V. 5. PIXE Analisis of Umeboshi (Dried Plum)

Tsuboi S.[1], Ishii K.[1], Matsuyama S.[1], Terakawa A.[1], Kikuchi Y.[1], Fujiwara M.[1], Kawamura Y.[1], Watanabe M.[1], Yamanaka K.[1], Arikawa J.[1], Okura S.[1], Fujikawa M.[1], and Yamazaki H.[2]

[1]Department of Quantum Science and Energy
[2]Cyclotron and Radioisotope Center, Tohoku University

Introduction

The self-efficiency ratio of food in major advanced country such as USA, France and Germany is 128%, 122% and 84%, respectively, whereas that in Japan is less than 40 %. It means that Japanese people rely strongly upon imported food and should take care of their safety. The Ministry of Health, Labor and Welfare reports of the total 2.0 million imported foods in 2007, only 10 percent were inspected. Under these conditions, imported foods whose concentration of contamination exceeds standard level based on food hygiene law are detected and food-poisoning cases arising from imported food also occurs. Heavy-metal contamination such as As, Cd, Hg, and Pb is especially important. These heavy-metal contaminations harm our health by mediating animals and plants grown in the polluted environment. In recent years, water and soil pollution are becoming more serious in China. On the other hand, Chinese-grown foods increase fourfold in two decades and Chinese agricultural products have a 50% share of the pie. Therefore, importance of Chinese-grown foods for Japanese has been increasing and its safety is a growing concern for Japanese.

In this study, we analyzed elemental concentration of *umeboshi* which is one of the traditional pickled foods in Japan. *Umeboshi* is very popular in Japan. Traditionally, many Japanese have *umeboshi* for breakfast or lunch. Recently, many Japanese eat *umeboshi* as a confectionery. *Umeboshi* is pickled *ume* fruits. *Ume* is a species of fruit-bearing tree in the genus *Prunus*, which is often called a plum, but is actually more closely related to the apricot. Almost all of *ume* for *umeboshi* are imported from China and its consumption per household has been increasing due to inexpensive price. Since *ume* is pickled without peeling, its contamination will directly affect our health. From these viewpoints, we analyzed *umeboshi* which was pickled using Chinese *ume* and domestic *ume* by PIXE.

Experimental

We analyzed seasoned *umeboshi* sold in convenience stores. Table 1 summarized the samples. KUr and USr are colored by new coccine ($C_{20}H_{11}N_2Na_3O_{10}S_3 \bullet 11/2H_2O$), and the other two are not colored by a food coloring. Seasoned *umeboshi* was divided into 3 parts for PIXE analyses as shown in Fig. 1. A wet ashing method was carried out to conventional PIXE analysis to know averaged elemental concentrations[1). Direct analysis using submilli-PIXE camera was also carried out to know elemental distribution in surface and cross section.

A dried mass of about 45 mg of *umeboshi* was heated with nitric acid by a microwave oven. 10 μ*l* dissolution was deposited on a backing film (Mylar, 2 μm) after adding indium (2000 ppm for a dried mass of *umeboshi*) as an internal standard. PIXE analysis was carried out by using an in-air PIXE system at Tohoku University. Proton beams of 2.4 MeV were extracted into air through a kapton film of 12.5 μm and irradiated on the target[2)]. Prepared samples were fixed to the target holder, and set just after the beam exit window. X-rays were detected two Si(Li) detectors. The one has a large sensitive area of 60 mm^2 and used for a high energy X-rays detection. To prevent piling up of high intensity low energy X-rays, a 500 μm Mylar absorber was used. The other detector has a thin Be window for low energy X-rays. A Mylar foil of 500 μm with a pin-hole of 0.7 mm in diameter was attached. In this set up, elements heavier than Al could be detected.

To know elemental distribution inside and skin of *umeboshi*, cross section and skin of *umeboshi* were directly analyzed by using an in-air submili-PIXE camera. These samples were sliced into thin sections (~1.5mm), fixed on the sample holder (500 μm thick Mylar) using epoxy resin, and set up just after the beam exit window of the in-air submili-PIXE camera[3)]. Two Si(Li) detectors were also used to cover wide range of X-ray energy.

Results and Discussion

Figure 2 and 3 show characteristic X-ray spectrum of *umeboshi* and elemental concentrations of *umeboshi*, respectively. Major constituent elements of *umeboshi* are Al, Si, P, S, K, Ca, and Fe. Since Al, Si, Ca, and Fe are major components of soil, *ume* sucked these elements in through their roots and accumulated. Calcium shows the highest concentration, which stems from the pickled process. During the process in making *umeboshi*, *ume* is dipped in Ca solution for several days and absorbs Ca. Phosphorus, sulfur, and calcium elements are major minerals in plants and play an important role in human health. Table 1 shows concentrations of toxic heavy metals, namely As, Cd, Hg and Pb. These concentrations were estimated by the detection limit of PIXE and were lower than standard values given by a food hygiene law in Japan. Thus, *umeboshi* analyzed in this experiment is safety for As, Cd, Hg and Pb.

Concentrations of elements heavier than Ca show similar trend. On the other hand, lighter elements than Ca show large difference. Elemental concentrations of CFT and US are 2 to 10 times higher than those of KUr and USr, which is related to food coloring. Although samples of US and USr are produced by the same company using *ume* which was cropped in the same area, there are large differences in elemental concentrations of P and S. On the other hand, elemental concentrations of KUr and USr are very similar and lower than other two ones. It means that these differences are related to the process of *umeboshi* and not to *ume* itself.

Elemental concentrations of Sr in US and USr were lower than that of CFT and KUr. MAFF (Ministry of Agriculture, Forestry and Fisheries) of Japan reported that concentration of Sr in Chinese soil is higher than that in Japanese soil[4]. Elemental concentration of Sr in *umeboshi* may indicate the area where *ume* is cropped.

Figure 4 and 5 show elemental distribution images of cross-sectional area and surface of *umeboshi*, respectively. Scanning area was 10×15 mm^2 for cross sectional and was 10×10 mm^2 for surface analyses. It is apparent that Fe is concentrated in hull. Chlorine is uniformly distributed around hull. Ca is concentrated in skin, which is related to the absorption of Ca solution. In Fig. 5, Ca is not uniformly distributed and will be deposition from a solution.

Conclusion

We analyzed *umeboshi* which uses Chinese and Japanese *ume* by using an in-Air PIXE system and an in-air submili PIXE camera at Tohoku University. Major constituent elements are Al, Si, P, S, K, Ca, and Fe. Concentrations of heavy metals such as As, Cd, Hg and Pb were lower than standard values given by a food hygiene law and *umeboshi* analyzed in this experiment is safety for these elements. Calcium shows the highest concentration, which stems from the pickled process. During the process in making *umeboshi*, *ume* is dipped in Ca solution for several days and absorbs Ca. Concentrations of elements heavier than Ca show similar trend. On the other hand, lighter elements than Ca show large difference, which is related to food coloring or processing technique. Even using *ume* which was cropped in the same area by the same supplier, there are large differences in elemental concentrations of P and S. On the other hand, elemental concentrations of colored *umeboshi* are very similar. It means that these differences are related to the process of *umeboshi* and not to *ume* itself.

References

1) Futatsugawa S., Hatakeyama S., Saitoh Y., Sera K., International Journal of PIXE **4** (1993) 319.
2) Iwasaki S., Ishii K., Matsuyama S., Murozono K., Inoue J., Tanaka M., Yamazaki H., Orihara H., International Journal of PIXE **6** (1996) 117.
3) Matsuyama S., Gotoh K., Ishii K., Yamazaki H., Satoh T., Yamamoto K., Sugimoto A., Tokai Y, Endoh H., Orihara H., International Journal of PIXE **8** (1998) 209.
4) Tsukada M., Fujihara M., Yamasaki Y., Miyatake M., Kobayashi T., http://www.famic.go.jp/technical_information/investigation_research_report/pdf/2802.pdf.

Table 1. Sample Informations.

Sample name	CFT	KUr	US	USr
Food Coloring	-	○	-	○
supplier	A	B	C	
Production Area	China	China	Gunma, Japan	

Table 2. Concentrations of toxic heavy metals.

	Concentrations[ppm]	Standard values[ppm]
As	<0.04	1.5-3.5
Cd	<0.84	1.0
Hg	<0.72	0.4
Pb	<0.90	1.0-5.0

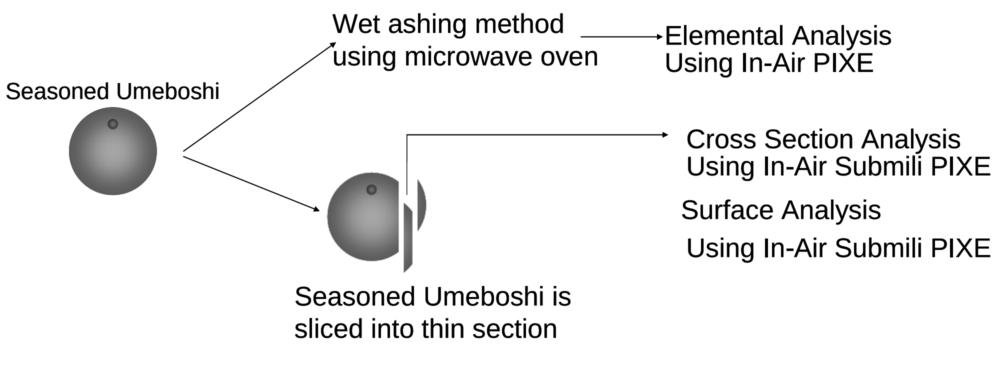

Figure 1. Flow of sample preparation.

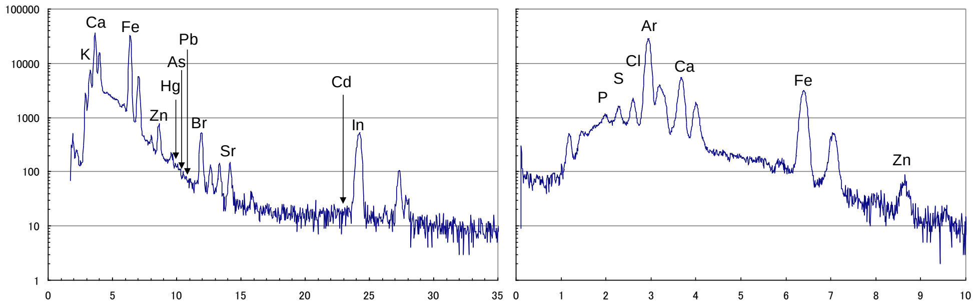

Figure 2. Characteristic X-ray spectrum of *umeboshi.*

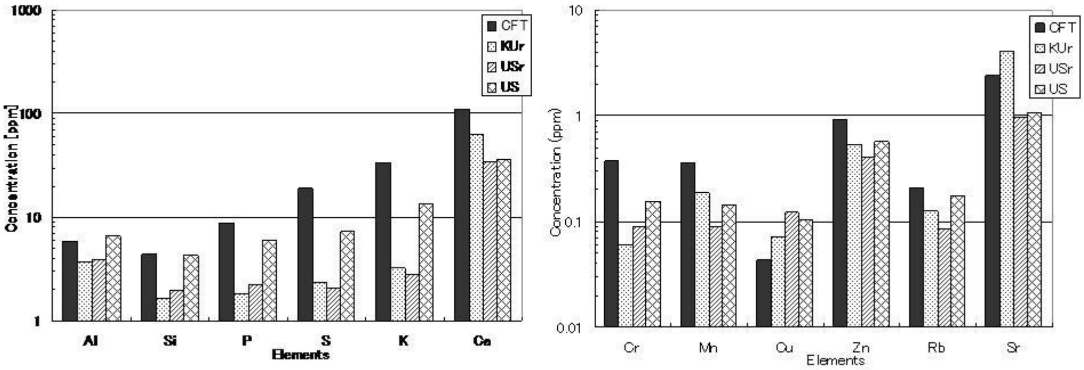

Figure 3. [left] Elemental concentration of *umeboshi.*(Al to Ca), [right] (Cr to Sr).

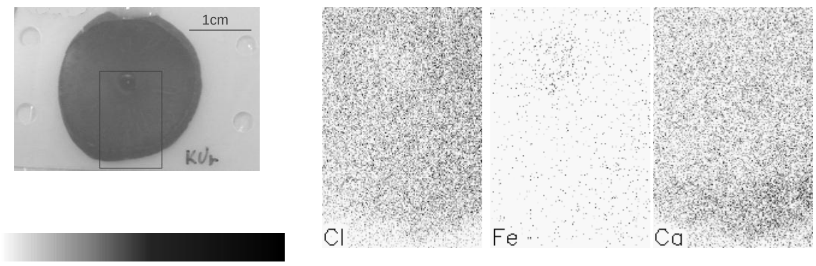

Figure 4. Elemental distribution of Cl, Fe and Ca in a cross sectional area.

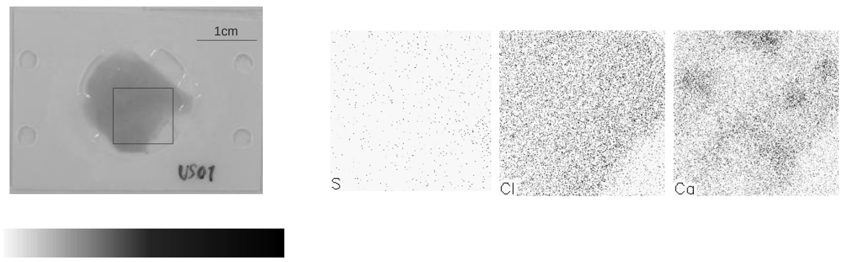

Figure 5. Elemental distribution of S, Cl and C on a surface of *umeboshi.*