

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

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ABSTRACT

Quantifying the trace elements in infinitesimal ambient liquid samples (e.g., single raindrop, cloud/fog water, and the soluble fraction extracted from the particles collected for a short time) is an important task for understanding formation processes, heating/cooling rates, and their health hazards. The purpose of this study is to employ an in-air micro PIXE system for quantitative analysis of the trace elements in a thimbleful of reference liquid sample. The bag type liquid sample holder originally designed with 10 μm thick Mylar[®] film retained the original shape without any film perforation and apparent peaks of film blank by the end of the analysis. As one of tasks to be solved, the homogeneity of the elemental distribution in liquid reference species was verified by the X-ray line profiles for several references. It was possible to resolve the significant peaks for whole target elements corresponding to the channel number of micro-PIXE spectrum. The calibration curves for the six target elements (Si, S, Cl, Fe, Ni, and Zn) in standard solutions were successfully plotted by concentration (ppm) and ROI of interest net counts/dose (nC).

Key words: Liquid sample, Cloud, Soluble fraction, Elements, micro-PIXE

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 radi-

ation 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 ($D_p < 100 \text{ nm}$) 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 refer-

ence 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.

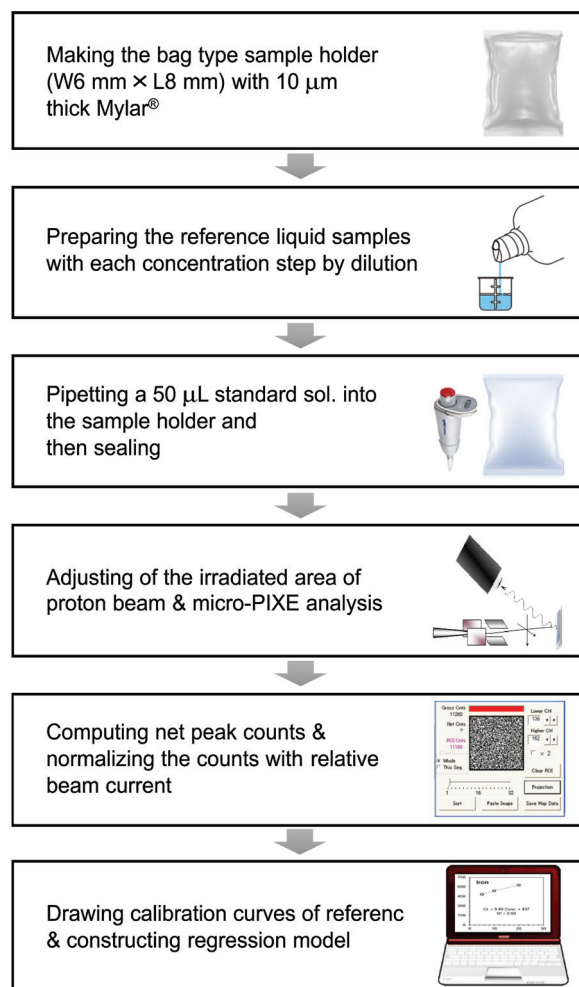


Fig. 1. Flow of preparation of standard species and their analysis.

Table 1. Target elements and their certified reference materials.

| Z | Reference material | Assay (%) | Concentration (ppm) steps | Sample holder |
|----------|---|--|---------------------------|---|
| Silicon | Si metal + HNO ₃ | ≥ 99.99 (metal basis) | 500/600/700 | (C ₁₀ H ₈ O ₄) _n |
| Sulfur | H ₂ SO ₄ + H ₂ O | ≥ 99.99 (H ₂ SO ₄ basis) | 200/500/700 | (C ₁₀ H ₈ O ₄) _n |
| Chlorine | Cl ⁻ + H ₂ O | ≥ 99.99 (Cl ⁻ basis) | 50/200/500 | (C ₁₀ H ₈ O ₄) _n |
| Iron | Fe, Ni metals + HNO ₃ | ≥ 99.99 (metal basis) | 5/10/20 | (C ₁₀ H ₈ O ₄) _n |
| Nickel | Ni, Zn metals + HNO ₃ | ≥ 99.95 (metal basis) | 5/10/20 | (C ₁₀ H ₈ O ₄) _n |
| Zinc | Zn, Ni metals + HNO ₃ | ≥ 99.95 (metal basis) | 5/10/20 | (C ₁₀ H ₈ O ₄) _n |

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 128×128 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-

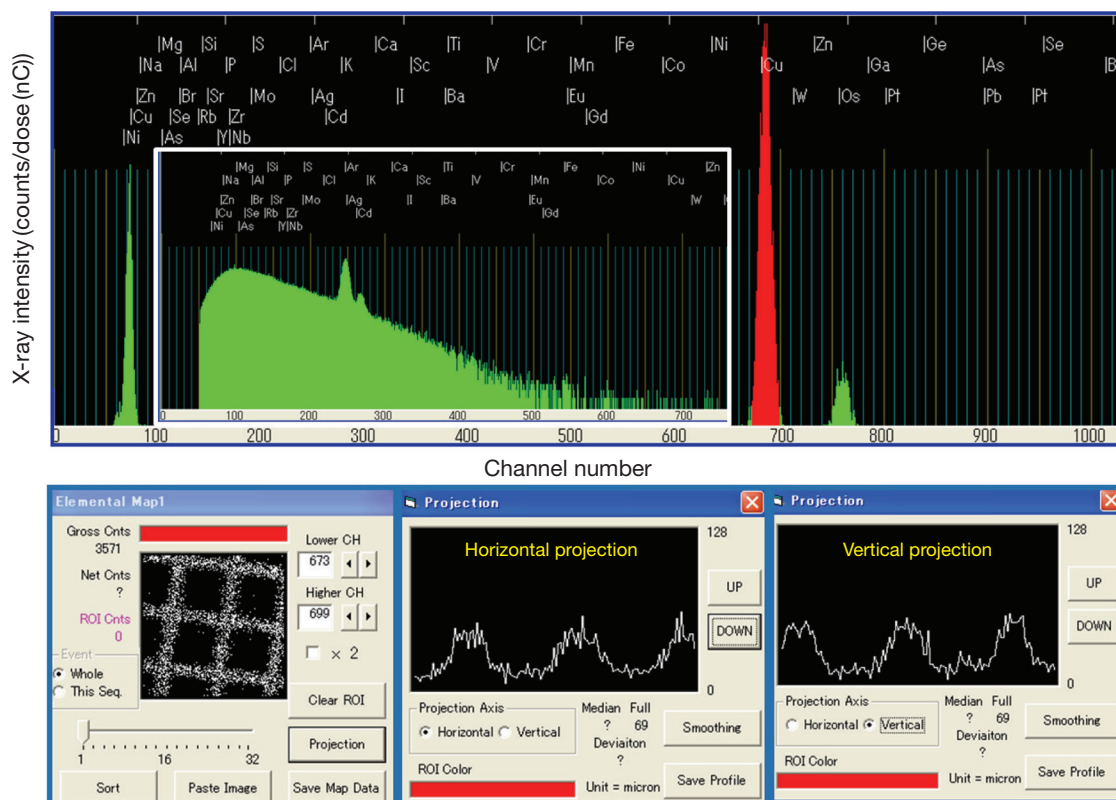


Fig. 2. The X-ray spectrum (top) drawn from the copper mesh for beam resolution test, its STIM image (bottom left), and its horizontal (middle bottom) / vertical localizations (bottom right). The inner is a spectrum of the sample holder made of Mylar[®] film of 10 μm thickness.

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 (K_{α} and K_{β}) 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 K_{α} 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

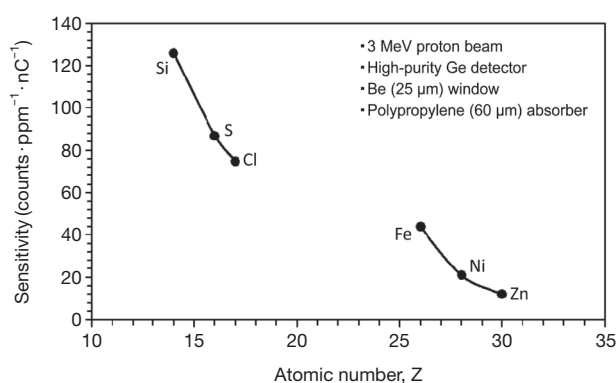


Fig. 5. Experimental sensitivity (counts · ppm⁻¹ · nC⁻¹) curve for liquid references.

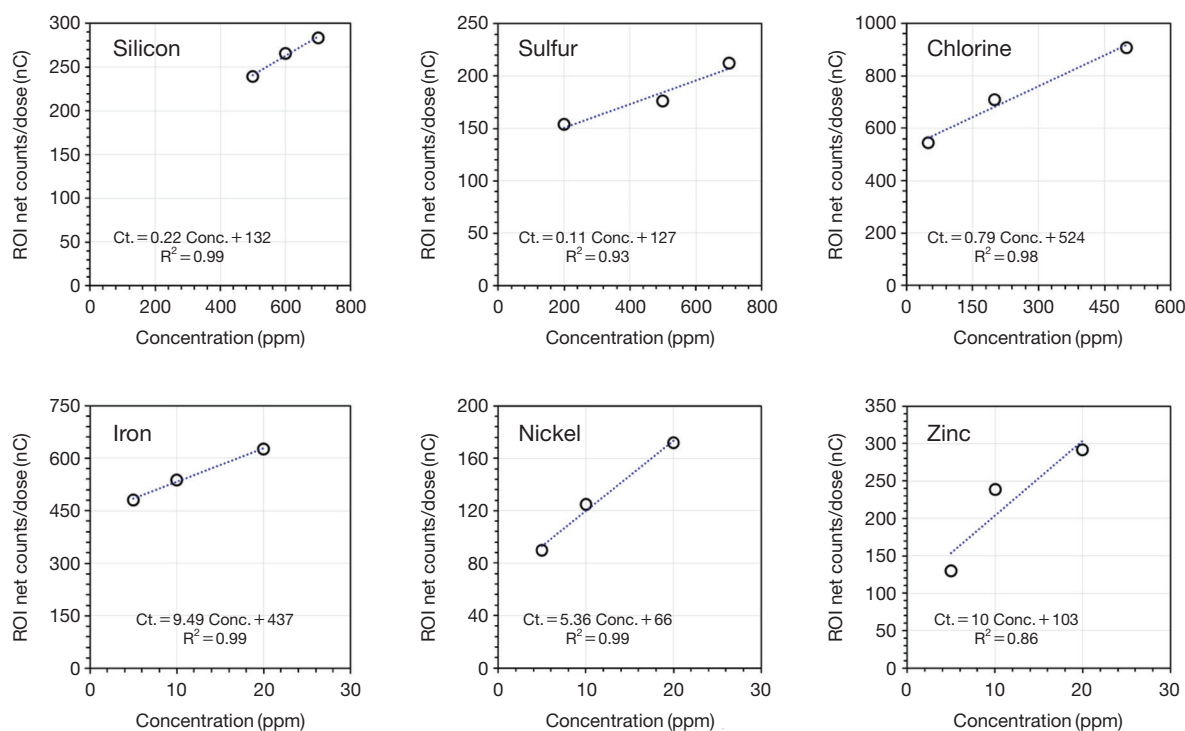


Fig. 6. Calibration curves of each liquid reference plotted by concentration and ROI net counts normalized with accumulated charge. Microbeam scan area of every sample was fixed with a 400 × 400 μm^2 .

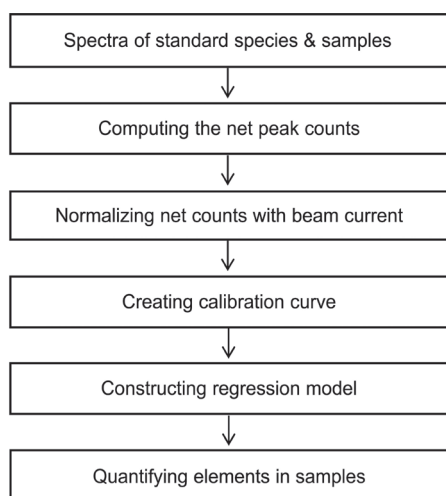


Fig. 7. Flow of elemental quantification from liquid samples by micro-PIXE analysis.

possible to resolve the significant peaks for whole target elements corresponding to the channel number of micro-PIXE spectrum.

Fig. 5 shows experimental calibration ($\text{counts} \cdot \text{ppm}^{-1} \cdot \text{nC}^{-1}$) curve for six kinds liquid standards. The sensitivity of each element S_i was calculated using the following equation:

$$S_i = X_i \cdot A_i^{-1}$$

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.

4. CONCLUSION

The quantification of elements in trace amounts of ambient liquid samples can provide new and interesting information on the heterogeneous multi-phase processes of the ambient droplets and their climate/health effects. However, at the present stage, a thorough interpretation is not possible due to technical restrictions for sampling, pretreatment, and, especially, analysis of a thimbleful of ambient liquid sample. In the present study, we made an attempt to quantify elements in ambient liquid samples of microliter volume using the micro-PIXE technique and report the outcomes of our preliminary trial. As the final outcome of our advanced attempt, the expected problems in the process of analysis, i.e., a burst of liquid-filled film bag and impurities contained in sample bag did not occur at all. Each element calibration curve, which is absolutely essential to an absolute quantification, was also successfully plotted by concentration and X-ray intensity with a high correlation coefficient. There still exist several points that must be clearly established for the proven method of quantitative analysis. Above all, to determine the matrix composition and then correct the micro-PIXE data for the self-absorption of X-rays (i.e., characteristic X-ray can be partially absorbed by the thick concentrated sample itself and then can exhibit severe spectral distortions) in the liquid sample is should be preceded. In the present study, no essential changes of sample holder appearance were observed, however, its stability and the boiling liquid sample have to be examined at more high-dose proton. In the future challenges, it is also expected to try to calculate the elemental concentration of various liquid samples.

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