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Development of an Ion Microprobe Setup for Complex Elemental Analysis of Individual Microparticles and Microstructures

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Abstract. Due to the growing need for extending the application capabilities of the Debrecen ion microprobe toward the quantitative determination of light elements, improvements of the Oxford-type scanning nuclear microprobe facility is in progress.

In this work we present the recently upgraded measurement setup and data evaluation system which is able to determine the quantitative elemental composition and distribution of individual microparticles and microstructures even for light elements by using complementary techniques. The available analytical techniques are STIM to determine the area density of the sample, ERDA to detect the H content, PIXE-PIXE to detect characteristic X-rays originating from elements with $Z \geq 6$, RBS to determine the sample thickness and matrix composition in order to crosscheck the validation of the data and the beam dose measurement, and DIGE for determining the light element ($3 \leq Z \leq 9$) content.

Although the driving force of the improvement was to establish a setup which is suitable for complex analysis of individual atmospheric aerosol particles, a complex study of inhomogeneous thin samples will also be achievable, opening up a wide range of applications in the field of materials science, biology, medicine, environmental science, geology and archaeometry.

Keywords: ion microscopy, complementary ion beam analytical techniques, light element detection

INTRODUCTION

Besides the bulk analysis of the airborne particulate matter, individual particle investigations performed on electron or nuclear microprobes provide useful additional information about the size, morphology and chemical composition of atmospheric aerosol particles [1-2]. Single particle analysis is routinely done on the Debrecen ion microprobe facility [3] by determining the particle size and its elemental composition for elements heavier than Na [4]. However, due to the new directions in atmospheric aerosol research it is no longer sufficient to determine the inorganic elemental composition of individual aerosol particles, but information about the light elemental (H, C, N, O) content together with the structure (morphology) of the particles is required.

In this work we present a measurement setup and data evaluating system installed at the Debrecen ion microprobe facility, which is based on complementary ion beam analytical techniques. The available methods are STIM (Scanning Transmission Ion Microscopy), PIXE (Particle Induced X-ray Emission), RBS (Rutherford Backscattering Spectrometry), ERDA (Elastic Recoil Detection Analysis), and PIGE/DIGE (Proton/Deuteron Induced Gamma Emission). STIM provides information on the density and structure of the sample, PIXE measures the concentration of elements with $Z \geq 6$, RBS serves to characterize the sample thickness and structure, the light element matrix and sometimes the beam dose. ERDA provides data about the H content, and the gamma emission techniques give accurate information about the Li, Be, B, N, O and F constituents with low detection limit.

With the combination of the above methods quantitative characterization of inhomogeneous samples containing both organic and inorganic component will be available.

DESCRIPTION OF THE SETUP

Within the frame of national and international projects the development of the Debrecen ion microprobe analysis facility is proceeding to fulfill the requirements of the new directions of research fields: to optimize the measurement and data evaluation conditions and to provide an opportunity for further extension of the application areas.

As a first step, a PIXE measurement setup and data evaluating system were developed to provide quantitative elemental concentrations and true elemental maps from B to U with a 1.5 - 2 μm lateral resolution, using the unique capability of the PIXE-PIXE technique [5,6].

As a second step, the sample chamber was improved by installing a 5-axis motorized HTP goniometer.

Parallel to the Oxford-type data acquisition system a new Canberra-type system is installed allowing a high spectral quality data collection as we showed in our previous paper [7]. As a new development, the conventional, home made analog amplifiers and analog signal processor units were replaced with modern digital X-ray signal processors (Titan DXP by Gresham Scientific Instruments Ltd), allowing high count rates without spectrum distortion and with controlled dead-time. With the appropriate combination of the electronic units the signals of various particle and X-ray detectors can be processed simultaneously. Signals from all detectors are recorded event by event in list mode files by the Oxford-type OM_DAQ system [8]

For RBS, ERDA and STIM measurements different detector geometries were tested, and the final arrangement was optimized to our requirements.

A new computer code (PIXEKLM-TPI) [9] based on the upgraded PIXEKLM program package [10] has been developed to generate offline quantitative true elemental maps that are free of image artifacts originating from the continuous background, overlapping X-ray lines, pile-up effects and detector response, and to calculate absolute concentration values considering the varying thickness of the sample.

In the following paragraphs detailed description of the measurement setups is presented.

X-Ray Detection: PIXE-PIXE technique

The PIXE-PIXE technique is based on the simultaneous use of an ultra thin windowed (UTW) and a conventional Be windowed Si(Li) X-ray detector. The UTW detector measures the X-ray lines with low and medium energy (0.2 - 9 keV), while the Be windowed detector detects the medium and high energy X-rays (> 4 keV).

A Gresham-type ultra thin windowed Si(Li) X-ray detector and a Gresham-type Be windowed detector with 30 mm^2 active area each are placed to the incident beam at 135º in IBM geometry. The beam dose is measured by a compact beam chopper [11].

For PIXE measurements usually a proton beam with 2 MeV energy and of 50-300 pA focused down to 2 x 2 μm^2 is used.

This way elements with atomic number higher than 5 can be detected simultaneously by at least one of the two detectors, reducing both radiation damage of the sample and measurement time. In case of thin, inhomogeneous samples with organic matrix (like in most biological and medical samples) the application of the UTW PIXE detector replaces the RBS technique in the determination of the matrix composition, which can be very useful when we wish to avoid of the sample damage by using only very low (<20 pA) beam currents or when the hydrogen content is not known. The PIXE-PIXE technique reduces the measurement time and increases the reliability of the data evaluation. As an example of light element PIXE detection, the characteristic X-ray spectrum of a kapton foil and O, N and Mg maps of single aerosol particles are presented in Figure 1.

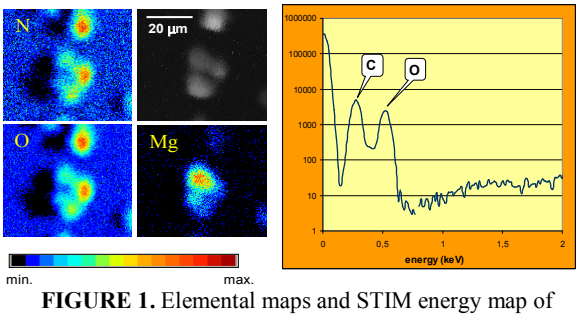

FIGURE 1. Elemental maps and STIM energy map of aerosol particles (left) & PIXE spectrum of a kapton-foil collected by the UTW detector (right). Note light element, C, N and O detection.

Particle Detection

For RBS, STIM or ERDA measurements the good particle energy resolution is vital, therefore 50 mm^2 Ortec-type "ULTRA" ion-implanted Si particle detectors with 11 keV nominal energy resolution are used.

These detectors have good energy resolution but they are rather expensive considering that they are sensitive to radiation damage, which is especially important when detecting the direct beam at scanning transmission ion microscopy. Applying much cheaper Si pin photodiodes can be a solution for these cases. A project is running whose aim is to investigate the capabilities and limitations of Si pin diodes as radiation detectors by high resolution ion beam methods [12].

STIM measurements

Usually the morphology and area density of thin, inhomogeneous samples are determined by STIM. STIM gives the best resolution when applied in on-axis geometry [13]. The disadvantage of the on-axis STIM, that it can be used only at very low currents (few hundred – few thousands protons/s) in order to avoid detector damage. To follow the damage on the sample caused by irradiation during PIXE measurements, off-axis STIM can be an ideal solution. To be able to use both on-axis and off-axis STIM, a rotatable detector holder were developed after the fashion of the Oxford-type. An Ortec ULTRA particle detector, a Hamamatsu Si pin photodiode and a Faraday-cup are mounted on a round plate, which can be placed at 0 degree to the beam direction 6 cm from the sample. Thus, the particle detector can be easily rotated to on-axis geometry when needed, and during PIXE irradiation it can be used in off-axis mode, while the Faraday-cup measures the beam dose. We use the pin diode to optimize the beam dose before applying the Ortec detector.

RBS and ERDA measurements

In environmental and biological research sometimes it is crucial to know the H and other light element content of the samples. Such case is the field of atmospheric aerosol research, when H, C, N, O are the major constituents of the particles influencing the human health or the global climate. RBS technique is used to detect C, N and O, and for H determination we have introduced the ERDA analytical technique.

Although micro-RBS has a 10 years old tradition at the Debrecen ion microprobe [14], ERDA measurements have been reported for the first time in this paper.

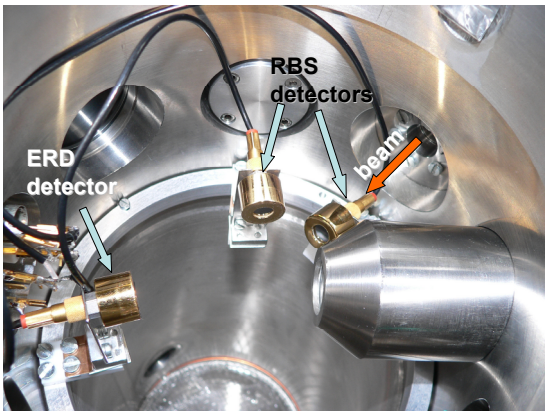

FIGURE 2. Particle detector arrangement for simultaneous RBS (135º IBM- and 165º Cornell-geometry) and ERDA (30º IBM-geometry) measurement.

For simultaneous RBS and ERDA measurements the detector arrangement shown in Figure 2 were installed. For the irradiation a He^+ beam of 2MeV energy was used with a current of 1nA. The sample was rotated with 70º while the ERDA detector was placed at 30º at IBM geometry. As a first step, spectra of different standard materials were recorded. As an example, RBS (135º) and ERDA spectra of a 36 μm thick Mylar foil are shown in Figure 3.

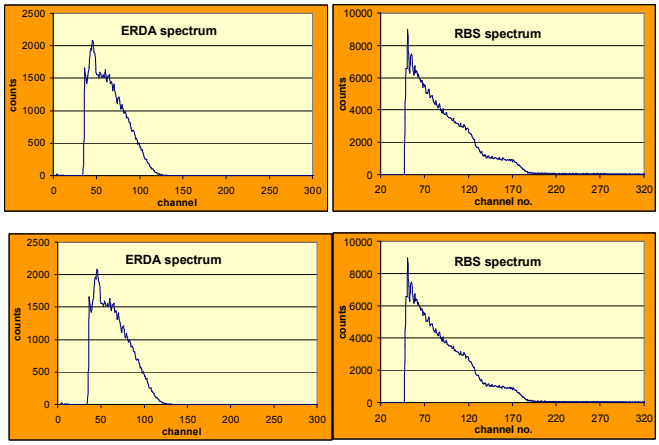

FIGURE 3. ERDA and RBS spectra of a 36 μm thick Mylar foil

The ERDA measurements were recorded in listmode and the off-line data evaluation shows the change of the H content of the foil during irradiation.

The complex analytical system was designed and built in such way that it gives opportunity to use the Be-windowed X-ray detector simultaneously with the ERDA and RBS measurement, so several characteristics of a sample can be detected at the same time. Although, in case of thin samples ERDA in transmission mode would be the best solution for simultaneous H, light element and trace element measurement, when at perpendicular incidence of the beam ERDA, STIM, PIXE and RBS analysis could be carried out simultaneously.

Gamma-Ray Detection: μ-DIGE

In those cases when the knowledge of light element (Li, B, C, N, O, F) distribution is needed with high precision and low detection limits, the DIGE technique can be applied.

Set-up for micro-DIGE Measurements

We have developed a relatively simple and inexpensive way of converting the sample chamber of a conventional Oxford-type microprobe into an easily useable μ-DIGE setup. The basic idea is to increase the image distance of the microprobe by moving the

focus out of the chamber into an extension tube. An outline of the modified chamber is shown in Figure 4. This new position of the sample enables the use of different type of gamma detectors in enlarged solid angle increasing the sensitivity of the technique.

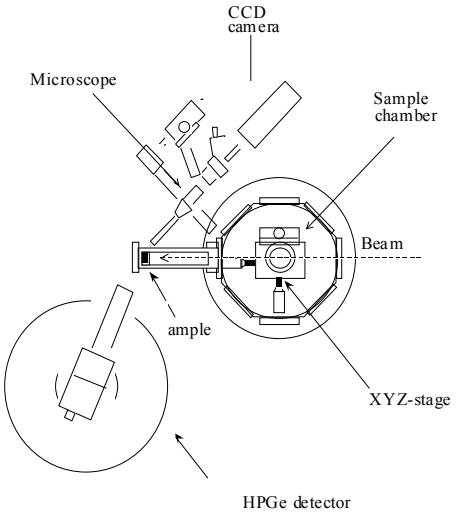

FIGURE 4. The micro-DIGE setup

More detailed description of the setup can be found in [14].

Absolutization of the DIGE technique

In order to eliminate the application of standards from routine analytical work, we measured thin target gamma ray yields of the $^{6}Li(d,p\gamma)^{7}Li$, $^{9}Be(d,n\gamma)^{10}B$, $^{11}B(d,p\gamma)^{12}B$, $^{16}O(d,p\gamma)^{17}O$ and $^{19}F(d,p\gamma)^{20}F$ nuclear reactions in the 0.6-2 MeV energy range with fine energy resolution. The yield data were converted into cross sections. The obtained systematic and uniform cross section curves and data set are useful for the analysis of thin targets and will serve as input parameters for the concentration calculus of thick and intermediate thick samples. For further details see [15].

SUMMARY

In this work we presented recent developments carried out on the Debrecen scanning ion microprobe facility toward an effective, complex analytical technique with high spatial resolution which covers the whole elemental range from H to U.

The simultaneous use of several particle and X-ray detectors, thus several analytical techniques, enables us to carry out complex studies.

Although the primary aim of the improvement was to establish a setup which is suitable for the complex analysis of atmospheric aerosol particles, the improved facility has numerous potential applications in the fields of materials sciences, biology, medicine, environmental science, archaeometry and geology.

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