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Rapid Screening for Uranium in Soils Using Field Portable X-Ray Fluorescence Spectrometer

A Comparative Study

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Abstract

Depleted uranium armor penetrating munitions are used on testing and training ranges leading to elevated concentrations of U in range soils. To prevent exposure on secure areas contaminated with depleted uranium (DU) hotspots, easy and rapid screening methods are needed. This study explores the feasibility of field portable X-ray fluorescence (FPXRF) spectrometry as a fast screening tool for locating hotspots of DU in the field. Direct comparisons of results were made for U concentrations in soil obtained using a FPXRF spectrometry and measurement of U using ICP-MS after acid digestion. The environmental samples included both field range contaminated soils collected at a munition testing facility and soils spiked with uranium dioxide, uranium trioxide and uranyl nitrate. Using U concentrations measured with ICP-MS from split samples, FPXRF operating procedures and conditions such as analysis time, soil moisture content, sample amount, and sample packing factors were optimized. Results showed that the FPXRF technique yielded similar U concentrations as ICPMS measurements after acid digestion in both standard soil (NIST) samples and DU contaminated range soils. In field contaminated soils, U values with FPXRF were 88.8% of the measurements with ICPMS with a significant correlation (R2: 0.98, n=8). Sample preparation affected the uranium concentration measurements made with FPXRF in the laboratory and in the field. A loose packing of the samples in the sample containers, higher sample occupancy as well as low soil moisture yielded significantly high U concentrations by 4-5%, 15-50% and 43%, respectively. The measured soil U concentrations were not affected by the variation of the sample analysis time. This study suggests that FPXRF is a promising fast screening tool for field DU hotspots as well as detection/location of penetrators in the fields that can increase the ability to rapidly and inexpensively manage DU on ranges and help ensure sustainable use of DU munitions on testing and training ranges.

Contents

Preface

This study was conducted for the U.S. Army Corps of Engineers under Project 458170, titled, "Depleted Uranium (DU) Clearance from DoD Ranges." The Grant Officer's Technical Representative was Mr. John H. Ballard, Office of the Technical Director for Installations and Operational Environments, ERDC-EL-EZT and the Technical Point of Contact was Dr. Steven L. Larson, Environmental Engineering Branch, ERDC-EL-EPE.

The work was performed by the Environmental Engineering Branch of the Environmental Processes Division, U.S. Army Engineer Research and Development Center, Environmental Laboratory (ERDC-EL). At the time of publication of this Miscellaneous Paper, Ms. Brooke Petery was Acting Branch Chief; Dr. Brandon Lafferty was Acting Division Chief; and Dr. Elizabeth Ferguson was the Technical Director for Installations and Operational Environments. The Acting Deputy Director of ERDC-EL was Dr. Justin Berman and the Acting Director was Dr. Jack Davis.

This report documents a collaborative study conducted under the sponsorship of the U.S. Army Futures Command with FY18 Congressional Program Increase Funds in PE 0603728A in the Fiscal Year (FY) 2018 Department of Defense Appropriations Act. Collaborative work was conducted by the U.S. Army Engineer Research and Development Center and Jackson State University via Cooperative Agreement W912HZ-16-2-0021.

The Commander of ERDC was COL Teresa A. Schlosser and the Director was Dr. David W. Pittman.

1 Introduction

Uranium is a naturally occurring radionuclide found in waters, soils, and sediments. Depleted uranium (DU) is a residuum of the uranium enrichment process with a majority of U as U-238 and a lower content of the fissile isotope U-235 than natural uranium U-235 is used as fuel in nuclear reactors and in the manufacture of nuclear weapons. In recent years, use of DU weapons such as DU containing penetrators have resulted in U contamination in soil and water on ranges [1]. Meanwhile, U mine tailings and ore wastes around abandoned mines are continuous sources of U in pollution of soils and groundwater. Yin et al recently reported that U release from U mine tailings increased with decreasing acidity in simulated acid rain with mechanisms of both dissolution and diffusion transport [2]. Rosen et al observed high concentrations (>30 µg/L) of U in the southeastern San Joaquin Valley, California, USA in some domestic, irrigation, and public-supply wells 3. High U in groundwater was due to the interactions of U in sediments of fluvial fans originating in the Sierra Nevada with seepage of irrigation water with high concentrations of HCO3 - that leaches U from the sediments [3]. U was also highly transported across the deep subsurface of these anthropogenic areas. Liu et al. reported that U partitioning in the depth soil profile in nearby former U mine tailings was possibly controlled by complicated interplay of leaching and precipitation cycles of U-bearing minerals [4].

Exposure to uranium can result in toxic effects in living organisms as both chemicaltoxicity and radiation danger [5]. In general, the chemical toxicity of DU, which is similar to thatof natural uranium, is far greater than DU radiological hazard with the kidney as the main targetorgan [6-7]. Normal functioning of the kidney, brain, liver, heart, and numerous other systems may be affected by DU exposure in its chemical toxicity and weakly radioactivity [8]. However, bothDU and natural U is less toxic than other heavy metals/metalloids, such as arsenic and mercury in its chemical toxicity. DU is weakly radioactive with its long half-life time of U-238 with alpha emission. Thus the radiation risk of DU is small relative to the chemical hazard [7].

The United States utilizes domestic firing ranges in several locations around the country for testing and training with DU penetrators. These firing ranges have soil that varies in soil types, depth of vadose zone and concentrations of U [9]. Therefore, DU munitions at firing range may lead to an increase in the concentration of U in the soil over time. Differentiation of the uranium residues from firing activities and soils with elevated levels of uranium from clean or low level uranium materials is critical for reducing both the environmental and wildlife risks associated with U on these ranges.

Removal of uranium items, residues from munitions use and soils containing high concentrations of U can reduce the risks posed by DU use in munitions. Limiting the amount of U present on ranges is a means of reducing the potential for contamination of ground water and surface water while also reducing exposure of range personnel and wildlife on these ranges. Personnel at testing and training ranges follow a policy to limit exposure to radioactive material known as ALARA (as low as reasonably achievable). ALARA policy is a means of reducing the risks associated with the presence of DU on firing ranges and workers in general in areas where radioactive materials are present [10]. Since the chemical toxicity of DU is much greater than its radiological danger due to its weakly radioactivity as discussed early [7], it seems more proper to use the FPXRF spectrometer to detect its presence than radiation dosimetry in the ranges.

U quickly oxidizes in the environment [9]. U-238 is the primary component of DU metal. When present at high concentrations, elevated uranium levels in soils can be easily identified by measuring elevated ionizing radiation from metals, oxides and soils. Using standard field NaI counters, U levels in highly contaminated soils can be identified in the field. When DU concentrations in soils drop below levels for which radiation is no longer detected by a field portable radiation sensing systems, laboratory techniques such as ICP-MS can be used to identify U concentrations in soils.

Inductively coupled plasma optical emission/ mass spectrometer (ICP-OES/MS) are two techniques used to determine U concentrations in environmental samples after acid digestion preparation [10-11]. These digestions and analyses take place in a laboratory setting with time consuming sample transportation, digestion and analyses. The concentration reporting is often not timely. This method of analysis could be expensive and the instrument is high maintenance [11]. Multiple analyses and dilutions of sample extracts are often required in order to accurately predict soil uranium concentrations using these techniques because there is also a narrow optimum operation range of concentrations in solutions for ICP-OES and even narrower range for ICP-MS.

In order to reduce the limitations inherited to ICPMS/ICPOES for soil U determination, a field portable X-ray fluorescence spectrometer (FPXRF) may be used when soils contain levels of uranium below those readily measured using scintillation detectors in the field. A FPXRF spectrometer can be used to determine elements in rocks, soils and other environmental samples. Comparative studies showed FPXRF spectrometry could be used to measure the concentrations of most heavy metals and trace elements in environmental samples [11-15]. These studies determined the detection limits, accuracies and precisions of multiple element concentration determinations using a handheld XRF spectrometer. Because the transparencies of many solid materials to Xrays is high, use of FPXRF spectrometry is a means of minimizing the matrix effects through measuring the characteristic emissions of analytes following excitation by X-rays. Since the technique is used to directly measure the solid samples without preparation, this makes FPXRF useful tool for measuring contaminants such as uranium in the field in order to get rapid determinations of soil concentrations. FPXRF spectroscopy has been shown to rapidly produce metal concentration information from environmental matrices with good accuracy and precision among measurements [11-12]. Optimum operation temperature for an FPXRF is at -10˚C to 50˚C and these temperatures are consistent conditions at which field measurement activities take place.FPXRF may be a fast, nondestructive and low-cost tool for fast screening the hotspots of heavy metals in the fields [11-12]. However, as a disadvantage FPXRF generated elevated detection limits of most trace elements when compared with ICP-OES [12]. In the case of DU in range soils, the field detection of concentrations of U during range management activities are significantly higher than the concentrations of general environmental interest. DU on firing ranges is known to be present. Therefore, DU management for sustainable range use requires rapid determination of U concentrations in the concentration range below that achievable using scintillation counting but above that for which ICP techniques are required.

No DU firing range-specific studies have been done on the optimization of FPXRF in measuring U in environmental samples. The use of FPXRF for

DU management on firing ranges requires the comparison of field portable XRF concentration determinations with methods such as ICP-OES or ICPMS. The objectives of this study are (1) To determine the detection limits, accuracy and precision of FPXRF for U in environmental samples; (2) To optimize the measurement protocol of U using FPXRF in the laboratory by varying sample analysis time, sample cup occupancy, and moisture content; and (3) To evaluate the feasibility of FPXRF for rapid screening U hotspots at a DU firing range.

Highlights are:

- Field Portable X-Ray Fluorescence (FPXRF) spectrometry was employed to determine uranium concentration in both field contaminated samples and laboratory soils spiked with UO2, UO3, and UO2(NO3)2 .
- The measurement process was optimized using comparisons with inductively coupled plasma mass spectrometry (ICPMS) through sample preparation techniques adjusted.
- Correlation between FPXRF and ICPMS results varied with changes in compaction and sample occupancy.
- Variations in sample analysis time did not show a significant shift on U measurements; however, soil moisture strongly affected U measurements.

2 Materials and Methods

2.1 DU Soil Samples from a Shooting Range

Yuma Proving Ground (YPG) is a United States Army proving ground and one of the largest military installations in the world. It is located in southwestern La Paz County and western Yuma County in southwestern Arizona, U.S. It encompasses 1,307.8 square miles (3,387.2 km^2) in the northwestern Sonoran Desert. DU soil samples were collected from four areas in the Yuma Proving Grounds. The contaminated samples were sieved into two different particles sizes <2 mm and 1-250 µm. For field testing of FPXRF, representative sites were selected based on locations of penetrators below ground and soils around the penetrators.

2.2 Spiked Soil Samples

Three soil samples were spiked with uranium dioxide, uranyl nitrate, and uranium trioxide. The original soil samples were taken from Mississippi Delta. The spiked U soils were cultivated for phytoremediation study. These uranium samples after a number of growing seasons of plants were used to optimize the measurement protocols for soil sample packing and occupancy of sample cups as well as soil moisture effects.

2.3 Standard Soils/Reference Soils

The two certified reference soil samples were used for investigating the accuracy, precision, and repeatability of the FPXRF method. They were NIST SRM 2710, Montana I soil and NIST SRM 2711a Montana II soil. Five to eight replicates were run on both soils.

2.4 Reagents

All chemical reagents are the trace-metal grade. The concentrated nitric acid and 30% H_2O_2 were purchased from Fisher Scientific for sample digestion and matrix-matching of calibration and quality control standards. Deionized water was used for the dilution of samples and standards. Deionized water with Nano-pure infinity ultrapure water systems was used (Barnstead International, Dubuque, IA).

2.5 Soil Digestion for ICP MS

Approximately 1.00 g of soil samples was ground and dissolved using acid digestion (EPA method 3050 B). Field soil samples were divided into two particle size ranges <2 mm and 2- 250 µm. For acid digestion of the samples, a hot block (Environmental Express) was employed.

A mixture of H_2O_2/HNO_3 was used when performing extractions. The samples were heated to 95±5°C to reflux for 10 to 15 minutes without boiling.

2.6 Soil Preparation for FPXRF in laboratory

The contaminated samples were ground into a fine powder and loaded into a 2.5-cm diameter disposable polyethylene micro X-ray cups (SPEX IND Inc.) and covered with a transparent polypropylene film and labeled. The samples were measured without further preparation after being lightly tapped on a solid surface to slightly compact the soil samples. Two portable handheld XRF devices, Bruker (S1 TITAN) (Billerica, MA) and Niton XL2 (Thermo Scientific) were used to determine the effects of packing on U readings in soils. In addition, both effects of sample occupancy and measurement time were studied. The sample occupancy in the sample cups included 10, 20, 40, 60, 80 and 100% of the cup volume. The measurement time were ranged from 15 sec, 30 sec, 60 sec to 120 sec.

The moisture effects on FPXRF measurements in soil samples were conducted with the formerly spiked soil samples after a number growing seasons of plants for phytoremediation. FPXRF readings were compared among the air-dried samples with hygroscopic moisture in range of 2-4% and the complete oven dried soils. The second moisture experiments were employed with the wet soil samples with the moisture in the range of 1-50%.

2.7 Direct Measurement of U in Soils and DU Penetrators in Range Fields with FPXRF

A plastic bag was covered in the front of FPXRF spectrometer for field U measurements. U was determined by direct shooting field soil spots, DU penetrators, and surrounding soils around penetrators. Often three U reading were set and the average of concentrations of U and other elements in mg/kg were presented with standard deviations on the screen.

3 Results and Discussion

3.1 Detection limits, Precision and Accuracy

High quality of pure quartz sands were washed with diluted acid overnight and washed with deionized water. A series of blanks (quartz sands) were run to determine the limit of detection (LOD) and limits of quantification (LOQ) [12]. The detection limit was expressed as the lowest analyte concentration that can be reliably measured using a specific instrument [11-12, 16-17]. In order to calculate the LOD, the standard deviation of blank values was multiplied by three, followed by the division of this value by the slope of the calibration curve. Similarly, the LOQ was calculated by multiplying the standard deviation by ten and then dividing this value by the slope of the calibration curve [18]. The LOD values of U calculated for FPXRF were 1.312 mg/kg and the LOQ was 13.12 mg/kg. In general, the values of FPXRF's detection limits were higher than those with ICP MS. However, since the LOD was traditionally determined with the blank samples and all natural soils contained some trace amount of natural uranium, the purified quartz sands were used in the current study to be a proxy to soil matrix to determine the LOD and LOQ.

The accuracy was determined by testing two certified reference soil standards. Two certified standard reference soils, NIST SRM 2710 and NIST SRM 2711a soils were run with ten replicates to determine accuracy and precision of the FPXRF spectrometer. The reference soils used for FPXRF for soils 2710 and 2711a had 30.02 ± 2.09 and 8.17 ± 1.12 mg/kg, respectively (Fig. 1). The relative errors between FPXRF measured values and the certificated values were 120% and 270% for standard soils 2710 and 2711a, respectively. This indicates that FPXRF may provide reasonable recovery for the soil samples with high U concentration than those samples with U concentrations near to the detection limit.

The reproducibility of FPXRF measurements was examined with ten measurements of the two standard soil samples. Relative errors measured as coefficient of variation (CV%) among ten measurements for U were shown in Fig. 2. The CV% for Reference Soil sample 2710 and 2711a was 6.96% and 13.69%, respectively.

FPXRF was reported to provide reasonable recovery for environmental contaminated samples with Hg, Zn and Cu at certain high concentrations

[11-12]. Kalnicky and Singhvi reported the detection limits of 22 major and trace elements in a NIST standard reference sample instead of the blank sample without these elements with XRF [19]. The values of detection limits determined with a representative soil sample were in general larger than the values with a blank sample (quartz sand) in the current study. Since any background soils still contain a significant amount of trace elements and heavy metals, the real soil sample might not be ideal for determining the detection limits as defined as blanks.

3.2 FPXRF measurements of U in DU contaminated soils

Uranium concentrations in the firing range soil samples were measured directly with FPXRF and compared with those with ICP-MS after acid digestion (Fig.3). FPXRF gave a reasonable measurement of U at levels between 500 to 8000 mg/kg. The average relative errors between the values of FPXRF and ICPMS was 17% ±16.9%. FPXRF values were relatively lower than those with ICPMS. A significant dilution factor was used for dilution of digested solutions for all samples before ICPMS measurements due to its narrow linear range of concentrations. This might contribute to the overestimation of actual U concentrations in the contaminated soils with ICPMS.

Formally spiked U contaminated soils with various UO_2, UO_3 and uranyl were measured with both FPXRF directly and ICPMS after acid digestion. The U spiked soils were used for phytoremediation study and soils were further used in this section for FPXRF measurement. FPXRF gave a good agreement with the values with ICPMS. For soils with UO2 and uranyl, the relative errors between values of FPXRF and ICPMS were -8.8% and -16.5%, respectively, but that for soil with UO_3 has a higher recovery (31%). The high relative errors might be related to the soil spatial variation as sampled for ICPMS as well as for FPXRF.

3.3 Effects of Sample Preparation on FPXRF Measurements

Packing of Samples. Samples were analyzed by two portable handheld FPXRF devices, Bruker and Niton without packing the sample. Analysis time for both instruments were set to 1:30 min for a reading. Two different FPXRF instruments were used to check for consistent readings among FPXRF devices, detection of U species and replicability of readings. Three different soil samples spiked with a U species (UO_2, UO_3 and Uranyl) were used. The three U species chosen were uranium dioxide, uranyl nitrate, and uranium trioxide. Similar measurement of U were found with two FPXRF instruments with packing of the samples. Samples were packed in the X-ray cups, covered with transparent polypropylene film. All settings for the instruments were the same as described above. There is a significant difference in measurements between samples that were packed in the sample cup and samples without packing. The packed soil samples had significantly higher readings than the unpacked samples as measured by two FPXRF with a large standard deviation with Bruker (Fig. 4). This was consistent between two different FPXRF devices. Uranium Trioxide concentrations were much higher with both FPXRF devices compared to ICP-MS concentrations (Fig. 4).

Sample Occupancy. The three spiked soil samples, uranium dioxide, uranyl nitrate, uranium trioxide, were loaded in individual sample cups from a least amount possible (0.50 g, 10% of the full cup volume) to full capacity (5.0 g, 100% of the cup volume) of the cups. As shown in Fig. 5 the U reading increased with the sample amount in the sample container, especially in low occupancy from 10% to 20%. When the sample occupancy increased up to 100% of the sample containers, the maximum U reading was generated. Thus, in the laboratory measurement, use of a full sample container of the samples is most effective.

Effects of FPXRF Analysis Time. Field soil samples were used to understand the impact of analysis time on uranium measurements in the soil. A series of samples were analyzed using 15 sec, 30 sec, 60 sec and 120 sec collection times with the Bruker FPXRF instrument (Fig. 6). There was not a significant difference in U measurements for samples when increasing the analysis time. Thus 15 sec provided useful and stable U reading from range samples, making field portable XRF measurements a rapid tool of obtaining U in range soils. For the increase of the live of X-ray tube, 15 sec measurements were recommended. However, Kilbride et al. reported that the XRF analyzer performance has been shown to improve with increased analysis time for metals such as Cu, Mn, and Pd [14]. Our previous study by McComb et al. stated that changing time measurement did not improve detection limits of the samples [12]. The current study indicates an independence on quantitation effectiveness with analysis time for these U contaminated range soils.

Moisture Effects on FPXRF Measurements. Significant effects of soil moisture on U measurement with FPXRF were noted. As moisture content increased, U values decreased as compared to ICPMS significantly due to less mass of soil present (Fig. 7). But a hygroscopic moisture shift (2-4%) showed no significant difference in uranium concentrations in soil samples. Kalnicky and Sanghvi stated that soil moisture strongly affected soil mass and that directly affected the apparent concentration of the sample due to the sample dilution [19].

3.4 Field application of FPXRF

On the same testing site, a DU penetrator, tungsten penetrator and the surrounding soils were directly measured for uranium concentrations. Both penetrators were discovered in close distance to each other. The DU penetrators had significantly higher uranium concentrations (37,000 ±342 mg/kg) than tungsten penetrators (201± 36 mg/kg). The surrounding soils near W and U penetrators showed the similar trend. The soil surrounding the DU penetrator contained U (301 ± 9 mg/kg) and the soil surrounding the tungsten penetrator did not detect the presence of U. This indicates that the FPXRF may be used in field for the fast screening the presence of DU penetrators. Actually the detection of DU with FPXRF was a useful tool to differentiate DU penetrators from non-DU penetrators.

4 Conclusion

A X-ray fluorescence spectrometer (XRF) requires little to no preparation for solid samples. It is a quick nondestructive analysis. The method minimizes production of hazardous waste. Samples are measured with FPXRF as rapid as 15secs per sample. FPXRF is durable and portable in the field and is cost effective. This study demonstrates FPXRF as a potential instrument for accurate and rapid screening uranium hotspots on ranges. The data shows that packing of the sample in the sample container significantly increased uranium concentrations for FPXRF instruments at laboratory. Sample container occupancy did affect measurements with FPXRF devices, but measurements correlated more closely with ICP-MS measurements when the sample container was at full capacity. Time analysis did not make a significant difference in U measurement correlation with ICPMS. Soil moisture strongly affected metal measurement by decreasing U concentrations as the moist level increased. As a tool for operating DU testing and training ranges sustainably, FPXRF has been shown to be effective to locate/measure/detect DU at levels of interest to range operators.

References

[1] Bleise, A.; Danesi, P.R.; Burkart, W. Properties, use and health effects of depleted uranium (DU): a general overview. *J. Environ. Radio.* 2003. 364, 93-112.

[2] Yin, M. ; Sun, J.; Chen, Y.; Wang, J.; Shang, J.; Belshaw, N.; Shen, C.; Lui, J.; Li, H.; Linghu, W.; Xiao, T.; Dong, X.; Song, G,; Xiao, E.; Chen,D. Mechanism of uranium release from uranium mill tailings under long-term exposure to simulated acid rain: Geochemical evidence and environmental implication. *Environ. Pollut.* 2019. 244. 174- 181.

[3] Rosen, M.R.; Burrow, K.R.; Fram, M.S.; Anthropogenic and geologic causes of anomalously high uranium concentrations in groundwater used for drinking water supply in the southeastern San Joaquin Valley, CA. *J. Hydrol.* 2019. 577. 124009.

[4] Lui, J.; Luo, X.; Wang, J.; Xiao, T.; Yin, M.; Belshaw, N.S.; Lippold, H.; Kong, L.; Xiao, E.; Bao, Z.; Li, N.; Chen, Y.; Linhu, W. Provenance of uranium in a sediment cofe from a natural reservoir, South China: Application of Pb stable isotope analysis. Chemosphere 2018. 193, 1172-1180.

[5] Adriano, D.C. *Trace elements in terrestrial environments: Biogeochemistry, bioavailability, and risks of metals,* (2nd ed.), Springer: New York, 2001.

[6] The Royal Society. The health hazards of depleted uranium munitions: Part II; The Royal Society: London, 2002.

[7] Miller, A.C.; Stewart, M.; Brooks, K.; Shi, L.; Page, N. Depleted uranium-catalyzed oxidative DNA damage: absence of significant alpha particle decay. *J. Inorgan. Biochem.* 2002. 91(1). 246-252.

[8] Craft, E.S.; Abu-Qare, A.W.; Flaherty, M.M.; Garofolo, M.C.; Rincavage, H.L.; Abou-Doria, M.B.; Depleted and natural uranium: Chemistry and oxicological effects. *J. Toxicol. Env. Health B.* 2004. 7 (4), 297-317.

[9] Etheridge, J.A.; Monts. D.L., Su. Y.; Waggoner, C.A. Sensor systems for precise location of depleted uranium in soil and for enhancing the recovery of both zero valence and uranium oxides. Waste Management Conference, Tucson, AS, United States. 2007.

[10] Bryan, J.C. *Introduction to Nuclear Science*, (2nd ed.). CRC Press: Boca Raton, FL. 2013.

[11] Kelly, j.; Han, F.X.; Su, Y.; Philips, V.; Monts, D.L.; Pichardo, S.T.; Rapid determination of mercury in contaminated soil and plant samples using Hg Direct Analysis without sample preparation. A comparative study. *Water Air Soil Pollut.* 2012. 223, 2361-2371.

[12] McComb, J. Q.; Rogers, C.; Han, F. X.; Tchounwou, P. B. Rapid Screening of Heavy Metals and Trace Elements in Environmental Samples Using Portable X-Ray Fluorescence Spectrometer, A Comparative Study. *Water, Air, Soil Pollut.* 2014. 225, 2169-2179

[13] Hannaker, P.; Haukka, M.; Sen, S.K. Comparative study of ICP-AES and XRF analysis of major and minor constituents on geological materials. *Chem. Geol.* 1984, 42, 319–324.

[14] Kilbride; C.; Poole, J.; Hutchings, T.R. A comparison of Cu, Pb, As, Cd, Zn, Fe, Ni and Mn determined by acid extraction/ICP–OES and ex situ field portable X-ray fluorescence analyses. *Environ. Pollut.* 2006. 143, 16–23.

[15] Marina, M. A.; Lopez, B. Determination of phosphorus in raw materials for ceramics: Comparison between X-ray fluorescence spectrometry and inductively coupled plasma-atomic emission spectrometry. *Analytica Chimica Acta.* 2001. 32, 157–163.

[16] MacDougall, D. Guidelines for data acquisition and data quality evaluation in environmental chemistry. *Anal. Chem.* 1980. 52, 2242-2249.

[17] Han, F.X.; Patterson, W.D.; Xia, Y.; Sridhar, B.B.M.; Y. Su. Rapid determination of mercury in plant and soil samples using inductively coupled plasma atomic emission spectroscopy, a comparative study. *Water Air Soil Pollut.* 2006. 170, 161-171.

[18] Skoog, D. A.; Holler, F. J.; Crouch, S. R. *Principles of instrumental analysis.* Thomson Brooks/Cole: Belmont, CA. 2007.

[19] Kalnicky, D.J.; Singhvi, R. Field portable XRF analysis of environmental samples. *J. Hazard. Mater.* 2001. 83, 93–122.

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14. ABSTRACT

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