Optimization of time for portable X-ray fluorescence analysis across different substrates

Vitalii Yatsenko[1], Oksana Datsko[1], Andrii Butenko[1*] ,
Ihor Kovalenko[1], Olha Bakumenko[1]

[1] Sumy National Agrarian University, 160, H. Kondratieva Str., Sumy, 40021, Ukraine
* Corresponding author's e-mail: andb201727@ukr.net

ABSTRACT

The soil environment plays a pivotal role in ecosystem sustainability, but industrialization and intensive agriculture contribute to heavy metal contamination. Portable X-ray fluorescence (pXRF) has emerged as an efficient tool for detecting heavy metal concentrations in soils and sands. This study evaluates the influence of measurement duration on the accuracy of pXRF results across soil and sand substrates. Measurements were performed using a Thermo Scientific Niton XL2 device on meticulously prepared samples with durations ranging from 5 to 220 s. Results demonstrated that optimal analysis times varied between substrates: 180–220 s for soils and 140 s for sands yielded stable and accurate data. Prolonged durations improved the statistical reliability of concentrations, particularly for trace elements like nickel and arsenic, which required extended times for detection. Findings emphasize the importance of calibrating analysis duration to enhance pXRF accuracy and applicability in environmental and agricultural research.

Keywords: heavy metals, sand, soil, pXRF, trace elements, contamination, ecosystem.

INTRODUCTION

The first methods for determining the content of heavy metals in soil were developed in the mid-20th century, driven by the growing need to monitor soil pollution. The primary methods included gravimetric analysis, one of the oldest chemical techniques, which involved precipitating heavy metals from a solution as insoluble compounds (e.g., sulfates or hydroxides). Soil samples were treated with acids to extract metals, which were then precipitated as compounds. The precipitate was dried and weighed to determine metal concentrations. Titrimetric analysis used reactions of metals with specific reagents in solution to determine their concentration; this method was relatively accessible but had limited sensitivity and specificity. Flame photometry measured the intensity of light emitted by metal atoms in a flame and was used primarily for alkali and alkaline earth metals. Visible and ultraviolet spectroscopy was based on detecting light absorption or emission by metal ions in solution. Polarography, an electrochemical method, determined metal concentrations by measuring the current generated during the electrolytic reduction of metal ions on a mercury electrode. Chemical extraction involved treating soil with acids (such as nitric or hydrochloric acid) to extract heavy metals, which were subsequently analyzed by other methods. These methods relied on classical analytical approaches that were refined over time. While they had their limitations, they laid the groundwork for modern analytical technologies such as atomic absorption spectroscopy, inductively coupled plasma spectrometry, and mass spectrometry. Contemporary methods provide rapid and accurate results, but historical approaches remain important for understanding the development of analytical chemistry [Environmental Technology Verification Report, 1998].

One of the emerging technologies that currently provides the best option for the rapid determination of heavy metal content is energy-dispersive X-ray fluorescence (ED-XRF), particularly in the form of portable instruments for portable X-ray fluorescence (pXRF). Such devices are

commonly used for determining metal content in metallic objects [Weindorf et al., 2014], the geochemical origin of minerals [Richardson et al., 1995], and soil analysis [Marguí et al., 2005; Dong et al., 2015]. Traditionally, ED-XRF has been employed as a fast and efficient method for analyzing trace and major elements in soil samples [Queralt et al., 2005; Munro et al., 2008]. Energy-dispersive X-ray fluorescence has also proven valuable in studies of the elemental composition of plants [Anjos et al., 2002; Tighe & Forster, 2014] and in identifying potentially hazardous trace metals in plants [Handson & Shelley, 1993; Paltridge et al., 2012].

Over the past 10 years, advancements in instrument components such as X-ray tubes, silicon detectors, and improvements in quantitative evaluation algorithms have established portable X-ray fluorescence spectrometers (pXRF) as a fast and cost-effective alternative to expensive and labor-intensive chemical analyses [Harvey et al., 2016]. The portable pXRF method is characterized by its simplicity in sample preparation, primarily requiring sample homogenization, and by its rapid multi-element analysis across a wide range of concentrations. This makes the procedure fast, affordable, and suitable for analyzing a large number of samples. The device can be used both in field and laboratory conditions, providing researchers with optimal results [Bernick et al., 1995; Hryhoriv et al., 2024].

Many studies highlight the advantages of pXRF, particularly for applications in agriculture and environmental research [Chimidza et al., 2001; Bako et al., 2005; McLaren et al., 2012]. However, the reliability of the data can be questionable, especially without properly prepared samples. Comparing data obtained using the pXRF method with traditional laboratory techniques such as atomic absorption spectroscopy, inductively coupled plasma spectrometry, and mass spectrometry, X-ray fluorescence spectrometry can sometimes lead to inaccurate assessments.

For this reason, pXRF users are encouraged to develop their own calibrations tailored to their specific needs. Factory settings often result in significant errors, and comparisons with reference methods have shown considerable deviations in results [Kenn et al., 2011; Hall et al., 2014; Piercey et al., 2014]. Experimental studies comparing data obtained via pXRF and laboratory methods have revealed discrepancies. Based on these findings, it is recommended to calibrate the device to align its performance more closely with laboratory analyses [Shackley 2012; Speakman & Shackley, 2013].

Measurement time also significantly affects the accuracy of pXRF results. The device allows for a wide range of measurement durations; for example, the analysis time ranged from 60 to 300 seconds, which greatly influenced the correctness of the obtained data [Forster & Grave, 2012; Frahm, 2013; Dong et al., 2015]. Studies by Shackley [2011] and Forster & Grave [2012] examined the effect of measurement duration on the accuracy of pXRF analysis in the study of mineral rocks. They found that the most accurate results were achieved with a measurement time of 300 s.

In general, the principles described by Forster & Grave [2012] are not fundamentally new. During analysis, the sample is irradiated with X-rays, which eject electrons from the inner shells of atoms. This causes electrons from outer shells to transition to the vacancies, accompanied by the emission of X-ray photons with energies characteristic of each element. The energy and intensity of this radiation are recorded by the detector, and based on the resulting spectrum, the elements present in the sample and their quantities are determined [Hughes, 1998; Shackley, 2010; Kolisnyk et al., 2024].

Theoretically, the instrument's algorithms convert fluorescence intensity into the concentration of substances in the sample. However, in practice, the relationship between fluorescence intensity and concentration is complicated by the sample matrix, preparation method, and measurement conditions [Stiko & Zawisza, 2012; Datsko et al., 2024].

Time, as one of the measurement conditions, is associated with the intensity of X-ray radiation, but it does not alter the relationship between intensity and concentration. As a result, time has minimal impact on the accuracy of data obtained via XRF; instead, the instrument's accuracy is determined by its calibrations [Angeles-Chavez et al., 2012; Towett et al., 2015]. Studies have shown that increasing analysis time does indeed reduce error (improving statistical reliability), which is inherent at every concentration level. Prolonged measurement time increases the likelihood of obtaining consistent results across multiple measurements of the same sample [Newlander et al., 2015; Rouillon et al., 2016; Voytovyk et al., 2024].

Overall, technological progress continues to enhance methods for measuring heavy metals in various environments. However, even the most advanced techniques, including instruments

based on these methods, require further refinement and calibration for specific tasks. Measurement time remains the simplest adjustable parameter to achieve reliable results.

MATERIAL AND METHODS

Equipment

The study was conducted using a portable X-ray fluorescence analyzer (pXRF), Thermo Scientific Niton XL2. The device was calibrated prior to analysis, and the readings on the standard sample corresponded to the data provided by the manufacturer.

Samples and sample preparation

The study was carried out on two types of substrates: soil and sand. Samples were meticulously prepared by drying in an oven at 100°C for 5 hours, grinding, and sieving through a mesh with 1 mm openings. A composite sample for analysis was collected following standard methodology.

Analysis duration

For each substrate and measurement range (high range and low range), a series of measurements was performed with varying analysis durations: 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, and 110 s. Each measurement duration was repeated three times. A detailed experimental scheme is provided in Table 1.

Procedure

The device was placed on a stable surface and calibrated. Prepared substrate samples (17 g each) were placed in sample holders. For each sample, three measurements were performed for each analysis duration within the corresponding analysis range.

Statistical analysis

Descriptive statistics were made at Statistica 10.0 (StatSoft Inc., Tulsa, USA).

RESULTS AND DISCUSSION

The graphs in Figure 1 illustrate the changes in the concentrations of chemical elements determined by the studied device, depending on the analysis time in soil. The concentration of Ba (Fig. 1a) starts at approximately 500 ppm and shows a gradual decrease until 100 s. After that, certain fluctuations are observed, particularly a significant decline at 180 s. However, at 200 and 220 s, the data stabilize. Zirconium, on the other hand, exhibits stable concentration throughout the experiment: starting at 20 s, the value remains at around 600 ppm with minimal deviation, except for a slight anomaly during the analysis at 120 s. The concentration of Mn has distinct features: the device cannot determine its concentration for an analysis time of only 10 s, and the first data appear only after 20 s. Between 40 and 100 s, the Mn concentration values are unstable, but they stabilize beginning from 120 s of the experiment.

Meanwhile, the measurement error is highest during the shortest analysis times and gradually decreases as the duration of the study increases (Fig. 1b). For instance, according to Duncan's criterion, the values obtained starting from 180 seconds and beyond do not statistically differ from one another. A similar situation is observed for manganese: the measurement error data show no significant statistical difference starting from 80 s of analysis. For zirconium, the device's error begins to significantly decrease from an analysis duration of 100 s.

Regarding the data obtained for strontium, its values stabilize beginning from 20 s of the experiment (Fig. 1c). A similar situation is observed for

Table 1. Experimental procedure

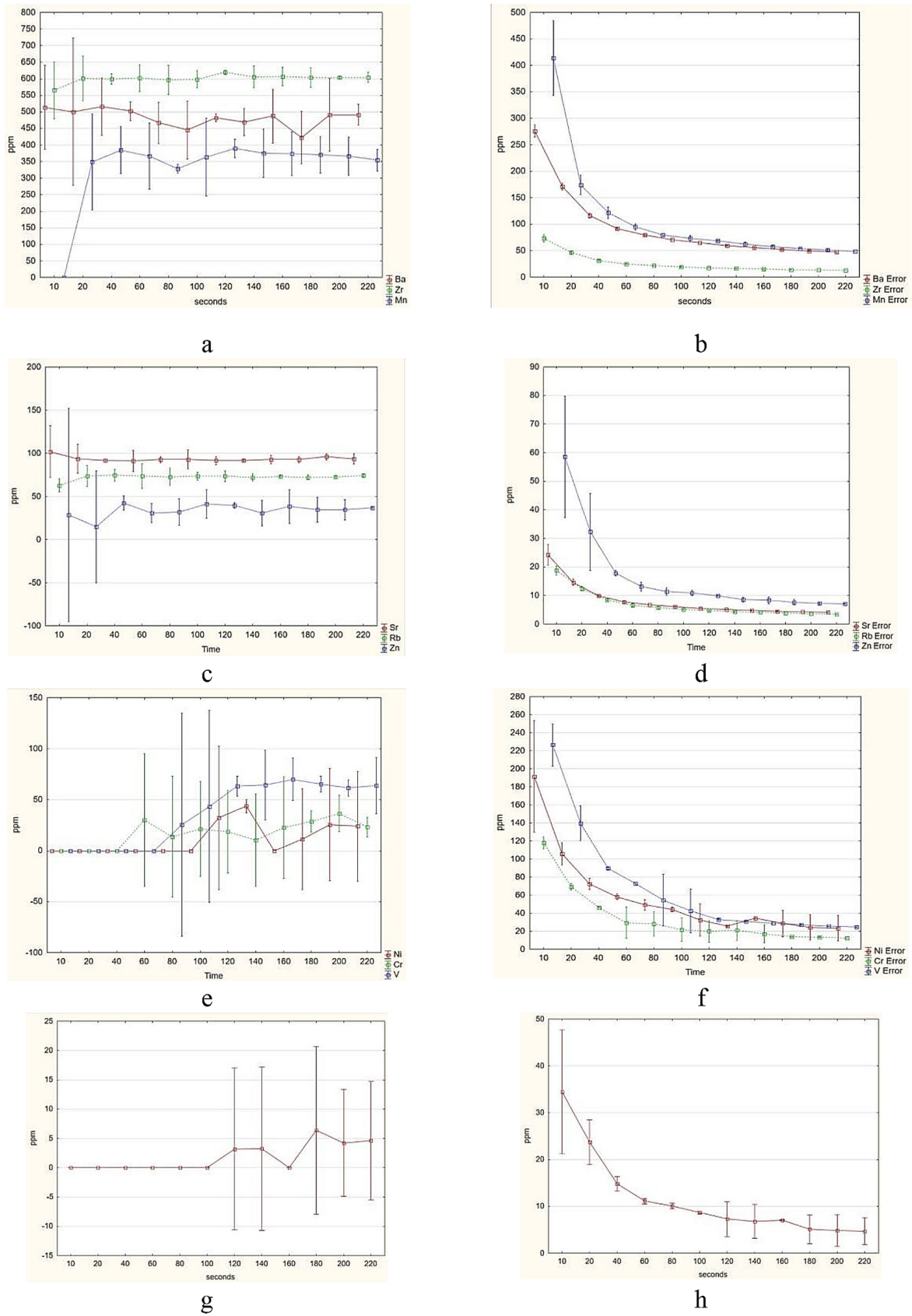| Substrate		Analysis range	Analysis duration, s
Soil		High	5, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110
		Low	5, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110
Total for soil			10, 20, 40, 60, 80, 100, 120, 140, 160, 180, 200, 220
Sand		High	5, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110
		Low	5, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110
Total for sand			10, 20, 40, 60, 80, 100, 120, 140, 160, 180, 200, 220

Figure 1. Average values and errors of chemical element concentrations in soil, where: (a) represents barium, zirconium, and manganese; (b) corresponds to the device errors for barium, zirconium, and manganese; (c) includes strontium, rubidium, and zinc; (d) refers to the device errors for strontium, rubidium, and zinc; (e) shows nickel, chromium, and vanadium; (f) represents the device errors for strontium, rubidium, and zinc; (g) indicates arsenic; and (h) corresponds to the device error for arsenic

rubidium, where the data stabilize starting from 20 s of the experiment. However, for zinc, it is worth noting that the data fluctuate, and stable values are obtained starting from an experiment duration of 140 s.

The error for these elements (Fig. 1d), particularly for strontium, ceases to change significantly beginning from an experiment duration of 80 s, while for rubidium, this occurs at 140 s. For zinc, the error stops significantly decreasing starting from 40 s of analysis duration. Special attention should be paid to the elements depicted in Figures 1e and 1g. It is worth noting that measurements for these elements can only be obtained after prolonged analysis. In particular, chromium content determination begins at an analysis duration of 60 s, but the data obtained show significant inaccuracies. At an analysis duration of 80 s or more, the data become more stable. Nickel data were first obtained at an experiment duration of 120 s; however, as in the case of chromium, the values showed considerable variability. Stable measurements were achieved at analysis durations of 200 and 220 s. The first results for vanadium were obtained at an analysis duration of 80 s, but stable data with minimal variation were recorded starting from the 120 s experiment. Arsenic data were first obtained at an analysis duration of 120 s, but stable values for this element were observed only at analysis durations of 200 and 220 s.

Regarding the device errors for these elements (Figs. 1f and 1h), the smallest fluctuations in error for nickel, chromium, vanadium, and arsenic were recorded at an analysis duration of 180 s or more. However, according to Duncan's criterion, a significant reduction in error for nickel was noted starting at 60 s. For chromium, this reduction occurred at 40 s, and for vanadium, at 120 s of the experiment.

Figure 2 presents data obtained from sand analysis. Since the concentrations of chemical elements in sand are generally lower, the detection time and measurement errors are also affected.

In particular, the amount of barium in sand is around 300 ppm, and the most stable values were obtained at an analysis duration of 100 s or more. It is worth noting that at 10 s, this element was not detected at all (Fig. 2a). The zirconium content in sand is also significantly lower, but, as with soil, stable and nearly identical values were obtained at an analysis duration of 20 s or more.

In terms of measurement errors, the lowest standard deviations for barium and zirconium were achieved at analysis durations exceeding 120 s (Fig. 2b). A distinctive feature observed during the sand analysis was the detection of antimony and tin, which were not found in the soil (Fig. 2c). Antimony was detected at 60 s of analysis, with stable values and minor fluctuations starting from 160 s. Tin was first identified at 20 s, but the device failed to detect it at 40 and 60 s. From 80 s onward, tin was consistently detected, with the most stable measurements recorded from 140 s. A similar situation occurred with vanadium, which was first detected at 100 s. However, at 140 and 160 s, the element was not identified, reappearing at 180 s of analysis.

Regarding device errors, the smallest deviations for antimony, tin, and vanadium were observed after 100 s of analysis (Fig. 1d). For strontium in sand, the first reliable concentration was obtained at 80 s, with minimal changes afterward (Fig. 1e). Rubidium was initially detected at 20 s, with its concentration gradually increasing until 140 s. The most accurate data were achieved at 200 and 220 s. Arsenic concentrations in sand were unstable: detected at 20 and 40 s, but not at 60 s. However, from 80 s onward, arsenic concentrations were consistently measured, with the most stable values achieved starting at 140 s.

Device error margins for strontium, rubidium, and arsenic are shown in Figure 2f. For strontium and rubidium, no statistically significant differences in deviations were observed from 40 s onward. The standard error for arsenic varied significantly, but changes became statistically insignificant from 80 s of analysis.

In general, such studies are highly relevant as results obtained with different devices and varying analysis durations can differ significantly [Brand & Brand, 2014; Hangen et al., 2019]. Similar research on optimal analysis duration has been conducted, but findings remain contradictory. Brazilian scientists, for instance, claim that pXRF analysis in field conditions can be conducted in just 2 s without compromising accuracy for detecting heavy metals in soil, providing rapid and reliable assessments [Tavares et al., 2023].

Li et al. [2022] investigated the efficiency of X-ray fluorescence spectroscopy for analyzing soil composition in laboratory and field conditions, assessing the effects of sample preparation, moisture content, and analysis duration. Their results showed that these factors significantly affect accuracy, with 60 s yielding the best results. Moisture impacted only finely ground samples.
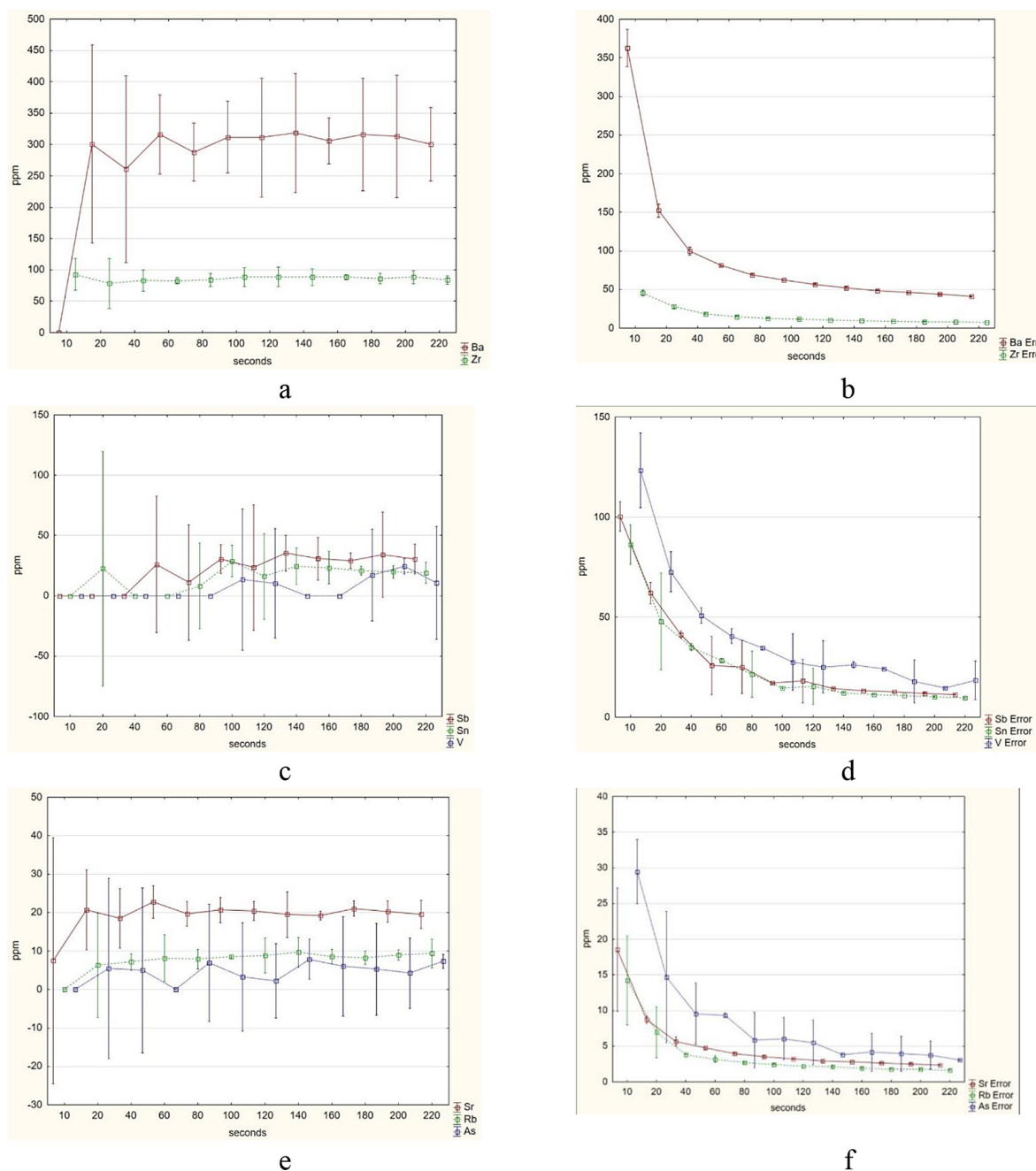
Figure 2. Average values and errors of chemical element concentrations in sand, where: (a) represents barium and zirconium; (b) corresponds to the device error for barium and zirconium; (c) includes antimony, tin, and vanadium; (d) refers to the device error for antimony, tin, and vanadium; (e) represents strontium, rubidium, and arsenic; and (f) corresponds to the device error for strontium, rubidium, and arsenic

The optimal conditions for field analysis involved measuring dry or slightly moist samples for 60 s.

Silva et al. [2021] emphasized that analysis duration should depend on the desired accuracy and the target elements. For example, their data indicate that 50 s is sufficient to determine iron content. The results of this experiment support such claims. Most elements showed stable values from 80 s, with device errors remaining minimal.

However, certain elements, such as nickel and arsenic in soil, and vanadium in sand, required at least 100 s for accurate detection.

Stable values for most elements were achieved at 180–220 s in soil and 140 s in sand. For example, barium concentrations in soil stabilized after 100 s, while zirconium stabilized at 20 s. In sand, lower concentrations delayed the detection of some elements, such as antimony and

tin, which became detectable only after 60 s. Errors significantly decreased with longer analysis durations, confirming the importance of extended experiments for obtaining accurate data.

CONCLUSIONS

The obtained results demonstrate that the accuracy of the analysis depends on the duration of the experiment, and the stability of most chemical element concentrations is achieved within specific timeframes. For soil, the optimal analysis duration is 180–220 s, while for sand, it is 140 s. For example, barium concentration in soil stabilizes after 100 s, zirconium shows stable values as early as 20 s, manganese stabilizes at 120 s, and zinc at 140 s. For elements such as nickel and arsenic, stable data in soil are achieved only at analysis durations exceeding 200 s. In sand, the concentrations of chemical elements are lower, requiring longer detection times. Antimony stabilizes after 160 s, and tin after 140 s. Regarding measurement errors, the highest values are observed during the early stages of analysis. Errors for most elements in soil decrease to acceptable levels after 80 s, while in sand, this occurs after 100 s. However, for elements with low concentrations, such as vanadium, accuracy improves after 120 s. Thus, to obtain the most accurate results, it is recommended to aim for an analysis duration of 180–220 s for soil and 140 s for sand, especially when considering device errors.

Acknowledgments

REFERENCES

1. Angeles-Chavez C., Toledo-Antonio J.A., Cortes-Jacome M.A. (2012). Chemical quantification of Mo–S, W–Si, and Ti–V by energy dispersive X-ray spectroscopy. In S. K. Sharma (Ed.), X-ray Spectroscopy. *Intech*, 119–136.

2. Anjos M.J., Lopes R.T., Jesus E.F.O., Simabuco S.M., Cesareo R. (2002). Quantitative determination of metals in radish using x-ray fluorescence spectrometry.

3. *X-Ray Spectrometry: An International Journal*, 31, 120–123. https://doi.org/10.1002/xrs.567

4. Bako S.P., Funtua I.I., Ijachi M. (2005). Heavy metal content of some Savanna plant species in relation to air pollution. *Water, Air, and Soil Pollution*, 161, 125–136.

5. Bernick M.B., Getty D., Prince G., Sprenger M. (1995). Statistical evaluation of field portable X-ray fluorescence soil preparation methods. *Journal of Hazardous Materials*, 43, 111–116. Retrieved from http://nepis.epa.gov/Adobe/PDF/30003LR0.pdf

6. Brand N.W., Brand C.J. (2014). Performance comparison of portable XRF instruments. *Geochemistry: Exploration, Environment, Analysis*, *14*(2), 125–138. https://doi.org/10.1144/geochem2012-172

7. Datsko O., Zakharchenko E., Butenko Y., Melnyk O., Kovalenko I., Onychko V., Ilchenko V., Solokha M. (2024). Ecological Assessment of Heavy Metal Content in Ukrainian Soils. *Journal of Ecological Engineering, 25*(11), 100–108. https://doi.org/10.12911/22998993/192669

8. Dong C., Taylor M. P., Kristensen L. J., Zahran S. (2015). Environmental contamination in an Australian mining community and potential influences on early childhood health and behavioral outcomes. *Environmental Pollution*, 207, 345–356.

9. Forster N., Grave P. (2012). Non-destructive PXRF analysis of museum-curated obsidian from the Near East. *Journal of Archaeological Science*, 39, 728–736.

10. Frahm E. (2013). Validity of "off-the-shelf" handheld portable XRF for sourcing Near Eastern obsidian chip debris. *Journal of Archaeological Science*, 40, 1080–1092.

11. Gladney E.S., Neifert P.E., Bower N.W. (1989). *Analytical Chemistry*, 61, 1834–1836.

12. Hall G.E., Bonham-Carter G.F., Buchar A. (2014). Evaluation of portable X-ray fluorescence (pXRF) in exploration mining: Phase 1, control reference materials. *Geochemistry: Exploration, Environment, Analysis*, 14, 99–123.

13. Handson P.D., Shelley B.C. (1993). A review of plant analysis in Australia. *Australian Journal of Experimental Agriculture*, 33, 1029–1038.

14. Hangen E., Čermák P., Geuß U., Hlisnikovský L. (2019). Information depth of elements affects accuracy of parallel pXRF in situ measurements of soils. *Environmental Monitoring and Assessment, 191*(11), 661. https://doi.org/10.1007/s10661-019-7869-2

15. Harvey P.J., Taylor M.P., Kristensen L.J., Grant-Vest S., Rouillon M., Wu L., Handley H.K. (2015). Evaluation and assessment of the efficacy of an abatement strategy in a former lead smelter community, Boolaroo, Australia. *Environmental Geochemistry and Health*, 1–14.

16. Hryhoriv Y., Butenko A., Solovei H., Filon V.,

Skydan M., Kravchenko N., Masyk I., Zakharchenko E., Tykhonova O., Polyvanyi A. (2024). Study of the Impact of Changes in the Acid-Base Buffering Capacity of Surface Sod-Podzolic Soils. *Journal of Ecological Engineering, 25*(6), 73–79. https://doi.org/10.12911/22998993/186928

17. Hughes R.E. (1998). On reliability, validity, and scale in obsidian sourcing research. In A. F. Ramenofsky & A. Steffen (Eds.), Unit Issues in Archaeology: Measuring Time, Space, and Material. *The University of Utah Press*, 103–114.

18. Chimidza S., Viksna A., Lindgren E.S. (2001). X-Ray Spectrometry, 30, 301–307.

19. Kenna T.C., Nitsche F.O., Herron M.M., Mailloux B.J., Peteet D., Sritrairat S., Sands E., Baumgarten J. (2011). Evaluation and calibration of a field portable X-ray fluorescence spectrometer for quantitative analysis of siliciclastic soils and sediments. *Journal of Analytical Atomic Spectrometry*, 26, 395–405.

20. Kolisnyk O., Yakovets L., Amons S., Butenko A., Onychko V., Tykhonova O., Hotvianska, A., Kravchenko N., Vereshchahin I., Yatsenko V. (2024). Simulation of High–Product Soy Crops Based on the Application of Foliar Fertilization in the Conditions of the Right Bank of the Forest Steppe of Ukraine. *Ecological Engineering & Environmental Technology*, 25(7), 234–243. https://doi.org/10.12912/27197050/188638

21. Li S., Shen J., Bishop T.F.A., Viscarra Rossel R.A. (2022). Assessment of the Effect of Soil Sample Preparation, Water Content and Excitation Time on Proximal X-ray Fluorescence Sensing. *Sensors, 22*(12), 4572. https://doi.org/10.3390/s22124572

22. Marguí E., Hidalgo M., Queralt I. (2005). Multielemental fast analysis of vegetation samples by wavelength dispersive X-ray fluorescence spectrometry: Possibilities and drawbacks. *Spectrochimica Acta Part B: Atomic* Spectroscopy, 60, 1363–1372.

23. McLaren T.I., Guppy C.N., Tighe M.K., Forster N., Grave P., Lisle L.M., Bennett J.W. (2012). Rapid, nondestructive total elemental analysis of Vertisol soils using portable X-ray fluorescence. *Soil Science Society of America Journal*, 76, 1436–1445.

24. Munro K.L., Mariana A., Klavins A.I., Foster A.J., Lai B., Vogt S., Cai Z., Harris H.H., Dillon C.T. (2008). Microprobe XRF mapping and XAS investigations of the intracellular metabolism of arsenic for understanding arsenic-induced toxicity. *Chemical Research in Toxicology*, 21, 1760–1769.

25. Newlander K., Goodale N., Jones G.T., Bailey D.G. (2015). Empirical study of the effect of count time on the precision and accuracy of pXRF data. *Journal of Archaeological Science: Reports*, 3, 534–548. https://doi.org/10.1016/j.jasrep.2015.07.007

26. Paltridge N.C., Palmer L.J., Milham P.J., Guild G.E., Stangoulis J.C.R. (2012). Energy-dispersive X-ray fluorescence spectrometry as a tool for zinc, iron and selenium analysis in whole grain wheat. *Plant Soil*, 361, 251–260. https://doi.org/10.1007/s11104-012-1423-0

27. Piercey S.J., Devine M.C. (2014). Analysis of powdered reference materials and known samples with a benchtop, field portable X-ray fluorescence (pXRF) spectrometer: Evaluation of performance and potential applications for exploration lithogeochemistry. *Geochemistry: Exploration, Environment, Analysis*, 14, 139–148.

28. Queralt I., Ovejero M., Carvalho M.L., Marques A.F., Llabrés J.M. (2005). Quantitative determination of essential and trace element content of medicinal plants and their infusions by XRF and ICP techniques. *X-Ray Spectrometry : An International Journal*, 34, 213–217. https://doi.org/10.1002/xrs.795

29. Richardson D.H.S., Shore M., Hartree R., Richardson R.M. (1995). The use of X-ray fluorescence spectrometry for the analysis of plants, especially lichens, employed in biological monitoring. *Science of the Total Environment*, 176, 97–105. https://doi.org/10.1016/0048-9697(95)04835-9

30. Rouillon M., Taylor M.P. (2016). Can field portable X-ray fluorescence (pXRF) produce high quality data for application in environmental contamination research? *Environmental Pollution*, 214, 255–264. https://doi.org/10.1016/j.envpol.2016.03.055

31. Sh.ackley M.S. (2012). Portable X-ray fluorescence spectrometry (pXRF): The good, the bad, and the ugly. *Archaeology Southwest*, *26*(2).

32. Shackley M.S. (2010). Is there reliability and validity in portable X-ray fluorescence spectrometry (pXRF)? *SAA Archaeological Record*, *10*(5), 17–18, 20.

33. Shackley M.S. (2011). An introduction to X-ray fluorescence (XRF) analysis in archaeology. In M. S. Shackley (Ed.), X-ray Fluorescence Spectrometry (XRF) in Geoarchaeology, *Springer*, 7–44.

34. Silva S.H.G., Ribeiro B.T., Guerra M.B.B., De Carvalho H.W.P., Lopes G., Carvalho G.S., Guilherme L.R.G., Resende M., Mancini M., Curi N., Rafael R.B.A., Cardelli V., Cocco S., Corti G., Chakraborty S., Li B., Weindorf D.C. (2021). Chapter One - pXRF in tropical soils: Methodology, applications, achievements and challenges. *Advances in Agronomy*, *167*, 1–62. https://doi.org/10.1016/bs.agron.2020.12.001

35. Speakman R.J., Shackley M.S. (2013). Silo science and portable XRF in archaeology: A response to Frahm. *Journal of Archaeological Science*, 40, 1435–1443.

36. Stiko R., Zawisza B. (2012). Quantification in XRF spectrometry. In S. K. Sharma (Ed.), X-ray Spectroscopy. *InTech Europe*, 137–162.

37. Tavares T.R., Molin J.P., Alves E.E.N., Melquiades F.L., Carvalho H.W.P.D., Mouazen A.M. (2023).

Towards rapid analysis with XRF sensor for assessing soil fertility attributes: Effects of dwell time reduction. *Soil and Tillage Research*, 232, 105768. https://doi.org/10.1016/j.still.2023.105768

38. Tighe M., Forster N. (2014). Rapid, nondestructive elemental analysis of tree and shrub litter. *Communications in Soil Science and Plant Analysis*, 45, 53–60. https://doi.org/10.1080/00103624.2013.848878

39. Towett E.K., Shepherd K.D., Drake B.L. (2015). Plant elemental composition and portable X-ray fluorescence (pXRF) spectroscopy: Quantification under different analytical parameters. *X-Ray Spectrometry*. https://doi.org/10.1002/xrs.2678

40. United States Environmental Protection Agency (US EPA). (1998). Environmental Technology Verification Report, Field Portable X-ray Fluorescence Analyzer: Metorex X-MET 920-P. Retrieved from. http://nepis.epa.gov/Adobe/PDF/30003LR0.pdf

41. Voytovyk M., Butenko A., Prymak I., Tkachenko M., Mishchenko Y., Tsyuk O., Panchenko O., Kondratiuk I., Havryliuk O., Sleptsov Y., Polyvanyi A. (2024). Mobile Phosphorus Presence of Typical Chernozems on Fertiliser System. *Rural Sustainability Research*, *51*(346), 58–65. https://doi.org/10.2478/plua-2024-0006

42. Weindorf D.C., Bakr N., Zhu Y. (2014). Advances in portable X-ray fluorescence (PXRF) for environmental, pedological, and agronomic applications. *Advances in Agronomy*, 128, 65–211. https://doi.org/10.1016/B978-0-12-802139-2.00001-9