Developments of muonic X-ray measurement system for historical-cultural heritage samples in Japan Proton Accelerator Research Complex (J-PARC)

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Abstract. Negative muon elemental analysis, which can measure depth-wise elemental composition from 100 nm to several centimeters with a depth resolution of order μm, is a revolutionary technology that enables the nondestructive analysis of materials. In recent years, this technique has begun to apply to understand historical cultural heritage. We have studied the Japanese archaeological heritage to provide new insights into Japanese archaeological research. Here, we report the progress on development of intense (high speed) negative muon X-ray measurement system at KEK Muon Science Laboratory (MSL) in the Japan Proton Accelerator Research Complex (J-PARC). For this purpose, the efficiency of detectors (wide energy range and high resolution) were improved by preparing a high-purity multi-arrayed germanium semiconductor detectors (HP Ge) to detect one photon or less per muon pulse available in J-PARC. In addition, by increasing the number of detectors and suppressing the noise sources, we have succeeded to enhance the detection efficiency by about 10 times compared to conventional systems.

1. Introduction

In the field of archaeology, quantitative evaluation of materials and elemental compositions of historical cultural heritage materials are used to reveal the place of production and the manufacturing process, and consider the historical background of the time. The most common non-destructive method for elemental composition is to analyze the spectra of element-specific fluorescent X-rays generated during the excitation and de-excitation of elemental atoms that compose the material by electrons or X-rays. The main examples where this method is difficult to apply are 1) bronze objects and 2) gold and silver coins. In the case of 1), the surface has been oxidized and its composition is different from that of the original object. To measure the fluorescent X-rays (copper 7.4keV, Tin 26.4keV lead 74.9keV for kα X-ray) by bombarding the rust-free deep layer with electrons, it is necessary for the X-rays generated from the depth of the bombardment to escape, but due to self-absorption during the escape, the X-rays do not penetrate to the surface at depths of 100 μm or more. In the case of 2), considering the robustness and economy as a coin, it was necessary to make it a gold-silver alloy by adding silver to gold. However, it was difficult to produce a gold color like that of gold coins. Therefore, a technique was developed to increase the gold content in the surface layer by applying a surface treatment to remove silver from the gold-silver alloy. To understand the historical background of this technique, it is necessary to analyze the gold/silver concentration ratio with a resolution on the order of micrometers from a depth shallower than 1 to 100 μm. In this case, the depth resolution is very poor because the area where X-ray fluorescence is generated is extended in the depth direction by electron bombardment. On the other hand, negative muon is very effective to study the elemental composition of cultural heritage materials that cannot be analyzed by electron excitation X-ray fluorescence.

When a muon enters into an object, it loses energy due to multiple Coulomb scattering and is stopped. Since negative muons have 1/9th the mass of protons, the stopping process is similar to that of protons, and the depth profile of stopped muons is localized in thin regions within the object. In the muon stopping region, muons are captured by the atoms in the material, forming muonic atoms. Muonic atoms emit atomic-specific X-rays (called to muonic X-rays) from the upper high energy levels, which cascade down to the lower energy levels. The muonic X-ray energy is very high compared to the fluorescent X-ray energy from electronic atoms due to the 200-fold difference in mass between the muon and electron. Therefore, even if muonic X-rays are launched into a bronze at a depth of 100 μm or more, they will penetrate to the surface. Kubo et al.[1] and Ninomiya et al.[2] have already used negative muons for bronze products and gold coins, respectively.

The energy range of muonic X-rays emitted by the cascade of muon de-excitation from the upper atomic orbitals to the lower atomic orbitals lies in the range between a few keV to MeV. Although the energies are discrete and vary from element to element, the energy spectra of different transitions of the elements in the same group of periodic table lies closer or even overlap to each other. The X-ray energies of the same transition of the elements of interest are often only a few keV to several 10 keV apart when Z-1 and its neighbor Z+1 elements are mixed together (exception for heavy elements with energies of MeV for the (2-1) transition). Therefore, in order to separate and analyze transition spectra from various elements, an X-ray detector with a wide energy range and high energy resolution is necessary. Currently, Ge semiconductor detectors are relatively inexpensive detectors that satisfy this requirement, but in order to analyze transitions emitted at energies below 100 keV, a detector with a resolution of the order of 1 keV or lower is needed.

2. Ge detectors choice required in J-PARC

The proton beam at J-PARC has a double pulse time structure with 25 Hz, 3 GeV, 100 nsec pulse time waveform and 600 nsec separation. This beam produces negative pions, which decay into muons and are transmitted through the beamline to the experimental area. Thus, a pulsed negative muon beam injected to the sample reflects the time structure of the proton beam. In this case, the time resolution of the Ge detector becomes an issue. The time required to collect the charge generated in the Ge crystal by X-rays and to form a signal to convert the charge into voltage and its amplification takes at least several microseconds. Therefore, one element can measure only one X-ray photon per pulse (single photon measurement). It is necessary to prevent two or more photons from entering the Ge element during the signal formation time (within a few microseconds). Also, except for capture X-rays, high-energy electrons emitted when muons decay in matter with a lifetime of less than 2 μs and their scattering, X-rays due to bremsstrahlung, and electronically excited X-rays derived from them cause the fatal noise. From this point of view, we have reduced the size of Ge crystals so that X-rays other than negative muonic X-rays are not included in the noise. The Low Energy Ge detector (LEGe, GL0110, Canberra) with Ge crystals of about 10 mm in diameter and 10 mm in thickness with a 1-inch diameter end-cap can be used efficiently for varieties of samples. The smaller crystal size helps to reduce the noise and increase the detection efficiency. On the other hand, the disadvantage is that the smaller the crystal size, the thinner the crystal, and therefore the detection efficiency at high energy range becomes poor. (A detector with a thickness of 15 mm and a diameter of 25 mm (GL0515) is also used because a detector with sensitivity up to as high energy as possible is desired, but its efficiency is lower than that of GL0110. Especially at energies less than 50 keV, the efficiency is about half of that of GL0110.)

3. Developments of the measurement system

Since the maximum efficiency of the Ge detector measurements at the J-PARC pulsed muon source is 25 photons/sec per detector, the number of detectors must be increased to improve the detection efficiency. We have conducted our experiments from 2014 to November 2020 using the AL chamber shown in Fig. 1 [3]. The large beam port of the chamber made it possible to accept the beam, but only two LEGe can be installed upstream of the beam to be able to measure X-rays from the sample surface. The number of detectors cannot be increased beyond due to placement issues. Therefore, we developed a new chamber that can accommodate a large number of LEGe. The main purposes of the design conditions are ① To measure the X-rays from the surface of the sample, a large number of Ge should be installed upstream of the beam as much as possible. ② Precise movement of the detector stage from 5 cm to 15 cm from the center of the chamber is possible. ③ Large multi-element detector with large diameter end-cap different from LEGe can be installed from left to right horizontally. ④ Usable in both vacuum and atmospheric air. ⑤ Possible to install and remove the entire system with the LEGe detector installed.

In condition ①, it is important to consider interference from liquid nitrogen tanks, preamplifiers, etc. carefully to promote the use of a large number of LEGe detectors. In this setup, seven LEGe detectors have permanently installed. Two additional LEGe detectors in horizontal ports, total nine LEGe detectors, can be installed. Negative muon elemental analysis is mainly performed at D2-area, D-line, MSL, where the chamber and instrument system must be replaced in every machine time, depending on the conditions of the measured data. Conditions ④ and ⑤ must be carefully considered in order to reduce the time required for these changes. In the previous setup, separate chambers and racks were used for vacuum and atmospheric air, which made the replacement complicated and time-consuming. In order to avoid these complexities, the experiment can be performed with the same system. Considering the above conditions, a hemispherical chamber system as shown in Fig. 2 was installed and used for negative muon experiments from January 2021 with two GL0110 Ge detectors and two GL0515 Ge detectors.

The change to a hemispherical chamber system was particularly effective in an experiment requiring negative muon irradiation at low momentum, the measurement of the depth profile of gold and silver concentration in gold coins excavated from a 16th century castle site. The Al chamber previously used had poor detection efficiency and could not perform measurements at even lower momenta where the muon intensity was lower than 6 MeV/c (muon stop depth: 1 μm). Experiments using hemispherical chambers showed that abundance of Au concentration in layers shallower than 1 μm is taking place. The results are shown in Fig. 3. It has been known from X-ray fluorescence analysis that the average gold concentration of gold coins used in the 16th century was high, and there was a question whether it was not necessary to increase the gold concentration on the surface since the amount of gold calculated for Japan at that time was considered to be abundant. The irradiation at 6 MeV/c took about 41 hours in the aluminum chamber, whereas it took 21 hours in the hemisphere chamber, about half of the time required for irradiation. Despite this, the measurement error of the muon X-ray ratio between Ag(7-6)

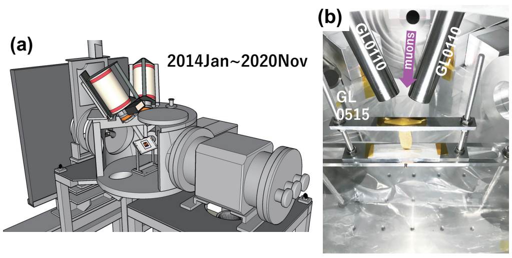

Figure 1. (a) Schematic drawings of the aluminum vacuum chamber, used for negative muon elemental analysis (vacuum mode) until November 2020.(b) Photograph of an experiment using gold coins excavated from a 16th century castle site in the aluminum chamber.

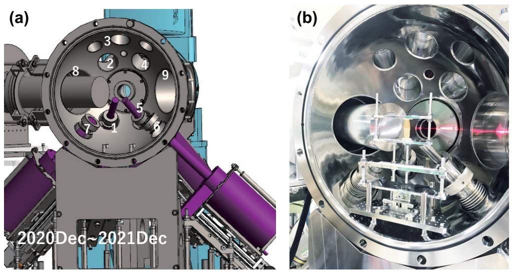

Figure 2. (a) Schematic diagram of the hemispherical chamber and Ge detectors (four LEGe units (purple)). The numbers in the chamber are port numbers (b). The picture of the experiment of gold coins excavated from a 16th century castle site using the hemispherical chamber.

and Au(10-9), Au41.3keV/45.9keV, has also improved by about 3 times. Regarding the ratio of Au(7-6) 129.95 keV to Ag(5-4) 140.23 keV, Ag(5-4) also has a peak split at 141.3 keV, which overlaps with Au(9-7) 141.88 keV. It is necessary to remove this Au(9-7) peak based on the other Au peaks. The error due to that removal operation is propagated.

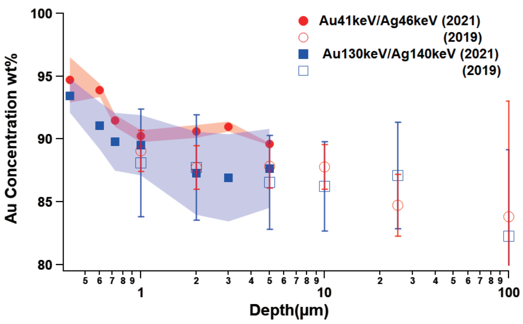

Figure 3. Depth profiles of gold coins excavated from a 16th century castle site. Solid points were measured in a hemispherical chamber and opened points were measured in an aluminum chamber. Circles points are obtained from the peak ratio of muon X-ray Ag(7-6) 45.9 keV to Au(10-9) 41.3 keV. Square points are obtained from the peak ratio between Ag(5-4) 140.23keV and Au(7-6) 129.95keV. While the aluminum chamber could only analyze down to 1 μm, the hemispherical chamber revealed Au enrichment down to a depth of 0.4 μm.

In January 2022, the beam duct was modified to a larger diameter (φ110 mm made of aluminum) as shown in Figure 4, and the remaining three LEGe units were added to the top of the duct for operation. After obtaining the beam profile and emittance in the beam direction, the effect of beam collisions on the inner wall of the duct was evaluated before and after the modification using the Monte Carlo simulation PHITS, as shown in Figure 5. Before duct modification, 40 % of the muons collided on the inner wall of the duct. After the modification, it was evaluated that 3 % of the muons collided on the inner wall of the duct and were suppressed. The only experiment that could be performed with the same sample before and after the hemispherical chamber modification to January 2022 is the gold-silver standard sample (50wt% gold), whose peak ratio Au(10-9)41.3keV/Ag(7-6)45.9keV is shown in Fig. 6. The comparison shows that doubling the number of Ge detectors improved the error bar by a factor of 3, as Fig. 6 shows. The better-than-expected error suppression is obtained likely due to the modification of the duct.

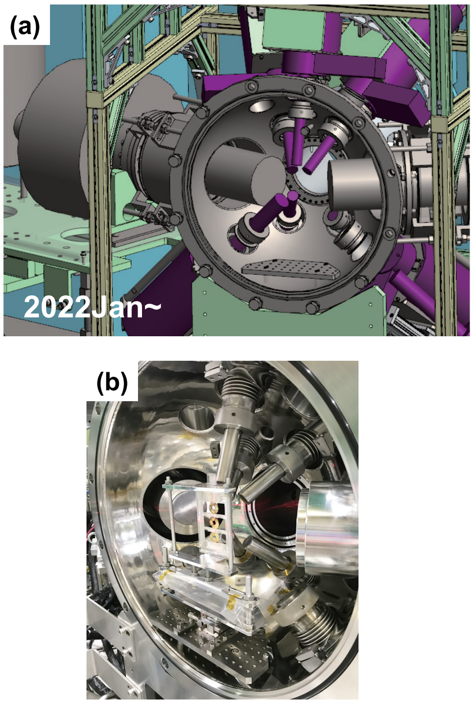

Figure 4. (a) Schematic diagram of the hemispherical chamber after modification in January 2022. (b) Analysis of archaeological samples (Ryukyu gold coins) after the modification. The upper ports, 2, 3, and 4 are now equipped with LEGe, enabling operation with a total of 9 units: 7 LEGe + 2 large Ge detectors.

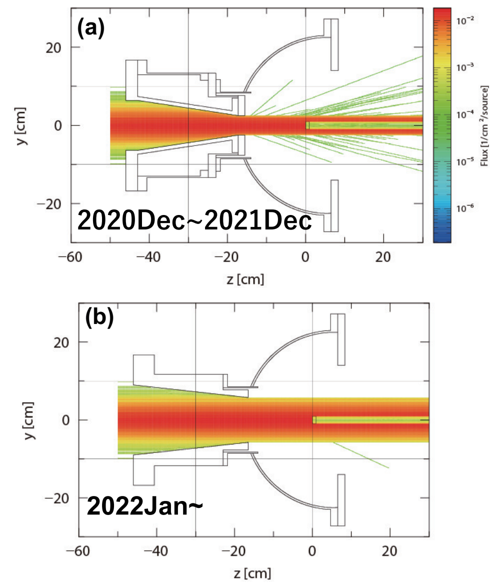

Figure 5. Calculations of the muon beam propagation in the beam duct modification before (a) and after (b) by using PHITS . (a) 40% of the muon beam collides with the inner wall of the duct. (b) Collisions are reduced to 3%. By modification of the duct, decay electrons generated before sample irradiation and their bremsstrahlung are suppressed by modification of the duct.

Although a precise comparison cannot be made as a result of the modification from the aluminum chamber used until November 2020 to the hemispherical chamber introduced by January 2022, since the experiment was not conducted using the same sample, at least the observed peak ratio, (Au(10-9)41.3keV/Ag(7-6)45.9 keV), the change from the aluminum chamber to the hemispherical chamber increased the detection efficiency by a factor of 3, and the modification of the hemispherical chamber increased it by a factor of 3, for a total increase of about 10. In the future, we will attempt to further increase the number of LEGe detectors by increasing the number of crystal elements, aiming for higher analysis efficiency. We will also try to use a large number of Ge detectors with high sensitivity to high-energy muonic X-rays, which can detect high-energy muon capture X-rays that pass from the irradiated surface of the sample to the backside of the sample.

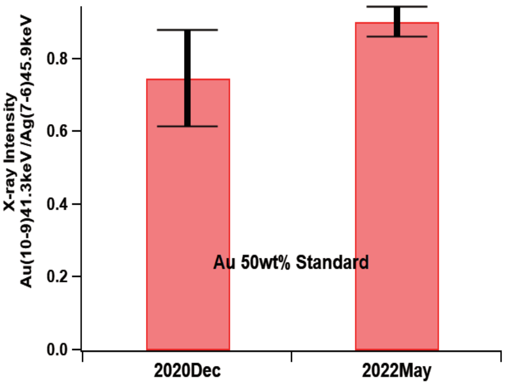

Figure 6. Results of gold-silver standard sample (50wt% gold) before (Fig.2 photo) and after (Fig.4 photo) hemisphere chamber modification. Before modification GL0110: 2 units + 0515: 1 unit. After modification 0110: 5 units + 0515: 1 unit. Measurement error improved by a factor of 3.

4. Summary

The advancement of the negative muon elemental analysis system at the J-PARC MSL facility is described. A hemispherical chamber that can accommodate a large number of LEGe semiconductor detectors to improve the resolution and efficiency of measurements from several keV to 150 keV has been developed. It will be efficient to use in the limited machine time and the characteristics of the pulsed muon source. The detection efficiency has been increased by about 10 times compared to the conventional systems. The new system will enable to respond to the demand of nondestructive analysis of a wide variety of cultural property samples in the future.

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