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Development of sample preparation method for engine lubricating oil analysis using in-air PIXE

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Abstract. We originally developed a preparation method of target sample for automobile engine lubricating oil (liquid sample) specifically designed for in-air PIXE analysis with Helium ions. In the developed preparation method, target samples were fixed by making the oil sample sandwiches with 1% collodion solution based ethanol. With this analytical method, elements such as Al, Si, P, S, Cl, Ca and Zn can be detected from the oil samples, where Si, P, S, Ca and Zn were the elemental components of the oil additives.

Keywords: Engine lubricating oil, Multi-elemental analysis, In-air PIXE, Helium ion beam

INTRODUCTION

Elemental particles (particle size: <10 nm) contained in automobile exhaust particles originated from the elements in the automobile engine lubricating oil, and may become a nucleus of atmospheric particles. Therefore, investigation of elements in automobile engine lubricating oil became our major consideration relating to chemical speciation of particles in the atmosphere. Detection of elements in automobile engine lubricating oil is one of the challenging subjects in environmental research. There are several reports concerning elemental detection of automobile engine lubricating oil using various analysis techniques, such as atomic absorption spectrometry (AAS)[1,2], reactor neutron activation analysis (RNAA)[3], X-ray fluorescence (XRF)[4] and PIXE[5] analysis method. Although, these previously performed techniques were unable to detect those relatively light elements such as P and S, which are the important components of additive elements in the engine lubricating oil[6]. For multi-elemental analysis of liquid sample, the in-air PIXE analysis method, which was introduced previously, may have advantages compared to the other techniques mentioned above. This PIXE analysis can be perform in air, and by using accelerated Helium ion, instead of proton, enables to obtain clear spectra of X-ray emission of those lighter elements than Fe[7]. The aim of our present studies was to develop a target sample preparation method which is suitable for multi-elemental analysis of automobile engine lubricating oil using in-air PIXE with Helium ion bombardment.

EXPERIMENTAL AND METHOD

Automobile engine lubricating oil of four different types of vehicle, heavy duty diesel vehicle, light duty diesel vehicle, gasoline vehicle, and motorcycle, were prepared. Samples of the engine lubricating oil were all the unused oil. Moreover, a mixed standard solution was prepared, which contained Al, K, Ca, Cr, Mn, Fe, Ni, Cu, Zn and Pb at five concentrations (0.1, 0.5, 1, 5 and 10 mg/L). Target samples were prepared on the 6 μm-thick polypropylene (PP) film, which was attached to backing film of 1 mm-thick polypropylene sheet (4 mm × 4 mm size). This backing film has a 3 mm diameter hole in the center and 10 μL of the engine lubricating oil were dropped into the hole. Since the sample has to be set in vertical position, the

centre hole was covered with 1% collodion solution diluted in ethanol (Figure 1). The background X-ray emissions of PP film and collodion layer by Helium bombardment were negligible, which was important in multi-elemental analysis using PIXE.

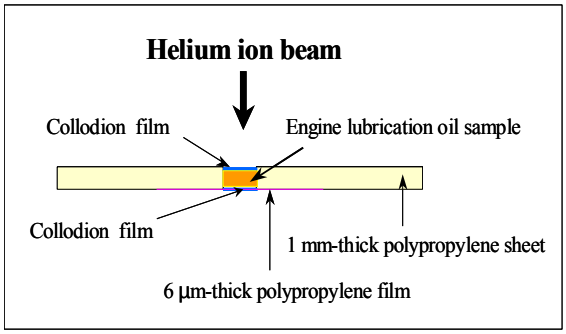


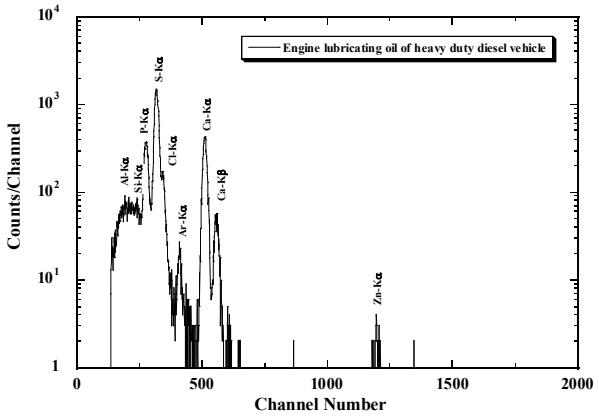
FIGURE 1. Schematic diagram of engine lubricating oil sample or standard solution sample prepared specified for in-air PIXE analysis.

In-air PIXE analysis with Helium ions of those samples were conducted at the National Institute of Radiological Sciences (NIRS). Each target sample was bombarded by 3.9 MeV Helium ion beam from a Tandetron (Model 4117MC, HVEE Co.)[8], and with the arrangements of the in-air Helium ion beam line, which was previously introduced as the droplet-PIXE system[9]. The Helium beam of approximately 2 mm diameter was introduced into a chamber filled by helium gas of atmosphere pressure. The dose irradiated to the target sample was controlled to 300 μC by monitoring with ionizing chamber installed at the beam exit. X-ray emission for each target sample were detected by Si(Li) X-ray detector and set at 30 mm (default position) away from the target sample and the X-ray spectra were analyzed using a software (SEIKO EG&G spectrum navigator).

RESULTS AND DISCUSSIONS

Multi-elemental spectra of X-ray emission by 3.9 MeV Helium ion bombardments are shown in Figure 2-5. Figure 2 shows the X-ray spectrum of engine lubricating oil for heavy duty diesel vehicle. In this oil, total of seven elements, Al, Si, P, S, Cl, Ca and Zn were identified. Especially, the peaks of P, S and Ca were clear. These elements, excluding Ar detected from the residual air in the chamber, are the major components of additive elements generally consisted in the engine lubricating oil[6]. The P, S, Zn, are the elements from the generally used antioxidant which is consisted of zinc dialkyldithiophosphate (ZnDTP). Another additive of oil, a friction modifier, has S as a component. The Ca is from the detergent-dispersant. The Si is a component of antifoaming agent included in the oil. The X-ray spectrum of engine lubricating oil for light duty diesel vehicle (Figure 3) was almost the identical to that of an engine lubricating oil for heavy duty vehicle shown in Figure 2. There was a significant difference in the engine oil of gasoline vehicle (Figure 4) from the engine oil of diesel vehicle. K and Fe were detected in the spectrum, along with the peak of Al and Si became more prominent. On the other hand, for the engine oil of motorcycle (Figure 5), only Si, S, K and Ca were detected.

The concentration of the major consisting elements in the oil were estimated from the spectra obtained from the measurement of the standard solution performed independently using the in air PIXE analysis with identical set-up. The concentration of P, S, Ca, and Zn were estimated to be 100 – 200 mg/L, 200 – 300 mg/L, 5 – 30 mg/L, and several mg/L, respectively, for the engine lubricating oil samples investigated in this study. The determination limit by the analysis method is 0.1 mg/L for elements from Al to Fe. For Zn, the determination limit is 0.5 mg/L.



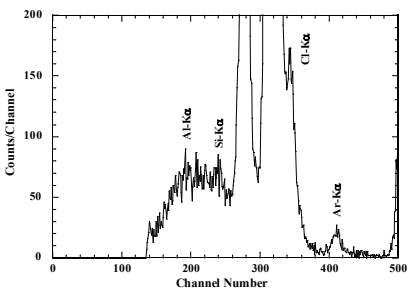
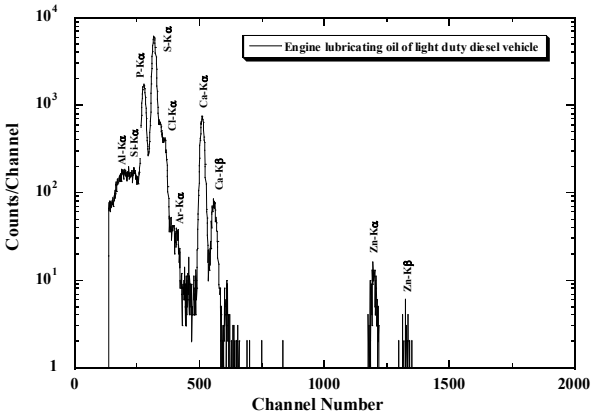


FIGURE 2. X-ray spectrum of the engine lubricating oil sample of a heavy duty diesel vehicle obtained by 3.9 MeV Helium ion bombardment.



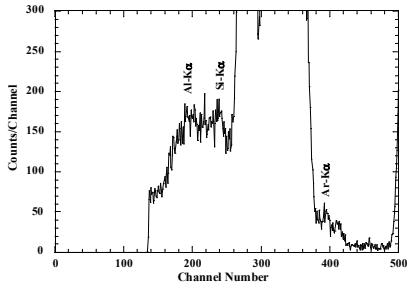
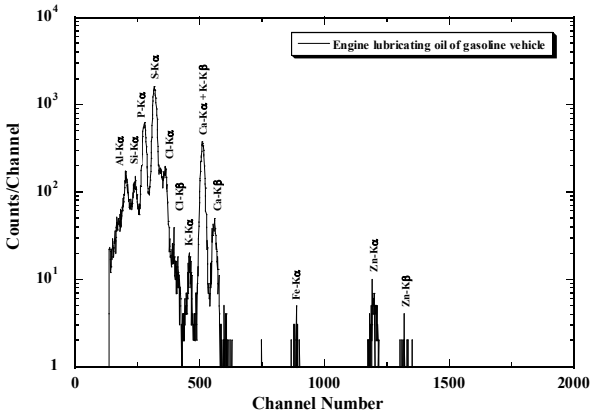


FIGURE 3. X-ray spectrum of the engine lubricating oil sample of a light duty diesel vehicle obtained by 3.9 MeV Helium ion bombardment.



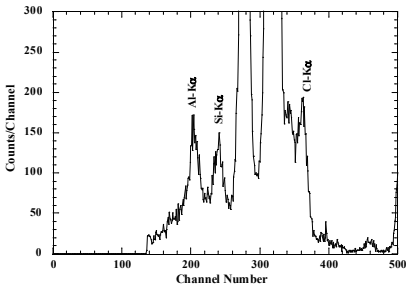
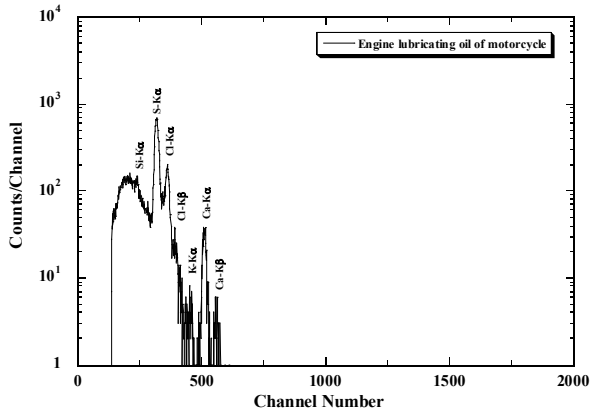


FIGURE 4. X-ray spectrum of the engine lubricating oil sample of a gasoline vehicle obtained by 3.9 MeV Helium ion bombardment.



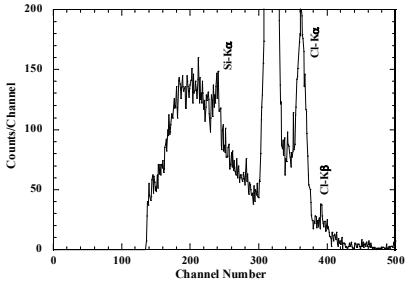


FIGURE 5. X-ray spectrum of the engine lubricating oil of sample a motorcycle obtained by 3.9 MeV Helium ion bombardment.

As we described in this paper, with our collodium sample preparation technique and in-air PIXE analysis using Helium ion enables to obtain a clear multi-elemental X-ray spectra of automobile engine lubricating oil. This technique may be the most convenient method for obtaining information of elemental components for various types of automobile engine lubricating oil. Therefore, this method has a possibility of contribution in advancement in atmospheric particles studies.

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