



A rapid screening of fluorine contents in soil with a consideration of chemical binding by wavelength dispersive X-ray fluorescence spectrometry



Seulki Jeong^a, Doyoung Kim^a, Youn-Tae Kim^{a,b}, Hye-On Yoon^{a,*}

^a Seoul Center, Korea Basic Science Institute, 6-7, Incheon-ro 22-gil, Seongbuk-gu, Seoul 02855, Republic of Korea

^b Institute of Earth-Atmosphere-Astronomy, Yonsei University, 50 Yonsei-ro, Seodaemun-gu, Seoul 03722, Republic of Korea

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ABSTRACT

Wavelength dispersive X-ray fluorescence spectrometry (WD-XRF) analysis is proposed as a powerful screening tool of fluorine-contaminated soil. Calibration curves of Na-F and Ca-F were compared, which showed that the sensitivity of Na-F was higher than that of Ca-F, thus the reliable dynamic ranges differed, ranging from 0.02 to 0.5% and 0.05 to 5% for Na-F and Ca-F, respectively. The calculated limit of detection (LOD) and the limit of quantification (LOQ) values were 14.7 mg/kg and 49.1 mg/kg for Na-F, respectively, and 51.6 mg/kg and 172.1 mg/kg. A correction factor (CF) was derived to compensate for the interference from iron and was applied to samples having > 10% Fe content. The results indicate that the use of the Ca-F calibration curve does not underestimate F contents in soil samples and is suitable for selection of the samples that require a more accurate analysis in widely contaminated sites. To verify the feasibility of the developed WD-XRF analysis tool, 15 soil samples were used, with all 15 samples acceptably screened. These findings can be helpful for screening over larger F-contaminated sites when accidental spillage is occurring and useful for continuous long-term monitoring.

1. Introduction

Fluorine has received increasing attention because of its toxicity to humans and the environment [1,2]. The Korea Ministry of Environment has established the regulatory level of F at 1.5 mg/L as fluoride (F⁻) in drinking water and 400 mg/kg as F in soil [3,4]. Various analytical techniques have been developed and the ion selective electrode (ISE) and UV/Visible spectrometric method are commonly applied to determine F contents in environmental samples including water and soil samples [5–7]. X-ray fluorescence (XRF) techniques have been applied to F analysis because the conventional methods such as UV/Visible spectrometric method require a disposal process of waste liquid generated during pretreatment such as perchloric acid (HClO₄) and sodium-2-(parasulfophenylazo)-dihydroxy-3,6-naphthalene disulfonate with zirconyl acid (Zr-SPADNS solution) and a long time for treatment. XRF techniques have the advantages of being fast (10 min for analysis) and nondestructive and having green analysis characteristics [8,9]. However, the application of wavelength dispersive X-ray fluorescence (WD-XRF) in F analysis has a limited detection range because of low fluorescence yield [10,11]. Our previous study focused on improvement of the pretreatment to lower the detection limit, and the sufficient low detection limit (approximately 20 mg/kg) was obtained by reducing the

dilution factor and optimizing the binder [12]. Elements in soil, such as high iron, manganese, and cobalt contents, having their L-Lines between 0.636 (Mn L α) and 0.790 (Co L β) can lead to increased background intensity at F-K α line at 0.677 keV in WD-XRF analysis. A correction factor (CF) to compensate for Fe interference effect in F analysis should be applied considering Fe contents in samples and a CF-derived method was suggested in our previous study [13]. An et al. [12] investigated the significant changes in normalized X-ray intensity in various matrices containing F and strongly recommend that calibration curves should be generated with the type of matrix studied because an absorption or enhancement effect caused by constituents of the matrix significantly affects F intensity. Gazulla et al. [14] and Kim et al. [11] also stated that the sensitivity, represented as a slope of calibration curve, was different according to the chemicals used to make the calibration standard.

The purpose of this study was to develop a new application of WD-XRF for screening F-contaminated soil to reduce the number of samples required for determination of F concentration via conventional analytical methods. This technique allows the soil sample to be screened rapidly and accurately over a site broadly contaminated with F, consequently saving time and cost. Sample preparation to a pressed pellet developed in our previous study was applied, and calibration curves

* Corresponding author.

E-mail address: dunee@kbsi.re.kr (H.-O. Yoon).

Table 1
Instrumental conditions of WD-XRF to determine fluorine contents in soil sample.

Parameter	Setting
X-ray tube	Rhodium (Rh) target 30 kV, 100 mA
Crystal type	PX-1 crystal
Window	Be ($d^a = 75 \mu\text{m}$)
Collimator	700 μm
Beam filter	Not used
Analytical line	F-K α ($2\theta = 43.174^\circ$)
Background offset ^b	1.5078°
Analyzing time	150 s

^a d = thickness.

^b Angular difference between peak of F-K α line and background.

were generated for two chemical forms of F (Na-F and Ca-F). This paper presents the detailed methods for preparation of the calibration standards: one is the solution spiking method using sodium salt (NaF) and the other one is the reagent addition method using reagent-binding calcium (CaF₂). The interference effect also was examined, and a CF value is suggested. Fifteen soil samples were collected and used to verify the application of the developed WD-XRF analysis as a screening tool for F-contaminated soil.

2. Experiment

2.1. Instrumentation

A wavelength dispersive X-ray fluorescence spectrometer (WD-XRF, PW2404, Phillips, Netherlands) was used to determine the F contents in soil samples. Table 1 represents the detailed instrumental conditions. A rhodium target X-ray tube was operated at 30 kV and 100 mA with a thin Be window (thickness = 75 μm). The instrument was maintained in vacuum state (< 3 Pa) to prevent the emitted X-rays from being absorbed by the air, subsequently increasing the sensitivity. A collimator with a diameter of 700 μm was used to increase the count rate. The beam filter was not used to increase the fluorescence intensity because the intensity of emitted fluorescence of the light element such as F was generally low. A PX-1 crystal ($2d = 4.9759 \text{ nm}$) was used, and the Bragg angle of the F-K α line was 43.174° and the background offset was 1.5078° . The analyzing time was set to 150 s.

2.2. Chemical reagents and reference materials

Calcium fluoride (CaF₂ $\geq 98\%$, analytical grade) and sodium fluoride (NaF $\geq 98\%$, analytical grade) were purchased from Junsei Chemicals Corporation (Japan). Boric acid (5%), obtained from Sigma-Aldrich (St. Louis, MO, USA), was used. Liquid Binder[®] was purchased from Chemplex[®] (Palm City, FL, USA), which contains a polymeric ingredient (C₆H₉ON) dissolved in dichloromethane. Two certified reference materials (CRMs) were used to evaluate the accuracy of the analytical procedures tested in this study: SDC-1 (mica schist) with $600 \pm 30 \text{ mg/kg}$ of F and NIST 694 (phosphate rock) with $32,000 \pm 1000 \text{ mg/kg}$ of F bought from the United States Geological Survey (USGS) and National Institute of Standards and Technology (NIST), respectively.

2.3. Sample preparation

Several binders, Liquid binder[®] (Chemplex[®], USA) with a polymeric ingredient (C₆H₉ON) dissolved in dichloromethane (100 mg/mL) and with a boric acid (Sigma-Aldrich, USA) dissolved in ethanol, Elvacite[®] 2046 (n-butyl/isobutyl methacrylate copolymer) (PANalytical, Netherlands) dissolved in acetone (20%, w/w), PVA (Sigma-Aldrich,

USA) dissolved in deionized water (10%, w/w), were tested considering drying time. A mixed liquid binder (i.e., 2 mL of Liquid Binder[®] dissolved in 1 mL of ethanol containing 5% of boric acid) was used to prepare the pressed pellets. This mixed liquid binder was selected as the most suitable for making mechanically stable and homogeneous pellets at a low dilution among various binder combinations. With 3 mL of prepared binders, 4 g of samples and standards were sufficiently mixed until it was completely dry, then it was pressurized at 20 ton for 10 s.

A base soil that consisted of 70.2% SiO₂, 14.4% Al₂O₃, 1.98% Fe₂O₃, and 0.594% CaO and had 4.18% of ignition loss was used for calibration. The F content in the base soil (220 mg/kg) was compensated for during calculation of the F concentration. Calibration standard samples were prepared via two methods to investigate the difference in chemical form of F in soil samples. Aliquots of the base soil were soaked in an equal volume of NaF solution at various F concentrations and then dried sufficiently at room temperature for two weeks. Because CaF₂ is rarely insoluble in water ($K_{sp} = 4.0 \times 10^{-8}$), the base soil was mixed with various contents of CaF₂ powder. Final F contents for calibration were 0.02, 0.1, 0.5, 1.0, and 5.0 (for Ca-F) wt%. All calibration standards were prepared in triplicate. The limit of detection (LOD) and the limit of quantification (LOQ) were calculated using Eqs. (1)–(2), respectively.

$$\text{LOD} = 3 \times (\sigma/p) \quad (1)$$

$$\text{LOQ} = 10 \times (\sigma/p) \quad (2)$$

where σ is the standard deviation calculated from seven replicates of base soil (net counts/s), and p is the slope of the calibration curve (net counts/s per unit concentration).

2.4. Soil sampling and characterization

Soil samples ($n = 14$, sample numbers 1–14) were collected within a radius of 1 km from the site of an accidental anhydrous hydrofluoric acid spill in Gumi, Korea. Soil was sampled at a depth of 0–30 cm, air-dried at room temperature, and then the grains under 2-mm in size were thoroughly pulverized below 60- μm in an agate mortar to minimize the grain effect. Physicochemical properties of the soil samples were characterized. Soil pH was measured at a soil:water ratio of 1:5, and organic matter content was determined using the Walkley-Black method [15]. Three textural fractions, namely clay, silt, and sand, were employed to determine the soil texture using the soil texture triangle recommended by the US Department of Agriculture (USDA). The total contents of 10 major elements (i.e., Al, Ca, Fe, K, Mg, Mn, Na, P, Si, and Ti) in the soil samples were analyzed via a WD-XRF (PW2404, Phillips, Netherlands) after preparing a glass bead using Li₂B₄O₇ (soil:Li₂B₄O₇ ratio of 1:10 (w/w)). The F concentration in the soil samples was determined using the standard method of the Ministry of Korea, i.e., the UV/Visible spectrometric method [16]. Briefly, 1.0 g of soil sample was passed through a 75- μm sieve and 1.0 g of soil and 5.0 g of CaO were placed in a nickel pot in a furnace at 500 °C for 5 h and then 800 °C for 2 h. Then, 50 mL of 70% HClO₄ and 25 mL of deionized water were added to the residue obtained in the previous step, and F ions were extracted via distillation at $135 \pm 2^\circ\text{C}$. Subsequently, 50 mL of distilled sample was mixed with 10 mL sodium-2-(parasulfophenylazo)-dihydroxy-3,6-naphthalene disulfonate with zirconyl acid (Zr-SPADNS solution) in a 100 mL volumetric flask, and aliquots were analyzed using a spectrophotometer at 570 nm. A soil sample contaminated with fertilizer ($n = 1$, sample number 15) also was applied, of which the major elemental contents and F concentration in soil samples were determined as mentioned above.

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