Preliminary Study on the Elemental Quantification of in Ambient Liquid Samples of Microliter Volume Using the In-air Micro-PIXE Technique

Chang-Jin Ma*, Cheol-Soo Lim1) and Takuro Sakai2)

Department of Environmental Science, Fukuoka Women’s University, Fukuoka 813-8529, Japan
1)Department of Air Quality Research, National Institute of Environmental Research, Incheon 22689, Republic of Korea
2)Advanced radiation technology center, Japan Atomic Energy Research Institute, Gunma 370-1292, Japan

*Corresponding author. Tel: +81-92-661-2411, E-mail: ma@fwu.ac.jp

1. INTRODUCTION

Due to the need to better characterize the ambient liquid samples and related influences, sometimes ambient liquid samples have to be analyzed even if they have only very small quantities. One of the best examples is the cloud droplets.

It is well known that clouds influence the earth radiation budget due to their optical reflectivity and absorptivity. This aerosol indirect climatic effect depends on both the in-cloud droplet size distribution and the chemical properties of the cloud droplets. A number of variables including the chemical properties of cloud droplets and the solute (or whole droplet) composition are essential prerequisites for understanding cloud formation processes and heating/cooling rates.

Moore et al. (2002) developed a multi-stage cloud water collector and made a field performance evaluation. It is not easy to collect enough amount cloud water for its chemical analysis, especially when it is separated as a function of drop size. Although it is possible to collect a quite sufficient amount by long time sampling duration, in this case, it cannot realize a high-time resolved data discussion.

In order to estimate rapid changes in chemical compositions, concentrations, and formation mechanisms of atmospheric particulate matter, in recent years, the high time-resolution collection is mainly being carried out. A short-time interval sampling naturally leads to collection of a small amount of sample. If, especially, particulate matters are size-fractionally sampled, a lower volume of samples will be collected. As a result, their chemical analysis will be restricted to the selected analytical instruments with very extraordinary capabilities. Moreover, ultrafine particles (Dp < 100 nm) that the importance of its study have been highlighted in recent years due to their possibly larger impacts on health when compared to coarse particles (Oberdörster, 2000) have very slight amount which then be under restrictions for pretreatment and analysis.

If particulate matters are soluble, most of them may deposit anywhere of our respiratory system and are able to dissolve and release the potentially harmful material to the body (Garrod et al., 1998; Morrow, 1992). Therefore, in order to fully understand the health risk of particulate matters, their water-soluble components have
to be comprehensively investigated.

Recently, as the increased demand for more precise characterization of the soluble fraction elements of particulate matters, the dried thin liquid sample have been the targets for ion beam analysis (Kikuchi et al., 2003). There were, however, a number of crucial flaws in the dried thin method. First of all, Poli et al. (2004) reported that as a result of a dissimilarity in the drying process of liquid samples on substrate film, the differences in adhesion and crystallization of the liquid sample may have occurred. Partially evaporation of components during drying process of liquid sample on a film layer can also create an unsound analytical result.

Given these realities, in this study, we made an attempt to quantify the trace elements in a small amount of ambient liquid sample using the in-air micro-PIXE technique and report the outcomes of our preliminary study.

2. EXPERIMENTAL METHODS

2.1 Liquid Sample Holder with a Micro-scale

The bag type sample holder (W6 mm × L8 mm) with 10 μm thick Mylar® (C10H8O4)n, 1.38-1.40 g/cm3) film was originally designed in this study to fill a small amount of liquid sample. The Mylar film is made of 100% polyester thus composed only by C, H, and O. It has a high transparency and is chemically neutral with low heavy metal contaminations. A 50 μL sample (the standard solutions in this study) was pipetted gently into the bag type sample holder and then allowed to sealed with a sealer.

After injecting liquid sample into the sample holder, it was secured on the sample mounting station of micro-PIXE. And then the exact location of the sample and the irradiated area of proton beam were better adjusted from the control room. Fig. 1 describes a new method for preparing durable and uniform sample with a very small quantity of liquid for the micro-PIXE analysis.

2.2 Preparation of Standard Solutions

Table 1 has a list of the different target elements and their certified reference materials. To prepare the reference liquid samples for six kinds of elements, a 1000 ppm of reference reagent (TraceCERT®) for AAS/ICP analysis was diluted as the levels of the concentration (ppm) steps described in Table 1. As shown in Table 1, among six reference samples, iron, nickel, and zinc contain the neighboring elements. Also, their assays are 99.95-99.99%, i.e., they contain 100-500 ppm of impurities.

Table 1. Target elements and their certified reference materials.

| Z   | Reference material                  | Assay (%)                      | Concentration (ppm) steps | Sample holder   |
|-----|------------------------------------|--------------------------------|---------------------------|-----------------|
| Si  | Si metal + HNO₃                      | ≥ 99.99 (metal basis)           | 500/600/700               | (C₁₀H₈O₄)ₙ     |
| S   | H₂SO₄ + H₂O                         | ≥ 99.99 (H₂SO₄ basis)           | 200/500/700               | (C₁₀H₈O₄)ₙ     |
| Cl  | Cl⁻ + H₂O                           | ≥ 99.99 (Cl⁻ basis)             | 50/200/500                | (C₁₀H₈O₄)ₙ     |
| Fe, Ni | Fe, Ni metals + HNO₃             | ≥ 99.99 (metal basis)           | 5/10/20                   | (C₁₀H₈O₄)ₙ     |
| Ni  | Ni, Zn metals + HNO₃               | ≥ 99.95 (metal basis)           | 5/10/20                   | (C₁₀H₈O₄)ₙ     |
| Zn  | Zn, Ni metals + HNO₃               | ≥ 99.95 (metal basis)           | 5/10/20                   | (C₁₀H₈O₄)ₙ     |

Fig. 1. Flow of preparation of standard species and their analysis.
Lin et al. (1979) carried out the studies on the variations of relative sensitivity in the external beam PIXE analysis of liquid samples due to the presence of large amounts of neighboring elements. And they reported that the variations of relative sensitivity for elements of $Z \geq 20$ were less than 1% if the Cu-concentration was less than 5 mg/mL (i.e., 5000 ppm). This means that there is no need to consider the matrix effect (i.e., the effect on the quantification of targeted element caused by all other components of the sample) from the impurities of our reference samples (i.e., iron, nickel, and zinc).

As the preliminary study, the concentration (ppm) steps of reference reagents were adjusted from the case of the unusually high concentration of ambient and workplace air in industries. The fog water collected in the Los Angeles basin and the San Joaquin Valley indicated unusually high concentrations of major ions (about 500 ppm of sulfate) and trace elements (about 24 ppm of iron) (Munger et al., 1983).

2.3 Micro-PIXE Analysis
For quantitative analysis of the reference standards, micro-PIXE analysis was performed at the division of Takasaki Ion Accelerator for Advanced Radiation Application (TIARA) in Japan Atomic Energy Research Institute (JAERI). Beam scanning, data acquisition, evaluation and the drawing of elemental maps are controlled by a computer on the basis of the system program. The beam scanning system generates control signals of high voltage applied to beam deflector electrodes, and also takes magnitude signals of secondary electron currents to display a secondary electron image of samples. X-Y beam scanning control signals, which indicate the beam position, are also digitized at the same time. These data are addressed to the 3D matrices in the memory space, that consist of 1024 channels for the energy spectra and $128 \times 128$ pixels for corresponding the beam scan area. Target portion of sample was allocated by STIM (Scanning Transmission Ion Microscope) method that can get the image of sample thickness by detection the transmitted beam amount, i.e. proton energy loss after irradiation of very weak beam current. Beam collection time was about 5-10 min.

The micro-PIXE system at the TIARA in Japan has been adapted for analysis of liquid samples. The hard-
ware design of the beam setup in TIARA has been already described in elsewhere (Sakai et al., 2002).

3. RESULTS AND DISCUSSION

3.1 Beam Resolution and Film Containing Impurities Tests

The energy-loss of transmitted protons depends on thickness and density of the sample and this can be obtained using a surface barrier Si detector behind the sample. It is possible to get the energy-loss map by scanning the sample surface with proton beams. Finally, the structure image of samples in the scanning area can be simultaneously structured with STIM system during PIXE analysis.

Fig. 2 illustrates the X-ray spectrum (top) drawn from copper mesh (1000 lines/inch) for beam resolution test, its STIM image (bottom left), and its horizontal (middle bottom) / vertical localizations (bottom right). From the analysis of reference copper mesh, it was possible to resolve not only the STIM spectrum, but the visual image including its horizontal / vertical localizations corresponding to the copper peak.

There are vague points for the application of micro-PIXE to the liquid sample filled in the sample holder.

![Fig. 3. Homogeneity of the elemental distribution in the liquid reference species.](image)

![Fig. 4. Examples of the X-ray spectra of the lowest concentration for six target elements.](image)
made of Mylar® film. One is the possibility of the sample holder rupture by a micro-PIXE beam intensity and the other is the elemental blank concentrations of Mylar® film. The inner spectrum of Fig. 2 is the X-ray spectrum of the sample holder made of Mylar® film with 10 μm thickness. As shown in Fig. 2, fortunately, no apparent peaks of Mylar® film blank which effect on the detection ability of PIXE analysis was found. As the characteristic peak of air, Ar (Kα and Kβ) was observed. And the sample holder made of Mylar® film kept the original shape without rupture under the PIXE analytical condition of beam charge from 100 to 150 nC for beam collection time of 5-10 min.

3.2 Homogeneity Test for Elemental Distribution

It is necessary to examine the homogeneity of the elemental distribution in liquid reference species. To solve this problem, X-ray line profile, i.e., the vertical and horizontal distributions of X-ray intensity for several references were estimated. Fig. 3 shows the line distribution of Kα characteristic X-ray intensity normalized with accumulated charge (count/nC) of chlorine, sulfur, and silicon depending on projection axis. The width of projection, i.e., the micro-beam scan width was 400 μm both horizontally and vertically. As a result, we could not find any difference in X-ray intensities among different locations of reference samples. This means the solute of each target element was uniformly distributed over the whole beam scan area.

3.3 X-ray Spectra and Calibration Curves of Target Elements

Fig. 4 shows the example of the X-ray spectra of the lowest concentration for six target elements. It was

![Experimental sensitivity (counts·ppm⁻¹·nC⁻¹) curve for liquid references.](image)

![Calibration curves of each liquid reference plotted by concentration and ROI net counts normalized with accumulated charge. Microbeam scan area of every sample was fixed with a 400 × 400 μm².](image)
possible to resolve the significant peaks for whole target elements corresponding to the channel number of micro-PIXE spectrum.

Fig. 5 shows experimental calibration (counts ⋅ ppm⁻¹ ⋅ nC⁻¹) curve for six kinds liquid standards. The sensitivity of each element $S_i$ was calculated using the following equation:

$$S_i = \frac{X_i}{A_i}$$

where $S_i$ is the sensitivity for element $i$, $X_i$ is the net counts per ppm, and $A_i$ is the charge (nC) accumulated during microbeam irradiation.

As the next step, each element calibration curve was successfully plotted by concentration (ppm) and ROI (region of interest) net counts/dose (nC) obtained from 3.0 MeV H⁺ microbeam (Fig. 6). Every calibration curve for target elements was drawn by three points concentration described in Table 1. As shown in Fig. 6, although a somewhat lower $R^2$ score (0.86) for zinc was obtained, every plotted point was lying on the straight line showing a high correlation coefficient ($R^2 = 0.93$ to 0.99) between X-ray net count and elemental concentration.

Fig. 7 show the flow of elemental quantification from liquid samples by micro-PIXE analysis. This elemental quantification will be conducted in the following order: drawing a spectrum with sufficient X-ray counts for standard species and samples - computing the net peak counts by subtracting the film background - normalizing the counts with respect to the relative beam current, exposure times, and microbeam scan area - creating calibration curve - constructing regression model - quantifying elements in samples.
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