

# Single particle transfer for quantitative analysis with total-reflection X-ray fluorescence spectrometry

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Received 3 April 2006; received in revised form 12 May 2006

Available online 10 July 2006

## Abstract

The technique of single particle transfer was applied to quantitative analysis with total-reflection X-ray fluorescence (TXRF) spectrometry. The technique was evaluated by performing quantitative analysis of individual Cu particles with diameters between 3.9 and 13.2  $\mu\text{m}$ . The direct quantitative analysis of the Cu particle transferred onto a Si carrier gave a discrepancy between measured and calculated Cu amounts due to the absorption effects of incident and fluorescent X-rays within the particle. By the correction for the absorption effects, the Cu amounts in individual particles could be determined with the deviation within 10.5%. When the Cu particles were dissolved with  $\text{HNO}_3$  solution prior to the TXRF analysis, the deviation was improved to be within 3.8%. In this case, no correction for the absorption effects was needed for quantification.

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PACS: 78.70.En

Keywords: Individual particles; X-ray fluorescence spectrometry; Total reflection; Quantitative analysis; SEM; Manipulator

## 1. Introduction

The characterization of particles is essential for studies in scientific and industrial fields. Atmospheric aerosol, soil and cosmic particles are extensively investigated to understand their origin, migration or influence on global climate in environmental science. The analysis of particles is important for the routine quality control of products and the characterization of products of powder metallurgy. The analysis is also useful to estimate the health hazard for workers exposed to toxic dust. Therefore, various kinds of analytical techniques have been employed [1,2]. For the analysis of particles, bulk analysis techniques such as X-ray fluorescence spectrometry (XRF) and inductively coupled plasma mass spectrometry (ICP-MS) have been

used. However, by these methods, only an average composition of many particles can be obtained. If the sample is a heterogeneous mixture of particles, individual particle analysis gives more valuable information than bulk analysis.

For the analysis of individual particles, scanning electron microscopy (SEM) combined with energy dispersive X-ray (EDX) analysis has been widely used [3,4]. The morphology as well as the elemental abundance ratios of individual particles can be analyzed. However, it is difficult by this method to determine elemental amounts in individual particles because the estimation of the interaction volume of an electron beam with the particle is difficult and suitable particle standards are absent.

Total-reflection X-ray fluorescence (TXRF) spectrometry is a technique for quantitatively measuring elements in a sample using an internal standard added to the sample in the form of a microdroplet [5]. This technique has been successfully applied to the analysis of particles as a bulk analysis

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method [6,7]. However, few studies have been performed for the analysis of elemental amounts in individual particles with TXRF analysis.

The aim of this work is to investigate a technique for quantitative analysis of individual particles by a combination of single particle transfer and TXRF analysis. Performing direct quantitative analysis of individual Cu particles, we then discuss the applicability and the limitation of the technique. Furthermore, the improvement of quantitative results by dissolution of the particles is also reported.

## 2. Experimental procedure

### 2.1. Sample carriers and samples

Polished Si carriers (Nihon Exceed Co., Japan) with a diameter of 25 mm and a thickness of 3 mm were used in this study [8]. The Si carriers were cleaned by immersing them in a 10% HNO<sub>3</sub> solution for 24 h and rinsing with Milli-Q pure water (Millipore Co., Massachusetts).

Cu particles (Nilaco Co., Japan) were collected onto a Si carrier by an impaction method [9]. As an internal standard, a 5  $\mu$ L droplet of a 0.2 ppm V solution prepared by diluting a 1000 ppm stock solution (Wako Chemical Co., Japan) was pipetted onto the center of another Si carrier with a micropipette (Eppendorf AG, Germany, accuracy is within 1.5% at 5  $\mu$ L). The microdroplet was evaporated to dryness at 100 °C.

To determine the detection limit of Cu in TXRF analysis, a 5  $\mu$ L droplet of a 0.2 ppm Cu solution prepared by diluting a 1000 ppm stock solution (Wako Chemical Co., Japan) was used in a same way as the V internal standard.

### 2.2. Particle transfer

Both carriers containing the particles and the internal standard were introduced into a scanning electron microscope (SEM, JSM-6700F, Jeol Co., Japan). A manipulator was attached to the chamber of the SEM. The needles for particle transfer were fabricated with a micropipette puller (PC-10, Narishige Co., Japan) from glass rods with a diameter of 1 mm [10]. The needles were coated with gold in a sputtering instrument (SC-701AT, Sanyu Electron Co., Japan). Finally, the tip diameter was approximately 1  $\mu$ m as shown in Fig. 1. The needle was positioned directly above the Cu particle. The stage of SEM was raised until the needle touched the particle. The particle was then picked up and transferred onto the center of the carrier containing the internal standard. The backscattered electron images of transferred Cu particles with the diameters of 3.9, 6.1, 9.4 and 11.0  $\mu$ m are shown in Fig. 2. In this study, the average value between the lengths of the major and minor axes of each particle determined with SEM was used as the particle diameter.

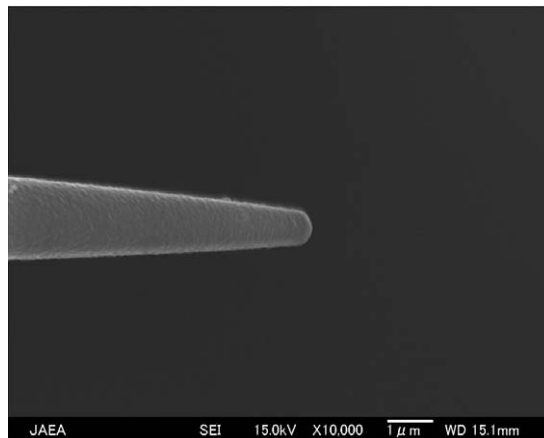


Fig. 1. The scanning electron image of a glass needle used for particle transfer.

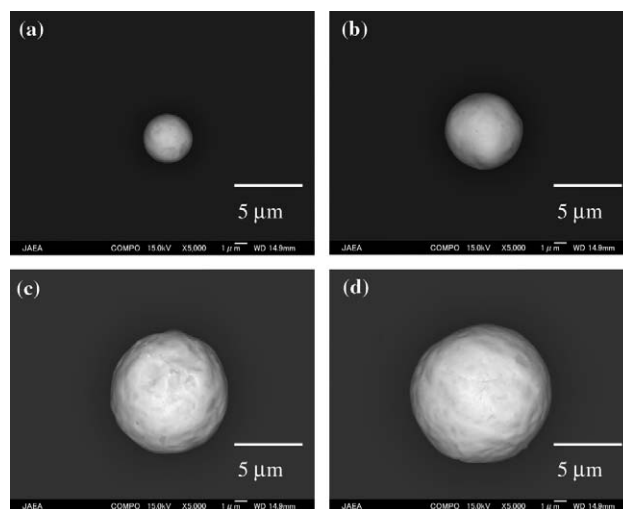


Fig. 2. The backscattered electron images of individual Cu particles with diameters of (a) 3.9  $\mu$ m, (b) 6.1  $\mu$ m, (c) 9.4  $\mu$ m and (d) 11.0  $\mu$ m.

### 2.3. TXRF analysis

The carrier containing the transferred Cu particle was removed from the SEM and introduced into a total-reflection X-ray fluorescence analyzer, TREX-610 (Technos Co., Japan). This instrument had an energy dispersive X-ray (EDX) spectrometer with a Si(Li)-detector. Sample holders were modified to fit the carrier. A tungsten X-ray tube was operated at 40 kV and 40 mA and the counting time was chosen to be 300 s. The quantitative analysis of the particle was then performed. Since the particle is fully irradiated with the primary X-ray beam, the interaction volume of the beam with the particle corresponds to the volume of the particle. In addition, the particle and the internal standard are irradiated with the beam simultaneously. This enables us to estimate the elemental amounts in individual particles by TXRF analysis. After the analysis, the carrier was once removed from the instrument for the dissolution of the particle with 20% HNO<sub>3</sub> solution. The carrier was

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