Strategies for overcoming limitations associated with fluorine determination in solid materials by conventional wavelength dispersive X-ray fluorescence spectrometry

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ABSTRACT

Potential ways to avoid limitations and improve analytical sensitivity in the determination of fluorine (F) in solid materials using wavelength dispersive X-ray fluorescence (WDXRF) spectrometry were investigated. Chemical shift was not significant in the F determination using WDXRF spectrometry, potentially because of high electronegativity of F. In a variety of matrices containing F, an absorption/enhancement effect noticeably altered the F intensity. A sample containing high-molecular-weight constituents seemed to absorb the emitted F-Kα line more than its counterparts. An additional calibration curve established using standards with similar matrices to samples is recommended. In addition, the intensity induced from the F-Kα increased by more than 9-fold by making a pressed pellet with a low dilution (9:1) method using polyvinyl alcohol and liquid binder. Peak overlap caused by the proximity between F-Kα and Fe-Lα or Mn-Lα is likely to disturb the quantitative F determination. It can be properly overcome by employing a correction factor derived from the slope of the measured X-ray intensity at the *Bragg* angle of 43.174° to Fe or Mn content in the sample. Consequently, WDXRF technique can be successfully used to assess the F content in solid materials by following the strategies proposed in this study.

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1. Introduction

Fluorine (F) has received increasing attentions due to its toxicity towards humans and the environment. Although F is known to play a crucial role in preventing dental caries, its excessive intake may cause skeletal and dental fluorosis in humans [1]. The accumulation of F in sheep and cattle by food, soil, and water intake induces emaciation, joint stiffness, and abnormal bond and teeth expression [2].

Various analytical techniques have been developed and successfully applied to investigate F levels in a variety of sample matrices [3–5]. In particular, the use of an ion selective electrode (ISE) followed by alkali fusion as a pretreatment method for extracting F from solid samples (e.g., soil and plants) has been thoroughly employed [6]. The required apparatuses (e.g., ISE, furnace, and nickel crucible) are commonly available in many laboratories, making this method versatile and inexpensive. Although this method is preferred to the conventional technique established by Willard and Winter [3] by omitting the burdensome distillation process, it still requires time-consuming, complex, and harsh procedures (e.g., the use of strong acidic/alkaline solution) and generates about 100 mL of wastewater per sample.

Green Analytical Chemistry (GAC) constitutes an important part of analytical chemistry [7]. GAC pursues the minimization of solvent use and excessive heating in an effort to decrease waste generation and conserve environmental resources. X-ray fluorescence (XRF) spectrometry was touted as a promising tool that meets this requirement, owing to its non-destructive properties [8]. As such, XRF spectrometry has been widely applied in the analysis of solid materials such as vegetal materials [9], plastic [10], ion exchange disks [11,12], and soil [13] without the need for tedious pretreatment steps.

Despite these advantages, XRF spectrometry can rarely be used for the determination of F. For elements with atomic numbers (Z) less than 15, the fluorescence yield is low [14], owing to signal loss resulting from the absorption of X-ray. In other words, the energy level of X-ray emitted from a low Z element is too low to escape the spectral pathway without loss. The absorption/enhancement effect also results in serious analytical biases [15]. Theoretically, XRF signals should exhibit a linear correlation with the concentration of the target element. However, it is altered due to the absorption of X-ray or secondary excitation by other atoms existed in the sample matrix [15]. Moreover, elements in the sample with similar X-ray energies compared to that of F-Kα (0.672 keV) may interfere with the F determination through peak overlap [16,17]. Finally, different chemical form of F in the sample may cause chemical shift, which alters the peak position as compared to the original location that was used to establish the calibration curve [18].

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Changes in electron density can be influenced by the surrounding environment of the target atom, resulting in substantial wavelength shifts (i.e., chemical or energy shift) of the emitted lines [18,19].

The purpose of this study was to clarify the limitations of wavelength dispersive X-ray fluorescence (WDXRF) spectrometry in the determination of F and to provide strategies to avoid them. Towards this end, the limitations of WDXRF analysis including (i) chemical shifts, (ii) absorption/enhancement effect, (iii) low intensity, and (iv) peak overlap and their impacts on F determination were assessed. Some available methodologies to improve analytical sensitivity and avoid such limitations were proposed and their feasibilities were discussed. This study will be advantageous in compliance with the concept of GAC through the use of conventional WDXRF technique with the strategies for the routine determination of F in solid materials.

2. Materials and methods

2.1. Reagents and sample preparation

Commercial reagents including AlF_3 (99.9%), BaF_2 ($\geq$98%), KF ($\geq$98%), LiF ($\geq$99%), and polyvinylidene fluoride (PVDF) purchased from Sigma Aldrich (St Louis, MO, USA), CaF_2 ($\geq$98%) and NaF (98%) from Junsei (Japan), and certified reference materials (CRMs; JK S10 (slag) and NIST 694 (phosphate rock)) from Brammer Standard Company were used to investigate the effects of the chemical form of F and the composition of the matrices on the measured F-Kα intensity in WDXRF analysis. Concentrations of F in NIST 694 and JK S10 are 32,000 and 344,000 mg/kg, respectively. In addition, a rice sample collected from the area directly affected by the anhydrous hydrogen fluoride (HF) spillage in Gumi City, Korea [20] was also used as a carbon based field sample. It was thoroughly ground in an agate mortar and its F concentration was determined using the alkali fusion-ISE method [6]. It contained 4173 $\pm$ 670 mg/kg of F [20]. To establish the F calibration curve in quantitative analysis using WDXRF system, standard materials were prepared by mixing 95% SiO_2 and the remaining 5% of CaO with varying concentrations (0, 0.1, 0.2, 0.5, 1.0, and 2.0%) of CaF_2 to mimic soil configuration. To observe peak overlap phenomenon, standard materials containing varying concentrations of Fe_2O_3 ($\geq$99%) and MnO ($\geq$99%) from Sigma Aldrich were used. Spectroblend® 44 μm cellulose powder ($C_6H_{10}O_5N$) obtained from Chemplex® (Palm city, FL, USA) and polyvinyl alcohol (PVA) from Sigma Aldrich were used as solid binders to enhance the mechanical stability of the pressed pellet in WDXRF analysis. A liquid binder from Chemplex® (Palm city, FL, USA) containing polymeric ingredient (C_6H_9ON) dissolved in dichloromethane was also used.

2.2. Analysis of chemical forms of F in solid materials

The chemical forms of F in several solid materials were assessed using X-ray diffraction (XRD) spectrometry (PW3040, Phillips, Netherland), X-ray photoelectron spectrometry (XPS) (Theta Probe AR-XPS system, Thermo Fisher Scientific, UK), and gas chromatography mass spectrometry (GC–MS) (6890 N, Agilent, USA) operating at Korea Basic Science Institute (KBSI). Specifically, a number of F containing compounds (AlF_3, BaF_2, CaF_2, KF, LiF, NaF, and PVDF) were analyzed by XPS. The changes in binding energy (BE) and full width half maximum (FWHM) of the F1s peak were used to distinguish whether or not a chemical shift occurred. XRD spectrometry was used to confirm the chemical form of F in the CRMs. The anode with a Cu-Kα1 (wavelength line of 1.5406 Å) was used. A generator was operated at 40 kV and 30 mA. The measurement temperature was set to 25 °C. The rice sample affected by the HF spillage was analyzed using both XPS and GC–MS. Methanol extraction with the aid of sonication was performed to recover F from the rice sample prior to GC–MS analysis.

2.3. WDXRF analysis

WDXRF spectrometry (PW2404, Phillips, Netherlands) operating at KBSI was used to determine the F concentrations in various solid samples. Rh target X-ray tube was operated at 30 kV and 100 mA with a thin Be window (thickness= 75 μm). The target was placed in a vacuum chamber (<3 Pa) to prevent the emitted X-rays from being absorbed by air, thereby increasing the sensitivity. The diameter of the X-ray collimator was 700 μm and a beam filter was not used. The Bragg angle of F-Kα line was 43.174° and the background offset was 1.5078°, when a PX-1 crystal (2d = 4.9759 nm) was used. The analysis time was set to 100 s. The operating conditions of WDXRF spectrometry were the same as those described previously [17].

Element scan program (IQ+ method) described by PANalytical [21] was performed for the qualitative determination of the elements in the samples. According to the target elements, this method was operated at 10 different conditions (Table S1). Each condition covers a certain range of Bragg angles by using various diffraction crystals (LiF220, Ge 111-C, PE 002-C, and PX-1).

2.4. Experimental procedures

2.4.1. Chemical shift effect

Seven different F containing compounds (AlF_3, BaF_2, CaF_2, LiF, KF, NaF, and PVDF), the field rice sample (i.e., contaminated with F owing to HF spillage), and two CRMs (JK S10 and NIST 694) were analyzed using WDXRF spectrometry to investigate the effect of chemical form of F on chemical shift. To make the pressed pellet, the samples were blended with a cellulose binder in a 1:1 weight ratio in an agate mortar and pressurized at 20 t for 6 min. The element scan mode (i.e., IQ+ method) was used to observe the change in peak positions (i.e., Bragg angle) of F-Kα that can be affected by the chemical shift.

2.4.2. Absorption/enhancement effect

The F intensities obtained from the IQ+ method in WDXRF analysis were normalized to express the X-ray intensity per unit F mass in the samples previously mentioned in Section 2.4.1. These values were used to assess the absorption/enhancement effect owing to elemental composition of the sample matrices. Furthermore, the feasibility of quantitative determination of F with a single calibration curve was assessed in a wide range of sample matrices.

2.4.3. Low intensity and development of pressed pellet with a low dilution

Conventionally, the pellet was prepared by 1:1 method that the soil sample was evenly mixed with a SpectroBlend® 44 μm cellulose binder at a 1:1 weight ratio (2 g soil to 2 g binder) and pressurized at 20 t over 6 min as same as our previous study [17]. In order to develop a method for the preparation of pressed pellet with a low dilution (for improving LOD value), several binders (boric acid, X-ray mix (lithium tetraborate), cellulose, PVA, and liquid binder) were tested with varying proportions. The mixture sample was pressurized at 20 t over 10 s after drying at room temperature for about 5 min. The calibration curve with varying F concentrations (i.e., 0, 0.2, 0.4, 0.6, 0.8, 1, and 5 g F/kg solid), prepared by the developed method in this study, was compared with that obtained from the existing 1:1 method.

2.4.4. Peak overlap effect and derivation of correction factor

By searching X-ray energy values of K and L lines of all elements, Fe, Mn, Al, Br, Se, As, Mg, Mo, Nb, P, Zr, Y, and Sr were determined to be potential interfering elements that may impact F determination. These elements have similar 2 theta values of K or L lines to that of F-Kα line (calculated using Bragg's law, n = 1, 2, and 3 with PX-1 diffraction crystal). As such, samples containing 95% of the oxide forms of the candidates with 2% F (added as CaF_2) were prepared to observe their effects on F intensities through the element scan mode (IQ+ method) [21]. To compensate the interfering effect, correction