

OPTICS AND SPECTROSCOPY

SYNCHROTRON RADIATION INDUCED X-RAY FLUORESCENCE FOR IDENTIFICATION OF LIGHT ELEMENTS IN PLANTS

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UDC 543.427.4

The paper considers analytical capabilities of synchrotron radiation X-ray fluorescence spectrometry of the elemental composition of plants with a view to detect light elements. The paper describes the experimental setup, experimental conditions, and the limit of detection for Si, S, Cl elements.

Keywords: X-ray fluorescence, synchrotron radiation, microelements.

INTRODUCTION

Synchrotron radiation X-ray fluorescence (SXRF) spectrometry is an elemental analysis technique which allows for the examination of different materials. For many years, this technique has been used in the Siberian Synchrotron and Terahertz Radiation Centre of the Budker Institute of Nuclear Physics (Novosibirsk, Russia). Although the SXRF spectrometry is universal, it cannot detect all elements at general settings. It is therefore important to optimize the equipment in the synchrotron radiation spectrum and detection conditions. Routine measurement methodologies of the chemical element concentration (from potassium to uranium) are tested on the local X-ray fluorescence beamline installed downstream the synchrotron radiation from the VEPP-3 storage ring [1]. It emits an X-ray energy spectrum between 12 and 25 keV. Hard radiation X-ray diffraction beamline installed on the VEPP-4 Ion Collider Facility [2], emits photons with an energy higher than 100 keV to use them for the excitation of fluorescence from rare-earth and heavy elements. Tentative measurements of light elements Al, Si, P, S, Cl (relevant for studying such plants as grass, roots, leaves, shoots, fruits) on these beamlines are not successful. The silicon (Si) distribution in plant parts is very interesting for studying the influence of Si-containing fertilizers and regulators on the plant growth and development [3]. At the excitation energy of 12 keV typical for the VEPP-3 storage ring, it is impossible to ensure a reliable estimate of the Si content in plant parts. This results from the fact that under routine experimental conditions at this beamline, the low-energy fluorescence radiation from light elements (e.g., 1.74 keV Si $K\alpha$ X-ray) is significantly absorbed by the ambient air and the background radiation suppresses a valid signal. In this work, we call elements light and heavy, that are lighter ($Z < 19$) and heavier ($Z \geq 19$) than potassium, respectively.

The aim of this work is to consider the possibility of expanding the opportunities of using the SXRF spectrometry for detection of light elements in plants.

MATERIALS AND METHODS

Experiments were conducted on the beamline installed downstream the synchrotron radiation (SR) from the VEPP-4M electron-positron collider [1]. It is intended for training students in the field of various SXRF techniques,

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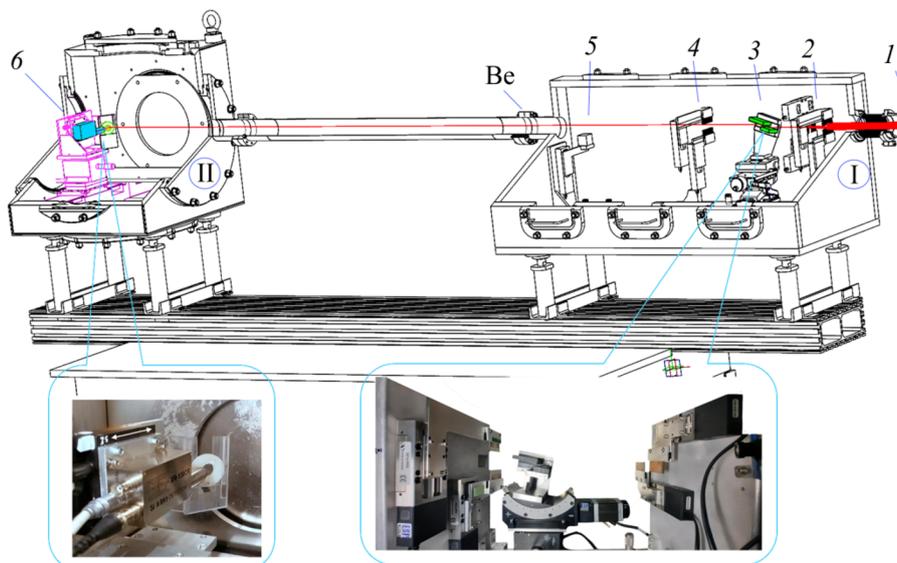


Fig. 1. Schematic illustration and photographs of the beamline main elements: 1 – SR beam, 2 – slit for X-ray input, 3 – crystal monochromator, 4 – slit for X-ray output, 5 – monitor photodiode, 6 – detector block.

equipment testing, and experiments. Figure 1 presents a schematic illustration and photographs of the beamline main elements. Motorized slits for X-ray input 2 and output 4, are situated in the chamber I. The material of the slit frame is 3 mm elkonite. A silicon (111) crystal monochromator is mounted to motorized slips, which provide a vertical displacement and tilt of crystal 3. A monitor photodiode 5 controls the position of the beamline elements relative to the synchrotron radiation beam. Chamber II incorporates the detector block 6 consisting of the sample holder and an X-ray detector XR100CR (Amptek Inc., USA). The holder and the XR100CR detector are mounted to a frame with the gap control between the sample and detector in the range of 19 to 35 mm.

Chambers I and II are separated from each other by a beryllium foil 200 μm thick and equipped with the pumping system providing pressure up to 10 Pa. To prevent the high vacuum in the storage from the internal air, beryllium windows with the total thickness of 800 μm are installed at the X-ray output.

The software was developed for motorized element control [5]. The XR100CR detector control was conducted by the ADMCA program included in the detector delivery set.

A standard herbage mixture Tr-1 (Russia) was used in this experiment to study the beamline capacity to detect light elements in plants [6]. Tr-1 samples as well as other samples, were compressed pills with a diameter 20 mm made of the plant product preliminary dried and pounded with a pestle.

A deflecting magnet in the VEPP-4M electron–positron collider serves as a synchrotron radiation source. The electron energy varies between 1.9 and 4.75 GeV, depending on the purpose. The most commonly used energy is 1.9, 3.5 or 4.5 GeV. It is found that at 1.9 GeV, beryllium foils absorb 99% of photon flux. Figure 2 presents synchrotron radiation spectra with respect to beryllium foils obtained at the energy of 3.5 and 4.5 GeV.

The sample is irradiated with monochromatic radiation at the energy higher than absorption edges of the element to be detected. At the same time, a simultaneous excitation is observed for all elements with absorption edges less than the excitation radiation. This determines a panoramic character of the technique, i.e., a detection of many elements at a time. The continuous SR spectrum makes it possible to choose the excitation energy closer to that of the absorption edge of the desired element, thereby minimizing the excitation of heavier elements and the scattered radiation background. Chemical elements, which are heavier than potassium, can be reliably detected in routine operation conditions using the SXRF beamline installed on the VEPP-3 storage ring [1, 7]. In this case, we observe the excitation of fluorescence from light elements Al, S, P, Cl. However, low-energy fluorescence photons emitted from

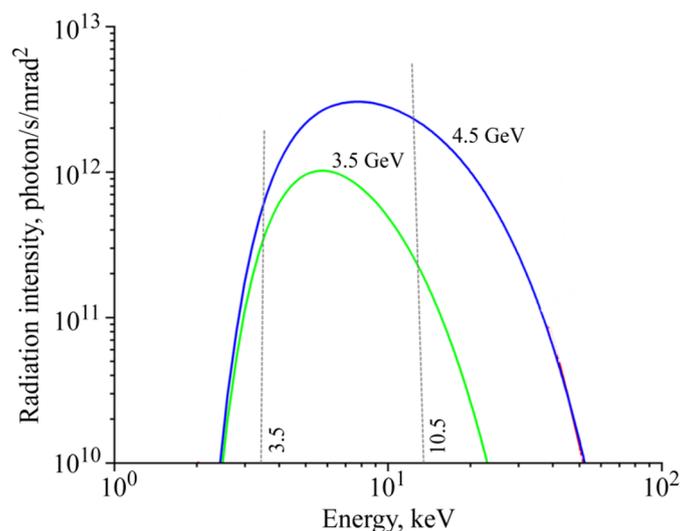


Fig. 2. SR spectra obtained on the VEPP-4M electron–positron collider at 3.5 and 4.5 GeV electron energy.

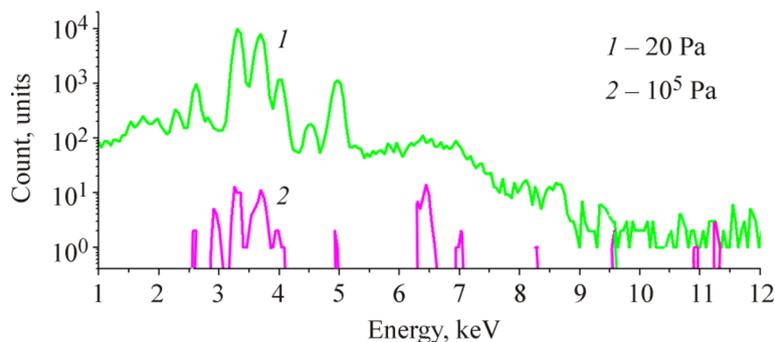


Fig. 3. XRF spectra of the standard herbage mixture at 5 keV excitation energy in vacuum and normal conditions.

these elements are largely absorbed by the ambient air in the gap between the sample and detector. The high-intensity excitation radiation generates a high scattered radiation background in the desired energy range. It should be noted that in the energy range from 1 to 4 keV, the fluorescence lines of neighboring elements approach to each other (the difference between peaks is 100 or 200 eV). Si-escape peaks overlap with peaks of elements. As a result, it is difficult to determine light elements by the SXRF technique at the excitation by high-energy photons (with energy higher than 5 keV) under atmospheric pressure.

RESULTS AND DISCUSSION

Reference samples were fabricated for testing and calibration of the energy scale of the XRD detector. A 0.1 μm thick Ti layer was sputtered onto a 370 μm thick Si plate, which was then covered with a 0.1 μm thick Al layer. The energy scale was calibrated by the fluorescent intensity of Si, Ti, and Al elements relative to the reference sample.

In order to illustrate the influence of the gas environment, Fig. 3 presents XRF spectra for the standard sample Tr-1 obtained under the atmospheric pressure and 20 Pa vacuum pressure at 5 keV excitation energy. Fluorescence

TABLE 1. Limit of Detection of Light Elements in Tr-1 Sample

| Elements | CO | Peak | Signal | LOD, $\mu\text{g/g}$ |
|----------|------|-------|--------|----------------------|
| Si | 5500 | 5690 | 2855 | 154.9 |
| S | 1800 | 9820 | 3292 | 31.6 |
| Cl | 3600 | 41859 | 3298 | 14.8 |

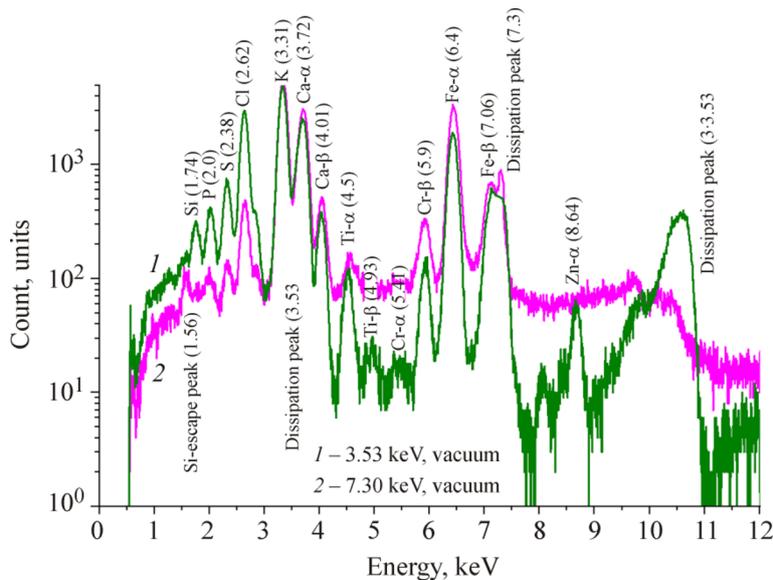


Fig. 4. SXRF spectra vs. excitation energy.

photons are significantly absorbed by the ambient air. All further experiments are conducted under the vacuum pressure of 20 Pa.

The matrix of plant samples is high in potassium (K-edge = 3.607 keV). It is therefore suggested to choose the excitation energy below the potassium K-edge to detect light elements, primarily Si. Thus, the VEPP-4M detector operates at the electron energy of 3.5 GeV, when the maximum SR intensity matches 5.7 keV, whereas at 4.5 GeV, the maximum intensity is observed at 8 keV. The excitation energy of 3.53 keV is selected below the indicated potassium K-edge and recorded by the emission monochromator. Since the silicon (111) crystal monochromator passes the third harmonic (10.63 keV at 3.53 keV), it is not possible to completely exclude the excitation of elements heavier than potassium, but the scattered radiation background is lower than at the excitation at high energy (e.g., 7.3 keV).

Figure 4 shows SXRF spectra at the excitation energy of 3.53 and 7.3 keV. In the first case, the photo peaks of heavy elements are lower, while photo peaks of light elements are more pronounced. Therefore, for the VEPP-4M it is preferable to operate in vacuum at the excitation energy less than 3.6 keV in order to analyze elements lighter than potassium.

The limit of detection (LOD) can be calculated from $LOD = 3CO \cdot \frac{\sqrt{peak}}{signal}$ ($\mu\text{g/g}$) [2], where CO is the element

concentration ($\mu\text{g/g}$) in the standard sample, *peak* is the photo peak integral, *signal* is the background signal under the photo peak. The phosphorus (P) purity is 99.5 %.

The XRF analysis performed in the AXIL (QAXS) program, determines the limit of detection for Si, S, and Cl concentration in plant samples. These data are presented in Table 1. It should be noted that the Al photo peak coincides with the Si-K α escape peak, and the P photo peak coincides with the Ca- α escape peak, which makes the detection of Al and P unreliable.

CONCLUSIONS

In this work, the experiments were conducted at the synchrotron radiation X-ray fluorescence beamline installed on the VEPP-4M storage ring equipped with the beam-forming and SXRF recording system in vacuum conditions. That allowed us to collect information about the content of light elements (Si, S, Cl) in addition to a panoramic character of SXRF imaging, which was implemented earlier in the Siberian Synchrotron and Terahertz Radiation Centre of the Budker Institute of Nuclear Physics (Novosibirsk, Russia).

COMPLIANCE WITH ETHICAL STANDARDS

Conflicts of interest

The authors declare no conflict of interest.

Funding

Research and the upgrade of the vacuum system of the SXRF beamline and automatic control for the experiment were financially supported by the government contract No. 075-15-2021-1348 (research lines 2.3.14 and 3.3.13) of the Ministry of Science and Higher Education of the Russian Federation.

Financial interests

The authors declare they have no financial interests.

Non-financial interests

None.

Acknowledgement

The authors like to express their gratitude towards the management of the Siberian Synchrotron and Terahertz Radiation Centre for equipment employed in these studies.

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