



## Technical Note

## X-ray fluorescence analysis with micro glass beads using milligram-scale siliceous samples for archeology and geochemistry

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## ABSTRACT

A micro glass bead technique was developed to assay precious siliceous samples for geochemical and archeological analyses. The micro-sized (approximately 3.5 mm in diameter and 0.8 mm in height) glass beads were prepared by mixing and fusing 1.1 mg of the powdered sample and 11.0 mg of the alkali lithium tetraborate flux for wavelength-dispersive X-ray fluorescence determination of major oxides (Na<sub>2</sub>O, MgO, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, P<sub>2</sub>O<sub>5</sub>, K<sub>2</sub>O, CaO, TiO<sub>2</sub>, MnO, and total Fe<sub>2</sub>O<sub>3</sub>). The preparation parameters, including temperature and agitation during the fusing process, were optimized for the use of a commercial platinum crucible rather than a custom-made crucible. The procedure allows preparation of minute sample amounts of siliceous samples using conventional fusing equipment. Synthetic calibration standards were prepared by compounding chemical reagents such as oxides, carbonates, and diphosphates. Calibration curves showed good linearity with *r* values > 0.997, and the lower limits of detection were in the 10s to 100s of μg g<sup>-1</sup> range (e.g., 140 μg g<sup>-1</sup> for Na<sub>2</sub>O, 31 μg g<sup>-1</sup> for Al<sub>2</sub>O<sub>3</sub>, and 8.9 μg g<sup>-1</sup> for MnO). Using the present method, we determined ten major oxides in igneous rocks, stream sediments, ancient potteries, and obsidian. This was applicable to siliceous samples with various compositions, because of the excellent agreement between the analytical and recommended values of six geochemical references. This minimal-scale analysis may be available for precious and limited siliceous samples (e.g., rock, sand, soil, sediment, clay, and archeological ceramics) in many fields such as archeology and geochemistry.

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## 1. Introduction

Elemental analyses for many types of siliceous samples have been performed in various fields. For example, in archeology, determining the components in ancient potteries [1] and obsidian [2] (used as a raw material of stone tools) is useful for provenance studies, which identify artifacts as local or nonlocal, whereas the elemental composition of natural rocks [3] is essential for geochemical and volcanological research. In many laboratories, the X-ray fluorescence (XRF) spectrometer has been routinely employed for the determination of major and minor elements in solid and powdered samples, since both the pretreatment and measurement are simple and convenient. In contrast, many techniques, such as conventional atomic absorption spectrometry (AAS), inductively coupled plasma-atomic emission spectrometry (ICP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS), require liquid samples and hence digestion at high pressure and high temperature with e.g. conc. HF or alkali fusion. In the former case, Si is often a major constituent of pottery, but it cannot be measured with liquefaction techniques after hydrofluoric acid (HF)

decomposition; in the latter case, the fused material needs to be dissolved again, which is a disadvantage for these methods. However, XRF analyses of archeological and geochemical samples have typically used a significantly greater amount of sample (hundreds to thousands of milligrams) than other destructive instrumental analyses, such as AAS [4,5], ICP-AES [6,7], ICP-MS [8,9], instrumental neutron activation analysis (INAA) [10,11], and particle-induced X-ray emission analysis (PIXE) [12,13]. For example, archeology and geochemistry researchers have submitted the following common specimens for XRF determination: (1) fused glass beads, mixing, fusing and vitrifying powdered sample and flux with a certain sample-to-flux ratio, using 300 mg of powdered ancient pottery [14] and 3000 mg of rock powder [15]; (2) pressed powder pellets, molding and pressing fine powdered sample, using 300 mg of powdered ancient pottery [16] and 3000 mg of powdered ceramic product [17]; and (3) loose powders, packing powdered sample into a sample cup and covering analytical surface by thin polymer film, using 3000 mg [18] and 8000 mg [19] of powdered soil. The requirement of large sample volumes is a disadvantage when analyzing precious and limited samples. Energy-dispersive XRF [20], including analysis via portable devices, has often been used for nondestructive direct measurements. Using this analytical method, however, erroneous results are often obtained due to limited analytical sampling depth related to X-ray absorption effects. These effects occur

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because natural rocks and siliceous artifacts are derived from geological materials that possess the following properties: chemical heterogeneity [21,22] resulting from inclusions of various geological components, elemental alterations by weathering effects [23,24], and structural unevenness resulting from variations in size and shape of the samples and inclusion particles [25]. Therefore, in many XRF analyses, archeological ceramic samples have commonly been prepared by homogenization, which destroys the sample. An alternative technique is total reflection XRF (TXRF) spectrometry, which has a high sensitivity and requires less sample amount than the previously mentioned techniques. The specimens for TXRF analyses have typically been prepared by dispersing a small powdered sample (e.g., 50 mg [26] of archeological ceramics and 50 mg [27] of soils) into high-purity water, and then placing the mixture on a sample holder where it is subsequently dried and analyzed. On the other hand, compared to the common specimens for XRF analyses, much less sample amount (tens to hundreds of milligrams) is typically required for analysis with other destructive instrumental analyses, such as AAS [4,5], ICP-AES [6,7], ICP-MS [8,9], INAA [10,11], and PIXE [12,13]. Some of these analytical methods are able to analyze very small samples. For instance, in graphite furnace AAS with a direct introduction technique, researchers prepared slurry specimens using small powdered samples (e.g., 5–40 mg [28] of soil and sediment samples). As a minimally destructive analytical technique, laser ablation ICP-MS has been used for the direct measurement of micro-sized archeological and geochemical samples, such as ancient pottery [29] and minerals [30], though this technique only probes the surface with localized analysis that is typically in the several tens of micrometers in size.

An improved XRF specimen preparation method for precious and limited samples such as ancient pottery and mineral fragments has been developed to reduce the required sample amounts for analysis. For instance, for fused glass bead preparations, 11 mg of archeological and geochemical sample powders has been used to prepare 35 mm diameter specimens with an extremely high sample-to-flux ratio of dilution of 1:300 [31], in addition to undersized (12.5 mm diameter) specimens [32] with a 1:36 sample-to-flux ratio using a special platinum crucible. Geological powdered samples (15 mg) have been fused for the production of small (6 mm diameter) specimens [33] with a 1:10 sample-to-flux ratio. Additionally, for loose powder preparation, 300 mg of powdered ceramics has been packed into a 10 mm-opening plastic cup [34], while a similar report molded 100 mg of powdered ancient potteries into an 11 mm-opening stainless steel disc (48 mm diameter  $\times$  0.8 mm height) [35]. Reducing the sample amount requirement for XRF analyses might allow for accurate determination of the chemical composition of more types of precious and limited samples with destructive pretreatment, rather than nondestructive direct measurements with increased analytical errors due to absorption effects.

The glass bead process involves fusing the sample of interest with a flux material to completely dissolve and homogenize the sample. For siliceous samples such as pottery and silicic rocks, application of the fusion method results in the formation of glass beads. This method has yielded excellent results, since a variety of samples with different physical and chemical differences can be converted to similar materials with the following characteristics: (1) a highly homogeneous glass body, (2) structural consistency by fusion, and (3) fully oxidized elemental constituents. In contrast, powder specimens such as loose powders and pressed pellets have low homogeneity and structural differences (e.g., grain size and shape of each specimen). Therefore, the precision and accuracy of the results obtained from XRF analyses with glass bead specimens are superior to those obtained from XRF analyses with the powdered specimens.

Although XRF analyses can be useful for determining the elemental composition of complex samples in archeology and geochemistry, there are noted difficulties with obtaining proper calibration standards. Siliceous samples such as ancient potteries and rocks have often been analyzed with XRF using calibration curves constructed from various

types of standards (e.g., rock, clay, and soil) [36,37]. However, these curves can be erroneous because of differences in the absorption and/or excitation effects resulting from compositional variabilities among the different sample matrices. In contrast, calibration curves constructed from mixtures of chemical reagents such as synthetic calibration standards [38] can provide composition ranges that are customized for a given sample type. This technique has been applied to XRF analyses of glass beads to determine 23 [39] and 42 [40] elements in silicate rocks, 15 elements in sludge ash from a sewage disposal plant [41], 10 major elements in ancient potteries [21], and 10 major elements in a minimal amount (11 mg) of natural rocks and archeological ceramics [31,32]. Calibration curves for XRF analyses of powder specimens also have been constructed to determine the following components: 18 elements in the fly ash of municipal solid waste [42] using powder pellet specimens, and 22 elements in ancient potteries [35] and 5 elements in scrapped printed circuit board ash [43] using loose powder specimens.

In this paper, we describe an alternative method to determine ten major oxides in 1.1 mg of a certain siliceous sample powder using XRF analysis with micro glass bead flux specimens based on a 1:10 sample-to-flux ratio. The discussion involves the following aspects: (1) development of a micro glass bead specimen using very small (1.1 mg) powdered samples with a commercial platinum crucible; (2) appropriate instrumental conditions for weakened fluorescence intensity, arising from the very small amount of sample and small size of the micro specimen; and (3) the reliability of calibration curves obtained from micro-sized synthetic calibration standards for determination of ten major oxides. The proposed method was subsequently applied to determine the major oxides in archeological and geochemical siliceous samples, including igneous rocks, sediments, ancient potteries, and obsidian. Additionally, the applicability of this method was discussed for various siliceous samples based on these analytical results.

## 2. Materials and methods

### 2.1. Geochemical samples

Major oxides in the following three igneous rocks and sediments, which are geochemical reference samples issued by the Geological Survey of Japan (GSJ), were determined: JA-1 (andesite), JB-1a (basalt), JR-3 (rhyolite), JSd-1 (stream sediment), JSd-2 (stream sediment), and JSd-3 (stream sediment). The powders were pre-dried at 600 °C for 1 h for rock samples [39] or 700 °C for 4 h for the sediment samples [21] using an electric furnace (FUM312PA; Advantec Toyo Seisakusho Kaisha Ltd., Chiba, Japan) prior to preparation of glass bead specimens.

### 2.2. Archeological objects

Major oxides in the following samples were determined: (1) a pottery sherd sampled at Hodogaya, Yokohama City, Kanagawa Prefecture, Japan on December 11, 2006; (2) another pottery sherd sampled at Daikata, Narita City, Chiba Prefecture, Japan on September 11, 2007; and (3) obsidian fragments sampled at Takayama, Nagawa City, Nagano Prefecture, Japan on August 30, 2009. For the ancient potteries, the sherds (3 g) were pulverized by an alumina mortar and pestle, and roughly crushed pottery grains under 500  $\mu$ m of diameter were ground by a mechanical grinder with an agate mortar and pestle. Subsequently, the powder was pre-dried at 700 °C for 4 h using an electric oven. The sample preparation details have been previously reported and discussed [21]. For the obsidian, the fragments (20 g) were pulverized by an alumina mortar and pestle, and roughly crushed grains under 500  $\mu$ m of particle size were pulverized by centrifugal ball milling with an agate bowl and balls. Subsequently, the obsidian powder was pre-dried at 600 °C for 1 h.

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