



Nondestructive Material Identification by Spectroscopic Methods and Application to Forensic Discrimination

Hashimoto, Takashi

(Degree)

博士 (工学)

(Date of Degree)

2010-09-25

(Date of Publication)

2012-05-07

(Resource Type)

doctoral thesis

(Report Number)

甲5072

(URL)

<https://hdl.handle.net/20.500.14094/D1005072>

※ 当コンテンツは神戸大学の学術成果です。無断複製・不正使用等を禁じます。著作権法で認められている範囲内で、適切にご利用ください。



Doctoral Dissertation

**Nondestructive Material Identification
by Spectroscopic Methods
and Application to Forensic Discrimination**

July 2010

**Graduate School of Engineering
Kobe University**

Takashi HASHIMOTO

博士論文

Nondestructive Material Identification
by Spectroscopic Methods
and Application to Forensic Discrimination

分光学的手法による非破壊物質同定と
法科学的識別法への適用

2010年7月

神戸大学大学院工学研究科

橋本 敬

(Takashi HASHIMOTO)

Acknowledgments

The author would like to express his sincere gratitude to Dr Minoru Mizuhata, Associate Professor of Department of Chemical Science and Engineering, Graduate School of Engineering, Kobe University, for his guidance and encouragement to accomplish and finish his studies for the doctoral dissertation.

The author would like to express his sincere gratitude to Professor Shigehito Deki of Yamanashi University and Professor Emeritus of Kobe University, and the late Professor Yukio Kanaji, Professor Emeritus of Kobe University, at the beginning of his study of discrimination of ceramics.

The author would like to appreciate the support given by Professor Donald P. Land, Mr. Frederic A. Tulleners, and Professor David G. Howitt of Forensic Science Graduate Group at the University California-Davis, Ms. Faye A. Springer, Criminalist IV of Sacramento Laboratory of Forensic Services, Dr. Shunlin Wang of Bruker Optics, Inc. for the study of morphological and spectroscopic Measurements.

The author would like to thank Professor Takashi Nishino and Professor Minoru Fujii of Kobe University, Professor Masayoshi Okubo, Professor Emeritus of Kobe university, and Dr Akihiko Kajinami, Associate Professor of Kobe University for valuable guidance and advice to my studies in Kobe University.

The Training Center of Forensic Science in Japan National Police Agency gave me The International Training and Research Award in 1995 to carry out this study at University California Davis.

For the study of plastic film, polyethylene domestic manufacturers, Sumitomo Chemical Co. Ltd., Ube-Maruzen Polyethylene Co. Ltd., Prime polymer Co. Ltd., Asahi Kasei Corporation, and Japan polyethylene Corporation cooperated with me for supplying test samples of polyethylene films.

For the study of Ceramics, nine domestic manufacturers cooperated with me for collecting ceramics.

In considering the oil collecting films, Sumitomo 3M Ltd. provided me with samples.

Finally, the author deeply thanks my superiors and colleagues of Forensic Science Laboratory of Hyogo Prefecture Police Headquarters for their cooperation on my research during the last two years.

July 2010



Takashi Hashimoto

Contents

	Page
Chapter 1 General introduction	1
Chapter 2 Morphological and Spectroscopic Measurements of Plastic Bags for the Purpose of Discrimination	7
Chapter 3 Discrimination of Transparent Polyethylene Films Based on Identification of Inorganic Antiblocking Agents for Forensic Purpose	23
Chapter 4 Microstructural Analysis of Ceramics for Forensic Discrimination	35
Chapter 5 Development of Collecting Expiration Equipment for Alcoholic Breath Inspection	49
Chapter 6 Establishment of Sampling Method of Oil Adsorption Film for Fire Scene	55
Summary	63
List of Publications	66

Chapter 1

General Introduction

Forensic science conduct an appraisal of the object which could be the evidence in court by scientific method and the judge will make decisions by referring it. In forensic chemistry, which is a branch of forensic sciences, we chemically analyze the objects and materials which are concerned in crime scene, and mainly conduct the identification and discrimination of them. Substance identification is to analyze and prove the evidences in chemical analysis. For example, it is the chemical examination whether the white powder which has been seized by law enforcement agencies is opium or not. On the other hand, discrimination is to give judgment to similarity of materials and substances. A typical case of discrimination is whether the fibers that were left behind at the crime scene are the same as clothing fibers of the suspect. Those are the application of mutual attachment theory known as Locard's exchange principle (1). In 1973, calculation method of discrimination power which is necessary for correlated attribution for discriminating analysis between a suspect and the scene of a crime for forensic science in the principal of probability functions (2). Such a discrimination analysis has been developed in various kinds of the materials for criminal cases.

Enormous research has been carried out for the discriminations of the fiber, sand, glass, metal, and paint. Especially, polymer films are packaging materials utilized in daily life, such as plastic bags. Also, the plastic bags are commonly used as container of objects at crime scene such as illicit drug or poison. It will help to clarify the crime if we can prove whether the plastic bag left behind in the crime scene and the one kept at the suspect's home are the same specification of plastic bag. According to this idea, I have been investigated to evaluate the identity of the polymer film. Compared to the study of the discrimination of fiber, few studies of discrimination identification of polymer film have been reported in spite of the importance for forensic purpose.

In 1957, Allen has released a way to examine the inhomogeneities of

transparent plastic film using the Schlieren technique in the viewpoint of physical properties; such as surface morphology and homogeneity, of plastic films (3). It gives the magnified image of inhomogeneities in the material which can not be identified by visual inspection. In 1975, von Bremen et al. clearly indicated that the spin traces of plastic bags by way of shadow graph technique (4). Ford studied detail analysis using three physical comparisons for the identification of plastic bags (5). In this paper, one is to compare the extrusion marks, which are made by blow molding using the projection images expanded by the photographic film developing machine. The second, it is shown that the heat seal of the bag was regarded as the evidence by examination of trace of a soldering iron and a laundry iron. Since the plastic bags are often heat-sealed by a special machine, the fabric texture pattern of heat sealing machine and the deformation texture of the cloth part by heating the metal crimp were compared and identified. The third is to compare the traces of cutting devices built in the sealing machine in producing plastic bags such as snags and the changes in cutting direction. In this case, we can consider whether the bags were manufactured by the same machine regardless of the dimensions of the bag. In 1981, Denton placed the film on the lighting grid and pictured from underneath (6). It was reported that the fine film extrusion mark was clarified and make as the identification. In 1991, Gilbert et al. applied infrared spectroscopy and a thermal desorption gas chromatograph to identify the plastic wrap such as polyethylene, polyvinyl chloride, and polyvinylidene chloride (7). The kinds of polymer were determined in infrared spectra for discrimination from fine difference among each spectrum at fingerprint range for each polymer. In 1994, Castle et al. presented the novel optical alignment for identification of a clear plastic bag and plastic wrap with comparison of the physical properties of transparent plastic films. Polarization tables, optical benches, and optical microscopy techniques were used for observations of birefringence(double refraction) colors, schlieren image, and shadowgraph of film (8). Many kinds of polymer show birefringence because of the polymer chain orientation made during extrusion. In the case of the film sandwiched between the polarization plates, polarization colors are appeared. Observed colors depend on the film thickness and birefringence change in the bag. In 1997, Tsukame et al. examined the fine

structure of polyethylene by differential thermal analysis (DSC) (9, 10). Blends of Low density polyethylene (LDPE), linear low density polyethylene (LLDPE), high density polyethylene (HDPE) were examined and the results showed blend of HDPE and LDPE or LLDPE have indicated that due to metastable microstructure which is caused by the co-crystallization of two different types of polymers. In 1998, Nissen et al. analyzed trace elements polyethylene film (colorless cling film and colored garbage bag), which are derived from pigments and fillers such as slip agents by way of ICP-MS for discrimination (11). In 2000, Roux et al discriminated plastic packaging for illicit drugs with an analysis of some optical inspections, crossed-polarized light, UV-visible spectrum and Fourier transform infrared spectrum in order to determine whether there are clear difference between the different sources, to establish the scientific value of such examinations and to build a data base of general drug packaging materials (12). It is shown that the visualization method of cross polarization was established for comparing machine marks in products. In 2002, Berx et al. scanned the surface of the plastic garbage bags using non-contact laser profilometry in order to do 3D measurement of manufacturing defects such as fish eyes, arrowheads, and surface scratches (13). In 2006, Causin et al. investigated plastic films of shopping bags using infrared spectroscopy and differential thermal analysis in addition to general tests such as the thickness measurement and microscopy (14). It is shown that the analysis of additives in films is effective for discriminated rather than IR absorption spectroscopy. In 2007, the same group performed wide angle X-ray diffraction measurements for their polyethylene films of shopping bags in which samples are mounted for two directions with the X-ray beam (15). Recently, Taylor et al. collected polyethylene grip-seal plastic bags that are used for packaging of contraband such as illegal drugs and explosives (16). In addition to infrared spectroscopy and physical comparison such as birefringence, mass spectrometry ^{13}C , ^2H stable isotope ratios (IRMS) were examined in order to discriminate and associate plastic bags. The infrared spectra primarily were performed to identify the main components of the bags.

As described above, there are many analytical methods have been developed about the discrimination of plastic films.

In forensic science, analysis or identification of the materials and sampling of materials need to be done in non destructive or semi destructive way, in order not to damage substances which might be the evidence in court.

Engaged in chemistry in the forensic science for a long time, mainly in the appraisal and analysis of specialized industrial products, the authors has been interested in analytical methods of artificial materials such as ceramics and polymer. This dissertation contains five chapters about nondestructive discrimination methods for industrial materials such as plastic films and ceramics using morphological and spectroscopic analytical methods. Additionally, nondestructive sampling techniques to forensic materials like breath containing alcohol and oil found in fire scene was also described for practical on-the-spot inspections during this research. The author has examined spectroscopic analysis of such substances, and tried to get useful information of material identification and discrimination. Discrimination of industrial products which are aiming to produce a uniform quality of products and are manufactured under strict quality control could not be done fully. In the appraisal inspection of the industrial materials, it should be said that forensic evidence and products in control experiments are the same kind of material, furthermore, it should be appraised from what aspects they are same. Under this limited situations, the author has been trying to approach the analytical method of ceramics and polymer film that have never performed, showed it to be useful in some cases.

In Chapter 2, morphological and spectroscopic measurements of plastic bags were discussed for the purpose of discrimination. The colorless, transparent plastic bags commonly found in the home and are often used to package drugs were examined. Measuring methods were chosen that were either non-destructive or consumed only a very small portion of the sample. Since the polyethylene used for these bags is typically a partially crystallized polymer we decided to consider not only the standard spectroscopic and optical methods but also x-ray diffraction.

In Chapter 3, we combined several kinds of observation and analysis methods for many polyethylene resins utilized for plastic bags containing antiblocking agents for an improvement of the forensic discrimination process. Morphological

analysis using optical microscope (OM) observation, comparison of main component and trace constituent by way of energy dispersive X-ray spectrometry with scanning electron microscope (SEM-EDX), and microscopic Raman spectroscopy were employed for analysis of molecular structure of the antiblocking agents and films.

In Chapter 4, Microstructural analysis of ceramics was carried out for classification of their sources in various supplier based on the surface characteristics cleared by acid or thermal etching method by means of SEM observation.

For following chapters, practical applications of various materials and equipments utilized in on-the-spot inspections was studied.

In Chapter 5, the equipment of collecting expiration equipment for alcoholic breath inspection for the policeman was invented to extract expiration mandatorily on the site as soon as the court issues the warrant in case of inspection refusal.

In Chapter 6, we studied the sampling method of oil adsorption film for fire scene using a oil clear film commercialized as face-oil absorbing paper containing the sample of a mixture of gasoline and lubricant oil, which is commonly used for two-stroke engine mowers. Adsorption and packing condition for the transportation was investigated.

References

1. G. Gupta, C. Mazumdar, M.S. Rao, R.B. Bhosale, *Digital Investigation*, **3**, 43 (2006).
2. W. Smalldon and A.C. Moffat, *J. Forensic Sci. Soc.*, **13**, 291(1973).
3. H. H. Allen, *Nature*, **180**, 50(1957).
4. U. von Bremen, *J. Forensic Sci.*, **20**, 109(1975).
5. K. N. Ford, *J. Forensic Sci. Soc.*, **15**, 107(1975).
6. S. Denton, *J. Forensic Sci. Soc.*, **21**, 259(1981).
7. J. Gilbert, J. M. Ingram, M. P. Scott, and M. Underhill, *J. Forensic Sci. Soc.*, **31**, 337 (1991).
8. D. A. Castle, B. Gibbins, P. S. Hamer, *J. Forensic Sci. Soc.*, **34**, 61(1994).

9. T. Tsukame, Y. Ehara, Y. Shimizu, M. Kutsuzawa, H. Saitoh, and Y. Shibasaki, *Thermochim. Acta*, **299**, 27(1997).
10. T. Tsukame, M. Kutsuzawa, H. Sekine, H. Saitoh, and Y. Shibasaki, *J. Therm. Anal. Calorim.*, **57**, 847(1999).
11. K. E. Nissen, J. T. Keegan, J. P. Byrne, *Can. J. Anal. Sci. Spectrosc.*, **43**, 122 (1998).
12. C. Roux, *J. Forensic Sci.*, **45**, 99(2000).
13. V. Berx and J. De Kinder, *J. Forensic Sci.*, **47**, 976(2002).
14. V. Causin, C. Marega, P. Carresi, S. Schiavone, A. Marig, *Forensic Sci. Intern.*, **164**, 148(2006).
15. V. Causin, C. Marega, P. Carresi, S. Schiavone, A. Marig, *Forensic Sci. Intern.*, **168**, 37(2007).
16. E. Taylor, J. F. Carter, J. C. Hill, C. Morton, N. N. Daeid, R. Sleeman, *Forensic Sci. Intern.*, **177**, 214 (2008).

Chapter 2

Morphological and Spectroscopic Measurements of Plastic Bags for the Purpose of Discrimination

2.1 Introduction

Plastic bags are often a component of evidence that may be recovered from crime scenes. Therefore there may be a need to distinguish them when one wishes to connect plastic bags from different criminal events. Polyethylene can be classified into one of three types: low density polyethylene (LDPE), linear low density polyethylene (LLDPE), and high density polyethylene (HDPE). The polyethylene available in Japan includes domestic as well as imported products, particularly from China, South Korea, and Southeast Asia. Since we wanted to correlate the results to particular processing methods we limited our study to Japanese manufacturers for which we could obtain information on both the grade and quality.

In this study, we chose the colorless, transparent plastic bags that are commonly found in the home and are often used to package drugs. Measuring methods were chosen that were either non-destructive or consumed only a very small portion of the sample. Since the polyethylene used for these bags is typically a partially crystallized polymer (1) we decided to consider not only the standard spectroscopic and optical methods but also x-ray diffraction.

2.2 Experimental

2.2.1 Samples

In this study, the five principal domestic manufacturers offered us the polyethylene films manufactured by the inflation method using their own production pellets whose properties are known as Table 1. Ultimately, 31 samples, including low density polyethylene (LDPE), linear low density

polyethylene (LLDPE), and high-density polyethylene (HDPE) were evaluated and compared using the different techniques.

Table 1 Crystallinity of polyethylene is calculated by diffraction strength and thickness.

Sample name	Grade	Thickness /mm	Peak height (110)	Degree at maximum value
F101-1	LDPE	0.039	3097	21.3
F218-0	LDPE	0.032	2896	21.32
F412-1	LDPE	0.030	2220	21.26
FS140	LLDPE	0.034	4709	21.38
FS370	LLDPE	0.034	6431	21.32
FR151	LLDPE	0.032	3568	21.32
F184	HDPE	0.015	14437	21.5
F1920	LDPE	0.038	3858	21.26
M2204	LDPE	0.039	3211	21.3
F019	LDPE	0.023	4072	21.28
F022	LDPE	0.028	1955	21.34
F023	LDPE	0.023	1638	21.12
F222	LDPE	0.024	1713	21.22
F522	LDPE	0.023	1395	21.24
R300	LDPE	0.045	3135	21.34
R500	LDPE	0.026	2411	21.38
2100J	HDPE	0.033	11070	21.52
7000F	HDPE	0.024	13675	21.52
640UF	HDPE	0.032	9251	21.54
0134M	LLDPE(C4)	0.030	4484	21.38
0238H	LLDPE(C8)	0.028	4540	21.38
0358CN	LLDPE(C8)	0.029	5436	21.48
SP2040	LLDPE(C6)	0.052	5869	21.4
SP1520	LLDPE(C6)	0.049	6074	21.38
20200J	LLDPE(C6)	0.032	4318	21.36
LF440HB	LDPE	0.024	1624	21.36
UF421	LLDPE(C4)	0.034	2473	21.38
SF232	LLDPE(C6)	0.031	3507	21.46
HF313	HDPE	0.024	22191	21.58
HF334	HDPE	0.033	4403	21.5
KF270	LLDPE(C6)	0.058	5212	21.38

2.2.2 X-ray Diffraction

In fabricating the polyethylene films by the inflation method there is the possibility of texture development so diffraction was initially carried out both in a flow and transverse direction. The measurements were performed using a copper source in an XDS2000 type X-ray diffractometer made by Scintag Inc. Tube voltage was 45kV and tube current was 40mA. Diffraction angle (2θ) was rotated from 4 to 80 degree. Films are cut to a rectangular piece and mounted on powder diffraction holder. The diffraction patterns taken along the direction of flow and the transverse direction were mostly in agreement, and did not show any significant texture as shown in Figs. 1 and 2. Thus after the first few specimens the sampling directions of the test pieces for X ray diffraction were taken at random.

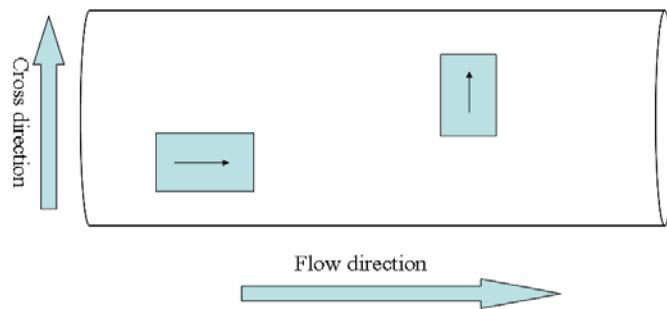


Figure 1. Directions of sample for X-ray diffraction measured along the flow and cross direction of the sample manufactured by the inflation method.

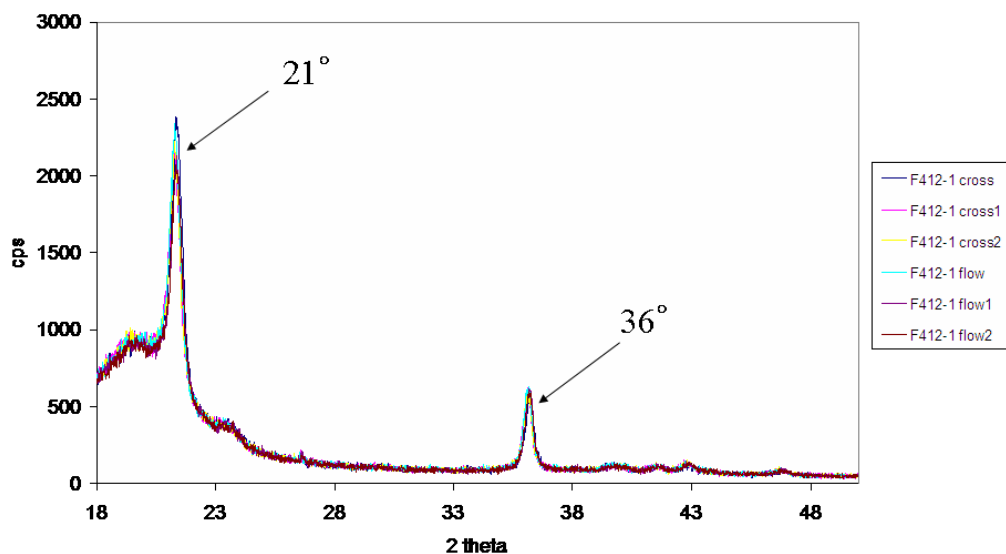


Figure 2 Comparison of x-ray diffraction to flow and cross direction.

2.2.3 Infrared Spectroscopic Analysis

Since the polyethylene films proved to be too thick for transmission analysis and because of the difficulties associated with mounting the films, we resorted to a single bounce attenuated total reflection technique (2). The diamond ATR prism produces a large absorption in the region of interest limiting the available spectral range. However we had good success with Zinc Selenide (ZnSe) at 45° incidence and measurements were taken utilizing a Pike Technologies constant-pressure gauge in conjunction with the Bruker Tensor 37 FT-IR. For each sample, 64 scans were co-added to enhance the signal-to-noise ratio for the smaller absorption features since the major spectral features showed little variation.

2.2.4 Optical Microscopy

Samples were observed using differential interference contrast microscopy (DIC) and phase contrast microscopy to highlight differences in the microstructure, refractive index and surface morphology, the most useful magnification range being around 200 times. DIC observation which can visualize surface concavity and convexity was performed using a Nikon LabOPHOT-2 microscope and the pictures were taken by PAXCAMERA. Phase contrast observations which can visualize the difference in density (3) were performed using an OLYMPUS BX51 microscope with a UPlanApo20x/0.70Ph2 objective lens and was conducted in the Sacramento County Laboratory of Forensic Services.

2.3 Results and Discussion

2.3.1 X-ray Diffraction

X-ray diffraction is an excellent method for distinguishing the different types of polyethylene as shown in Fig. 3. In the linear low density and high density polyethylene, there are recognizable peaks around 23 and 36 degrees, the former being more pronounced in the high density form with the linear low density having an additional shoulder peak at 19 degrees. The peak at 19 degrees appears alone in the general low density form (LDPE) and as a general rule one can fairly easily recognize the different types. In LLDPE a peak appears near 23 degrees and the

peak near 36 degrees decreases. In HDPE, the peak near 23 degrees becomes larger, and the peak near 36 degrees decreases further.

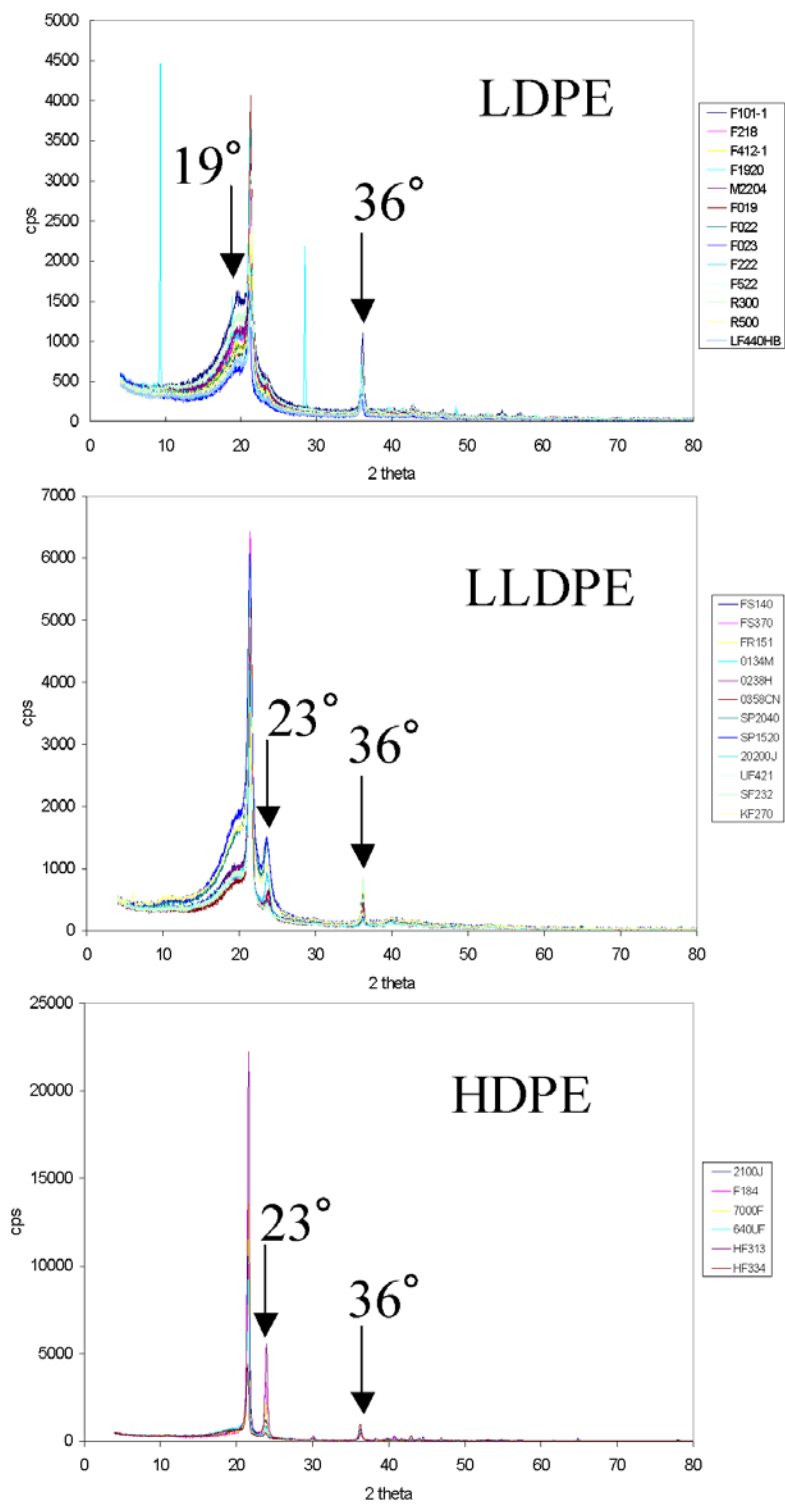


Figure 3. Comparison of X-ray diffraction patterns according to PE grade, LDPE, LLDPE and HDPE.

In terms of distinguishing the products from the different manufacturers in LDPE and HDPE there was one sample in each batch that could be clearly distinguished, but the rest were similar. These were sample F1920 amongst the 13 samples of LDPE and sample 2100J from the 6 samples of HDPE as shown in Figs. 4 and 5, respectively. In LLDPE none of the 12 samples showed any individuality that could be recognized. All of the samples also displayed a peak at about 21 degrees as shown in Table1. Nevertheless such distinctions would certainly not be obvious.

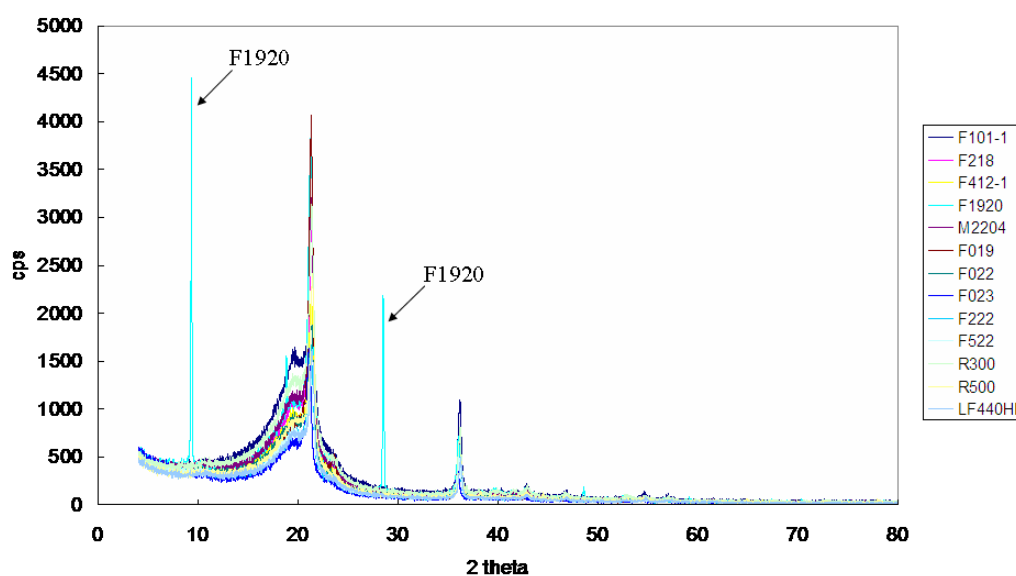


Figure 4. Distinguishable XRD pattern of F1920 from the other LDPE films.

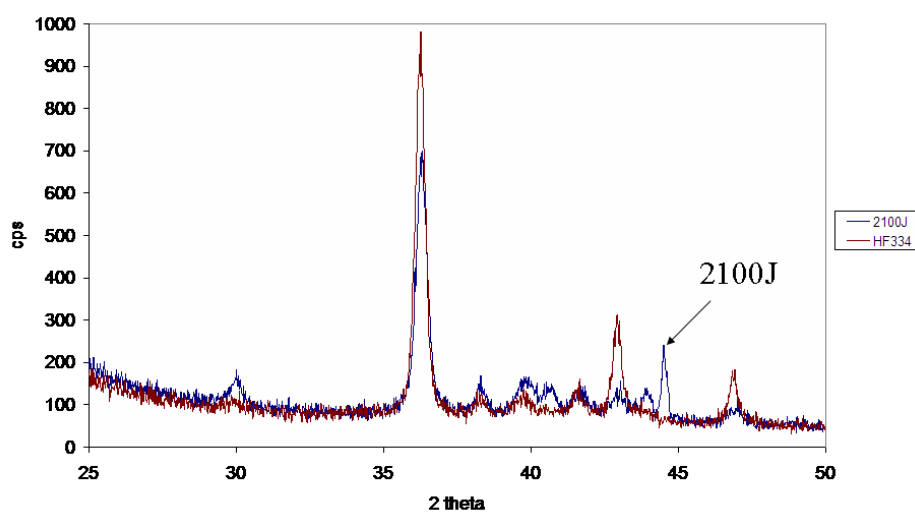


Figure 5. Distinguishable XRD pattern of 2100J from the other HDPE films.

2.3.2 Infrared Spectroscopic Analysis

The infra red spectra from the samples produced similar results in that in LDPE, one of the 13 samples was clearly distinguishable (Fig. 6) as was one of the 12 samples of LLDPE (Fig. 7) and one of the six samples of HDPE (Fig. 8). Using the Bruker classification software, all 31 of the samples were recognized individually. The difference in the spectral were subtle and, for the most part, not recognizable to the naked eye.

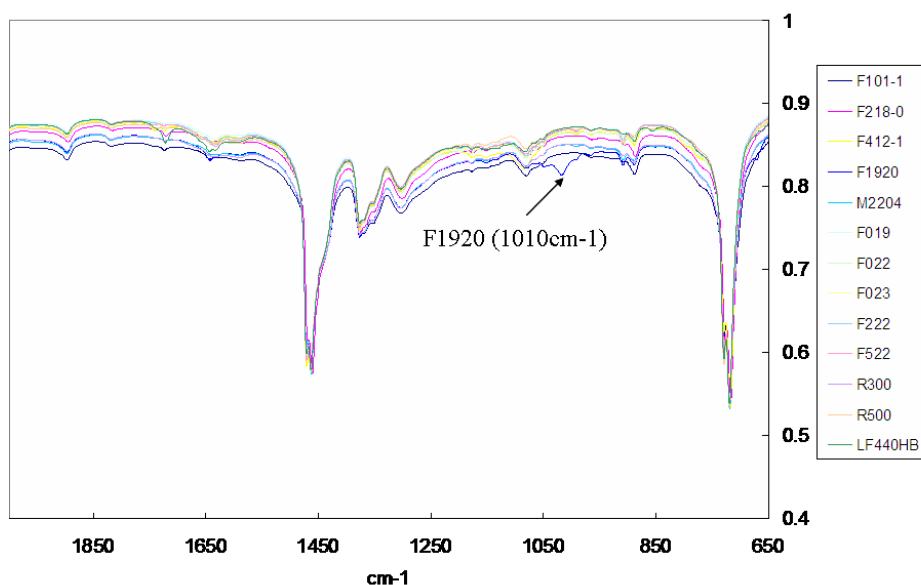


Figure 6. Distinguishable XRD pattern of F1920 from the other LDPE

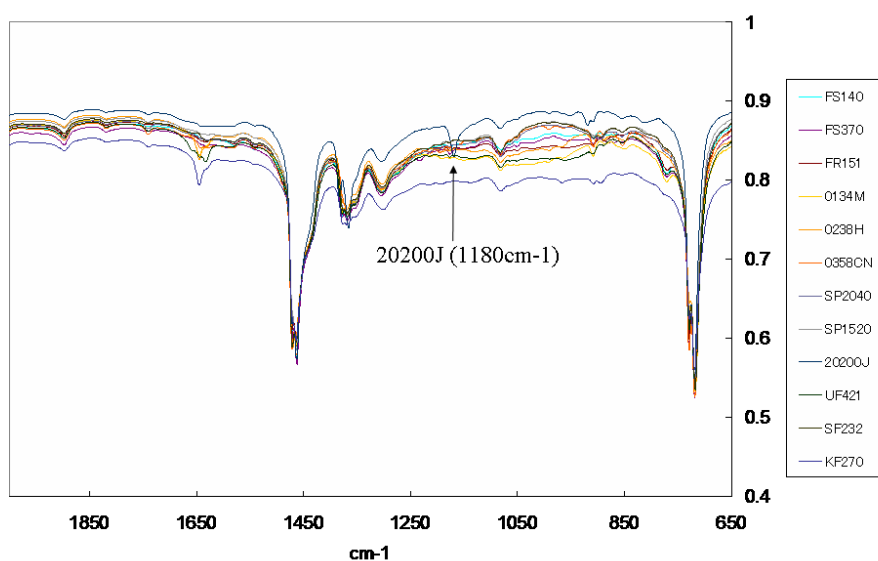


Figure 7. Distinguishable XRD pattern of 20200J from the other LLDPE

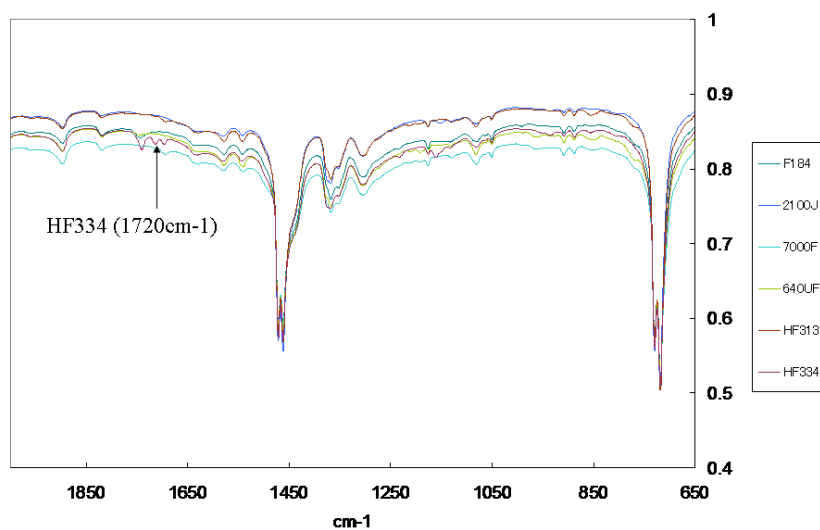


Figure 8. Distinguishable XRD patterns HF334 from the other HDPE

2.3.3 Optical Microscopy

Using DIC images and phase contrast images, each image was compared to the others in the same type of polyethylene: low density polyethylene (LDPE), linear low density polyethylene (LLDPE), and high-density polyethylene (HDPE).

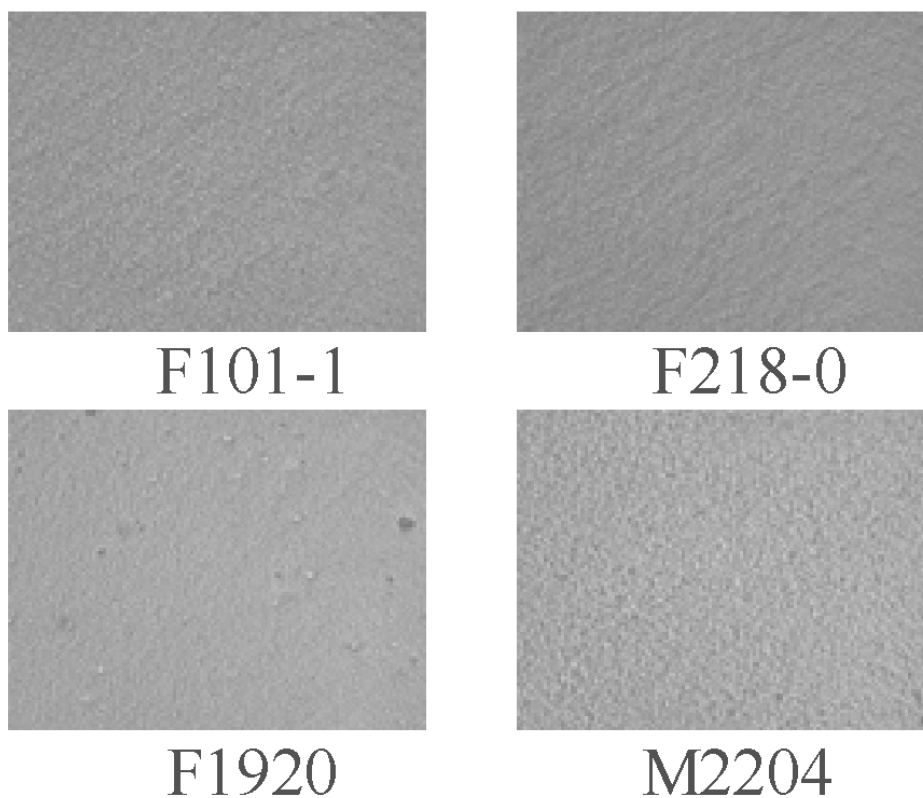
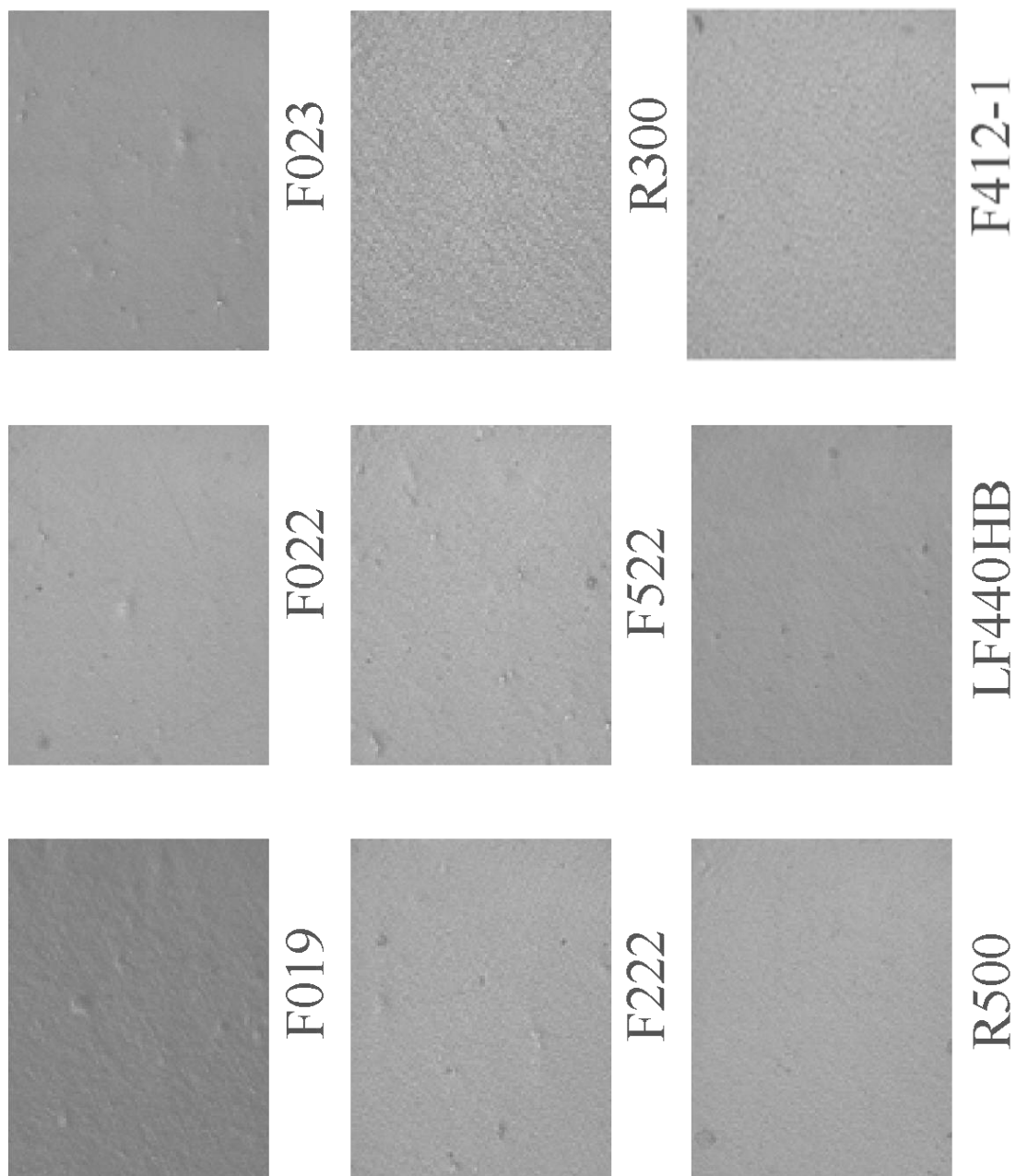


Figure 9. Typical DIC images of LDPE.

Figure 9. (Continued)



There are 78 combinations in low density polyethylene, 66 combinations in linear low density polyethylene and 15 combinations in high density polyethylene. Optical Microscopy (DIC and phase contrast microscopy) was the most powerful of the discriminatory tools. Using DIC observation; 72 of the 78 combinations were distinguishable (Fig.9). However five combinations between F101-1 and R300, between F1920 and F522, between F022 and F023, between F023 and F522,

between F522 and LF440HB, are indistinguishable in all of the possible 78 paired polyethylene samples.

In the LLDPE group, 62 of the 66 combinations were distinguishable (Fig. 10). Three combinations between FS140 and 0358CN, between FR151 and UF421, between UF421 and 0238H are indistinguishable in all of the possible 66 paired polyethylene samples.

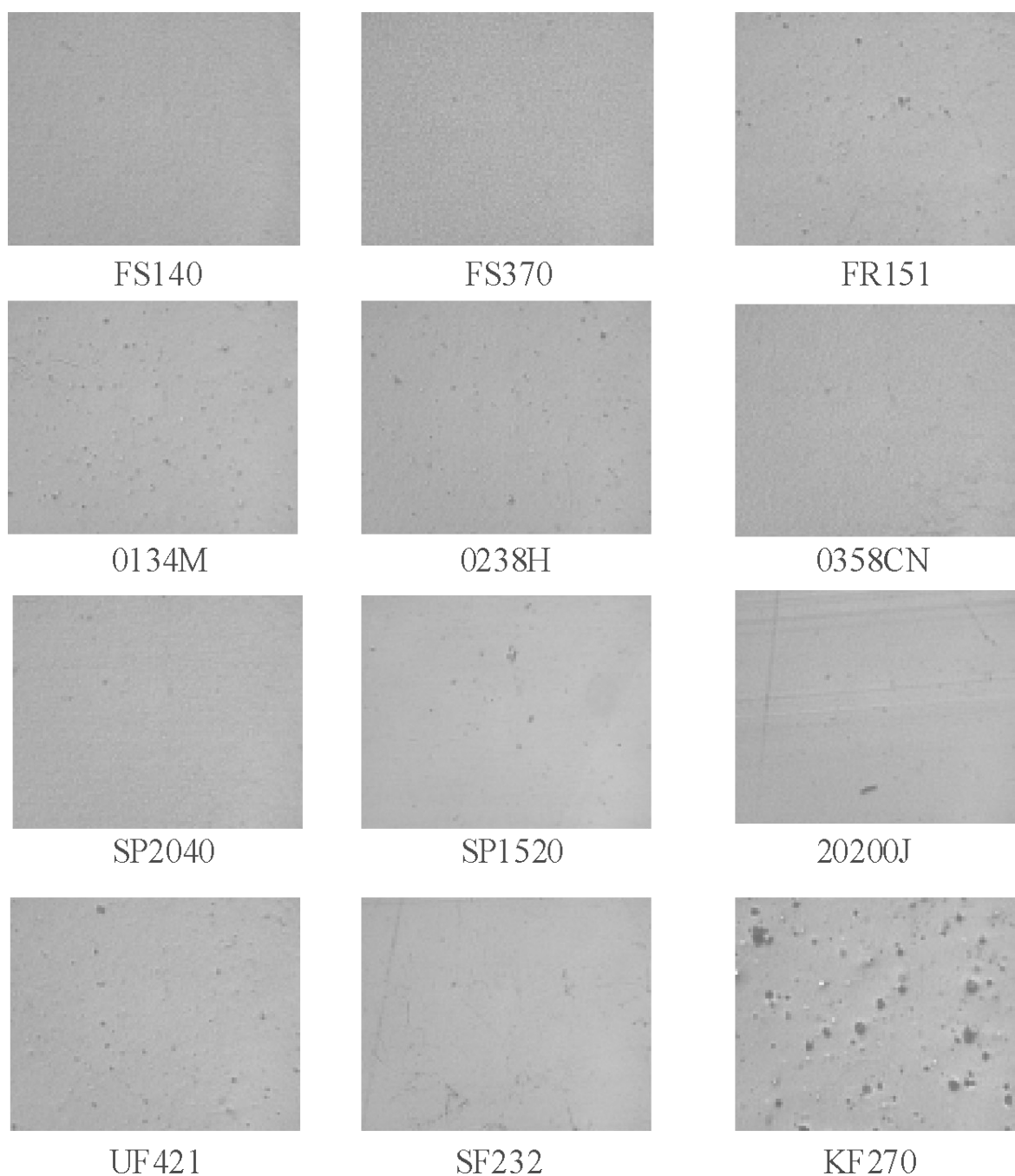


Figure 10. DIC images of LLDPE film samples.

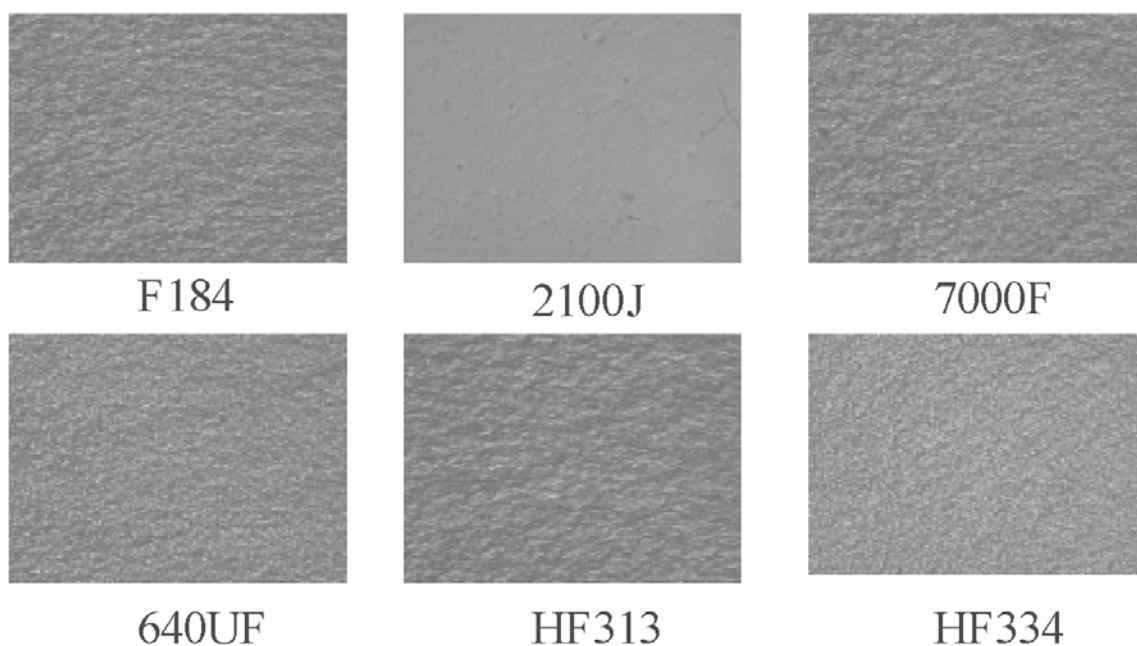


Figure 11. DIC images of HDPE film samples.

In the HDPE samples, it was 11 out of the 15 combinations that were distinguishable as shown in Fig. 11. Combination among F184, 7000F, and HF313 is indistinguishable in all of the possible 15 paired polyethylene samples. Using phase contrast observations, each sample can be distinguish among all samples for LDPE, LLDPE, and HDPE samples as shown in Figs. 12-14, except for F022 and F023 in 78 combinations of the LDPE samples, 0134M and 0238H in 66 combinations of the LLDPE samples, and F184 and 7000F in 15 combinations of the HDPE samples, respectively.



Figure 12. Phase contrast images of LDPE film samples.

Figure 12. (Continued)



F222



F522



R300



R500



F101-1



F218-0



F412-1



M2204



F1920



LF440HB

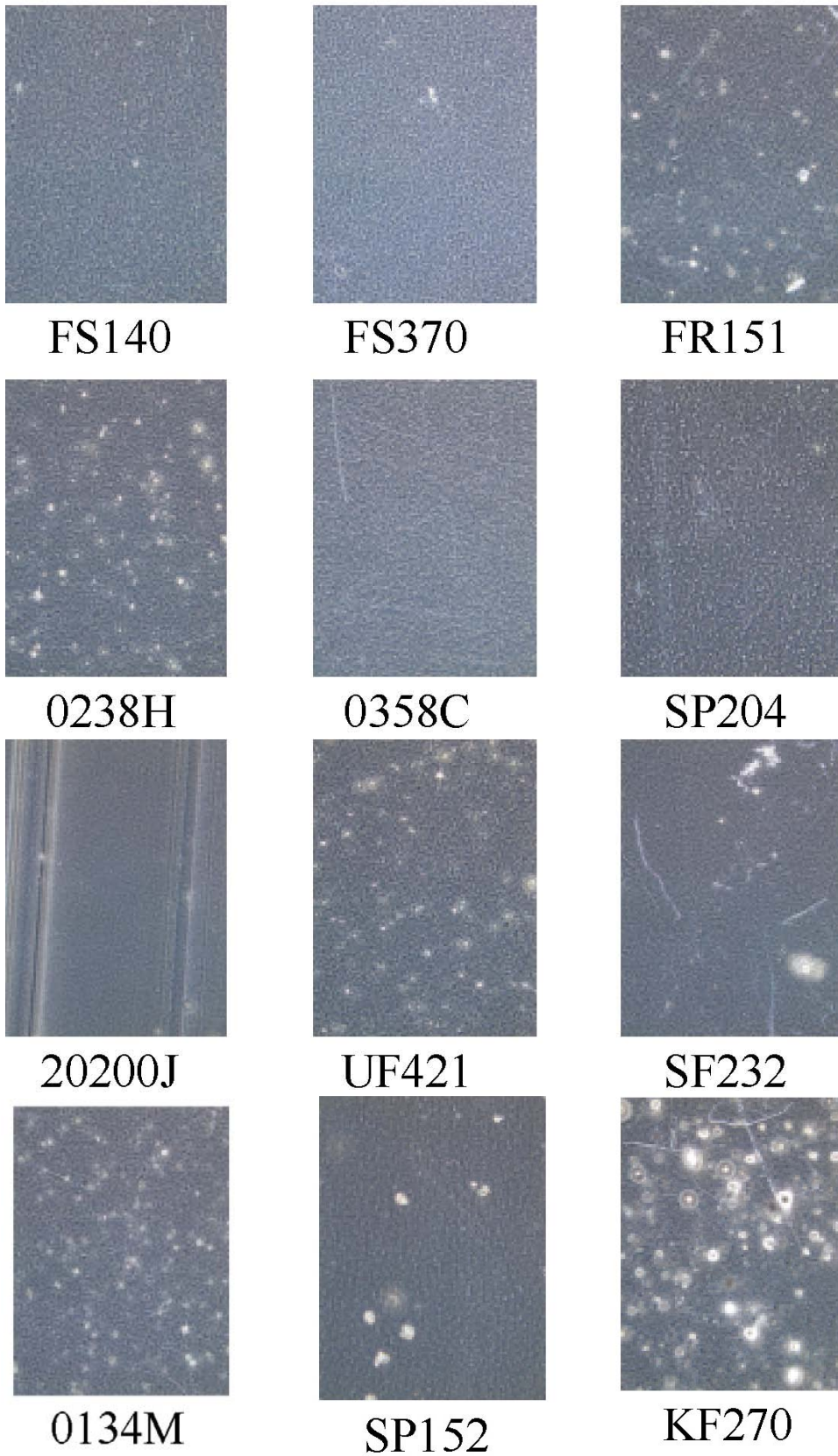
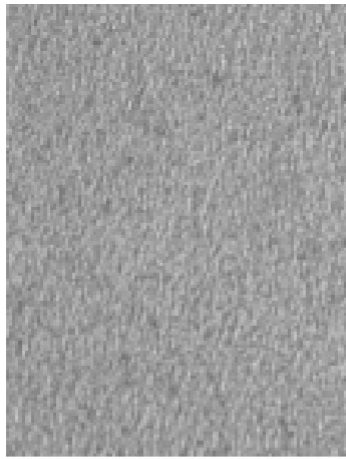
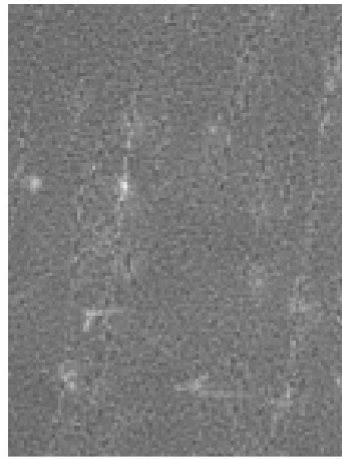


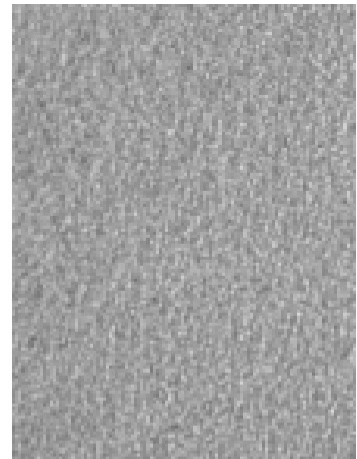
Figure 13. Phase contrast images of LLDPE film samples.



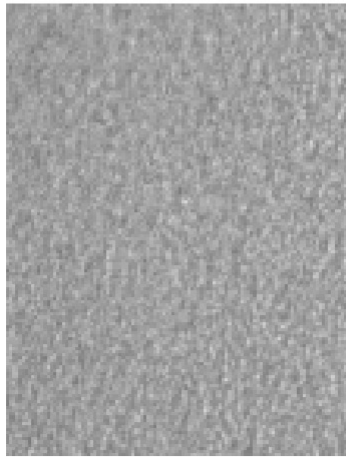
F184



2100J



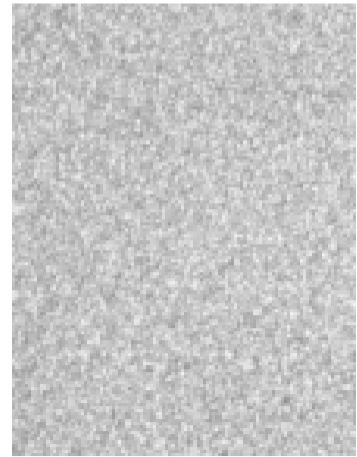
7000F



640UF



HF313



HF334

Figure 14. Phase contrast images of HDPE film samples.

2.4 Conclusions

X-ray diffraction would seem to be effective in classifying the type and category to which the polyethylene belongs, that is, low density, linear low density and high density. In terms of individualizing these films, there is reasonable discrimination using ZnSe ATR infra red spectroscopy. Using classification software, one can easily classify samples individually. It would seem that for comparison purposes if standards are available optical microscopy would seem to be by far the best method for discrimination. Clearly the structural and chemical differences between the films are somewhat marginal, but the different manufacturing processes clearly produce distinctly different morphologies and textures in the films that can be readily identified using optical microscopy. Phase contrast microscopy may be a little better to DIC microscopy.

References

1. K. M. Furuheim, D. E. Axelson, H. W. Antonsen, and T. Helle, *J Appl. Polym. Sci.*, **91**, 218(2004).
2. A. W. Hartshorne and D. K. Laing, *Forensic Sci. Intern.*, **26**, 45(1984).
3. M. Abramowitz, "Phase contrast microscopy" in "Contrast methods in microscopy -transmitted light-. Vol.2", Basics and Beyond Series, Technical Information, Olympus America Inc.; pp.19-23 (1985).

Chapter 3

Discrimination of transparent polyethylene films based on identification of inorganic antiblocking agents for forensic purpose

3.1 Introduction

Since plastic bags made of polyethylene film are the common packing materials in daily life, they are generally used for packing food and medicine. They are also used for packing crime evidential materials such as illegal medicine or arms. Discrimination among various kinds of the plastic bags containing crime evidences and unused plastic bags kept in the house of the suspect is often requested.

On the other hands, the comparison of morphology, color, major component and trace constituent is necessary in forensic discriminations of materials (1). Whereas colored films can be discriminated by their own color, transparent films need other methods for the discrimination. Especially, both non-destructive and semi-destructive methods are necessary to analyze crime evidences. Many polyethylene resins for plastic bags contain antiblocking agent added at the stage of blow molding. Materials of antiblocking agent are various inorganic oxides such as silica, aluminosilicate, talc, zeolite, and so on. An identification of antiblocking agents is the important procedure in discriminating plastic bags. For the classification of the various kinds of polymer samples, vibrational spectroscopy such as IR absorption and Raman scattering are useful. However, since particles of antiblocking agents are scattered and buried in the films, it was difficult to apply an infrared spectrometry with any attachments such as ATR and microscopic FT-IR (2). On the other hands, the microscopic Raman (Micro-Raman) might be applicable for analysis of the antiblocking agents in the transparent and thin films due to small focusing area including the agents and strong scattering intensity which can be controlled by a laser intensity of localized

light source in the small target on the film samples (3).

In this study, we combined several kinds of observation and analysis methods for many polyethylene resins utilized for plastic bags containing antiblocking agents for an improvement of the forensic discrimination process. Morphological analysis using optical microscope (OM) observation, comparison of main component and trace constituent by way of energy dispersive X-ray spectrometry with scanning electron microscope (SEM-EDX), and microscopic Raman spectroscopy were employed for analysis of molecular structure of the antiblocking agents and films.

3.2 Experimental

3.2.1 Samples

Polyethylene films have been classified into three kinds; such as low density polyethylene (LDPE), linear low density polyethylene (LLDPE), and high density polyethylene (HDPE) which can be classified by near infrared spectroscopy (4). Since adhesion of HDPE is rarely occurred, most of commercialized HDPE does not include antiblocking agents. Therefore we focused on LDPE and LLDPE samples mainly in this study as shown in Table 1. Fifteen kinds of film samples blow-molded from their own resins are collected from five Japanese suppliers by necessity of confirming information of antiblocking agent without unknown compositions or natures. Original samples of the antiblocking agents contained in those films were also examined and compared each other.

3.2.2 Optical microscope observation

Antiblocking agents were observed by the optical microscope (OM) because polyethylene films are transparent. Particle size and dispersion of the antiblocking agents can be examined by digital microscope KEYENCE VHX-1000/1100. A characteristic shape, morphology, and diameter of particles of antiblocking agents are analyzed from OM images using image analysis software Scion image (Scion Corporation) statistically. Since each thickness of supplied polyethylene films was around ca. 30 micrometers and contained

antiblocking agents were dispersed in every region, focus point was slid from lower surface to upper surface of each film and the OM images were collected at several steps and merged. Consequently, clear images containing all particles were obtained in the focusing area.

Table 1 Component of antiblocking agents and assignments of vibrational mode in Raman spectra.

Supplier Sample	Kinds of PE	Kinds of antiblocking agents(AB) and analyzed contained elements	Assignments in Raman spectra
Sumitomo Chemical			
F412-1	LDPE	Silica	Si-O E(t)+E(1) (128 cm ⁻¹) A ₁ (205 cm ⁻¹) A ₁ (463 cm ⁻¹) *Ref. 7
F208-3	LDPE	Silica	
Ube-maruzen			
F019	LDPE	Natural silica	
F022	LDPE	Natural silica	
F023	LDPE	Natural silica	
F222	LDPE	Natural silica	
F522	LDPE	Natural silica	
Sumitomo Chemical			
FR151	LLDPE	Aluminosilicate	Si-O bridging (485 cm ⁻¹) Al-O (ca.700cm ⁻¹) *Refs. 8, 9
FR153	LLDPE	Aluminosilicate	
CL1083	LLDPE	Aluminosilicate	
Prime Polymer			
0134M	LLDPE	Aluminosilicate	
0238M	LLDPE	Aluminosilicate	
Asahi Kasei			
F1920	LDPE	Talc	O-H-O(199 cm ⁻¹) v ₅ (e)SiO ₄ (388 cm ⁻¹) v _s Si-O _b -Si(680 cm ⁻¹) *Refs. 10, 11
Japan Polyethylene			
LF440HB	LDPE	CaSO ₄	v ₂ (SO ₄) (412 cm ⁻¹ , 492cm ⁻¹) v ₄ (SO ₄) (605 cm ⁻¹ , 621 cm ⁻¹) *Ref. 12

3.2.3 Observation and element analysis of antiblocking agents using SEM-EDX

Morphology and element analysis of the antiblocking agents were carried out by energy dispersive X-ray spectrometry with scanning electron microscope (SEM-EDX) using QUANTA200F with EDAX QUANTA400 EDX spectrometer (FEI Company). Acceleration voltage was 15kV under low vacuum condition of 90Pa. Magnification for EDX analysis was mainly at 800.

3.2.4 Microscopic Raman spectrometry

Although the size of many particles of antiblocking agents was very small; from a few microns to about 10 microns, by optical microscope observation, we were able to obtain characteristic micro Raman spectra of various antiblocking agents buried in the polyethylene films within twenty-second exposure time using high sensitive microscopic Raman equipment. Microscopic Raman spectroscopy was performed by microscopic laser Raman spectrometer SENTERRA™ (Bruker Optics) equipped with microscope BX51 (Olympus, Japan). Sample was excited by second harmonic Nd:YAG laser of which wavelength was 532 nm. Scattered light from the sample was detected by CCD with 1024 × 255 pixels. The laser power, integration time are 20mW and 2-20 seconds, respectively. Laser was focused into the specified area of ca. 1 μm x 1 μm which includes a single particle of the antiblocking agents.

3.3 Result and discussion

3.3.1 Optical microscope

Digitally merged images of LLDPE FR151 sample observed by optical microscope were shown in Fig.1. Internal distribution of antiblocking agents of transparent plastic film can be observed. It is possible

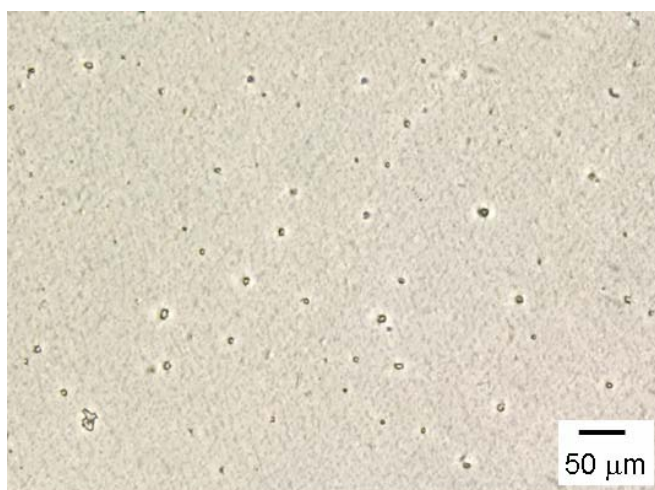


Figure 1. Digital microscope image of LLDPE film with antiblocking agent of aluminosilicate (FR151).

to determine the type of antiblocking agents to some extent by visually observing the shape and size of the particle. It is also possible to sort out the differences between the evidence and the film needed to be contrasted. In addition, the image was captured in analysis software Scion Image and the numerical information was available about the size of the particle. Typically, the particle size distributions of two kinds of films containing aluminosilicate antiblocking agents such as F151 and CL1083 are shown in Fig. 2. Particle size distributions of these films are obviously different. Such information of the particle size distribution is useful in roughly discrimination as the first procedure.

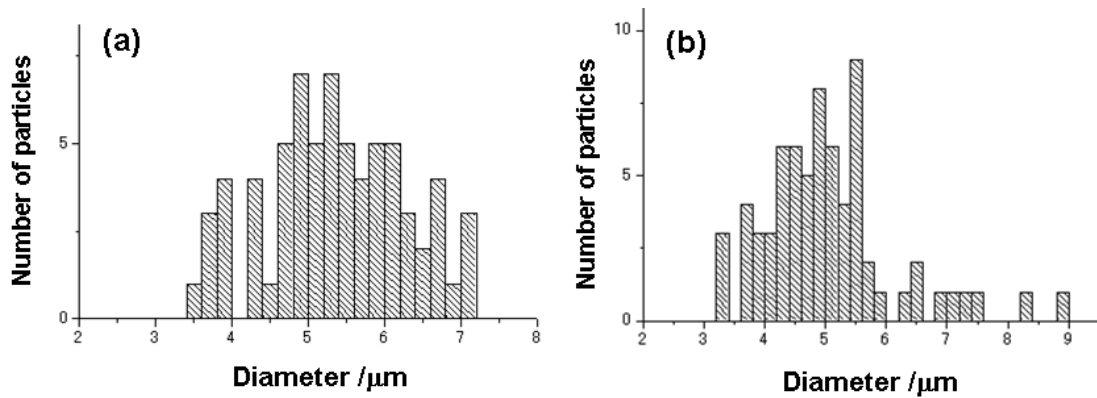


Figure 2. Particle diameter distributions of antiblocking agent using Aluminosilicate; (a)FR151 and (b) CL1083.

3.3.2 Observation and elemental analysis of antiblocking agents using SEM-EDX

In the observation using optical microscope, the sub-milli order structure and its size distribution can be discriminated. However, various kinds of samples have resembled size distribution and sometimes it is necessary to classified by the elemental analysis. Since most antiblocking agents consist of light elements as shown in Table 1, an EDX analysis is applicable for detail analysis of the antiblocking agents. Comparing the EDX profiles of the samples for F208-3 containing silica and CL1083 containing aluminosilicate which have similar size distribution, containing elements are assigned by EDX spectra as shown in Fig.3.

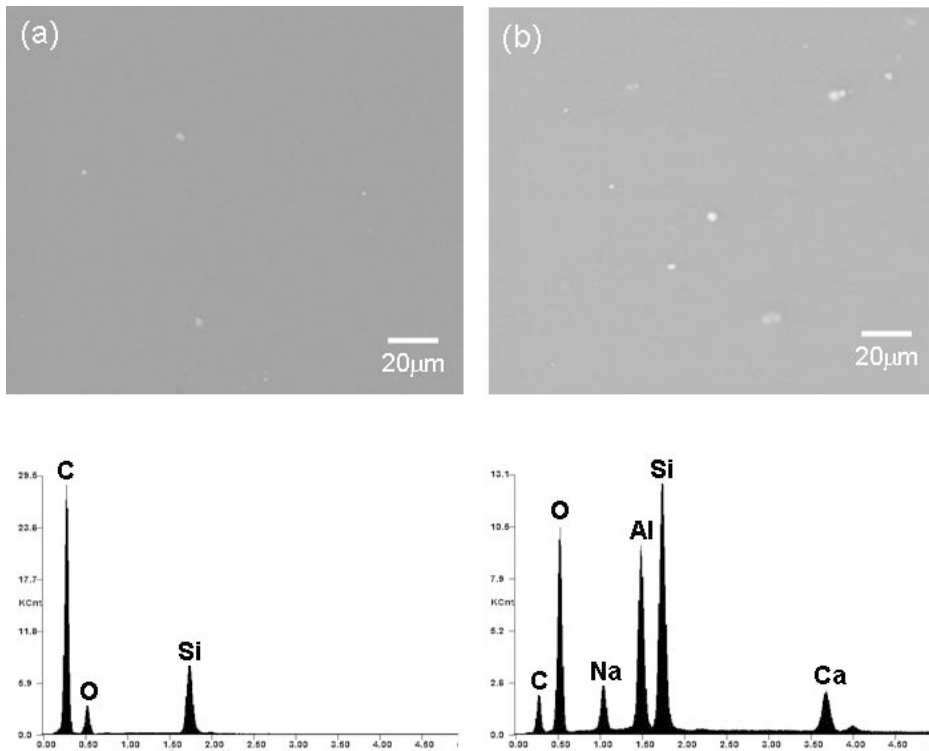


Figure 3. SEM images and EDX spectra of antiblocking agent in polyethylene films (a)F208-3 (Silica) and (b) CL1083 (Aluminosilicate).

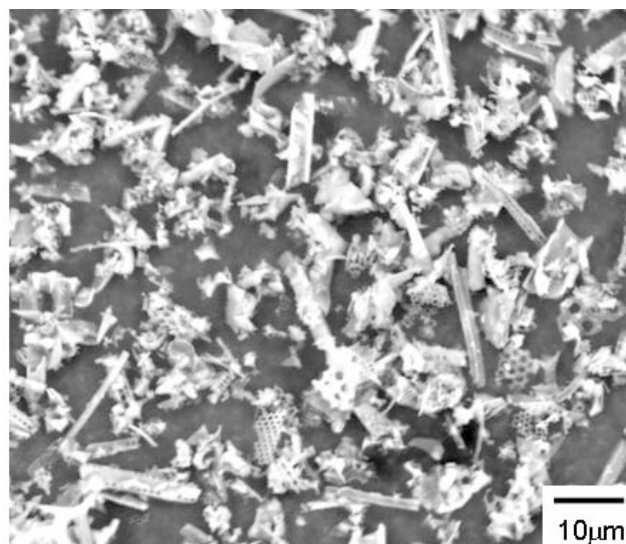


Figure 4. Characteristic morphological discrimination of natural diatomite silica mineralized from diatoms.

Some agents have a peculiar shape due to the origin of the samples such as natural diatomite silica mineralized from diatoms as shown in Fig. 4. Although samples of F019, F022, F023, F222, and F522 containing the diatomite silica have a similar composition with the film containing silica such as F412-1, F208-3, it is necessary to be classified by not only the composition analysis but also the direct observation under high magnification.

It is noticed that the SEM-EDX observation should be carried out under the low vacuum condition at 90 Pa in order to avoid the charge-up of the polymer film without sputtering treatment for non-destructive observation. Therefore, the SEM-EDX observation of the polyethylene samples is not more predominant than the OM analysis on the forensic purpose requesting to maintain the original status of the samples.

3.3.3 Microscopic Raman spectrometry

Normal Raman spectra of various inorganic compounds have been measured by numerous studies. Some compounds are summarized in the spectroscopic articles and it seems to be possible to discriminate based on the database (5, 6). However, since little amount of the antiblocking agents is contained in each polyethylene film, it is necessary to control the optical alignment to apply the laser to single or few particles of the agents focused enough to be observed visually and measured (3). In Fig.5, the focusing area of the micro-Raman spectra of the films containing antiblocking agents such as (a)silica (synthesized; F412-1) (b)natural silica (F019), (c)aluminosilicate (CL1083), (d)talc (F1920), and (e)calcium sulfate (LF440HB) are shown. We have confirmed that such size of area is enough to obtain the Raman spectra covering each fingerprint range of the antiblocking agents without hiding in the fingerprint region of polyethylene, which ranged in ca 1000-1400 cm^{-1} . As shown in Fig.6, the micro-Raman spectra of the films containing antiblocking agents are shown. As a reference, the spectra of original antiblocking agents are also shown in the same figures. It is possible to distinguish among the inorganic compounds which were used using pattern analysis of the spectra in the fingerprint range of the agents. For silica sample, the Raman peak assigned to E(t)+E(1) at 128 cm^{-1} , A₁ at 205 cm^{-1} , A₁ at 463 cm^{-1} ,

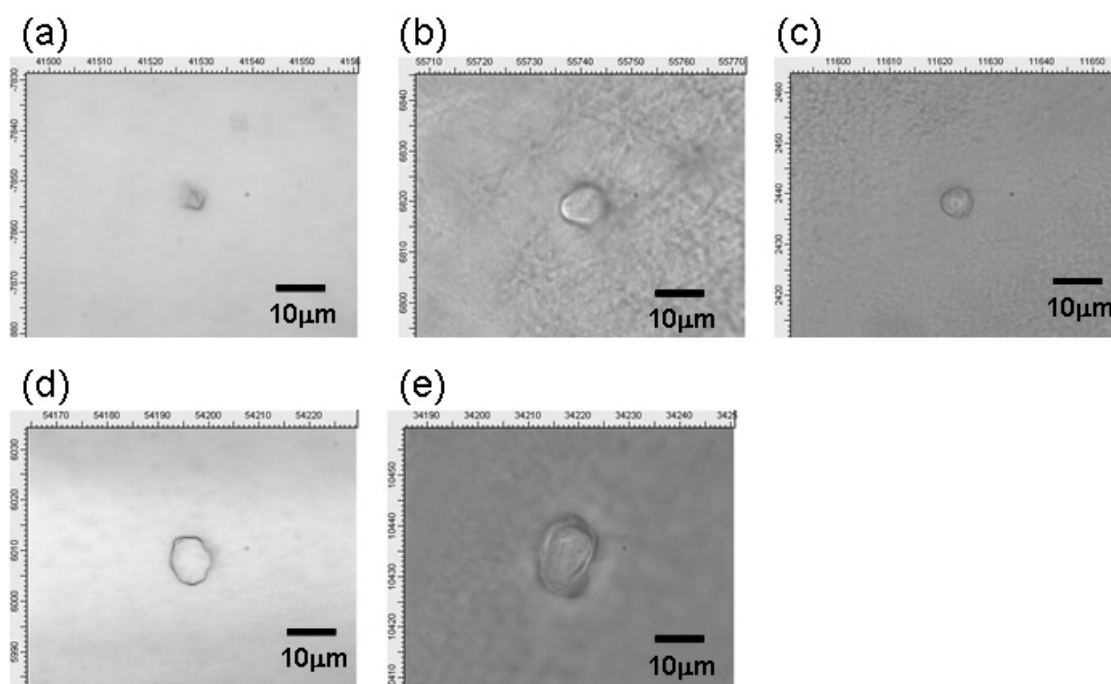


Figure 5. Microscopic view image of antiblocking agent (silica) for Raman spectra measurement of polyethylene films containing antiblocking agents; (a) F412-1(silica), (b)F019 (natural silica), (c) CL1083 (aluminosilicate), (d)F1920 (talc), and (e)LF440HB (CaSO_4).

and so on, were observed clearly as shown in Fig.6a (7). As shown in Fig.6, the micro-Raman spectra of the films containing antiblocking agents are shown. As a reference, the spectra of original antiblocking agents are also shown in the same figures. It is possible to distinguish among the inorganic compounds which were used using pattern analysis of the spectra in the fingerprint range of the agents. For silica sample, the Raman peak assigned to $E(t)+E(1)$ at 128 cm^{-1} , A_1 at 205 cm^{-1} , A_1 at 463 cm^{-1} , and so on, were observed clearly as shown in Fig.6a (7).

Similarly, each major peak was observed in the fingerprint range for the other samples as shown in Table 1. It is suggested that the micro-Raman spectroscopy can be applicable to the discrimination of the polyethylene films containing antiblocking agents, since most inorganic compounds which are utilized for antiblocking agents are oxides under the non-destructive spectroscopic analysis.

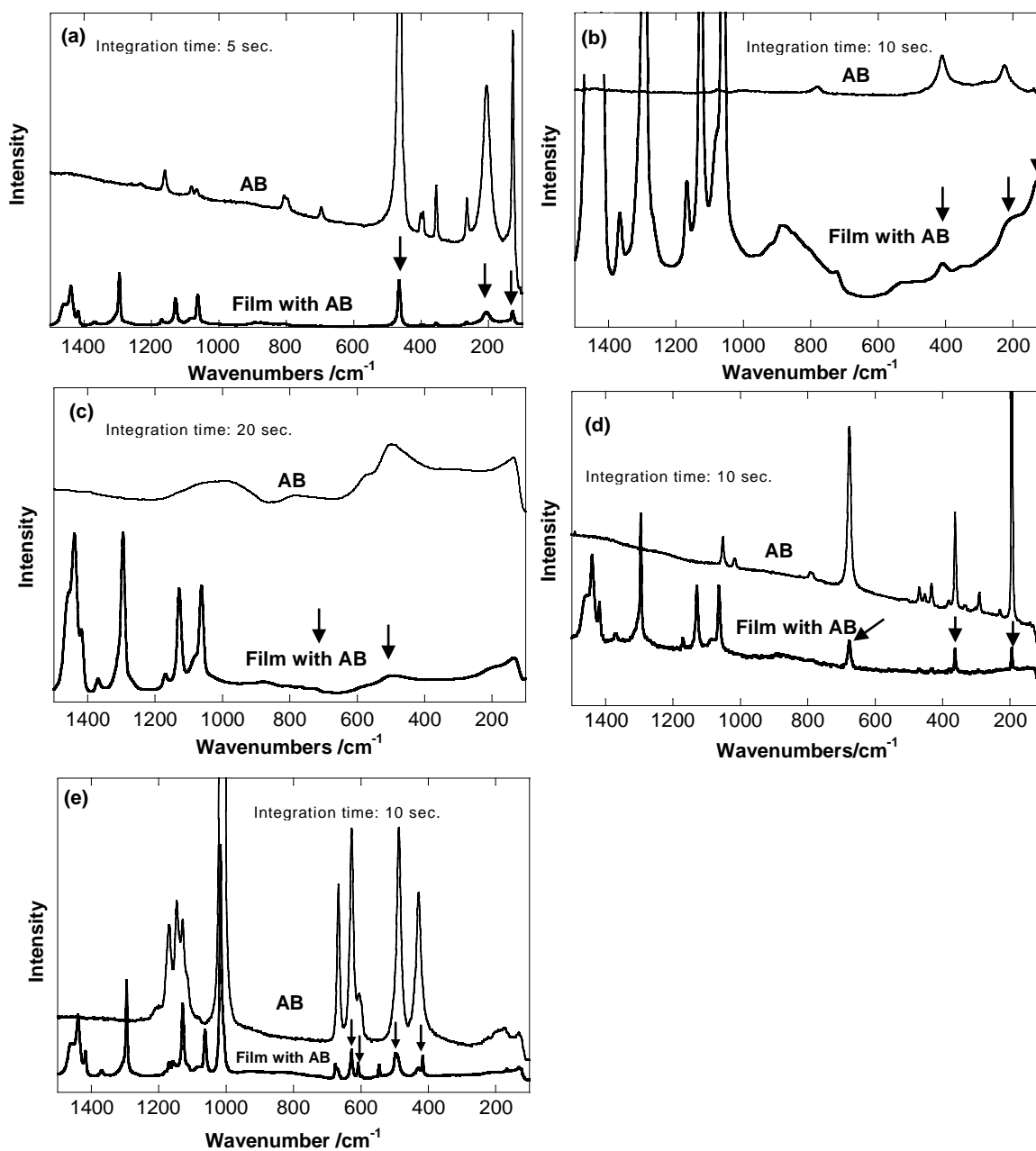


Figure 6. Raman spectra of polyethylene films containing antiblocking agents (Film with AB) and the powder of the original antiblocking agents (AB). Kinds of films and contained antiblocking agents: (a) F412-1(silica), (b)F019 (natural silica),(c) CL1083 (aluminosilicate), (d)F1920 (talc), and (e)LF440HB (CaSO_4). Assignments of vibrational modes indicated by arrow are shown in Table 1.

3.4 Conclusions

The optical microscope (OM), SEM-EDX, and micro-Raman spectroscopic analysis are applied to the polyethylene films in order to discriminate the antiblocking agents. The antiblocking agents are observed by the optical microscope, and by using resemble optical alignment, Raman spectra of inorganic compound which is included in antiblocking agents in commercialized polyethylene films. Using EDX measurement, the elemental analysis of the agents are measured and analyzed with the Raman spectra mutually. We hope this should be useful in forensic discrimination of plastic bags. There are also other additives to plastic bags such as antioxidant, lip, and antistatic agent. It might be necessary to consider how to identify such additives as well as this report.

References

1. Y. Nir-El, *J. Forensic Sci.*, **39**, 758(1994).
2. T. Hashimoto, D. G. Howitt, D. P. Land, F. A. Tulleners, F. A. Springer, and S. Wang, *J Forensic Sci*, **52**, 1082(2007).
3. R. Tabaksbrat, R. J. Meier, and B. J. Kip, *Appl. Spectrosc.*, **46**, 60(1992).
4. H. Sato, M. Shimoyama, T. Kamiya, T. Amari, S. Šašić, T. Ninomiya, H. W. Siesler, and Y. Ozaki, *J. Near Infrared Spectrosc.*, **11**, 309(2003).
5. L. Burgio, and R. J. H. Clark, *Spectrochim. Acta. A* , **57**, 1491(2001).
6. K. Nakamoto, “*Infrared and Raman Spectra of Inorganic and Coordination Compounds, 5th Edition, part A: Theory and Applications in Inorganic Chemistry*”, pp.153-319, John Wiley & Sons, NY (1997).
7. R. K. Sato and P. F. McMillan, *J. Phys. Chem.*, **91**, 3494(1987).
8. P. K. Dutta and B. D. Barco, *J. Chem. Soc. Chem. Commun.*, 1297(1985).
9. D. A. McKeown, F. L. Galeener, and G. E. Brown Jr, *J. non-crystalline Solids*, **68**, 361(1984).
10. J. J. Blaha and G. J. Rosasco, *Anal. Chem.*, **50**, 892(1978).
11. C. Rinaudo D. Gastaldi, and E. Belluso, *The Canadian Mineralogist*, **41**,

883(2003).

12. E. Knittle, W. Phillips, and Q. Williams, *Phys. Chem. Minerals*, **28**, 630(2001).

Chapter 4

Microstructural Analysis of Ceramics for Forensic Discrimination

4.1 Introduction

Ceramics are synthetic materials, produced from non-metallic inorganic solid bound together by sintering at high temperature. Since they possess several useful characteristics such as heat-resistance, corrosion-resistance, reasonable strength, insulation, or semiconductivity, fine ceramics have become widely employed as industrial materials. These uses include alumina ceramics as IC substrates, translucent alumina as optical materials, zirconia ceramics as edge tools and silicon carbide and silicon nitride as a heat-resisting materials. Sapphire(alumina singlecrystal) and hydroxy apatite which exhibit high strength are referred to as bioceramics and are used as artificial teeth or bones (1-3). The ever growing use of ceramics has resulted in these materials or articles composed of ceramics being encountered more commonly as physical evidence in criminal cases (4, 5), in one case a fragment of the dental porcelain(artificial tooth) found in the murder site was identified the artificial tooth of the suspect in a murder case, and in another case the manufacturer was determined from a minute fragment of a zirconia ceramic cutleries by means of scanning micro photography. Establishment of forensic science methods for distinguishing the characteristics of these materials is needed for criminal investigations. The scanning electron microscope(SEM) is well suited for the observation of the microstructure of ceramics materials. It is well known that size and shape of grains of sintered polycrystalline ceramics are affected by the condition of the sintering process and nature of the original ceramic powder (6-12).

In this study, the aim was to classify ceramics from different sources by SEM observation of their microscopical surface characteristics which was cleared by acid or thermal etching method.

4.2 Experimental

4.2.1 Materials

Nineteen alumina ceramic samples manufactured by nine ceramic companies in Japan were collected. Their alumina content varied and was divided into three groups according to alumina content (Low purity approximately 92%, Medium purity 96~98% and High purity more than 99% see Table 1).

Table 1. Density of alumina ceramics.

Supplier	Grade name	Purity(%)	Density
S	A-392	92	3.627
	A-396	96	3.736
	A-399	99	3.997
NK	SSA-A	92	3.895
	SSA-990	99	3.904
NT	KP-990	99	3.859
I	----	96	3.753
	----	99.5	3.991
N	----	92	3.545
	----	96	3.768
	----	99.8	3.919
O	----	92	3.618
	----	97	3.770
	----	99.5	3.920
T	AL-170	97	3.767
	AL-197	99	3.882
K	A-471	97	3.686

4.2.2 Measurement

Rectangular solid samples ca 1×2 cm and 0.5cm thick were prepared by cutting them from the exhibits with a diamond saw. After the measurement of the density of samples by Archimedian method, the samples were ground in turn on #600 diamond pad, with #4000 SiC powder and #6000 alumina powder. This polishing process is essential to make the grain boundary structure of the sample clear,

because the irregular original surface(whether from cut surface, polished surface or broken surface) obscures the morphology of microstructures as shown in Fig.1.

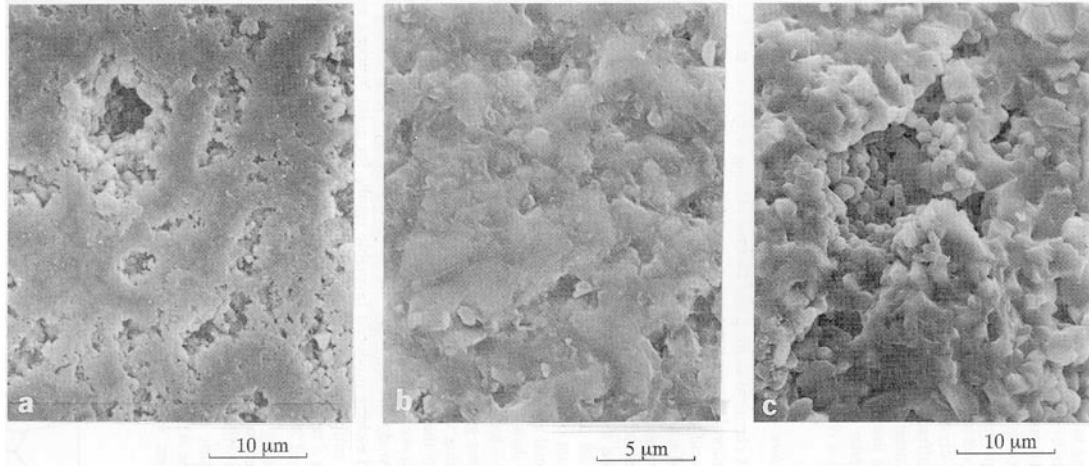


Figure 1. Comparison of micrograms of each surface: (a) Cut off surface; polished surface; fractured surface. Samples are alumina (92%) from Company S.

After cleaning in an ultrasonic cleaner, each sample was treated to make grain boundary conspicuous by acid or thermal etching procedure as shown in Fig.2. Each prepared sample was sputter coated with Pt-Au and observed with HITACHI S2500 SEM; secondary electron image operating at 25kV. The image processing for determination of the area distributions of the micrograin structure was performed by the micrograin structure analysis program previously developed for metal crystals supplied by the Iron and Steel Institute of Japan (13). The X-ray diffraction (XRD) measurements were made by using a SHIMAZU XD-D1(X-ray diffractometer) with Cu- α source operating at 40kV-30mA, scanning rate is 0.125 deg/min and an integrating time is 4 sec (14-16). For this measurement, samples

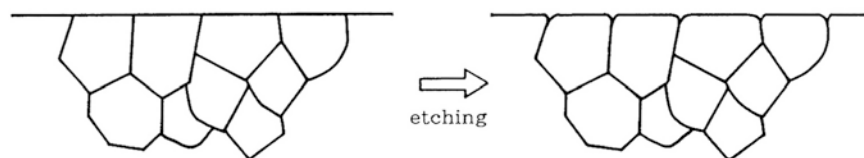


Figure 2. Schematic drawing of grain boundary etching of polished surface etching.

were cut to be a rectangular solid specimen ca 1×2 cm and 0.5cm thick fixed on the holder with a clay compound.

4.2.3 Etching Procedure

Two kinds of chemical etching and thermal etching were evaluated for their usefulness in elucidating morphological structure. Phosphoric acid etching was evaluated by dipping samples in 60% and 80% boiling phosphoric acid under standard atmospheric pressure for several minutes. Typical SEM micrographs are shown in Figs.3a and 3b. Control of the etching time and temperature of this phosphoric acid etching procedure was found to be too difficult to obtain reproducible results. Either increasing the acid strength from 60 to 80% or extending of etching time from 5 to 15 minutes caused an excessive amount of grain boundary etching as shown in Figs.3a and 3b. For the thermal etching, samples were heated at 1400°C for 10 min. The temperature is 100°C lower than the sintering temperature of alumina ceramics. A long time of half a day was needed for heating and cooling of the sample. This etching treatment gave a desirable result for the purpose, however slight grain growth due to the heating was observed as shown in Fig.3c. According to these results, it was concluded that both phosphoric acid etching and thermal etching were not suitable for the observation of the microstructure of surfaces in the present study. Sulfuric acid etching produced favourable results for grain structure analysis by SEM. To evaluate sulfuric acid etching, samples were immersed in 4.5 mol/L or 6mol/L sulfuric acid in a teflon capsule, sealed in a stainless steel pressure vessel and heated to between 150 and 200°C for 2 to 4 hours. Etching with 4.5 mol/L sulfuric acid at 200°C for 2 hours generated good grain boundary etching, while the increase of acid concentration to 6 mol/L resulted in attack of the internal portions of grains as shown in Fig. 4. Experiments with high temperature sulfuric acid etchants resulted in the adoption of 4.5 mol/L sulfuric acid at 150 to 200°C as the best alternative. The degree of etching depended on the Al₂O₃ purity of ceramics. Two hour treatments for low alumina samples seemed adequate, while up to four hours were required for the high alumina materials as shown in Fig. 5. These results suggest that etching for long time makes it difficult to identify grain

boundary, and high concentrations of sulfuric acid is not suitable for alumina ceramics etching. Based on these results, the most suitable conditions for chemical etching of alumina ceramics was determined; to be, sulfuric acid (4.5 mol/L) at a temperature range is of 150~200°C, carried on for 2 hours on low purity alumina ceramics and for 4 hours on high purity alumina ceramics. Therefore it is

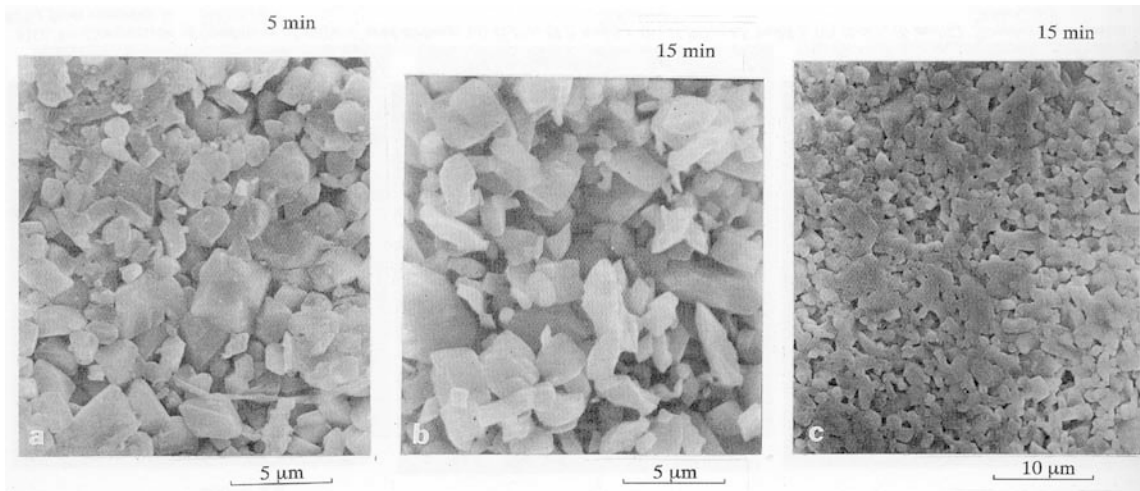


Figure 3. Comparison of each etching method: (a) boiling phosphoric acid(60%); (b) boiling phosphoric acid(80%);(c) thermally etched at 1400°C. Samples are alumina (92%) from company S.

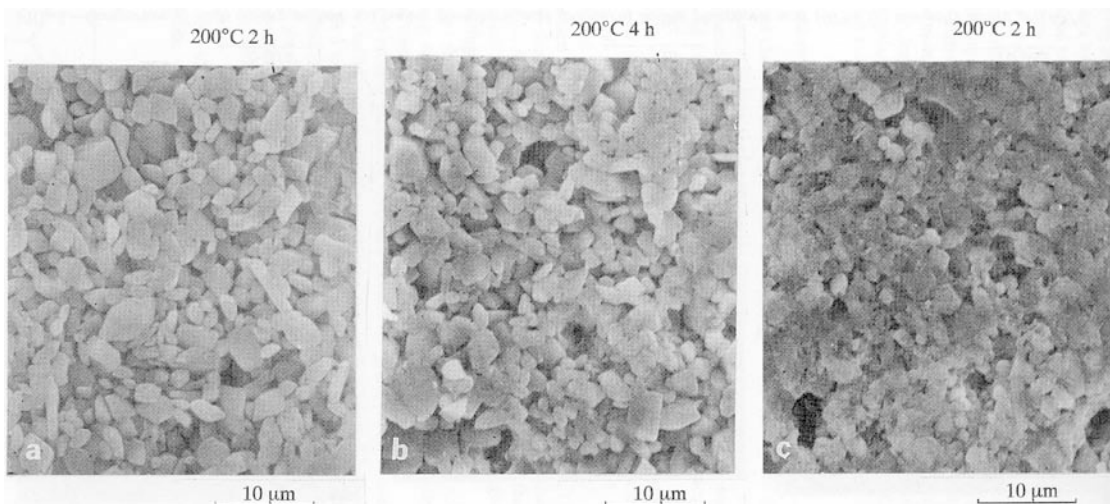


Figure 4. Comparison of conditions of sulfuric acid etching: (a) H_2SO_4 (4.5 mol/L); (b) H_2SO_4 (4.5mol/L) ; (c) H_2SO_4 (6 mol/L). Samples are alumina (92%) from company S.

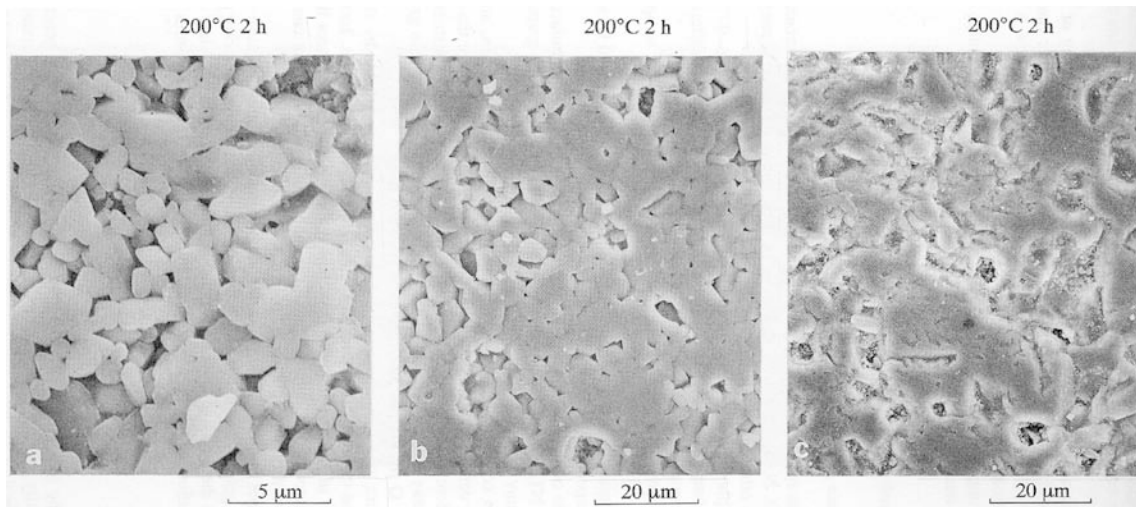


Figure 5. Comparison of clarity of sulfuric acid etching on different purity: (a) alumina (92%) ; (b) alumina (97%) ; (c) alumina (99%). Samples are alumina (99%) from company S.

apparent that for sample of unknown content of alumina, suitable etching conditions must be established.

4.3 Results and Discussion

4.3.1 Observation of Grain Morphology

Photomicrographs of low alumina content ceramics samples (92%) manufactured by three companies(O,N,S) are shown in Fig. 6. In them the one from company S was discriminated from other makers through feature of grain

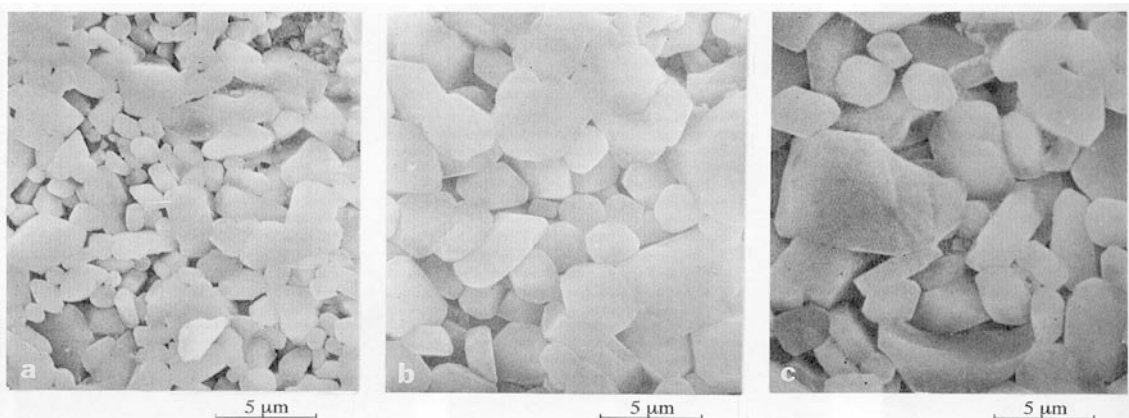


Figure 6. Comparison of microstructure of alumina ceramics (92%) from different supplier: (a) company S; (b) company O; (c) company N.

morphology. The surface morphology of middle purity alumina ceramics samples (96-97%) manufactured by five companies(S,O,N,I,T) are shown in Fig. 7. Distinct differences of grain morphology were observed among makers. Pits in the grain brought from the grain growth were observed for the sample from company T. The existence of pits enabled discrimination between samples from T and O, although those had similar aspects in their grain morphology.

Photomicrographs of high alumina content ceramic samples(>99%) manufactured by six companies(N,NT,I,O,T,S) are shown in Fig. 8. The large size of grains in the sample from company I was similar to that from the company T. The sample from company I, however, contained some small size grains, and it indicated that the raw ceramic powder had different particle size distribution, or the ceramic was sintered in different conditions from others. Although the grain size distribution in sample from company NT was similar to that from company O, some grain growth in that from company O resulted in discrimination between them. The microstructure of low alumina content ceramics is distinguishable by the SEM observation, because of clear differences in their grain boundary structures. Increase in the alumina content of the ceramics produces less grain boundary differences therefore identification of microstructure differences of the high and middle alumina content ceramics were problematic. Grain size becomes large as the purity of alumina powder increases, because the lack of impurities at the grain boundary promotes large grain growth during sintering process. Since increase in the purity of alumina ceramics produces less grain boundary etching, identification of microstructure on high and middle purity of alumina ceramics is more difficult.

4.3.2 Density

The measured density of alumina ceramics are shown in Table 1. The density generally increased proportionally with the increase of the purity of alumina in the ceramics. The grain growth observed in the high alumina content ceramics decreased the porosity. The density measurements showed the possibility of generating information about the different manufacturing processes thereby leading to identification of the source manufacturer.

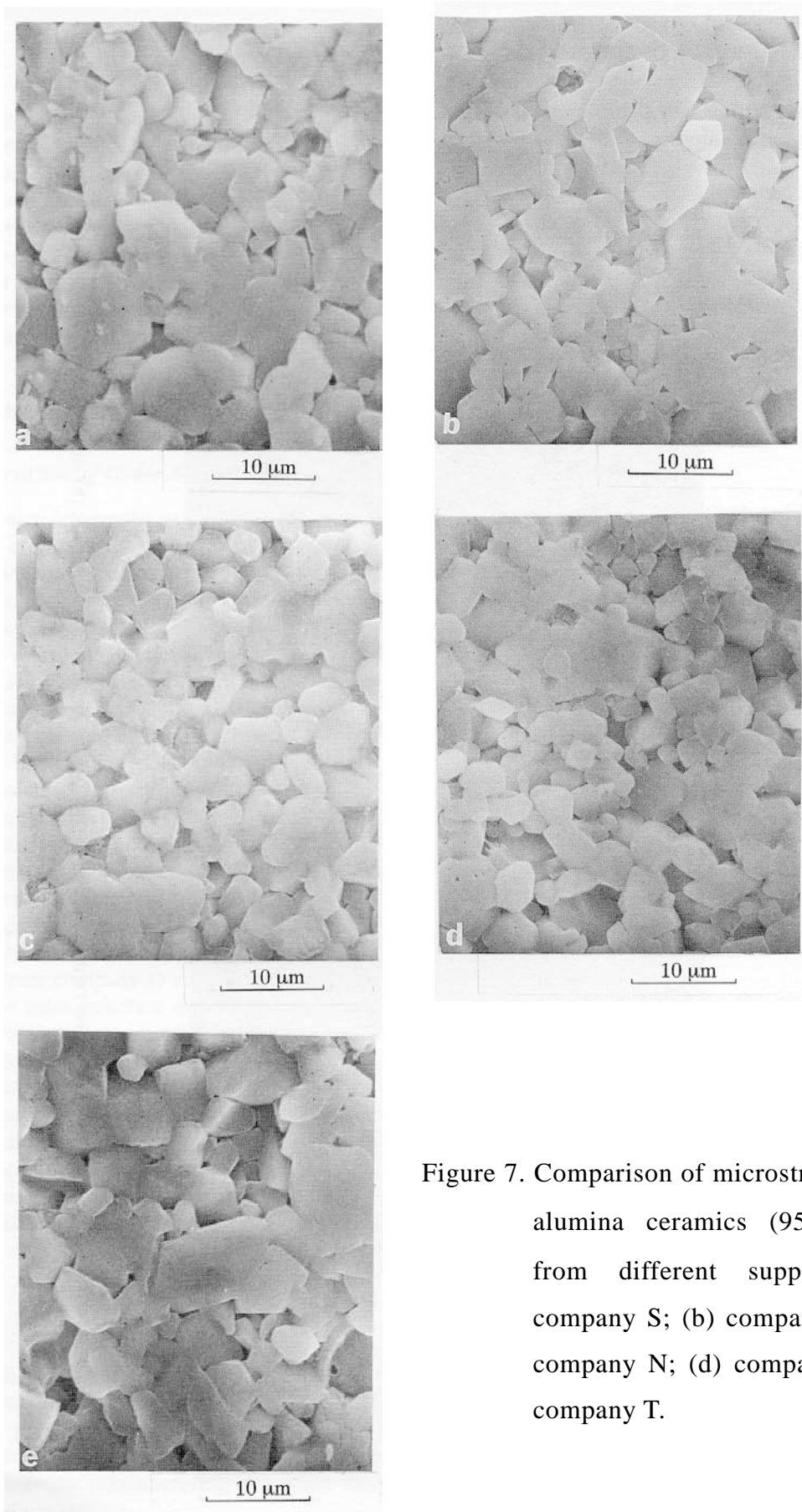


Figure 7. Comparison of microstructure of alumina ceramics (95 ~ 97%) from different supplier: (a) company S; (b) company O; (c) company N; (d) company I; (e) company T.

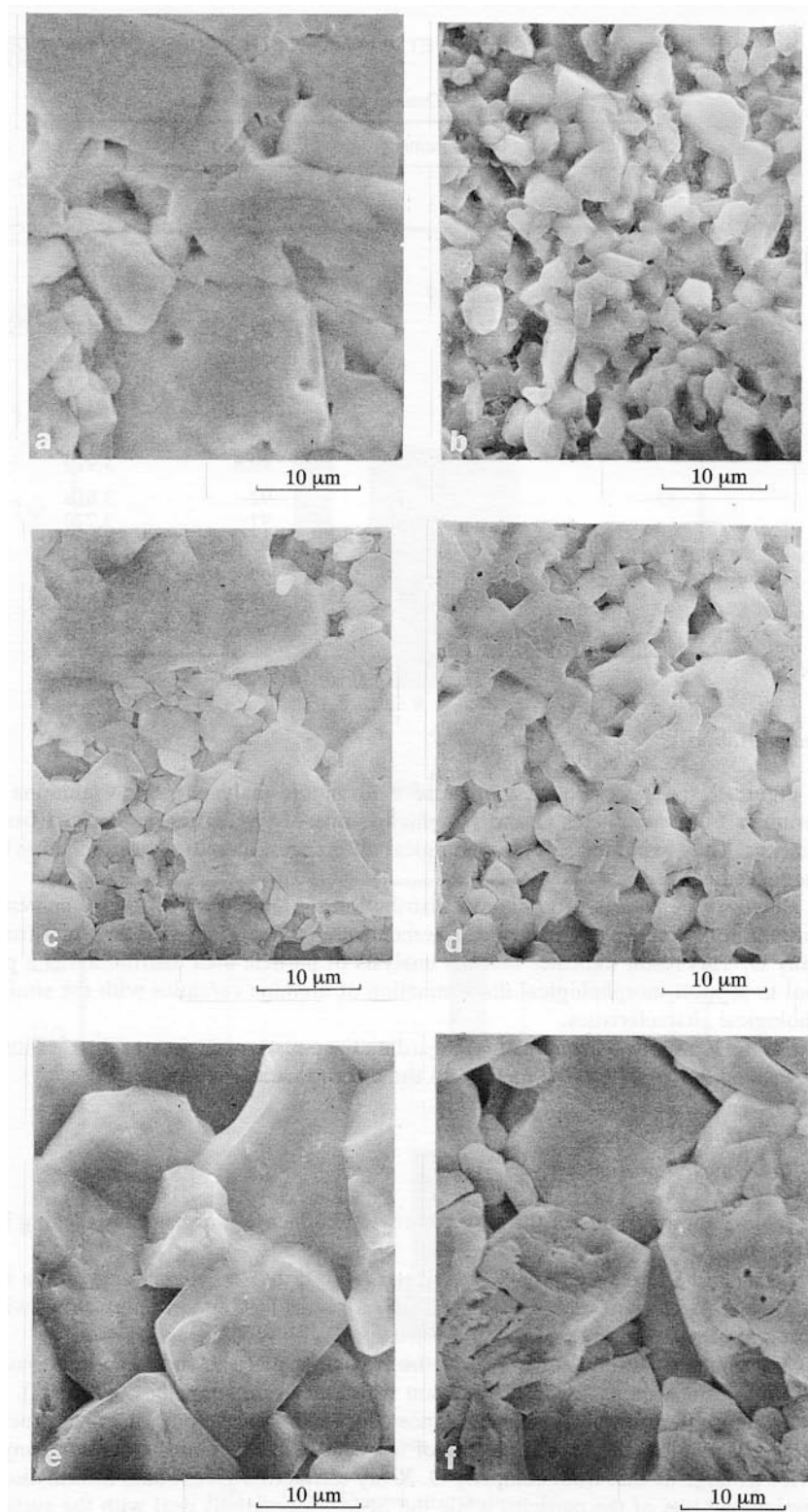


Figure 8. Comparison of microstructure of alumina ceramics ($> 99\%$) from different supplier: (a) company N; (b) company NT; (c) company I; (d) company O; (e) company T; (f) company S.

4.3.3 Image Analysis

Fig. 9 shows results of grain size distribution analysis for low alumina content ceramics from companies O and N, which is one of typical results derived from some analysis. They exhibited less morphological differences, therefore discrimination between them seemed difficult.

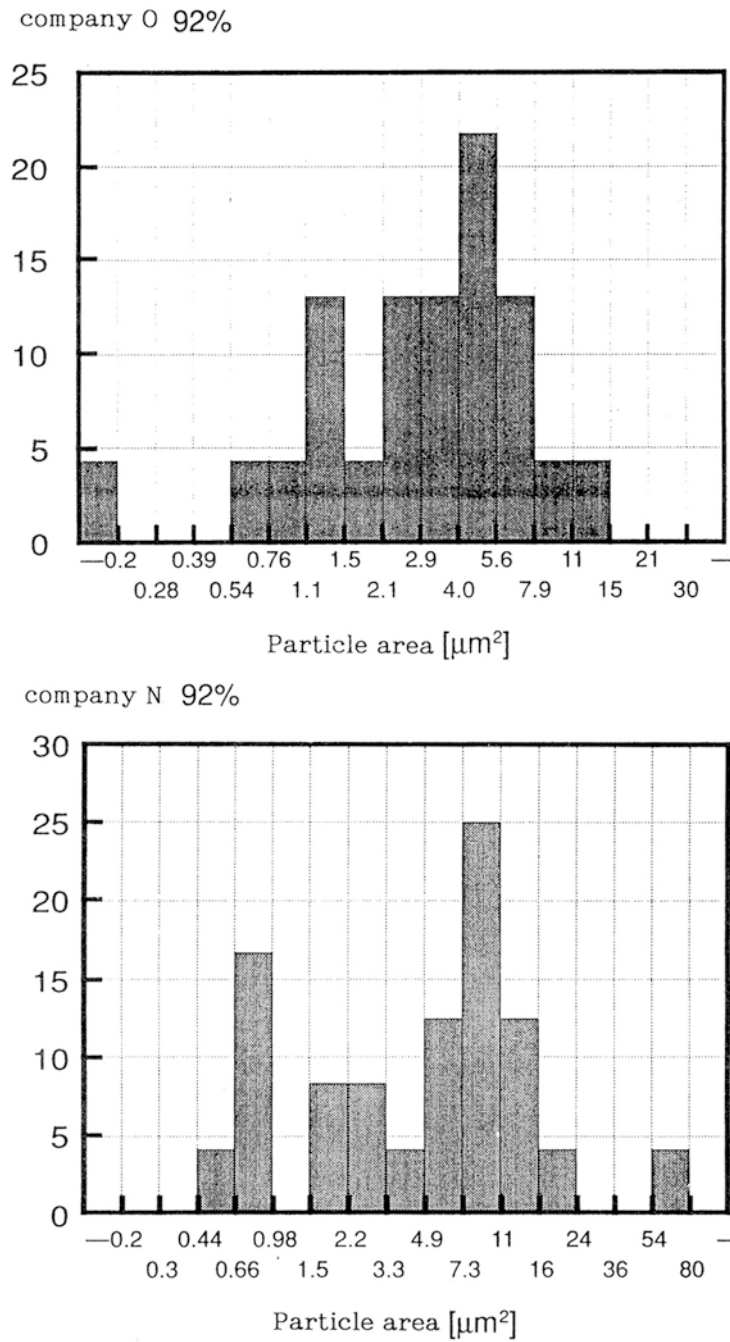


Fig. 9 Grain size distribution of alumina ceramics.

However the pattern of grain area distribution for them were different apparently. The sample from company N had higher percentage of large grain size than that from company O. This result indicates that the analysis of particle area distribution is a powerful tool to support morphological discrimination of alumina ceramics with the similar morphological characteristics.

For the future, data accumulation regarding the pattern of grain area distribution should be desired for applying this method to the discrimination of ceramics.

4.3.4 X-Ray Diffraction Analysis

Table 2 shows results of the half wave width, a measure of band broadening in X-ray diffraction. Since the half wave width is reflected mainly by the average crystallite size, the half wave width by X-ray diffraction analysis seems to be an good index along with grain observations to discriminate the microstructure of alumina ceramics. The sample(alumina content 92%) from company N showed large half wave width of three diffraction peaks, in comparison with that from company O(Table 2). Although these samples showed almost the same morphology of grain structures on SEM observation, the crystallite size of alumina in the ceramics from company N was twice as large as that from company O. X-ray diffraction gives some informations about the internal pits of the particles while the SEM observations deal with the surface. For these samples, the shift of d-value spacing of lattice plane, caused by a crystalline strain was not observed.

Table 2. Half wave width of three X-ray diffraction peaks for two alumina ceramics that show similar morphology of microstructures. Alumina content: 92%

Plane Index (hkl)	(116)	(113)	(104)
Company O	0.125	0.106	0.184
Company N	0.277	0.267	0.275

4.4 Conclusion

The morphological observation of ceramics surfaces was performed to discriminate their microstructure. The etching during preparation of samples was an important factor in determining morphological differences among specimens. Image analysis and X-ray diffraction analysis supported the results obtained by examining microstructure. Density measurements suggested the degree of grain growth, which was related to the purity of alumina powder. Further analytical determinations of the elements which are added to ceramic formulations in order to control the grain growth on sintering, or to improve ceramics' characteristics may be useful. Surface study would support the discrimination of ceramics established by the morphological observation (3-6). And therefore these further studies are recommended.

References

1. N. Soga, "Basic of Ceramics (in Japanese)", Agune, Tokyo (1990).
2. H. Yanagida, "Fine Ceramics(in Japanese)", Blue Backs, Kodansha, Tokyo, (1987).
3. Japan Chemical Society Ed., Engineering Ceramics(in Japanese), Chemical Review No.37, Publishing Center of The Chemical Society of Japan(1982).
4. K. Suzuki, Y. Hanaoka, K. Minaguchi, M. Inoue and H. Suzuki, *Jpn. J. Leg. Med.*, **45**, 330 (1991).
5. M. Kudoh, *Act. Crim. Japan* **54**, 200(1988).
6. J.Y.H. Ming-Ting, R. Y. Lin, and Y. H. Ko, *Ceramic Bull.*, **70**, 1167(1991).
7. R. L. Coble, *J. Appl. Phys.*, **32**, 793(1961).
8. C. A. Powell-Dogan and A. H. Heuer, *J.Am.Ceram.Soc.*,**73**, 3670(1990).
9. C. A. Powell-Dogan and A. H. Heuer, *J. Am. Ceram.Soc.*,**73**, 3677(1990).
10. C. A. Powell-Dogan and A. H. Heuer, *J. Am. Ceram. Soc.*, **73**, 3684(1990).
11. O. H. Kwon and G. L. Messing, *J. Am. Ceram. Soc.*,**73**, 275(1990).
12. J. S. Chappell, T. A. Ring, and J. D. Birchall, *J. Appl. Phys.*, **60**, 383(1986).
13. Image measurement software supplied the Iron and Steel Institute of Japan.

14. B.D. Cullity, "Elements of X-ray Diffraction", Addison-Wesley Publishing Company Inc., Reading, Massachusetts, USA (1956).
15. S. Kato, Basic Course of Ceramics 3 "X-ray Diffraction Analysis" (in Japanese), pp.246-248, Uchida Rokakuho Publishing, Tokyo, 1990.
16. H. Okashita, A. Uota, H. Sato, *Shimadzu Review*, 48, 23(1991).

Chapter 5

Development of collecting expiration equipment for alcoholic breath inspection

5.1 Introduction

The method of alcoholic inspection differs whether the driver agrees to the expiration inspection or not. If the driver agreed to it, the he inspires the expiration spontaneously into the expiration picking sack, then the alcoholic density will be measured on regulation site with the alcoholic detecting tube or alcoholic meter. If it exceeds the limit, he will be decided to have driven under the influence of alcohol. In case that the driver denied the inspection it, the police ask for the court to issue a warrant, accompany the driver to the hospital, for the doctor to extract his blood and convey the blood to the forensic science laboratory. Finally, the alcoholic density in this blood will be measured and if it exceeds the limit, the driver is decided to have driven under the influence of alcohol. Since this procedure takes a several hours or more which is too long for inspection of alcoholic density in the body. There was an actual case that the driver who was reeky of liquor at the regulation site was acquitted of a charge. In this study, the collecting expiration equipment was invented for the policeman to extract expiration mandatorily on the site as soon as the court issues the warrant in case of inspection refusal.

5.2 Experimental

5.2.1 Legal study of expiratory sampling

Preceding the trial manufacture of the collecting expiration picking device, legal consideration of expiration picking was done. There were several cases in the past of picking expiration from the unconscious subject who caused the traffic accident. There are judicial precedents that judge it legitimate (1, 2): such as the

Fukuoka high court December 16th 1981 decision, Urawa district court Koshigaya branch November 6th 1981 decision, Fukui district court June 10th 1981 decision and Tokyo high court June 7th 1976 decision. In each case, they collected the expiration by opening up one end of the expiration picking sack and press it to the subject's face. These were decided to be legitimate without the warrant. In this way, however, the alcoholic density in the expiration will decrease because of mixing with outside air. The current expiration picking sack can be used only when the subject grips the tube spontaneously and inspire the expiration, but never by force. Therefore the instrument to pick expiration naturally without depending on the intention of the subject was made on an experimental basis.

5.2.2 Development process of collecting expiration equipment

Expiration picking device which is used for exercise stress testing in research of physiology- the combination of the expiration picking mask of Rudolf mask and the expiration retention container such as the Douglas bag- gave me a hint in developing the trial manufacture. However, Rudolf mask and Douglas bag were large-scale. First the inlet valve and the exhaust valve of the kerosene pump for home use was installed in the transparent plastic make for the respirator, connecting the inspiring tube of the expiration picking sack on the exhaust valve side. As the subject breathes naturally while the mask is applied to the face, expiration accumulates automatically in the picking sack as shown in Fig.1 (3). Next the expiration picking technique using the device of the combination of aforementioned Rudolf mask and the Douglas bag was attempted is shown in Fig.2. Since it is desirable to make the picking bag for drinking inspection as small as possible, the improved model of expiration picking kit combining the respirator (A), the plastic made connecting hose (B), three-way cock (C), the rubber made



Figure 1. Prototype of the mask for collecting expiration.

expiration picking sack(D) was made with reference to the combination of the Rudolf mask and the Douglas bag as shown in Fig.3. Usage is as follows: put the mask on the subject's face and expel the first several breath outside from the three-way cock together with the fresh air inside the mask. Then after switching the three-way cock, accumulate the expiration into the picking sack. When the expiration



Figure 2. Rudolf mask and Douglas

enough, remove the mask from the subject immediately. Since there is a check valve at the mask outlet, the expiration cannot flow back from the picking sack, so you don't need to do the job in haste. Connect the alcoholic detecting tube or alcoholic meter to the pickup hole (E) of the sack, measure the alcoholic density according to the usual drinking inspection routine.

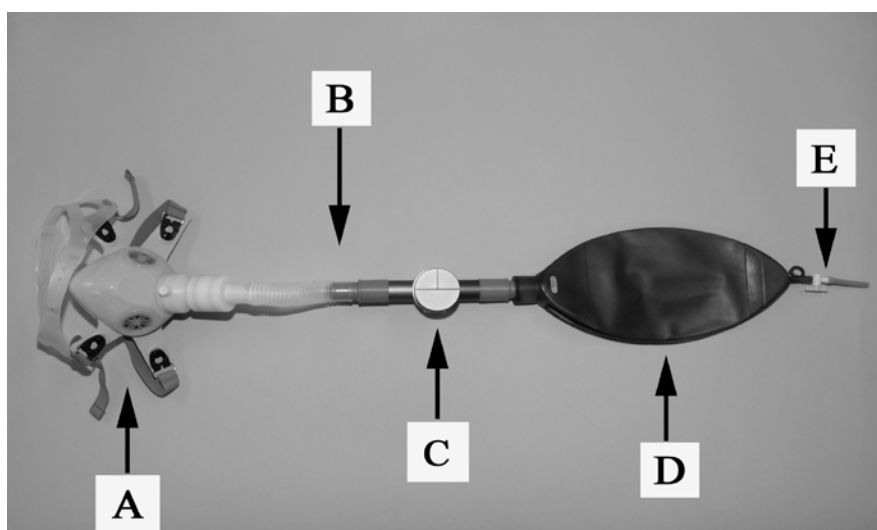


Fig.3 The mask and bag for collecting expiration

5.2.3 Drinking Experiment

After taking alcoholic drinks, expiration was extracted using the expiration picking kit every 20 minutes.

In our experiments, the subject took 1000ml of 5% alcohol beverage spending 10 minutes. After drinking, we collected the extracted expiration every 20 minutes up to 100 minutes later. We used Yanagimoto-made alcoholic meter to measure the alcoholic density in expiration as shown in Fig.4.

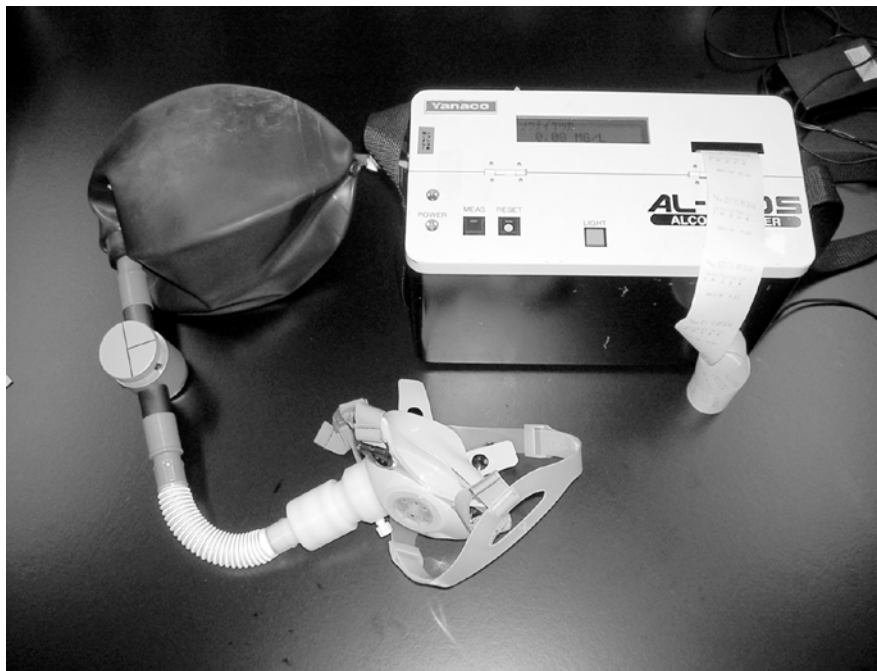


Figure 4. Measuring alcoholic concentration of expiration using alcohol meter.

5.3 Results

5.3.1 Performance Evaluation of Expiration Picking Devices

Because the aperture of the blowing mouth of the simple type expiration picking sack is small, the subject met with big resistance exhaling and hard to breathe naturally, so it is not of practical use. By using the expiration picking device which combines Rudolf mask and the Douglas bag, there is no resistance in breathing and can collect expiration easily. However, the capacity of the Douglas bag is 50 liters at the smallest, so the whole device will become very big in size

and cannot handle with ease. With reference to the improved expiration picking kit, breathing resistance is little and the subject can breathe naturally with the mask on as shown in Fig.5. In addition, the capacity of the expiration picking sack is approximately 4L, which is sufficient for the alcoholic inspection in expiration and so we can handle with ease.



Figure 5. The scene of using the mask and bag for collecting expiration.

5.3.2 Drinking Experiment

The contrast of the measurement result of alcoholic density between the picked expiration using the usual picking sack and the improved expiration picking kit is

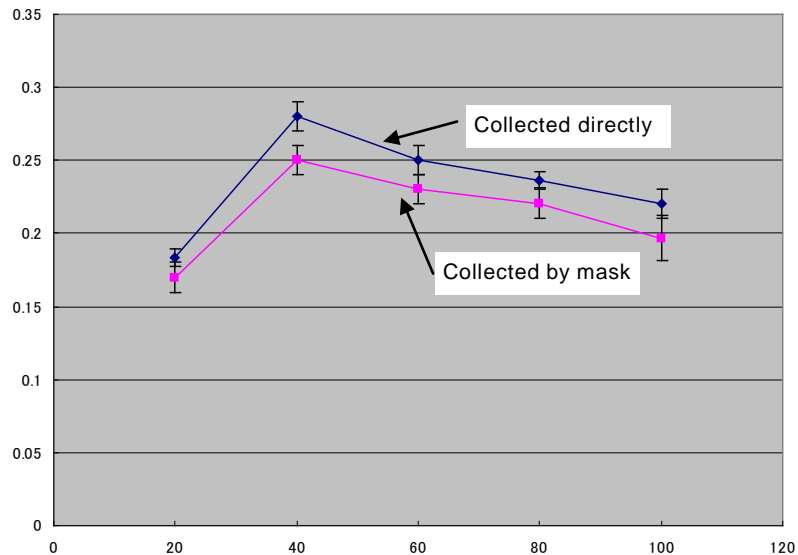


Figure 6. Measured results of alcoholic concentration from expiration collected directly and collected by mask and bag.

shown in Fig.6. The measurement result using the improved expiration picking kit tends to lower slightly in comparison with using the usual expiration picking sack. This is probably because the fresh air inside the tube from the life plug to the expiration picking sack barely diluted the alcohol. By shortening the tube and decreases the spatial cubic measure, this difference can be lessened. Under present conditions, however there was not a big difference between the two measurement results, so we considered it to be practical use.

5.4 Conclusion

As an expiration picking device for drinking inspection, the expiration picking kit was developed. In developing, I got a hint from Rudolf mask and the Douglas bag which is used in expiration picking of motion load test in research of motion physiology. By using this picking kit, we can pick the expiration of the driver who refuses the alcoholic inspection justifiably and quickly. Moreover, it gives less burden to the subject compared to blood picking. In addition, with the unconscious suspect who was hospitalized right after the accident and impossible to grip the blowing mouth of the usual expiration picking sack by himself, we could pick his expiration under the permission of the doctor. The picking sack of the expiration picking kit developed this time is a rubber- made medical article, but it is also possible to convert it to the disposable transparent polyethylene bag used in present drinking inspection.

References

1. K. Harada, Separate judicial precedent times, 9, 94 (Nov. 20, 1985).
2. A. Saka, Separate judicial precedent times, 10, 127 (Sep. 30, 1988).
3. T. Hashimoto, *Jpn. J. Sci. Tech. Iden.* , **9**, 167 (2004).

Chapter 6

Establishment of Sampling Method of Oil

Adsorption Film for Fire Scene

6.1 Introduction

It is important to collect and maintain the oil residue at the fire site for inspection for the cause and origin of fire cases. To examine whether the combustion residue of the fire site contains oil or not, it is difficult to bring the samples to the laboratory when they are huge, containing large amount of water, or nondestructible materials such as flooring. In previous study, we found that porous polypropylene film of which color changed by oil adsorption was the most appropriate for collecting materials for combustion oil residue at the fire site (1). The oil clear film is commercialized as face-oil absorbing paper. Oil adsorbed in the film volatilize in order from low boiling component and composition changes. Gasoline, kerosene and diesel oil were loaded to the film and recovered after appropriate time (2). However, in the previous study, we found that the volatile component might be changed cause by vaporization during transfer from the fire site to laboratory. Additionally, since the oil clean film includes some petroleum heavy oil as a component, which is equivalent to lubricating oils, we need to estimate the effect of the lubricating oils as the contamination for quantitative analysis of the adsorbed oil in the sheet. In this study, we choose the sample of a mixture of gasoline and lubricant oil, which is commonly used for two-stroke engine mowers, and adsorption and packing condition for the transportation.

6.2 Materials and Methods

6.2.1 Materials

As the oil extraction equipment, oil clear film which has been used as facial oil absorbent supplied by Sumitomo Corporation was used. This product is being

marketed under the name of "oil blotting film" and can be purchased at pharmacies. Oil clear film contain high-boiling petroleum component (equivalent lubricant) during the production process. So it was degreased using ultrasonic cleaning immersed in solvent (*n*-pentane). After the oil was added to oil clear film, it was sealed in the bags for collecting volatile materials. These plastic bags are used for the collection and storage of combustion residue samples in our laboratory, which are made of nylon and polyethylene laminated film as shown in Fig. 1, and are impermeable to volatile oil such as gasoline, kerosene and so on (3).

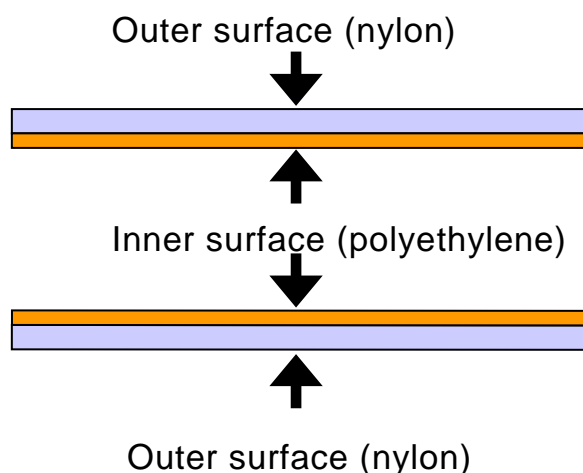


Figure 1. The layer structure of the gas barrier plastic bag.

6.2.2 Sampling

Oil sample was dropped using micropipette in order to load a certain amount as shown in Fig.2. Film specimen was cut to the size of 3cm×3cm and 10 μ l of oil was dropped on it. After a specified time exposure to air at room temperature, oil was extracted 10ml of *n*-pentane. Extract was concentrated to 1ml by way of blowing nitrogen stream. Injection amount of extract to gas chromatograph was 2 μ l. Gas

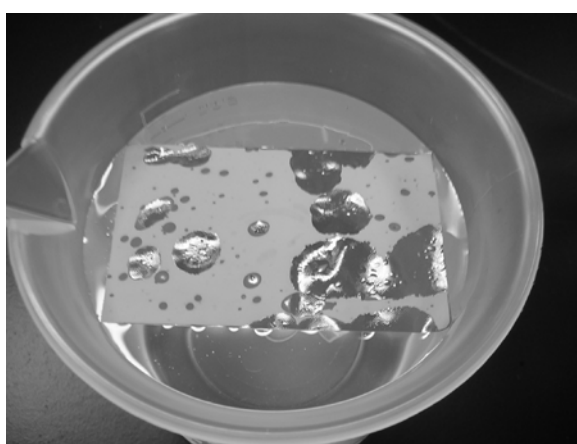


Figure 2. The film which adsorbed the floating oil on the water surface.

chromatograph analysis was performed with a Agilent Technologies model 6890N gas chromatograph combined with DB-5 column (length 30m, inner diameter 0.25mm, thickness of liquid layer 0.25 μ m). The GC was temperature programmed from 50 $^{\circ}$ C to 300 $^{\circ}$ C at a rate of 10 K/min; the injection and detector temperature 280 $^{\circ}$ C and injection split ratio 1:50. For the mixture of gasoline and lubricant oil, Gas chromatograph analysis was performed with a Shimadzu model GC2010 gas chromatograph combined with Ultra Alloy PLUS-1 HT (length 15m, inner diameter 0.25mm, thickness of liquid layer 0.25 μ m). The GC was temperature programmed from 50 $^{\circ}$ C to 350 $^{\circ}$ C at a rate of 10K/min, with a final hold of 20 min; the injection and detector temperature 300 $^{\circ}$ C and injection split ratio 1:50.

6.2.3 Use of bag for collecting volatile materials

For highly volatile gasoline sample, two experiments were conducted. After oil was loaded on the film, one was left in the air at room temperature and the other was stored in the volatile materials collecting bag. (Fig.3) In this way, oil keeping ability was compared between the two preservation methods.

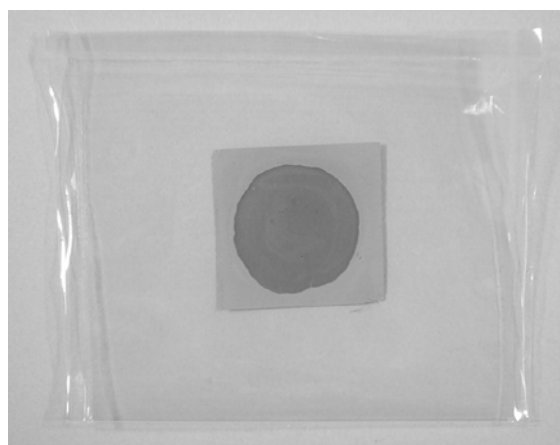


Figure 3. Film which adsorbed oil is contained in the gas barrier plastic bag.

6.2.4 Mixing of gasoline and lubricant oil

For mixture of gasoline and lubricant oil, normal oil clear film and degreased oil clear film were used in order to examine the effect of lubricant containing in the oil clear film originally. Both films were recovered after the addition of the mixture oil. Although gasoline – oil ratio (20:1) is common in mixture oil, we made gasoline-oil ratio (2:1) sample in order to get close to the gasoline –lubricant ratio of oil containing in the combustion residuals.

6.3 Results

6.3.1 Effect of sealing bag on exposing the additional oil samples

At first, the exposing conditions after oil addition were compared for the cases of exposing in air and sealed condition. The results of gas chromatograph analysis are shown Fig. 4 after the addition of oil to oil clear films in air, and recovering the oil by solvent extraction. Extraction was analyzed by gas chromatograph for gasoline, kerosene, and diesel. As for Gasoline in Fig.4a,

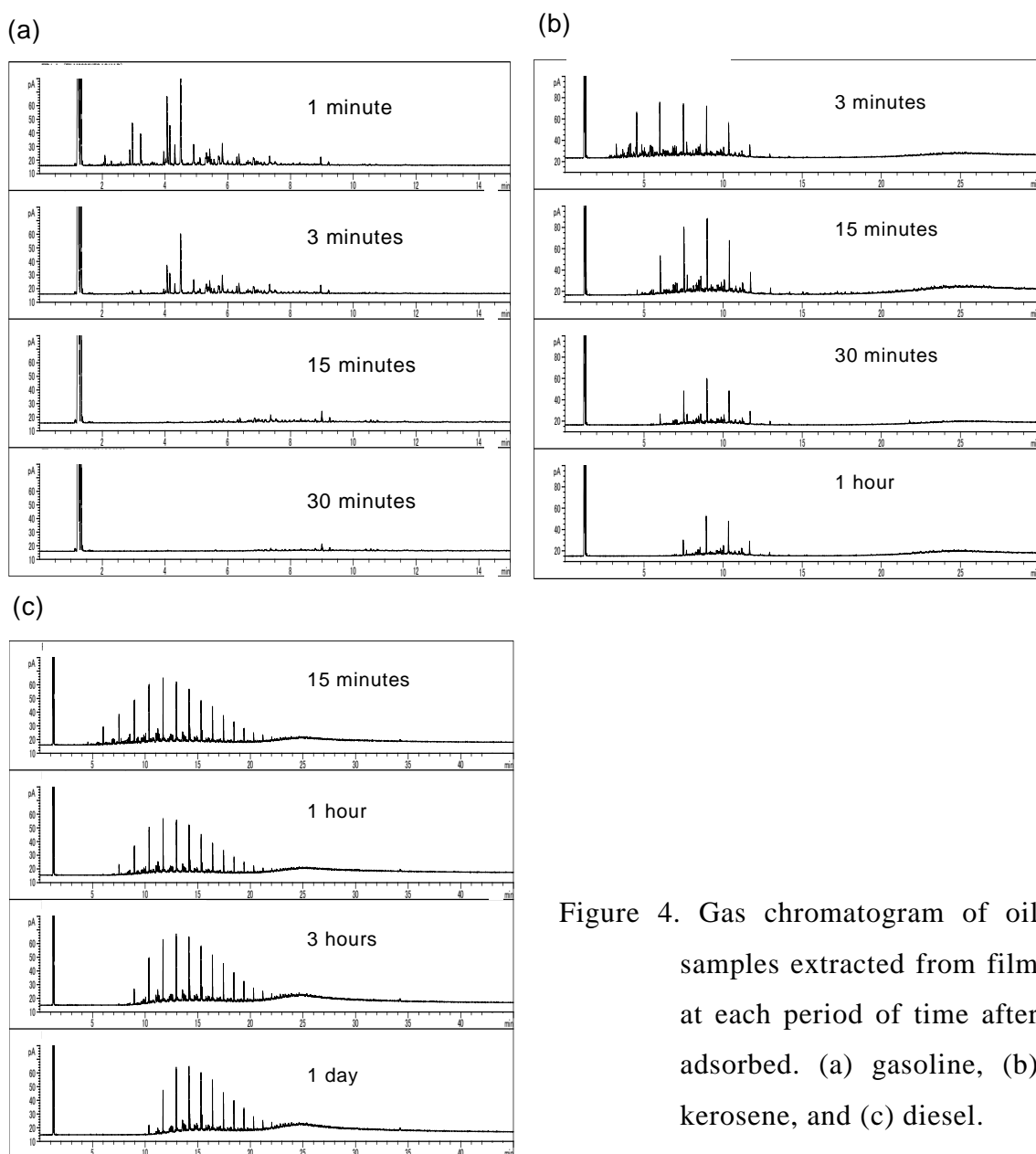


Figure 4. Gas chromatogram of oil samples extracted from film at each period of time after adsorbed. (a) gasoline, (b) kerosene, and (c) diesel.

retention time has decreased significantly within 3 minutes after addition. However, it was recognizable as gasoline. As for kerosene in Fig.4b, lower boiling point element of 0 to 5 minutes of gas chromatography retention time has diminished 15 minutes after addition, No major changes in composition ratio were measured within 30 minutes after addition. Although three major peaks of the components of lower boiling point were lost, kerosene can be fully identified even one hour after addition. Diesel fuel having a lower boiling point elements of 5 to 10 minutes of retention time of the gas chromatograph have diminished 15 minutes after addition as shown in Fig.4c. There were no major changes in composition ratio only the major two peaks of lower-boiling disappeared 3 hours after the addition. Although the lower boiling point elements of up to 10 minutes of retention time diminished from three hours to 24hours, diesel oil can be fully identified.

On the other hand, after the addition of gasoline, film was sealed in the volatile materials collecting bag. It was extracted after a specified time and analyzed. Results were compared with the film exposed in the air after addition of oil and it is shown in Fig.5. Gas chromatogram of the oil extracted from the former film

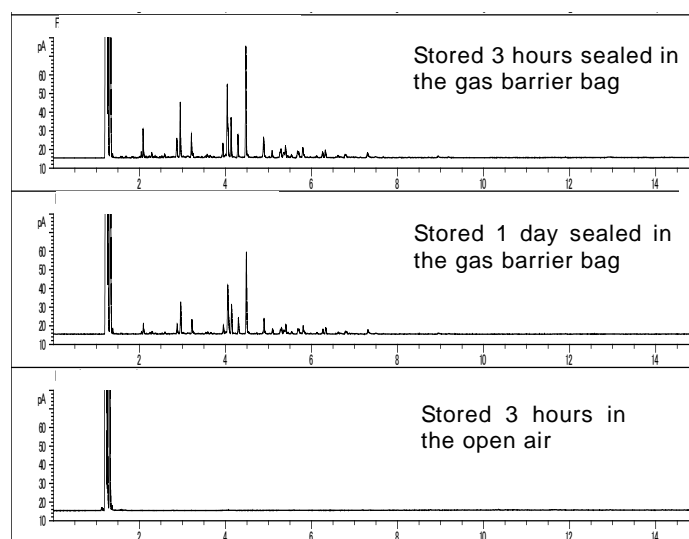


Figure 5. Comparison of gas chromatogram of gasoline extracted between with sealing bag and in the air from film at each period of time after oil adsorption.

stored 1 day after sealed was no less than the latter film exposed 1 minute in the air. In contrast, the film exposed 30 minutes in the air, was difficult to identify.

From the experiments mentioned above, volatile oil, especially gasoline, should be stored in a sealed container impermeable material volatiles after the collection of oil clear film (describe as film hereafter). Kerosene and diesel oil are held on he film for a while (about 1 hour for kerosene, about 3 hours for diesel oil) even when they are left in the air after collection. However, practically, it should be sealed immediately in a bag for collecting volatile materials.

6.3.2 The mixture of gasoline and lubricant oil

As for mixture of gasoline and lubricant oil, the oil added and extracted from unprocessed film and degreased film are shown in Fig. 6. The time to extraction was 3 minutes from addition of oil to the film. Some of the peaks between high-boiling petroleum component (equivalent lubricant) of oil clear film and lubricant mixed oil are identical. Therefore, it is necessary to degrease the film when we try to extract the oil such as mixture oil from gasoline and lubricant, that

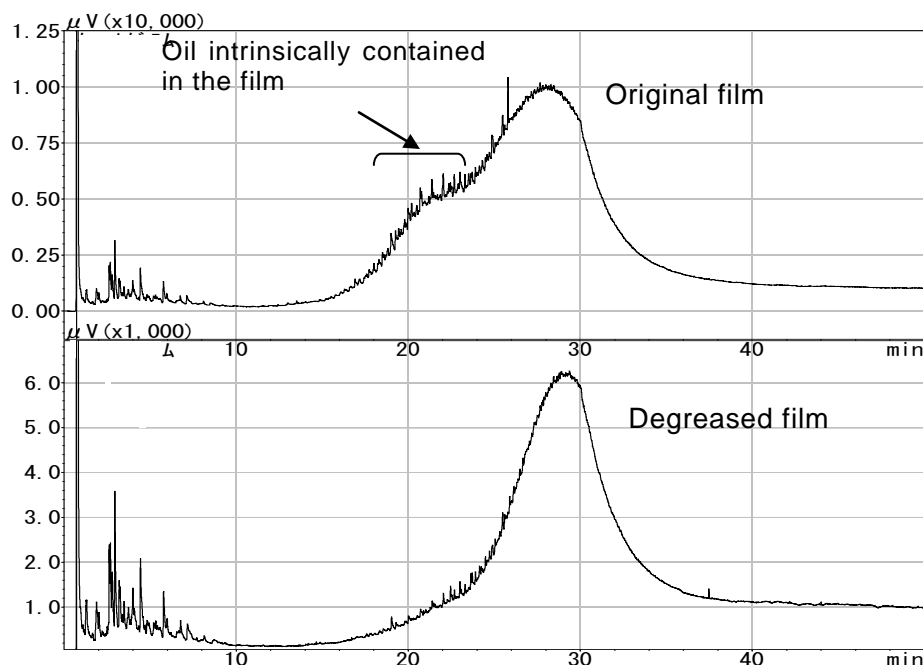


Figure 6. Gas chromatogram of gasoline extracted from original film and degreased film 3minutes after adsorbed on the film.

is found to be necessary to do a film processing of degrease. However, qualitative inspection whether the sample contains lubricant or not may be possible when the oil amount of the sample is larger than the experimental dosage (10 micro liter oil amount in 3cm × 3cm film), because the oil included in the film is little. But if quantitative analysis is necessary, degreasing process is required.

6.4 Conclusion

Experiment of addition and collection of oil such as gasoline, kerosene, and diesel oil to oil clear film were conducted. In order to identify the recovered oil sample by gas chromatography analysis, exposure limit time of each oil was investigated. Gasoline was identifiable up to 3 minutes from collection. Kerosene was identifiable even after 1 hour from collection. Diesel was identifiable even after three hours to 24 hours. When the film was sealed in the volatile materials collecting bag after addition of oil, the remaining of oil was very long. Even gasoline was identifiable until the next day. Therefore, all volatile samples should be stored in the volatile materials collecting bags right after the collection. It is recommended to use the oil clear film when the mixture of gasoline and lubricant oil was sampled.

References

1. T. Hashimoto, T. Nakanishi, M. Takatsu, A. Miyawaki, M. Fukushima, *Jpn. J. Sci. Tech. Iden.*, Proceeding of 5th annual meeting, 50 (1999).
2. T. Hashimoto, *Jpn. J. Sci. Tech. Iden.*, **8**, 43(2003).
3. T. Hashimoto, Proceedings of forensic science work shop at national research institute of police science (chemistry department committee), 28 (1987).

Summary

In this dissertation, studies on non-destructive or semi-destructive analytical techniques and sampling techniques to forensic materials were described in the viewpoints in forensic science in which the analysis or identification of the materials need to be done in non-destructive or semi-destructive ways, in order not to damage substances for the usage as the evidence in court.

In Chapter 1 (Introduction), the purpose of analysis in forensic science, which is the identification and discrimination of materials and its implications were discussed. The identification and discrimination of polymer film which is the central theme of this paper, the examples of forensic inspection that has been conducted in the past were summarized.

In Chapter 2, several analytical methods such as X-ray diffraction and optical microscope, used for identification of the polyethylene film for plastic bags were examined. As the experimental samples for this study, blow molded films for plastic bags were collected in cooperation with the domestic manufacturers. They include Low-density polyethylene (LDPE), linear low density polyethylene (LLDPE) and high density polyethylene (HDPE). All of these films all have different specifications of the resin. X-ray diffraction, infrared spectroscopy and optical microscopy (differential interference contrast microscopy and phase contrast microscopy) were used to analyze. By X-ray diffraction, we were able to tell whether the film was made of LDPE, LLDPE, or HDPE from the crystal structure. By infrared Spectroscopy using the method of the ATR with ZnAs crystal, every samples were attributed to every different groups using cluster analysis software. Optical microscope observation was performed by differential interference microscopy and phase contrast microscope. Each image was characteristic and they have large discriminating power.

In Chapter 3, the discrimination method of transparent polyethylene films based on non-destructive analysis of inorganic antiblocking agent contained in the film was described. After the observation of the particle morphology and distribution status of antiblocking agent in the film by optical microscopy, they were analyzed

using SEM-EDAX elemental analysis and molecular vibration spectra by Raman microscopy. The accuracy of identification could be improved by specifying the contained antiblocking agent.

In Chapter 4, discrimination of ceramic was made mainly by the morphological observations. 19 kinds of alumina ceramics which were produced by nine ceramics manufacturers in Japan were collected as samples. They were classified into three groups by the amount of alumina. (low purity of about 92%, middle purity 96% to 98%, and high purity of 99% or more). After polishing and etching the surface of these ceramics, deposition of Pt-Au was observed by SEM secondary electron image. It was possible to identify a visual image from this observation. Structural analysis program of microscopic particles, which Japan Iron and Steel Industry Association developed, performed image processing of microscopic particles of Japan Iron and Steel Industry Association, and computed the distribution of fine particle size of the structure. Since X-ray diffraction (XRD) FWHM reflects the raw material particle size which is hard to identify from observations of sintered ceramics, it is expected to adapt and improve the ability to identify morphological observation.

In Chapter 5, the development of a mask for collecting expiration compulsorily was reported. The equipment for breath alcohol sampling can be said as non-destructive(or non-invasive medically) method , since the sample is a person consuming alcohol. According to this method, we can collect the breath and measure the density of alcohol from the person seriously injured and unconscious in a car accident. There is no need to collect blood, and the way of collecting their breath is natural, non destructive and admissible in some cases law has recognized. By using this method towards people (human) refusing alcohol tests and do not voluntarily provide their breath, we don't have to measure blood alcohol concentrations in blood samples collected with a legal warrant, but take their breath compulsorily.

In Chapter 6, the performance test samples of oil adsorption film at the fire scene are reported. Oil extraction film can be collected oil contained in the material remaining at the fire sight but difficult to bring back. Large fire sight evidences such as carpet and large bed material had to be cut brought laboratory.

This oil extraction film, which is the same material as facial oil remover marketed, has the performance not to adsorb moisture but oil. Using this feature, we are able to collect oil efficiently from the large materials containing water by non-destructive method. In using at the spot, we must be sure of the necessary amount of sampling to determine the analysis time limits of the collected material. Volatile oil such as gasoline were maintained on this film, it was stored in the plastic bags made of transparent polyamide to which volatile organic compounds do not penetrate and the temporal limits of detection were examined. In this way, the necessary amount and the way to keep the samples were revealed and the usage of the on-site sampling activities.

List of Publications

Chapter 2

“Morphological and Spectroscopic Measurements of Plastic Bags for the Purpose of Discrimination”

Takashi Hashimoto, David G. Howitt, Donald P. Land, Frederic A. Tulleners, Faye A. Springer, and Shunlin Wang

Journal of Forensic Sciences, **52(5)**, 1082-1088 (2007).

Chapter 3

“Discrimination of transparent polyethylene films based on identification of Inorganic antiblocking agents”

Takashi Hashimoto, and Minoru Mizuhata

Journal of Forensic Sciences, in press.

Chapter 4

“Discrimination of Ceramics -Study on the Microstructure of Ceramics-”

Takashi Hashimoto, Shigehito Deki, and Yukio Kanaji

Journal of Forensic Sciences, **39(3)**, 824-838 (1994).

Chapter 5

“Development of Collecting Expiration Equipment for Alcoholic Breath Inspection” (in Japanese)

Takashi Hashimoto

Japanese Journal of Forensic Science and Technology, **12(1)**, 147-151(2007).

Chapter 6

“Performance of Assessment of Oil Collecting Film Used at an Arson Scene” (in Japanese)

Takashi Hashimoto

Japanese Journal of Forensic Science and Technology, **13(1)**, 93-99 (2008).