JLT-46) results of samples processed with Ca(OH)₂. (a) JLT-46 results of samples processed with Ca(OH)₂ (mg-As L⁻¹). (b) Relative elution ratios when the elution ratio of the original ash is 1.

X-BF2 by calcium hydroxide are shown.

Y-CY satisfied the environmental standards by 0.5% calcium hydroxide addition, and X-BF and Y-BF satisfied the standards by addition with 1% addition. However, X-BF2 did not satisfy the standards in this study. Between the pH value of these elution and arsenic concentration (Fig. 5.3(b)), the arsenic concentration decreased as the pH increased up to pH 9-10; at pH 10 or higher the concentration became below minimum quantification limit, or did not decrease any more. In the result of IC-ICP-MS (Table 5.5), As(III) concentration was under lower limit of determination (0.002 mg L^{-1}) or less. On the other hand, As(V) was 0.019 mg L^{-1} in the condition of 1% calcium hydroxide, which did not meet the standard. As the samples other than X-BF2 met the standard in the condition of 1% calcium hydroxide, it was assumed that there were differences in samples, which were collected from the same incinerator and the same sampling points, depending on the sampling periods.

Figure 5.4 shows the XANES spectra and the results of LCF for the calcium hydroxide insolubilization materials. Every sample has the peak top at 11,870-11,871 eV and this indicated that the arsenic in the samples was predominantly pentavalent. Additionally, the samples besides Y-CY had a shoulder on the low energy side, which indicated that the arsenic was partially trivalent. In the LCF results (Fig. 5.4(b)), the portion of As(III) and As(V) almost did not change as to X-BF, X-BF2 and X-BF; in X-BF and Y-BF, 1% of As(V) increased, and in X-BF2, 5% of As(V) increased. As to Y-CY, on the other hand, 14% of As(V) decreased contrary to the other samples.

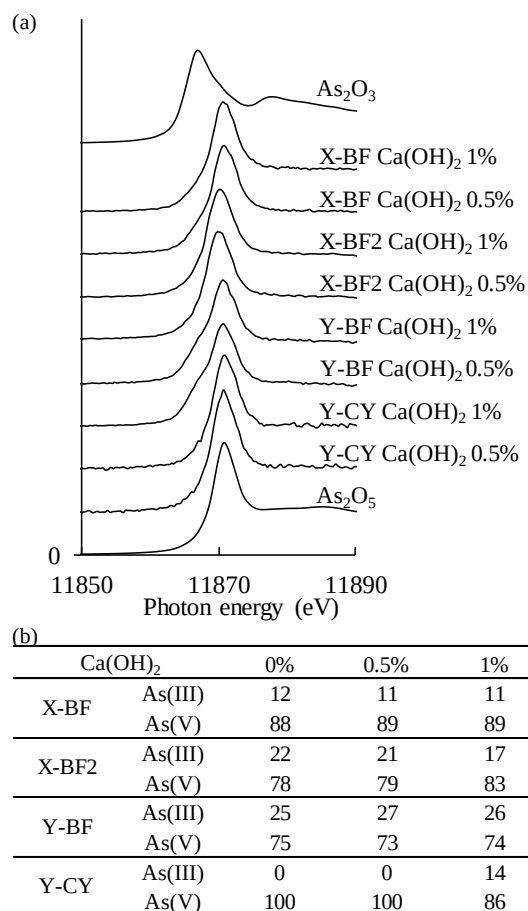


Fig. 5.4 Results of XAFS analysis for Ca(OH)_2 -processed samples. (a) XAFS spectrum of the samples. (b) XAFS pattern fitting results of the samples (%).

5.3.2.2 Insolubilization with ferrous sulfate

Table 5.6 shows the results of JLT-46 for the insolubilized materials of X-BF, Y-BF and Y-CY by ferrous sulfate. In Table 5.7, the JLT-46 and the IC-ICP-MS result for the insolubilized material of X-BF2 by ferrous sulfate are shown. The arsenic elution decreased by ferrous sulfate as calcium hydroxide. The arsenic concentration of X-BF2 and Y-CY satisfied the standards (0.01 mg L^{-1}) by 1% ferrous sulfate treatment. The arsenic concentration of X-BF and Y-BF exceed 0.01 mg L^{-1} in the condition of 5% ferrous sulfate treatment, that indicated that 5% or more ferrous sulfate was needed to meet the standard. However, it was assumed that elution of heavy metals other than arsenic increased, because the ferrous sulfate adding decreased pH value. In fact, it is difficult to insolubilize the heavy metals of the sewage sludge incineration ash only with ferrous sulfate. It is necessary to adjust pH value with the other insolubilization agents, like alkali (calcium hydroxide etc.)

Table 5.5 JLT-46 results for X-BF2 processed with Ca(OH)_2 (mg L^{-1}).

Element	Ca(OH)_2			Method
	0%	0.5%	1%	
Na	140	140	100	ICP-MS
Mg	110	48	2.1	
Al	<2	<2	4.7	
K	75	71	66	
Ca	19	28	44	
Ti	<0.76	<0.76	<0.76	
V	0.48	0.18	0.088	
Cr	<0.0022	<0.0022	<0.0022	
Mn	0.69	0.019	<0.00066	
Fe	15	9.5	7.9	
Co	0.04	0.00098	<0.0012	
Ni	0.048	<0.0079	<0.0079	
Cu	<0.0056	<0.0056	<0.0056	
Zn	<0.44	<0.44	<0.44	
Se	0.24	0.18	0.13	
Sr	0.19	0.12	0.32	
Mo	1.4	1.5	1.2	
Cd	<0.0041	<0.0041	<0.0041	
Sn	<0.018	<0.018	<0.018	
Sb	0.0044	0.005	0.0027	
Cs	<0.0012	<0.0012	0.01	IC-ICP-MS
W	0.041	0.088	0.15	
Pb	<0.002	<0.002	<0.002	
As(V)	0.25	0.063	0.019	IC
As(III)	0.013	<0.002	<0.002	
F ⁻	0.64	2.2	2.3	IC
Cl ⁻	47	57	31	
NO_2^-	<0.75	<0.75	<0.75	
Br^-	3.7	4.2	4.3	
NO_3^-	<1.5	1.5	<1.5	
SO_4^{2-}	700	840	410	-
pH	6.76	8.37	11.67	

Table 5.6 JLT-46 results of samples processed with FeSO_4 (X-BF, Y-BF, and Y-CY) (mg-As L^{-1}).

FeSO_4	0%	0.3%	1%	5%
X-BF (pH)	1.43 (5.4)	0.77 (5.4)	0.40 (4.4)	0.03 (3.3)
Y-BF (pH)	1.67 (4.2)	0.91 (4.4)	0.67 (4.3)	0.14 (3.4)
Y-CY (pH)	0.16 (6.8)	0.01 (5.6)	<0.01 (4.1)	<0.01 (3.3)

Table 5.7 JLT-46 results for X-BF2 processed with FeSO_4 (mg L^{-1}).

Element	FeSO_4			Method
	0%	1%	5%	
Na	140	85	93	ICP-MS
Mg	110	87	88	
Al	<2	<2	5.8	
K	75	42	56	
Ca	19	11	18	
Ti	<0.76	<0.76	<0.76	
V	0.48	0.012	0.011	
Cr	<0.0022	<0.0022	<0.0022	
Mn	0.69	3	3.7	
Fe	15	59	620	
Co	0.04	0.1	0.13	
Ni	0.048	0.12	0.16	
Cu	<0.0056	0.22	0.97	
Zn	<0.44	6.9	11	
Se	0.24	0.082	0.047	
Sr	0.19	0.3	0.32	
Mo	1.4	0.11	0.03	
Cd	<0.0041	<0.0041	<0.0041	
Sn	<0.018	<0.018	<0.018	
Sb	0.0044	0.0039	0.0035	
Cs	<0.0012	<0.0012	<0.0012	
W	0.041	0.0085	0.0078	
Pb	<0.002	<0.002	<0.002	
As(V)	0.25	<0.002	<0.002	IC-ICP-MS
As(III)	0.013	<0.002	<0.002	
F ⁻	0.64	0.75	1.5	IC
Cl ⁻	47	21	23	
NO_3^{2-}	<0.75	<0.75	<0.75	
Br^-	3.7	2.9	0.81	
NO_3^{3-}	<1.5	<1.5	<1.5	
SO_4^{2-}	700	460	1300	-
pH	6.8	5.3	4.5	

Figure 5.5 shows the XANES spectra and the results of LCF for the ferrous sulfate insolubilization materials. In Fig. 5.2, Fig. 5.4 and Fig. 5.5, every sample has the peak top at 11,870-11,871 eV like original ash and the calcium hydroxide insolubilization materials. This indicated that the arsenic in the samples was predominantly pentavalent. Additionally, the samples besides Y-CY had a shoulder on the low energy side, which indicated that the portion of the arsenic was trivalent. In the LCF results (Fig. 5.5(b)), 2% of As(V) in X-BF, 5% of As(V) in X-BF2, and 8% of As(V) in Y-BF, respectively, increased. As to Y-CY, on the other hand, 2% of As(V) decreased contrary to the other samples, like the calcium hydroxide treatment.

5.3.3 The results of chemical equilibrium model calculation

The chemical species in the calcium hydroxide insolubilization material of X-BF2 were estimated using a chemical equilibrium model. Input conditions were based on the component concentrations and leachate

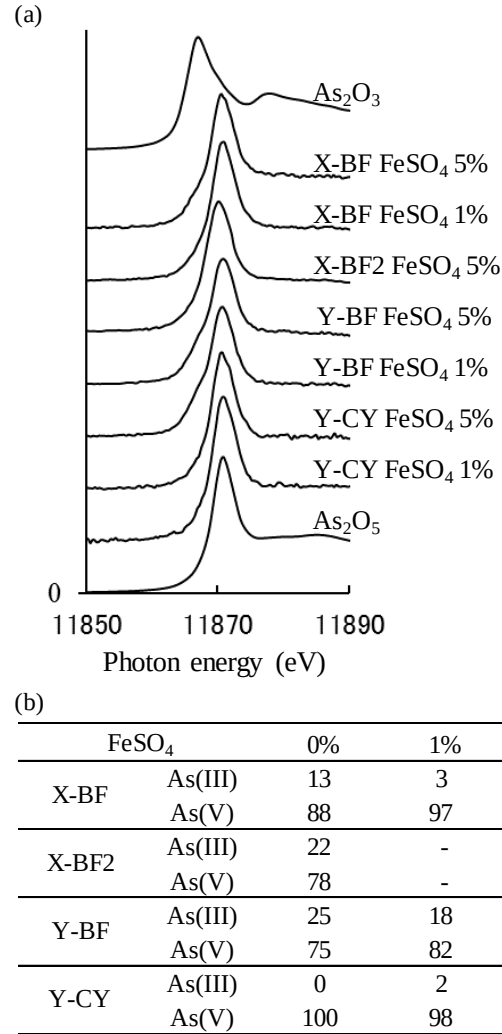


Fig. 5.5 Results of XAFS analysis for FeSO_4 processed samples. (a) XAFS spectrum of the samples. (b) XAFS pattern fitting results of the samples (%).

concentration of X-BF2. On the basis of the LCF results, 22% of the arsenic existed as trivalent form and 78% existed as pentavalent form. Therefore, $6.9 \times 10^{-3} \text{ mmol L}^{-1}$ (1.0 mg-As L^{-1}) As_2O_3 and $2.4 \times 10^{-2} \text{ mmol L}^{-1}$ (3.7 mg-As L^{-1}) As_2O_5 were used to calculate the composition. It was assumed that all calcium hydroxide could be dissolved at least once into solution. Thus, $540 \text{ mg L}^{-1} \text{ Ca}^{2+}$

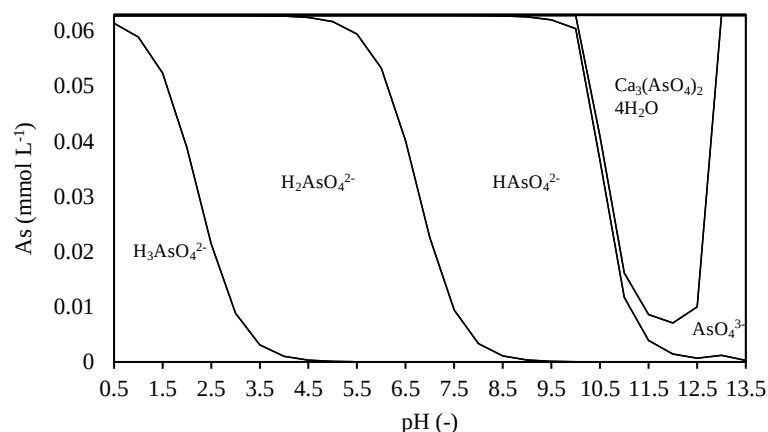


Fig. 5.6 Result of Visual MINTEQ modeling in the CaOH_2 -processed sample.

($1,000 \text{ mg-CaOH}_2 \text{ L}^{-1}$) was used in the calculation where 1 wt% calcium hydroxide was added at liquid-solid ratio 10. The pH was entered as a fixed value, ranging from 0.5 to 13.5 at 0.5 intervals. Oversaturated solutions were allowed to precipitate. As the oxidation-reduction reaction could occur, I set the arsenic oxidation-reduction reaction ($\text{H}_3\text{AsO}_3/\text{AsO}_4$) on Redox menu of the visual MINTEQ. The pe value was left as the initial condition ($\text{pe} + \text{pH} = 15$). Fig. 5.6 shows the results of calculation. In the results of the calculation, it was found that the arsenic precipitate by forming $\text{Ca}_3(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}$ within the range of pH 10.5-12.5. In Fig. 5.3(b), the elution amount decreased as the pH value raise to 10 and became lower than determination limit in the range of pH 10 or more. In the results of calculation (Fig. 5.6), $\text{Ca}_3(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}$ was formed within the range of pH 10 or more. Accordingly, it is assumed that the arsenic elution amount decreased by precipitating with calcium in the addition of calcium hydroxide. On the other hand, the arsenic dissolved in the range of acidity and neutrality. From the above, the arsenic can elute from the materials insolubilized by calcium hydroxide in the case of exposure to acid condition.

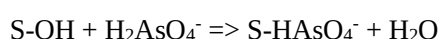
The chemical species in the ferrous sulfate insolubilization material were estimated by calculation. As in the case of calcium hydroxide, Table 5.7 was used as the initial input condition. In the addition, $6.9 \times 10^{-3} \text{ mmol L}^{-1}$ (1.0 mg-As L^{-1}) As_2O_3 and $2.4 \times 10^{-2} \text{ mmol L}^{-1}$ (3.7 mg-As L^{-1}) As_2O_5 were used to calculate the composition. $370 \text{ mg L}^{-1} \text{ Fe}^{2+}$ and $630 \text{ mg L}^{-1} \text{ SO}_4^{2-}$ ($1,000 \text{ mg-FeSO}_4 \text{ L}^{-1}$) was used in the calculation where 1wt% ferrous sulfate was added at liquid-solid ratio 10. The pH was entered as a fixed value, ranging from 0.5 to 13.5 at 0.5 intervals. Oversaturated solutions were allowed to precipitate. I set the oxidation-reduction reaction of arsenic ($\text{H}_3\text{AsO}_3/\text{AsO}_4^{3-}$), sulfur ($\text{HS}^-/\text{SO}_4^{2-}$) and iron ($\text{Fe}^{2+}/\text{Fe}^{3+}$) on Redox menu of the visual MINTEQ. In the result of calculation for all pH region, the arsenic dissolved. This calculation result is conflict with the fact that the arsenic was insolubilized by the addition of ferrous sulfate. In this calculation result, focusing on the iron, in the

region of pH 1 or higher, iron was 99% or more as hematite (Fe_2O_3). As described in the previous study^{21,22}, it was assumed that arsenic did not precipitate as FeAsO_4 , but co-precipitated with iron hydroxide, which was Fe_2O_3 in the simulation, or was adsorbed on the surface. The absorption of arsenic onto the solid surface was simulated using absorption program in Visual MINTEQ. The same input condition as the ferrous sulfate case was used. HFO model (Dzombak & Morel) or Goethite model (Weng et al.), which were predefined in Visual MINTEQ, were used as absorption model. In former model the arsenic was absorbed onto hydrous ferric oxide (HFO,

ferrihydrite) in former model and onto goethite in the latter. The calculations were conducted assuming that the concentrations of ferrihydrite and goethite were 0.01, 0.05, 0.1, 0.2, and 0.5 g L^{-1} , respectively. The pH value was set to 5.3, which was obtained in the condition of 1% ferrous sulfate addition. The pe value was left as the initial condition as insolubilization by the calcium hydroxide. Fig. 5.7 shows the results of calculation. Similarly to the previous result where the adsorption was not considered, the arsenic did not precipitate in the all pH range. However, 99% of arsenic was absorbed in the 0.1 g L^{-1} HFO model and in 0.5 g L^{-1} goethite model. Actually, the dissolution ratio was suppressed to 1% or less under the condition of adding 1% ferrous sulfate, that agreed with these calculation results. At pH 5.3, the arsenic predominantly existed as H_2AsO_4^- , that is an anion (about 97% of arsenic is H_2AsO_4^- in the calculation). The reaction formula is as follows.



In addition, this anion reacts on the surface of a solid (S) such as ferrihydrite as follows and is absorbed.²³



In the condition of 1% ferrous sulfate insolubilization, 370 mg L^{-1} iron was added to the JLT-46 extraction liquid as ferrous sulfate, and the ash X-BF2 originally contained 7% iron (7 g-Fe L^{-1}). In this study, it is not clarified how the iron solidifies in solution, but even if the iron in solution becomes hematite in the final equilibrium state,

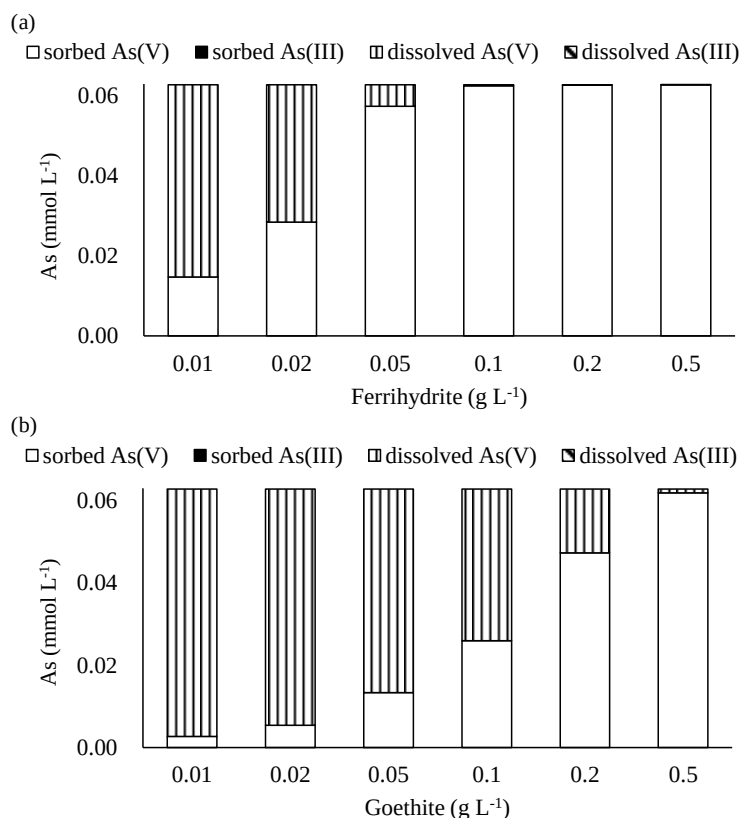


Fig. 5.7 Results of the adsorption reaction calculated by Visual MINTEQ. (a) Ferrihydrite. (b) Goethite.

ferrihydrite, it was indicated that it formed iron hydroxide compound such as ferrihydrite or goethite and insolubilized arsenic by uptake while adsorbing. However, adsorption of arsenic to iron hydroxide did not occur when temperature, atmosphere, redox potential or pH changed, so that arsenic could be eluted if there was a change in the environment.

5.4 Conclusion

I analyzed 4 kinds of sewage sludge incineration ash collected from two incinerators in operation by JLT-46 leaching test, XAFS, IC-ICP-MS and chemical equilibrium calculation to identify the chemical species of arsenic and its insolubilized material. In XAFS, chemical state of arsenic at a low concentration of 32 mg kg^{-1} could be clearly analyzed, and in IC-ICP-MS, the lower limit of quantifications of both As(III) and As(V) were $2.0 \text{ } \mu\text{g L}^{-1}$. The arsenic contained in the samples excess the environmental standard. There were differences in samples, which were collected from the same incinerator and the same sampling points, depending on the sampling periods. The arsenic in the samples was predominantly pentavalent. In addition, the chemical state of trace arsenic compounds in complex matrix could be nondestructively analyzed by using XAFS. Therefore, because XAFS enables chemical state analysis of trace arsenic contained in complex matrix samples such as biological samples, foods, and drinks in addition to recycled materials, this technique is valuable in arsenic analysis for forensic science. Furthermore, XAFS can be applied to forensic analysis of other trace elements contained in complex matrix samples.

Three species of samples satisfied the environmental standards by calcium hydroxide addition and X-BF and Y-BF satisfied the standards by addition with 1% addition. On the XAFS results, the arsenic in the insolubilization materials by calcium hydroxide was predominantly pentavalent. In the results of calculation, the arsenic formed $\text{Ca}_3(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}$ and precipitated within the alkaline range.

Two kinds of the samples satisfied the standards by ferrous sulfate treatment, but the other samples did not satisfy the standards in the condition of 5% addition. Though more ferrous sulfate was needed to meet the standard, it was assumed that elution of heavy metals other than arsenic increased by this. On the results of XAFS, the arsenic in the insolubilization materials by ferrous sulfate was predominantly pentavalent. In the chemical equilibrium model calculation, the arsenic was adsorbed on the surface of iron hydroxide and was insolubilized.

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Chapter 6 Concluding Remarks

6.1 Summary of this thesis

In this study, analysis methods were developed for the glass and rubber from industrial products and ash from waste.

In Chapter 1, the present situation of crime, traffic and forensic science in Japan was explained. X-ray absorption fine structure (XAFS) and its application was showed. The background and aim of this study were described.

In Chapter 2, automobile window glass manufacturers were identified based on refractive index (RI), X-ray fluorescence spectrometry (XRF), XAFS analyses. The samples were classified into the corresponding groups using XRF, which should be the first step for identification. Samples manufactured at different times showed differences in the refractive index. Based on XAFS, the amplitude of the extended X-ray absorption fine structure (EXAFS) spectra and the intensities of Fourier transforms differed between manufacturers. In the scheme for manufacturer identification proposed in this study, performing XRF and refractive index analyses is the first step. The concentrations of CeO_2 , MgO , Al_2O_3 , and K_2O allowed us to distinguish among manufacturers. Second, for samples containing cerium, the manufacturer was discriminated based on the amplitude of the EXAFS spectra and the intensities of Fourier transforms. As a result, the manufacturers of the 75 samples used in this study were identified multilaterally. In this study, the amount of sample required was 1.5 mm square and the concentration of cerium was 0.5 wt%.

In Chapter 3, tire rubbers were analyzed using pyrolysis-gas chromatography mass spectrometry (Py-GC/MS) and X-ray absorption near-edge structure (XANES) to discriminate various tire rubbers. The Py-GC/MS results confirmed that the sample can be identified by the ratio of the pyrolytic monomer. In sulfur XANES, the shape and height of the peaks varied among the tires, and tire rubbers could be discriminated. Based on t-test results, Py-GC/MS showed superior sample discrimination capability. However, because XANES is a non-destructive analysis, XANES should be performed as the first forensic analysis, and Py-GC/MS should be carried out when samples cannot be distinguished by XANES. In this study, the amount of sample required was 10mm * 1 mm in XAFS, and 0.5 mm square in Py-GC/MS.

In Chapter 4, chemical state analysis for cadmium and lead in fly ash was conducted to address aims: to acquire the cadmium chemical states in fly ash, and to examine the quantitative determination of lead chemical species in fly ashes. Furthermore, analysis method of the chemical state by sequential extraction procedure alone was examined. XANES results indicated that cadmium in fly ash was represented by CdCl_2 : 94% + Cd: 6%. When the pH in the first fraction of the sequential extraction procedure (water-soluble fraction) is highly alkaline, CdCl_2 dissolves and then precipitates in the form of $\text{Cd}(\text{OH})_2$, which is dissolved

in the form of an ammine complex in the ammonium acetate fraction of the sequential extraction procedure. When the pH in the water-soluble fraction is neutral, CdCl_2 is dissolved without precipitation. The experimental result of the sequential extraction procedure, the pH-dependent leaching test, and XAFS results were consistent with chemical equilibrium modeling calculations by Visual MINTEQ. XANES analysis showed that PbSiO_3 , PbCl_2 , or $\text{Pb}_2\text{O}(\text{OH})_2$ was the predominant chemical species of lead in fly ash. The result of the sequential extraction procedure was strongly affected by the pH and sample matrix, and did not necessarily reflect the chemical state accurately. Considering re-precipitation, chemical forms easy to dissolve, such as CdCl_2 and PbCl_2 , could be estimated by the first three fractions. It was difficult to quantitatively examine the chemical species using EXAFS alone. XANES fitting enabled direct quantification of the chemical species. Assuming to testify the chemical states of samples at trial, analysis by XAFS should be performed. It was concluded that multiple analyses should be compared multilaterally to improve the accuracy of the final analysis. In this study, the concentrations of cadmium and lead were 360 mg kg^{-1} and 1100 mg kg^{-1} , respectively.

In Chapter 5, the chemical states of arsenic contained in sewage sludge incineration ash and insolubilized materials were analyzed. Four kinds of sewage sludge incineration ash and their insolubilized materials were analyzed using a leaching test (Japan Environment Agency Notification No. 46: JLT-46), XAFS, ion chromatography inductively coupled plasma mass spectrometry (IC-ICP-MS), and a chemical equilibrium model calculation. The arsenic in samples existed mainly as As(V). Three of the four kinds of insolubilized materials meet the environmental quality standards for soil after hydroxide calcium insolubilization treatment, and it is suggested that the arsenic formed $\text{Ca}_3(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}$. Two kinds of insolubilization material meet the standards after ferrous sulfate treatment, and it is inferred that arsenic was absorbed onto iron hydroxide. In XAFS, chemical state of arsenic of 32 mg kg^{-1} could be clearly analyzed, and the lower limit of quantifications of both As(III) and As(V) were $2.0 \mu\text{g L}^{-1}$ by IC-ICP-MS.

Finally, in Chapter 6, based on the results of Chapters 2–5, the analysis methods including synchrotron radiation analysis were summarized and compared, along with a discussion of the problems associated with and prospect of using synchrotron radiation analysis in forensic science analysis.

6.2 Findings obtained by X-ray absorption fine structure analysis

In this study, XAFS analysis was part of the method used to examine glass and rubber, which are industrial products, and ash, which is waste. The findings obtained are as follows.

EXAFS was an effective method for identification of the manufacturer of automobile window glass, and made it possible to identify each manufacturer. However, the accuracy was inferior to that of XRF analysis. In addition, because XRF can be conducted at a general laboratory level, whereas XAFS requires

the use of a synchrotron radiation facility, the application of XAFS is not necessarily feasible in some cases. Notwithstanding, because XAFS was only used to analyze cerium in this study, improvement of the discrimination accuracy by XAFS using other elements remains possible in the future. In the analysis scheme, XRF should be performed first, and RI and XAFS should be performed to reinforce XRF analysis.

On the basis of the chemical state analysis of sulfur by XAFS, it was possible to differentiate automobile tire rubber. Because the oxidation state of sulfur was used as an index, it was assumed that even the same product could be identified. However, the results showed that the accuracy was less than that of Py-GC/MS. Py-GC/MS is a destructive analysis method, whereas XAFS is non-destructive; thus, XAFS should be performed first. If samples cannot be identified by XAFS, Py-GC/MS may be useful. To that end, it will be necessary to conduct research to distinguish between new and old sample on the same item. By X-ray photoelectron spectroscopy (XPS), the chemical states information can be obtained, like XAFS. Since the chemical states of sulfur on the surface of tire rubber can be analyzed by XPS, it will be necessary to analyze tire rubber by XPS in future. In this study, the two chemical states of sulfur were used as an index of identification, but because the original XAFS spectrum is considered to contain more information, it is necessary to prepare additional types of standard samples suitable for analyzing the chemical states of sulfur in the tire rubber in the future.

XAFS was effective for analyzing the chemical states of heavy metals contained in ash. By analyzing the chemical states of cadmium in ash by XANES, cadmium in fly ash was presented as CdCl_2 : 94% + Cd: 6%. PbSiO_3 , PbCl_2 , or $\text{Pb}_2\text{O}(\text{OH})_2$ was the dominant lead in the ash. As for the results of other methods, it was difficult to use the sequential extraction method for chemical state analysis because this procedure was affected by the pH of the extract solution. EXAFS analysis cannot measure up to a sufficiently high energy region depending on coexisting elements. On the other hand, XANES can directly and quantitatively analyze the chemical state. By XAFS, it was found that the arsenic contained in sewage sludge incineration ash and the insolubilized materials were predominantly pentavalent; it was possible to quantitatively analyze trivalent and pentavalent arsenic using XAFS. By the chemical equilibrium thermodynamic calculation with XAFS, it was possible to clarify the chemical states of insolubilized matter.

6.3 The analysis protocol obtained in this study

The analysis protocol obtained in this thesis are described below. In the following, the criterion for judgment should be set based the accuracy on measurement. The measurement should be performed multiple times as necessary.

6.3.1 Automobile window glass

The protocol to identify manufacturer of automobile window glass sample is presented in Fig. 6.1.

1. Purpose

This protocol is created to identify manufacturer of automobile window glass sample in forensic science.

2. Range of application

This protocol is applied when all the following are satisfied.

- (1) The sample is like an automobile window glass in appearance.
- (2) The analysis is conducted to identify the manufacturer of the sample.
- (3) The sample must have a sufficient amount for examination.

3. Examination

- (1) The sample is subjected to RI analysis.
- (2) The sample is subjected to XRF analysis.
- (3) When it is confirmed that cerium is contained in the sample by XRF, the sample is subjected to XAFS analysis, and the chemical state of cerium is measured.

4. Database: control samples

The control samples whose manufacturers, date of manufacture, and manufacturing lot are known are examined.

5. Reference material

$\text{Ce}_2(\text{CO}_3)_3$ and CeO_2 are prepared as reference materials.

6. Judgment

When the followings are satisfied, it is judged that the sample is from the control manufacturer. Judgment criteria must be set according to the number of the control samples.

- (1) In XRF analysis, the composition of the sample is within those of the control samples. Examples of target elements: Na, Mg, Al, Si, K, Ca, Fe, Ce.
- (2) In RI analysis, the RI of the sample is within those of the control samples.
- (3) In XAFS analysis, the XANES spectrum of the sample is similar to those of the control samples. Additionally, in the FEFF simulation, the obtained result is within those of the control samples.

When any one of the above is not satisfied, it is judged that the manufacturer of the sample is unknown.

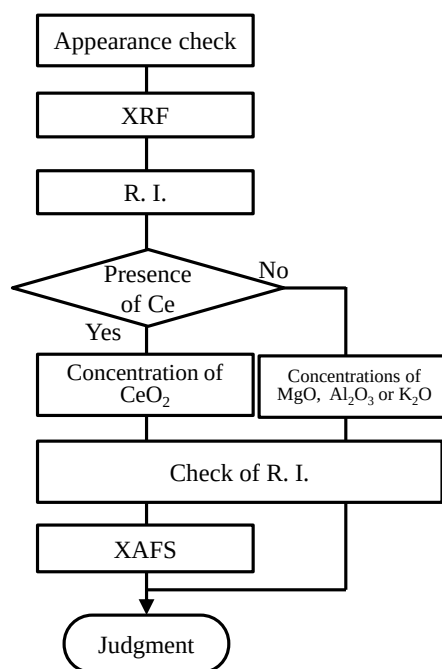


Fig 6.1 The Identification method of automobile window glass manufacturers.

6.3.2 Tire rubber

The protocol for discrimination of automobile tire rubbers is presented in Fig. 6.2.

1. Purpose

This protocol is created to discriminate automobile tire rubbers in forensic science.

2. Range of application

This protocol is applied when all the following are satisfied.

- (1) The sample is like a tire rubber in appearance.
- (2) The analysis is conducted to discriminate between the sample and control sample.
- (3) The sample must have a sufficient amount for examination.

3. Examination

The repetition number of examination should be set appropriately.

- (1) The sample is subjected to XAFS analysis for the chemical state of sulfur.
- (2) The sample is subjected to Py-GC/MS.

4. Reference material

The reference materials to check the valence of sulfur are prepared appropriately.

5. Judgment

When the followings are satisfied, it is judged that the sample and the control sample are of the same type. The discrimination standard should be set appropriately based on the measurement accuracy: e. g.

two times the standard deviation (2SD), or three times standard deviation (3SD).

(1) In the XAFS analysis, the ratio of the peak height derived from sulfide and sulfate is similar.

(2) When the above item (1) is satisfied, XAFS analysis is performed. In Py-GC/MS, the ratio of the pyrolysis product of the sample is similar to that of the control sample.

When any one of the above is not satisfied, it is judged that the sample and control sample are of different type.

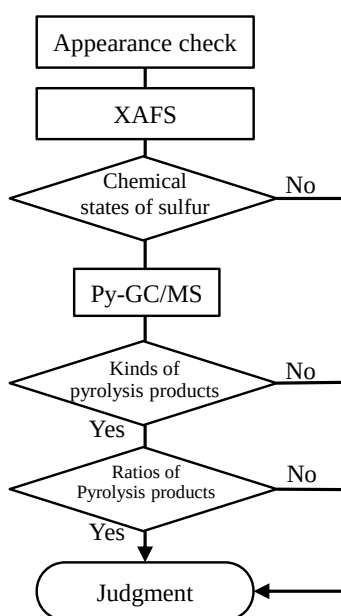


Fig 6.2 The discrimination method of automobile tire rubber.

6.3.3 Chemical state of heavy metals contained in fly ash

1. Purpose

This protocol is created to analyze chemical state of heavy metal contained in fly ash in forensic science and environmental engineering. Along with chemical state, elution behavior can be additionally evaluated.

2. Range of application

This protocol is applied when all the following are satisfied.

- (1) The sample is ash.
- (2) The analysis is conducted to analyze the chemical state of sample.
- (3) The sample must have a sufficient amount for examination.

3. Examination

The repetition number of examination should be set appropriately.

- (1) The sample is subjected to XAFS measurement for the chemical state of target element.
- (2) When evaluating the dissolution behavior, a sequential extraction procedure or pH dependent leaching test may be conducted.

4. Reference material

The reference materials are prepared according to the target element. The type of control sample should be selected based on sample composition and chemical thermodynamics.

5. Judgment

- (1) On the basis of XANES, the species are identified and quantified using the linear combination fit (LCF).
- (2) Based on chemical thermodynamics, the result of the LCF is checked. When inconsistency is caused, LCF is conducted again.
- (3) When the sequential extraction procedure is performed, the result of the LCF and the procedure are compared. When inconsistency is caused, LCF is conducted again.
- (4) When the sequential procedure is conducted, the result of the procedure should be checked with the LCF for re-precipitation.

6.4 Analysis method in forensic science

In this study, the analysis and identification of various samples using XRF, RI analysis, Py-GC/MS, and XAFS were compared. The findings are described below.

XRF is extremely useful from a forensic science viewpoint because the measurement provides a large amount of information, the method is non-destructive, and the identification accuracy is superior to that of RI and XAFS. The method shows great power in analyzing with the classification such as discrimination between manufacturers. However, there are cases when it is not possible to distinguish samples from the same manufacturer. Further, the amount of glass specimen examined in this study was about 1 cm², which is very large for forensic science. It will be necessary to determine a technique that can analyze principal components even in minute amounts, such as scanning electron microscopy-energy dispersive X-ray spectroscopy.

Py-GC/MS showed higher discrimination ability than XAFS in rubber identification. Because Py-GC/MS provides rich information, similar to XRF, it was possible to distinguish samples by setting indices matching the samples with high accuracy. The amount of sample required in Py-GC/MS was about 0.5 mm³, and the amount required in XAFS was about 10 mm * 1 mm square. However, because Py-GC/MS is a destructive analysis method, it cannot always be carried out for reasons other than analytical conditions, such as samples that cannot be consumed. Though XAFS is inferior to Py-GC/MS, it is able to non-

destructively discriminate samples by XAFS. Analysis by XAFS should be conducted at first step.

6.5 Issues and prospect of using XAFS analysis in forensic science

XAFS is a non-destructive analysis method that was an effective identification method for glass and rubber samples in this study. It was also effective for analyzing the chemical state of trace elements contained in a complicated matrix like ash, as it is traditionally referred. However, the identification accuracy was inferior to that of conventional XRF and Py-GC/MS because the XAFS method used less information as indicators than XRF and Py-GC/MS. That is, in the study of glass, the chemical state of one kind of cerium was used as a discrimination index; thus, the result was based on less information compared with XRF analysis. Thus, it is necessary to confirm whether the presence of other elements contained in the glass can be used as indicators for identification. Second, the shortage of standard samples is also a problem. Sulfur in the R-S-S' and SO₄ states were used as an index in the analysis of rubber; however, additional states are included in the XANES spectrum. As such, standard samples suitable for the analysis are required. In addition, because there are few research examples of synchrotron radiation analysis, especially XAFS, it will be necessary to adapt the standards and technique moving forward.

Regarding the application of XAFS in forensic science, the findings of this study suggest that supplementation of XAFS analysis with non-destructive analytical methods and methods with good analytical accuracy, such as XRF, should be considered. Additionally, it would be ideal to conduct XAFS analysis before a destructive approach and to examine the application of more accurate destructive methods depending on the results.

The individual issues of each chapter in this research are described below. In chapter 2, automobile window glass was analyzed by XAFS in transmission mode. However, this approach requires 2 cm square sample, which is fairly large as a sample in forensic science. In future, in order to utilize XAFS in forensic science, the research for fluorescence mode will be necessary. In chapter 3, it was shown that tire rubber can be identified by XAFS. It will be necessary to examine discrimination among the same kinds of product of different production lots. Additionally, since it is also possible to obtain chemical form information by XPS, it will be necessary to examine the identification method by XPS in future. In chapters 4 and 5, the chemical state of heavy metals (cadmium and lead in fly ash, and arsenic in sewage sludge incineration ash), were analyzed by XAFS. It was possible to analyze the chemical species directly and quantitatively by XANES. With the respect to fly ash, since the other elements, such as chromium, may cause a trouble, the research for them will be needed in forensic science as well. For the sewage sludge incineration ash, because it is necessary to pay attention to elution of selenium, which is a harmful element, the research for it will be necessary.

In utilizing XAFS in forensic science, the following problems should be considered. First, the measurement will be carried out at an external facility such as a synchrotron radiation facility by lack of XAFS apparatus in a general laboratory. Therefore, the sample must be taken out of the affiliation. Since the sample traceability may be problem, it is necessary to keep a strict record on the situation of the sample movement and storage. Next, it takes time from the examination for usage to the measurement. The case must be sent to prosecutor within 48 h. In addition, the period of detention is 20 days. Considering the time required for the experimental preparation, such as sampling or selection of the analysis scheme, it will be difficult to complete analysis using XAFS within these periods. It is not realistic to have a beamline in synchrotron radiation facility for irregular forensic analysis. The importance and necessity of the experiment should be judged quickly.

I studied the analyses for glass, rubber, fly ash, and sewage sludge incineration ash. Regarding these samples, the information to be analyzed in forensic science is identification of samples, origin of samples, or dissolution behavior of harmful metals. The analyses of these types may be conducted for samples of other kinds. There are a variety of samples in forensic science, and there are many conventional methods such as Fourier-transform infrared spectroscopy and gas chromatography mass spectrometry. This study was the few attempts for XAFS in forensic science. Therefore, it will be necessary to apply XAFS to various kinds of samples in the future and accumulate information of them. As is clear in this research, combining the conventional method and XAFS will be able to perform the advanced analysis.

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List of Related Published Papers

Original Papers

- 1) Speciation Analysis for Cadmium in Fly Ash.

Atsushi Funatsuki, Masaki Takaoka, Daisuke Kokubu, Kazuyuki Oshita, Nobuo Takeda, *Bunsekikagaku*, **2010**, 59, pp.801-810 (in Japanese).

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