Enhancement of electron-induced X-ray intensity for single particles under grazing-exit conditions

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Abstract

Grazing-exit electron probe microanalysis (GE-EPMA) was performed for single Al\textsubscript{2}O\textsubscript{3} and atmospheric particles, deposited on a flat Si substrate coated by gold, by using an aperture (1 mm in diameter) in front of an energy-dispersive X-ray detector. Silicon K\textsubscript{α} X-rays from the Si substrate were strongly observed at an exit angle of \(45^\circ\). However, they disappeared at grazing-exit angles about \(0^\circ\) and only the X-rays from particles were detected. Furthermore, Al K\textsubscript{α} and O K\textsubscript{α} intensities from single Al\textsubscript{2}O\textsubscript{3} particle were enhanced approximately three- and sixfold at the grazing-exit angles (\(\approx 1^\circ\)), respectively, in comparison with those at large angle (\(\approx 7^\circ\)). The background intensities at the energy of Al K\textsubscript{α} and O K\textsubscript{α} almost monotonously decreased with decreasing exit angle. As a result, the intensity ratios of Al K\textsubscript{α} and O K\textsubscript{α} X-rays to the background intensities were enhanced five- and sixfold, respectively. This enhancement is considered to be caused by the interference effect of both directly detected X-rays and reflected X-rays on the flat substrate. The similar results are also obtained for Al K\textsubscript{α}, Si K\textsubscript{α}, K K\textsubscript{α} and Ca K\textsubscript{α} emitted from single atmospheric particle. The significance of the matrix effect in the particle is also pointed out.

Keywords: Electron probe microanalysis; Grazing exit; Aerosols; Interference effect; Particle analysis

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1. Introduction

Recently, it has been gradually recognized that aerosols (atmospheric particles) have an influence on the global climate. Aerosols of several μm in diameter reflect solar radiation by scattering, and also transfer the solar energy by light absorption \[1\]. Aerosols of less than 1 μm including toxic elements are easily taken into human body, harming human health. To understand influences of aerosols on climate and human body, elemental analysis of individual particles is important. Atmospheric particles have been measured by inductively coupled plasma optical emission or mass spectrometry \[2\], X-ray fluorescence (XRF) and total reflection XRF (TXRF) \[3,4\]; however, only the averaged elemental composition is obtained by these analytical methods. Single-particle analysis gives more information about the type and source of aerosols. Thus, micro-analytical methods such as: electron probe microanalysis (EPMA) \[5,6\], micro-particle-induced X-ray emission (μ-PIXE) \[7,8\] and laser microprobe mass analysis (LAMMA) \[9\], have been applied to single aerosols analysis. An X-ray spectrum with low-background is obtained by PIXE; however, PIXE needs a large and expensive accelerator. The drawback of LAMMA is in the lack of stability for quantitative analysis. Compared with PIXE and LAMMA, EPMA makes qualitative and quantitative analysis possible with a commercially available common and small-size instrument. The bremsstrahlung background intensity in EPMA X-ray spectra, however, is much higher than that in PIXE. This affects the detection limits in EPMA. Lower detection limits would be achieved both by enhancement of X-ray intensity and by reduction of background intensity.

It is well known that the background intensity in TXRF analysis is reduced under total-reflection conditions \[10\]. That is, the primary X-rays are totally reflected on a flat substrate when the grazing incident angles are below the critical angle for total reflection. Therefore, the X-ray analysis can be performed with extremely low background by using an energy-dispersive X-ray detector (EDX). Grazing exit (or emission) X-ray fluorescence (GEXRF), where characteristic X-rays are measured at grazing exit angles, also makes trace-analysis possible for a flat substrate \[11–13\]. From an analogy of this, we recently proposed a new analytical method: grazing-exit EPMA (GE-EPMA), in which electron-induced X-rays are detected at grazing exit angles \[14\]. It has been demonstrated that a surface-sensitive analysis of a Si wafer and a surface layer analysis of a single particle are possible by GE-EPMA \[14\]. In GE-EPMA measurement, the solid take-off angle for X-ray-detection should be quite small, because X-ray intensity is sensitive for the take-off angle under the grazing exit conditions. To limit the solid angle below the critical value, the use of aperture or slit systems would be desirable. Since we could not use an aperture in the previous work \[14\], the obtained exit-angle dependency was not clear. In this work, an Al aperture of 1 mm in diameter was attached in front of the EDX detector. As a result, it is found that the X-ray intensity emitted from single particles is enhanced at the grazing exit angles. In this article, the details of this experiment will be shown and the mechanism of an enhancement will be discussed.

2. Experimental section

2.1. GE-EPMA instrument

The details of GE-EPMA experiment have been described previously \[14\]. The commercially available EPMA instrument (Superprobe-733, JEOL, Tokyo, Japan) was used with an ultra-thin window EDX (Link Pentafet model 5373, sensitive area: 30 mm², Oxford Instruments, England). To detect the X-rays emitted only from the limited exit angle, an Al aperture (1 mm in diameter, an attachment of EDX) was attached in front of the X-ray detector. Furthermore, the X-ray detector was taken away at a maximum distance of 100 mm from the sample. Under these experimental conditions, the solid take-off angle for X-ray detection is approximately 0.5°, which would allow the grazing-exit EPMA (GE-EPMA) experiments. The EPMA instrument used was designed to measure the X-rays at the exit angle of approxi-
mately 40°. Thus, a custom-made brass attachment having an inclination of 45° was put on the sample holder to make it possible to measure the X-rays at the grazing exit angle around zero [14]. The incident angle of the electron beam was also changed to be approximately 45° due to the use of this attachment. The EPMA apparatus was operated under a vacuum of 7.5 × 10⁻⁶ torr, at a beam current of 1 nA and at an accelerated voltage of 15 kV, which was suitable for the detection of low-Z elements in atmospheric particles. This EPMA apparatus has two operation modes: spot mode and scanning mode. In the case of spot mode, in which the electron beam is fixed in the diameter of several tens nanometer, the irradiated area of the particle is cruelly damaged and the part of the particle is volatilized during the measurement. Therefore, X-ray measurements were performed at scanning mode, in which the electron beam was scanned in the area of about 1 μm square. The measuring time for each exit angle was chosen at 300 s. It was possible to change the exit angle with a step angle of 0.25° by tilting the sample holder.

2.2. Sample preparation

Two kinds of particles; artificial Al₂O₃ particles and ambient atmospheric particles, were deposited on flat Si substrates, which had been cut from a Si wafer with a size of 5 × 10 mm². The Al₂O₃ particles (Aluminum oxide G, type 60/E, particle size: ~2 μm, Merck, Germany) were suspended in pure water Milli-Q; a few microliters of the suspension were pipetted and dried in air. Atmospheric particles were collected at the campus of University of Antwerp (UIA), Belgium. Air was sucked with a rotary vacuum pump into a multiple-orifice impactor (Bernertype, Hauke, Austria), and spots of deposited atmospheric particles were collected at the campus of University of Antwerp (UIA), Belgium. The Al₂O₃ sample was coated by Au of different thicknesses (30, 50, 80 and 100 nm) by a vacuum-evaporation method. This Au coating was useful to obtain electrical conductivity, and also to investigate the possibility of surface-layer analysis by GE-EPMA. The closest particle to the edge of the substrate was chosen for measurements, because if there are other particles between the analyzed particle and the X-ray detector, the characteristic X-rays emitted from the analyte are absorbed by them.

3. Results and discussion

3.1. X-Ray spectra under grazing-exit conditions

In conventional EPMA, the electron beam irradiates the individual particle collected on a sample carrier, and part of electrons passes through the thin particle and then bombards the substrate. Therefore, X-rays emitted from the sample carrier are also observed, although only the X-rays from the particle are necessary. In this case, a substrate including the same elements as the main components of atmospheric particles is not suitable as a sample carrier for particle analysis. The characteristic X-rays from the sample carrier overlap with the significant X-ray peak from the particle, and obstruct the X-ray analysis of the particle.

Fig. 1a–c show the X-ray spectra obtained for single Al₂O₃ particle at the exit angles of 40°, 3.5° and 0.0°, respectively. Al₂O₃ particles were coated with Au thin film of about 80 nm. Since it was difficult to determine the absolute zero angle in this work, the zero angle was simply defined as the angle where Si Kα originated from the Si substrate disappeared. In the physical meaning, zero angle should be defined in the plane of the flat Si surface. The observed characteristic X-ray peaks are C Kα, O Kα, Al Kα and Au Mα. The intensity of Au Mα changes in comparison with Al Kα, as shown in Fig. 1a–c. This is probably because the thickness of Al₂O₃ particle is not the same in each analyzed position that is also slightly changed for each measurement. The Si Kα peak disappears at the grazing angles below 0.0°, as shown in Fig. 1c. It is well known in GEXRF that X-ray intensity becomes extremely small at the exit angles smaller than the angle corresponding to the critical angle for total reflection. This phenomenon, which can be understood from the analogy of X-ray total reflection, is also observed in GE-EPMA. Fig. 1 indicates that particle analy-
Fig. 1. X-Ray spectra obtained for a single Al$_2$O$_3$ particle at different angles of 40° (a), 3.5° (b), and 0° (c). The Al$_2$O$_3$ particles were deposited on a flat Si substrate, and then the sample was covered with a Au film of 80 nm in thickness. Characteristic X-rays of Si Kα decrease as the exit angle decreases. At the exit angle near 0°, only the X-rays emitted from the particle are observed.

sis with reduced background from the substrate is possible at the grazing angles near zero.

At the exit angles below zero, only the top of the particle is observable [14], because X-rays emitted from other places are obstructed at the edge of the Si substrate. Fig. 2 shows the intensity ratio of Au Mα to Al Kα for the different Au thicknesses (30, 50 and 100 nm). The intensity ratio abruptly increases at negative exit angles. The angle where the intensity ratio increases is different for each measurement, because this angle simply depends on both the particle height and the distance between the position of the measured particle and the edge of the Si substrate. After Al$_2$O$_3$ particles had been deposited on the Si substrate, the sample was covered with Au. The Au layer existed only outside of each Al$_2$O$_3$ particle. Therefore, Fig. 2 clearly indicates the possibility to analyze only outside of each Al$_2$O$_3$ particle. This would be useful for understanding reaction processes between the particle and the atmosphere.

3.2. Enhancement of X-ray intensity from Al$_2$O$_3$ particle

The characteristic radiation intensity from an Al$_2$O$_3$ particle coated with a Au thin film about 80 nm was measured at the different exit angles. The angle-dependencies of net intensities of Al Kα, O Kα, Au Mα and Au Lα and their background intensities are shown in Fig. 3a,b. X-Ray intensity fluctuates, and high X-ray intensities at an exit angle of 40° are observed. This is caused by the fact that the observed position was changed at each angle, because it was difficult to exactly adjust the surface of the sample at the center of the tilting stage, in addition, the thickness of the particle was also not identical. When the sample holder was tilted, the incident angle changed. This also influenced the intensity of characteristic X-rays.

Al Kα and O Kα intensities were enhanced approximately three- and sixfold at the grazing exit angles (~ 1°), respectively, in comparison with those at large angle (~ 7°), as shown in Fig. 3a. Noma et al. [15] reported ‘interference effects of fluorescent X-rays’ at grazing exit angles. They used a Cr/Au layered sample, and observed an oscillation structure in the angular-dependent
Fig. 2. Intensity ratios of Au Mα to Al Kα for different Au thicknesses of 30, 50 and 100 nm as a function of exit angle. Au layers were deposited on the Al₂O₃ particle after they were collected on the Si sample carrier.

curve of Cr Kα fluorescence intensity. This result was explained in a similar way for X-ray standing waves using the reciprocity theorem [16]. Sasaki et al. [17,18] also reported interference effects of fluorescent X-rays for a sample of a Langmuir–Blodgett film including a Zn layer. The interference fringes were observed in the angular-dependent curve of Zn Kα. This interference effect is caused by both the direct X-ray beam and the X-ray beam reflected on the flat substrate, and it is also expected in GE-EPMA measurement of particles. Fig. 4 illustrates a simple model of a particle on the Si substrate in order to explain the interference effect in GE-EPMA experiments. Electron-induced X-rays are directly detected; in addition, a part of the X-rays are reflected on a flat substrate, and then detected. Therefore, interference effects occur due to both X-ray beams at grazing angles.

Klockenkämper and Bohlen [19] described the critical thickness to avoid X-ray absorption of the matrix for TXRF analysis. De Boer [20] also discussed the critical sample thickness for practical TXRF analysis. X-Ray absorption depends on both the density of the substrate and mass absorption coefficients for the incident X-ray energy. The critical thickness for mineral powders is estimated to be about 50 nm for Mo Kα [20]. A similar discussion is possible for interference effect in GE-EPMA. The X-rays, emitted from positions far more than several tens of nanometers from the substrate surface, would not contribute to the interference effect. Au existed only outside of the particle. Fig. 3b shows the exit-angle dependency for Au Mα and Au Lα intensity, where any enhancement is not observed at grazing exit angles. Since the thickness of Al₂O₃ was approximately several μm, Au Mα and Au Lα were emitted from the positions far from the substrate surface. Therefore, X-rays, emitted only from Al₂O₃ near the substrate, contribute to the enhancement of the X-ray intensity, as shown in Fig. 3a.

The angular dependency of background intensities for each X-ray peak is also shown in Fig.
Fig. 4. Illustration of a single particle on a flat substrate in GE-EPMA arrangement. Two paths for X-ray detection are shown: directly detectable X-ray beam and the X-ray beam reflected on the substrate. When the distance between the substrate surface and the position where X-rays are emitted are smaller than approximately 50 nm, interference effect due to two X-ray beams would be remarkably observed.

3a,b. The background intensity decreases with decreasing angle, and it is not enhanced at grazing exit angles. The small background intensity is advantageous for the trace analysis by GE-EPMA.

Fig. 5 shows the angular dependency of the intensity ratios of the net intensities of Al Kα, OKα and Au Mα to the background intensities for each characteristic peak. These intensity ratios for Al Kα and O Kα are enhanced five- and sixfold at grazing exit angles, respectively, in comparison with those at the normal take-off angle of 40°.

3.3. GE-EPMA of atmospheric particle

Atmospheric particles were collected on a flat Au film (~ 120 nm) deposited on a flat Si wafer. When the Si wafer is used as the substrate, there are two possibilities for observation of Si Kα line: one is from the Si wafer and another is from particle itself, because Si is one of the most common elements of atmospheric particles. Of course, as shown in previous sections, it is possible to decrease signals from the substrate by the application of grazing-exit technique. However, the use of the Au film as the sample carrier makes it easy to detect Si Kα only from particles. In addition, the measurement of X-rays from Au is useful to determine the absolute zero angle, because it can be defined as the angle where Au Lα disappears. Furthermore, the Au layer is useful to obtain the enhancement effect. Au has large density, leading to large critical angle, therefore, characteristic X-rays from particles reflect can reflect on an Au surface.

Fig. 6 shows the angular dependency of X-rays mainly observed for a single particle. The X-ray intensity of Si Kα at 40° is large. This is probably because Si Kα X-rays emitted from the substrate were also detected. At the grazing angles below about 2°, X-ray intensities are enhanced due to an interference effect. The critical angle can be considered in a similar way as in GEXRF or TXRF. The refractive index n is defined with the use of real and imaginary parts by 

\[ n = \sqrt{1 - \frac{\delta}{\lambda} + \frac{\beta}{\lambda}}. \]

The critical angle \( \theta_c \) for total reflection is given by the following approximations: 

\[ \theta_c = \left(\frac{2\delta}{\lambda}\right)^{1/2} \text{ or } \theta_c (\text{degrees}) = 1.65/E \times (Z\rho/A)^{1/2}, \]

where

- \( E \) (keV) is the energy of characteristic X-rays,
- \( Z \) is the atomic number,
- \( A \) is the atomic weight, and
- \( \rho \) (g/cm³) is the density of the substrate [21]. Under grazing exit conditions, the energy of observed X-rays is applied as \( E \) in this equation [16,22]. Therefore, the critical angle in GE-EPMA should change depending on the energy of each characteristic X-ray peak: the smaller the energy, the larger the critical angle. The energies for Al Kα, Si Kα, K Kα and Ca Kα are 1.49, 1.74, 3.31 and 3.69 keV, respectively. As shown in Fig. 6, each curve has maximum peak at the different exit angle. Apparently, the angular positions for maxi-
Fig. 6. Net intensities of Al Kα, Si Kα, K Kα and Ca Kα for an atmospheric single particle as a function of the exit angle. The Si Kα X-ray intensities were divided by a factor of 10.

3.4. Matrix effect in GE-EPMA of single particle

Atmospheric particles are composed mostly of low-Z elements, such as C, O, Na, Al, and Si. The energies of X-rays for these elements are so low that they are absorbed in the particle itself. This matrix effect should also be considered when a large particle is analyzed by GE-EPMA [23]. To investigate the matrix effect in GE-EPMA, the Al2O3 particle shown in Fig. 7 was used. The size of this particle and the diameter of the electron beam were approximately 12 and 1.2 μm, respectively. Thus the GE-EPMA measurements were carried out at different five positions shown in Fig. 7. The X-ray detector was put at the right side of the particle, and the exit angle was fixed at approximately 0.5°. The X-ray intensities of Al Kα and O Kα detected at each position are shown in Fig. 8. The X-ray intensities change depending on the position, and they increase from position 2 to position 5. The X-ray intensity at position 1 is stronger than that at position 2, probably because the particle was thickest at position 1. The X-rays emitted from position 5 are detected by EDX without any absorption by particle, while the X-rays from positions 2 and 3 are absorbed by the particle itself before they are detected. Therefore, the increase of X-ray intensities from position 2 to position 5 would be caused by the decrease of absorption in the particle. When the analyzed particle is large enough, this matrix effect will be more significant in GE-EPMA, because the X-ray path in the particle under grazing exit conditions is longer than that at the normal take-off angle of 40°.

4. Conclusions

EPMA is a powerful method for single-particle analysis. Its detection limits could be improved by both enhancement of characteristic X-rays and reduction of background intensity. In this article, we demonstrate that X-ray intensities from single particle are enhanced at grazing exit angles due to interference effect between the direct X-ray beam and the reflected X-ray beam. Furthermore, it is also shown that the X-ray intensity emitted from the substrate decreases and almost disappears under grazing-exit conditions. In practical quantitative analysis of a single particle,
Fig. 8. The position-dependency of the X-ray intensities of Al Kα and O Kα, which were measured at the different positions of an Al₂O₃ particle shown in Fig. 7.

reduction of X-ray intensity from the substrate would be more significant and interesting than an enhancement of the characteristic X-ray intensity. The enhancement of X-ray intensity occurs at different exit angles depending on the X-ray energy of each element. Therefore, simultaneous quantitative analysis for multi-elements may be difficult at a fixed grazing exit angle. However, the increase of characteristic intensity of analytes in GE-EPMA would be useful for trace elemental analysis. In addition, attention should be paid to matrix effects in GE-EPMA analysis of large particles.

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