

# DEVELOPMENT OF DROPLET-PIXE SYSTEM FOR ENVIRONMENTAL MONITORING SAMPLES \*

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## Abstract

A Behaviour of radionuclides in the environment and organisms has been investigated to evaluate the radiation effect on human using stable isotopes using PIXE (particle induced x-ray emission) analysis at the PASTA (PIXE analysis System and tandem accelerator) facilities in the NIRS (National Institute of Radiological Sciences). Since some of the environmental monitoring samples are in the liquid state, pre-treatment of the samples such as filtration, drying and solidification are necessary prior to the PIXE analysis. During sample preparation process, there may be loss of element due to sublimation or evaporation that must be taken care for quantitative analysis. To avoid such problems, we have developed a suitable droplet-PIXE system. It is based on the following points: (i) development of equipment with a good stability to supply a droplet of good reproducibility, (ii) optimisation of all equipments that includes a stable beam line (proton, 2.8MeV) and (iii) to evaluate irradiation dose for quantitative analysis. It will be advantageous to many researchers since it is very simple and save time during the sample preparation. However, there are some disadvantages in the detection range compared to conventional PIXE. The droplet-PIXE system has been applied to a few case studies. Limits of detection with or without any chemical preparation and its superiority or advantages over other PIXE system will be discussed in this paper. Application of the droplet-PIXE system can be expanded in future to other possibilities.

## INTRODUCTION

During the sample preparation process for PIXE analysis, there may be loss of element due to sublimation or evaporation that must be considered for quantitative analysis. To avoid such problems, suitable droplet PIXE system has been developed for determination of elemental abundances of liquid samples in atmospheric condition. This system is designated as “droplet PIXE system” which is constructed under the following concepts: (i) keep a fixed droplet size during measurement of one cycle, (ii) optimisation of all equipments during operation that includes a stable beam line (proton, 2.8MeV) (iii) to evaluate the amount of irradiation dose for quantitative analysis and (iv) its application to environmental and biological samples.

The droplet PIXE method can offer advantage to many researchers since it is a very simple method and save time during the sample preparation. The droplet PIXE system has been applied to a few case studies in this dissertation. Limits of detection with or without any chemical

preparation and its superiority or advantages over other PIXE system will be discussed.

## PIXE EQUIPMENT

The PASTA facilities of the NIRS are used for development of droplet PIXE system. [1] The accelerator is Tandetron (Model4117MC) manufactured by High Voltage Engineering Europa B.V. For PIXE, the facility provides three beam lines, which are a conventional-PIXE line, a micro beam scanning PIXE line and in-air PIXE line. The development of droplet PIXE system is explained as below.

### *Geometrical arrangement of the droplet PIXE beam line*

The beam line has been optimized by modification of existing in-air PIXE system for a droplet PIXE measurement such as (a) suitable design of beam collimator, (b) layout of irradiation chamber, and (c) the attachment angle of a Si(Li)detector, and final geometrical arrangement. Figure 1 shows the layout of this droplet PIXE beamline.

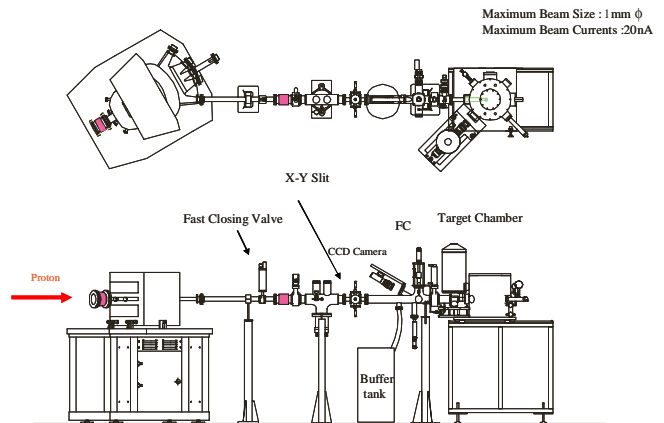


Figure 1: Layout of Droplet PIXE beam line and Si(Li) X-ray detector.

### *Control system for droplet PIXE equipment*

The system is composed of a pumping unit to generate constant size droplets, stable supply of a 2.8 MeV proton beam, and an irradiation control for quantitative analysis. The system has several dripping modes in order to enhance advantage of dripping method over static liquid target method. The features of the system are divided into three categories; (i) precise flow control system that corrects a non-linearity of pumping unit controller, (ii) by monitoring droplet size, image capture has been carried out using CCD (charge-coupled device) camera, and (iii)

keyboard emulation program that enables utilization of a commercial MCA (multi-channel pulse height analyzer) software and integration of a current integrator and a beam shutter control and a MCA. Figure 2 and 3 show the schematics of Droplet PIXE control system.

### EXAMPLE OF PRACTICAL USE OF THE DROPLET PIXE SYSTEM

It has been proposed that a droplet PIXE system can be a practical method to analyze elements in liquid environmental and biological samples in the liquid state.

### Measurements method of an environmental sample with low elemental concentration and large amount

Although it is known that the concentration of elements in river water is relatively low, the water sample has been selected to demonstrate the ability of this proposed technique. In this case, the amount of the samples is large.

The sample was collected from the sluice gate (Edogawa river origin) of the Kuriyama water purification plant of Chiba prefecture. Nitric acid was added, in order

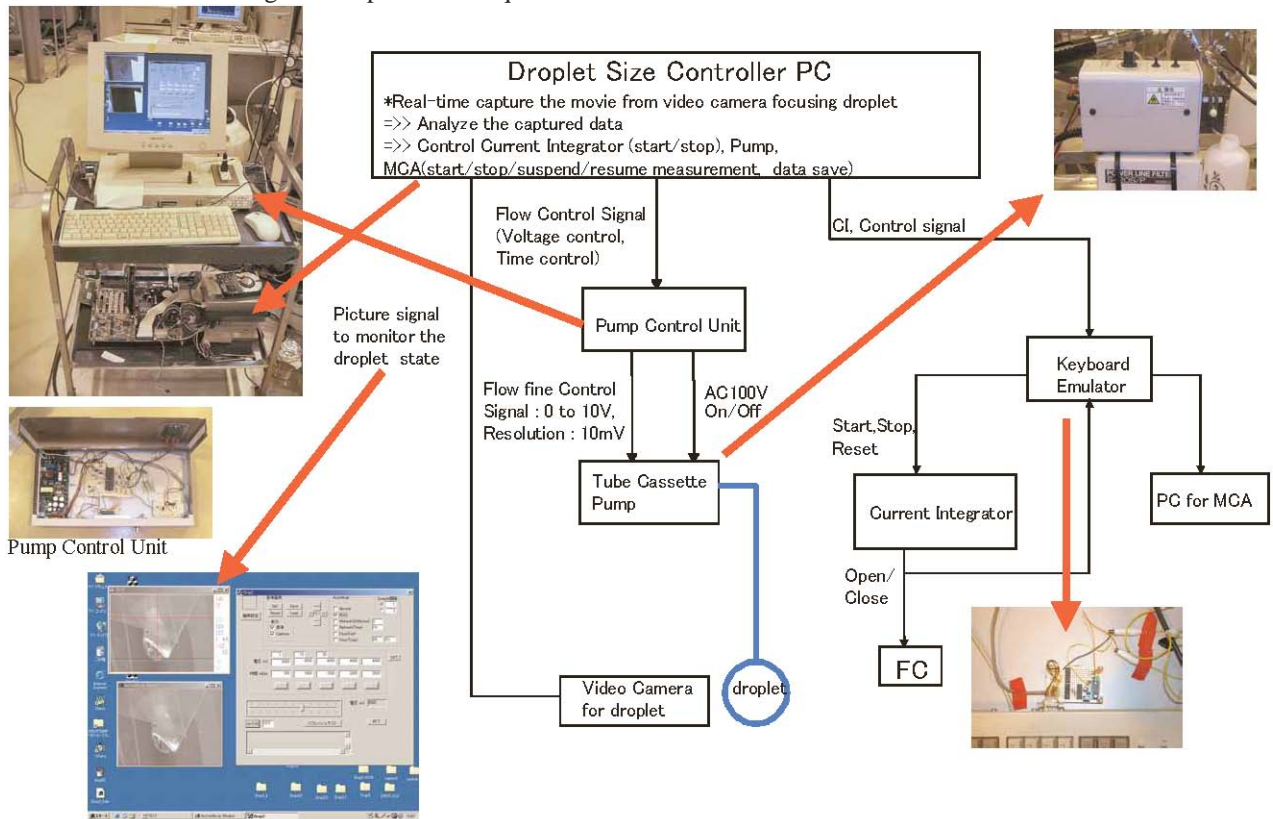


Figure 2: Schematic Diagram of Droplet PIXE System.

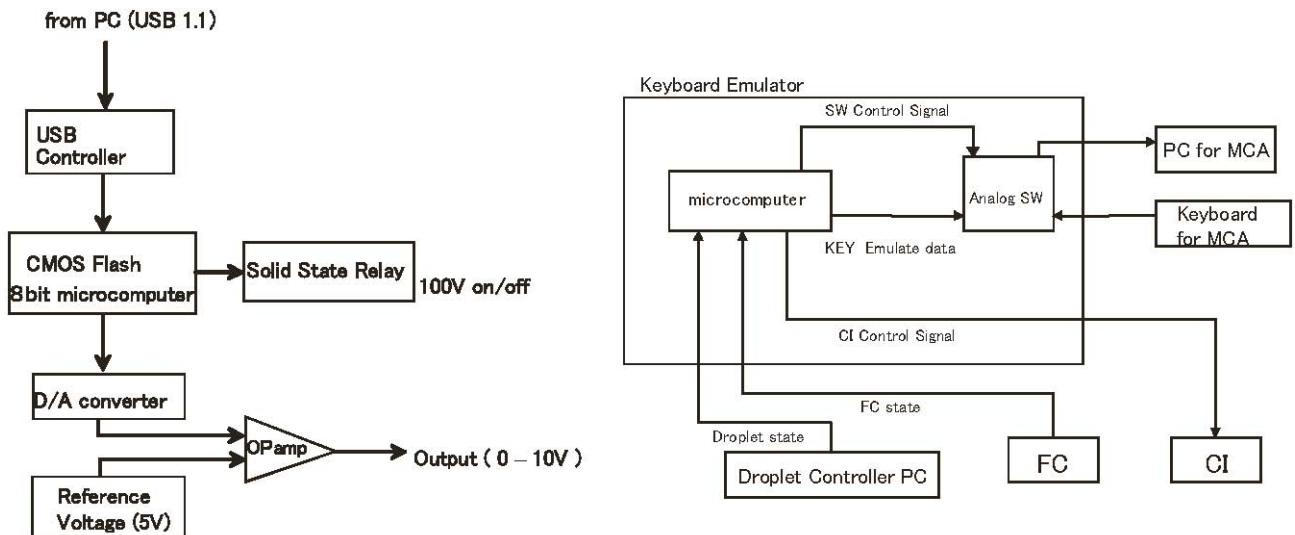
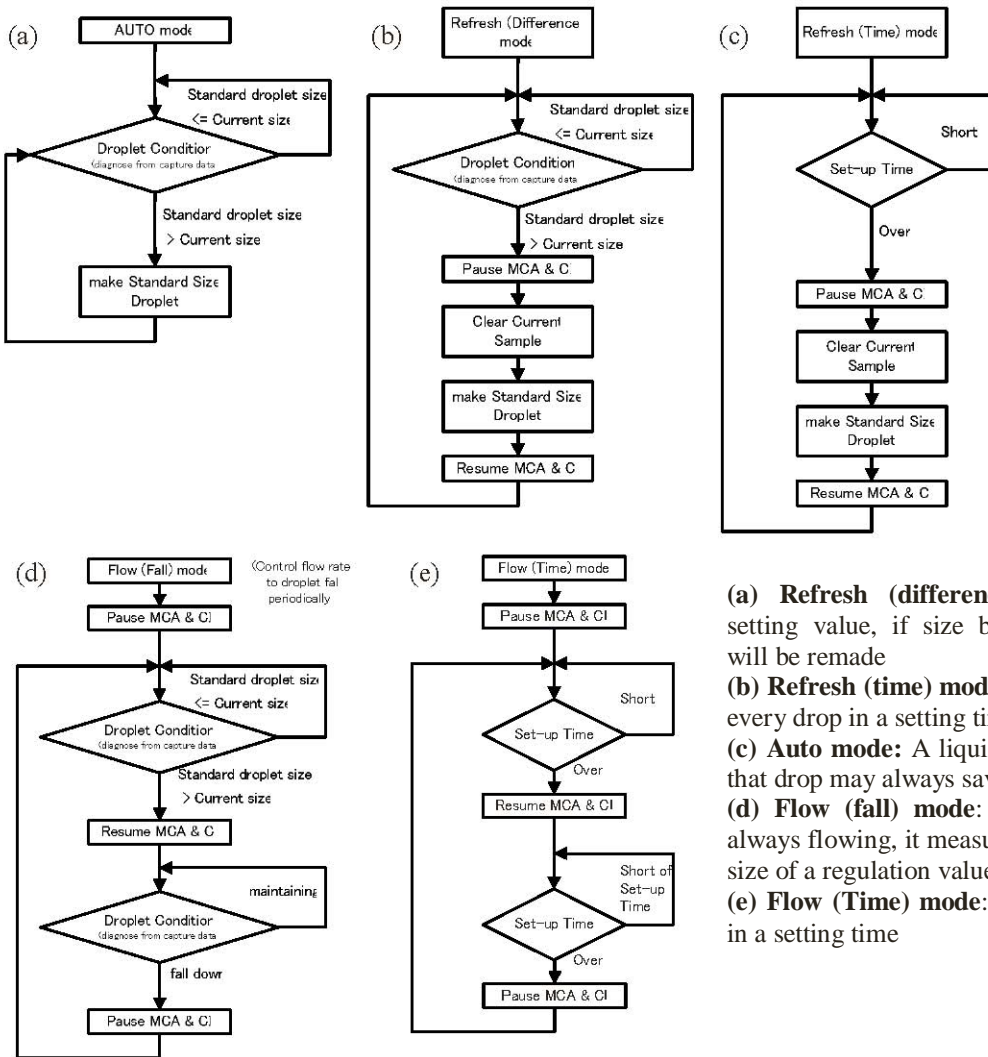


Figure 3: Schematic Diagram of Pump Control Unit and Keyboard Emulator.



- (a) **Refresh (difference) mode:** from a setting value, if size becomes small, drop will be remade
- (b) **Refresh (time) mode:** drop is remade for every drop in a setting time
- (c) **Auto mode:** A liquid is always added so that drop may always save a fixed size
- (d) **Flow (fall) mode:** where the liquid is always flowing, it measures at the time of the size of a regulation value
- (e) **Flow (Time) mode:** A liquid is replaced in a setting time

Figure 4: Flow chart of the droplet size control mode of this system.

to avoid adsorption elements to the container wall. The water sample was filtrated with the Millipore filter (0.45 micrometer-HA) to remove a charcoal and an insoluble substance before analysis. The sample volume ranged from 1ml to 150ml. Although the elemental concentrations are low, it is necessary to lengthen the measurement time, without employing evaporation method to avoid any loss in their concentration. For this purpose, following methods were developed. When the drop becomes smaller than a fixed size, or when it falls by the middle, once, MCA has been stopped, and after remaking water drop, it has been carried out in the Refresh (difference) mode (see Fig.4) that resumes measurement. Only calcium peak has been observed in the date of MCA in this measurement.

*Measurement method considering influence of the concentration change by evaporation of a sample during irradiation*

Liquid sample evaporate during the irradiation, and the elemental concentrations change every second. Water drop was made in the Refresh (time) mode (see Fig.4)

compulsorily measured while remaking at intervals of fixed time. For testing the mode, sea water was measured.

The sample was collected from the beach of Chiba Kujuukuri- Hama of Chiba prefecture. The pretreatment procedure is the same as describe for river water. The peaks of chlorine (Cl), potassium (K), calcium (calcium), and sulfur (S) have been observed.

*Measurement method of a liquid sample of very small quantity with the necessity of it being stabilized for a long time*

Human Cu, Zn- SOD (superoxide dismutase) has been selected as an example due to its importance in field of biological materials, and the sample amount obtained was very small. Therefore, the Auto measurement mode (see Fig.4) has been applied. The quantity used for this measurement was about 90 µl (three drops). Peaks of Cu and Zn have been observed. A significant peak of Cd could not be identified contrary to the expectation. Figure 5 shows X ray spectrum of SOD.

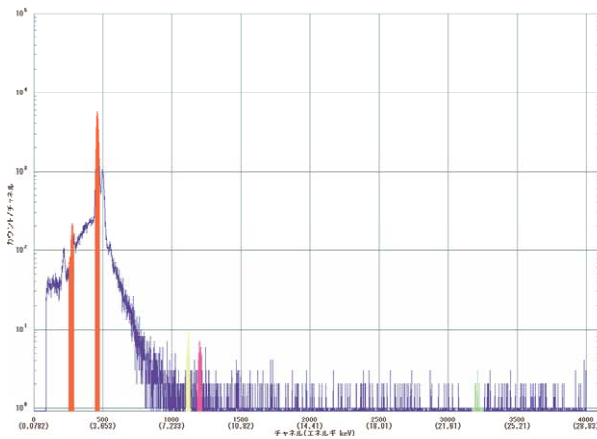


Figure 5: X ray spectrum of SOD.

*Measurement method of a living body sample where element concentration changes with time*

This method is to measure the liquid while sample is always flowing, and it is expected that the element contained in a liquid changes with time.

Flow measurement mode is followed. Drop has been changed into the state of flowing at a fixed speed, and during fixed time (fixed in the range with size) measurement. In this paper, we have selected healthy rat bile without giving any stress, such as irradiation of X-rays, to find out any change in the concentration of element with time. However, no change has been noticed in the bile.

*Measurement method recording variation of element concentration with time change*

It is expected that the element contained in a liquid changes with time, and it has been proposed, as an example, in this case to obtain the measurement results of the process precisely in the form in which it is carried out at a time rate and also to notice any changes during the procedure. A capsule containing CuSO<sub>4</sub> has been applied to this measurement.

Water drop has been dropped for the measurement of fixed time (at this time, the quantity to drop can also be set up arbitrarily), and measurement will be resumed if the water drop of same standard size is made. It is the Flow (Time) mode (see Fig.4), where it can be repeatedly measured and saves all the measurement data in a separate file.

Ten water drops have been dropped for the measurement within 15 minutes. During this period, it has been saved in another file which records the measurement result and time interval with a new file name for every stop. After a period of 20 minutes, the concentration of Cu was observed which indicates that concentration of Cu from the capsule started to melt slowly and after 120

minute, it has been recorded that CuSO<sub>4</sub> has been completely melted and released from the capsule. This measurement is completely automated. Figure 6 shows temporal response of element concentration.

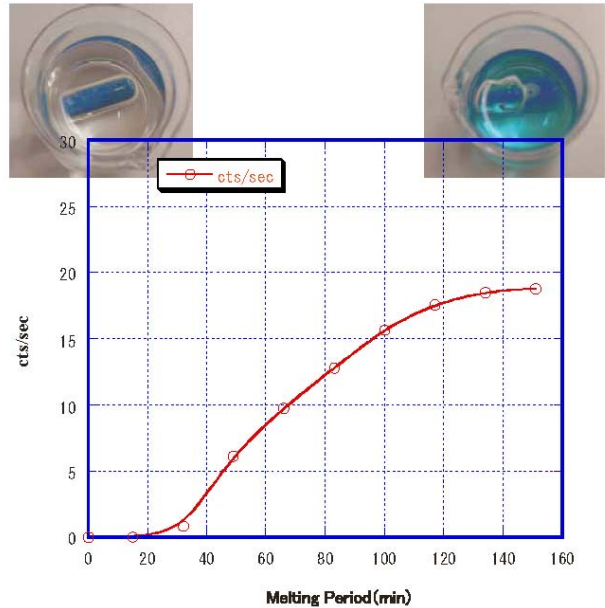


Figure 6: Temporal response of element concentration: pump control mode flow (time).

**SUMMARY**

The results obtained during development of a droplet PIXE system are as follows.

- (i) Detection limit obtained using this method is about 1 ppm (Fe) and successfully has been compared with a conventional PIXE system. This is a significant achievement from the view point of detection limit.
- (ii) To monitor beam current, ion chamber is suitable for droplet PIXE analysis equipment.
- (iii) In addition to the above point when we consider analyzing liquid samples, the practicality of droplet PIXE analysis equipment has been superior to various other developed methods.

This study demonstrates that the droplet PIXE analyzing method is a new technique for liquid analysis. Droplet PIXE system shows the advantages over other equipments where burden on a researcher for chemical pretreatment of a sample can be reduced. Application of droplet PIXE system can be expanded in future and it's suitability to other possibilities.

**REFERENCES**

[1] 1. H. Imaseki, and M. Yukawa, "Introduction of PIXE analysis system in NIRS," International Journal of PIXE, 10, Nos. 3 & 4 77-90 (2000)