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Optimization of exposure time in pXRF protocols for high-precision geochemical mapping of heavy metals in soils

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Abstract

This study provides a scientific substantiation of protocols for the use of portable X-ray fluorescence (pXRF) spectrometry for monitoring agricultural soils degraded by anthropogenic impacts, focusing on optimizing exposure time to enhance the reliability of in-situ heavy metal determination. Experimental work conducted with a Niton XL3t GOLDD analyzer on soil samples, with dwell times ranging from 30 to 300 seconds and the application of analysis of variance (ANOVA), established that for elements with low concentrations (below 50 ppm), such as molybdenum (Mo), uranium (U), arsenic (As), copper (Cu), and scandium (Sc), a measurement duration exceeding 240–300 seconds is critical for signal stabilization above the limit of detection (LOD). Conversely, for elements with concentrations of 50-100 ppm (strontium (Sr), rubidium (Rb), zirconium (Zr), barium (Ba), and vanadium (V)), stability of the mean values is achieved in as early as 60 seconds, although increasing the detection time remains a universal tool for minimizing random variability and narrowing confidence intervals. Based on the results, a differentiated approach to pXRF analysis regulation is scientifically justified: for rapid screening of elements with concentrations above 50 ppm, 60–90 seconds is sufficient, whereas for more precise monitoring of elements below this threshold, an extension of analysis time to 240–300 seconds is necessary to ensure data reliability for subsequent land remediation.

Keywords:

anthropogenic degradation; environmental monitoring; exposure time; instrumental error; limit of detection (LOD)

1. Introduction

Modern challenges require advanced solutions. The primary task of humanity today is process optimization–for instance, achieving higher crop yields while consuming fewer resources and simultaneously preserving the environment (**Butenko et al., 2025**). Another example is the transition from labour-intensive manual soil sampling to the use of mobile samplers (**Lukowska et al., 2019**), or moving from time-consuming laboratory analyses, such as atomic absorption spectrometry, to the rapid determination of heavy metal content in soil using the X-ray fluorescence method (**Poljak et al., 2024**). Research by **Rouillon & Taylor (2016)** confirms that modern portable X-ray fluorescence (pXRF) systems not only provide operational efficiency but also achieve accuracy levels comparable to the Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) method. Specifically, for 15 out of 19 elements, the highest level of data quality was recorded, and for elements such as titanium (Ti) and chromium (Cr), pXRF demonstrated even higher efficiency than traditional atomic emission spectrometry. Specifically in this study, it was mentioned that, for 15 out of 19 analyzed elements (including lead (Pb), zink (Zn), Cu, and manganese (Mn), a high level of data quality was recorded, with results showing a strong correlation to laboratory standards. For elements such as Ti and Cr, portable X-ray fluorescence provided more consistent analytical data compared to traditional atomic emission spectrometry. This is attributed to the non-destructive nature of the technique, which avoids errors associated with the incomplete acid digestion of stable mineral phases – a common limitation in sample preparation for plasma-based methods.

XRF technology has been known for a long time; however, its active implementation as a reliable field tool for agricultural soil assessment began only in the late 1990s and early 2000s (**Weindorf et al., 2012**). So, what is pXRF? Many researchers are familiar with this instrument, and it is frequently used for assessing the content of various heavy metals in soil, sand (**Datsko et al., 2025**) and minerals (**Balaram & Sawant, 2022**) or metal alloys (**Vianello & Tykot, 2017**). Its most signifi-

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cant advantage is the ability for scientists to evaluate the chemical element content in a material directly on-site, both *in-situ* and *ex-situ*, although it was primarily designed for "field conditions".

However, one of the most debated issues in the scientific community remains the balance between analysis duration and the accuracy of the obtained results. Detection time is a critical parameter that significantly affects the instrument's sensitivity–specifically, whether a quantitative indicator of an element will be determined. In field conditions, this issue is vital as it dictates whether short-term scanning (e.g. 30–60 seconds) provides sufficient statistical reliability, or if longer detection (90 seconds and more) is required to obtain dependable data on soil elemental composition.

At the same time, in laboratory conditions, the question of duration becomes even more acute, taking on a different methodological significance. Since the stages of field sampling and thorough sample preparation (drying, grinding, homogenization) have already been completed, the factor of speed moves to the background. In this context, a slight increase in the analysis time for each sample no longer has a critical impact on overall energy consumption or personnel workload. Instead, longer detector operation becomes a justified investment in analytical quality, as it allows for a significant reduction in measurement error, improves the signal-to-noise ratio, and achieves higher precision in determining the concentrations of heavy metals present in the test sample.

Despite the significant influence of this factor on analysis, relatively few scientific works have focused on this issue. Specifically, **Newlander et al. (2015)** state that an analysis duration exceeding 180 seconds is not expedient and indicate that measurement time has practically no effect on the accuracy or validity of the obtained data. However, **Towett et al. (2016)** argue that a duration of 180 seconds is the standard for accurate quantitative analysis, ensuring the stability of results.

Modern technological solutions, such as the use of helium purging and graphene detector windows, allow for radical optimization of the analysis process. According to recent studies of **Adams et al. (2020)**, scanning time can be reduced from the traditional 60–180 seconds to as little as 20 seconds without a significant loss of accuracy. This ensures the transmission efficiency of X-ray radiation for light elements such as sodium (Na) and magnesium (Mg) at a level close to 100%, which was previously unattainable for field methods.

Therefore, the aim of this article is to determine the optimal analysis duration for the Thermo Scientific Niton XL3t GOLDD X-ray fluorescence analyser and to identify the threshold at which the measurement error ceases to fluctuate significantly.

2. Methods

Experimental studies were conducted using a Thermo Scientific Niton XL3t GOLDD pXRF analyzer operating in the factory-calibrated 'Soil Mode', which utilizes the Compton Normalization algorithm for matrix interference correction. The device is equipped with a Silver anode X-ray tube and a high-performance Silicon Drift Detector (SDD), which ensures superior resolution and light element detection compared to traditional sensors. To ensure high data quality and check for instrumental drift, a standard SiO_2 blank and a Certified Reference Material (NIST SRM 2709a) were measured at the beginning of the session and after every 5 samples. For each measurement, three independent replicates were conducted. To account for micro-heterogeneity within the cuvette, the sample was repositioned and slightly shaken between replicates, ensuring that each of the three scans targeted a different area of the soil surface within the measurement window.

The object of the study was soil collected using a standard sampling technique in the form of a composite sample. Specifically, the sampling was performed using a stainless steel soil auger from the upper horizon (0–20 cm depth). To ensure the representativeness of the area, 20 individual sub-samples were collected from a 1-hectare plot using a zigzag pattern and then thoroughly mixed in a plastic container to form a single composite sample of approximately 0.5 kg. The sample preparation process involved thermal treatment of the soil substrate in a drying oven at 100°C for 5 hours until a constant mass was reached to ensure the complete removal of hygroscopic moisture. Subsequently, the dry matter was thoroughly ground and homogenized by sieving through a 1 mm mesh to minimize grain-size effects and ensure a uniform analytical surface for portable X-ray fluorescence measurement. To evaluate the analytical performance of the instrument across different geochemical backgrounds, the studied elements were categorized into three distinct concentration ranges: low concentrations (0–50 ppm), medium concentrations (50–100 ppm), and high concentrations (100–500 ppm).

The soil used in this study was a Typical Chernozem, characterized by a heavy loamy texture and an organic matter content of 3.2% (determined by the Tyurin method), pH_{H2O} – 6.5, pH_{KCl} – 6.2. The soil matrix analysis, pre-evaluated with pXRF at 300 s exposure, revealed total concentrations of key matrix-forming elements: Iron (Fe) at 18,434.52 ± 134.14 mg/kg, Mn at 536.03 ± 54.44 mg/kg, and Calcium (Ca) at 3,846.54 ± 117.89 mg/kg. These parameters, were consistent throughout the experiment to minimize physical matrix effects and ensure the reproducibility of the dwell-time optimization results. For the analysis, 17 g of the prepared soil was placed into specialized cuvettes, ensuring the necessary representativeness of the measured layer.

The experimental design was focused on determining the effect of exposure time on the accuracy of results across three energy ranges: the main filter, high range, and low range. Measurements were performed in series with a 10-second increment for each filter individually, ranging

Table 1: Experimental design and exposure time settings

Substrate	Analysis range	Duration per single filter, s	Total sample analysis duration, s
Soil	Main, High, Low	10, 20, 30, 40, 50, 60, 70, 80, 90, 100	30, 60, 90, 120, 150, 180, 210, 240, 270, 300

from 10 to 100 seconds per filter. This approach allowed for tracking the evolution of the analytical signal within a total sample analysis duration ranging from 30 to 300 seconds (see **Table 1**). The exposure times mentioned (e.g. 30 s, 60 s, 180 s) represent the total analysis duration per sample, encompassing the sequential operation of all active beam filters (Main, High, and Low).

For each time interval, measurements were performed in triplicate. The obtained results were subjected to statistical processing using one-way analysis of variance (ANOVA) with Statistica 10.0 software (StatSoft Inc., Tulsa, USA).

3. Results and Discussion

The results of the study indicate a direct correlation between the duration of the measurement filters' operation and the detector's ability to identify heavy metals with concentrations within background or low ranges (0 to 50 ppm). The analysis established that with insufficient exposure time, the instrument is often unable to distinguish the useful signal from background noise, resulting in data classified as "limit of detection" (LOD). In **Figure 1**, such data are represented as zero values, which does not actually imply the absence of the element, but rather the inability to detect it.

Among all the tested heavy metals, Pb demonstrated the highest detection stability, being consistently recorded from the first 10 seconds of measurement with an average value of approximately 14.96 ppm. A similar trend was observed for Th, with indicators fluctuating between 6.21 and 8.57 ppm regardless of exposure time. This suggests that for elements with well-defined fluorescence lines, such as Pb and Th, even a minimal analysis duration yields reliable data. Their characteristic X-ray emissions and relatively high energy levels result in a high signal-to-noise ratio (SNR), which quickly overcomes the background noise of this heavy loamy Typical Chernozem matrix, characterized by a total Fe content of ~18,434 ppm and organic matter of 3.2% (**Gu et al., 2019**).

In contrast, a group of elements including Cu, As, and Mo exhibited a critical dependence on signal accumulation. Specifically, Cu remained at the LOD level during the first 40 seconds of exposure; only after reaching 50 seconds did the device begin to provide stable average values at 16.18 ppm. As showed detection instability at short intervals (10–40 s), where results frequently fell below the detection limit, and its measurement only became regular after 50 seconds, with values around 6.2–6.8 ppm. This confirms the necessity of extending the operation time of the corresponding filter to obtain valid

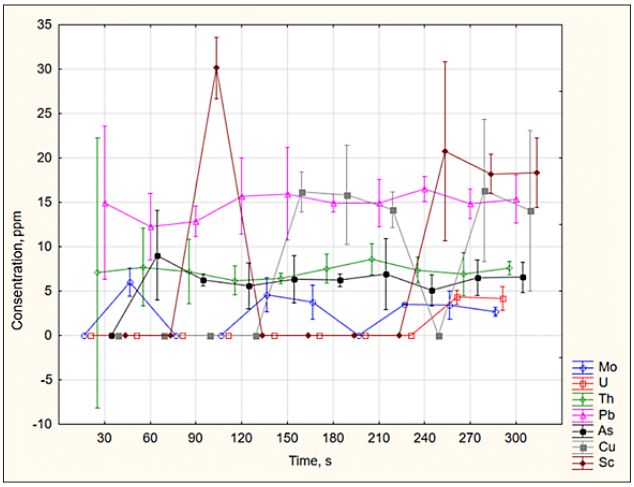


Figure 1: The relationship between the detection frequency of heavy metals (0–50 ppm range) and total analysis duration

results for these heavy metals. For Mo, the analytical signal exhibits significant instability but the concentration readings are allways in a narrow range of 3–5 ppm.

U and Sc proved to be the most challenging to determine, as their detection threshold was reached only under the longest instrument operating modes. U began to be recorded only after 90 seconds of exposure at a level of 4.1–4.3 ppm, indicating an extremely high limit of detection for this element with this analyser model. The situation with Sc was even more specific, as the device produced sporadic high values (18.1–30.1 ppm) only at certain time intervals, which may be attributed to instrumental errors or spectral overlaps under conditions of low pulse accumulation.

Statistical processing of the results using ANOVA allowed for a quantitative assessment of the effect of measurement duration on the stability of the obtained data (see **Table 2**). The results indicate that for Mo, U, As, Cu, and Sc, the significance level is well below the confidence threshold ($p < 0.05$). This indicator mathematically confirms that the choice of detection time for these elements is crucial: short analysis duration Pbs to statistically different results compared to prolonged scanning.

Specifically, at low time values (up to 120–150 s), the instrument demonstrates unstable detection, frequently yielding LOD values. Sharp fluctuations in concentrations, such as the Sc peak at 90 seconds of analysis or the appearance of Cu only at 150 seconds, create significant intergroup variance.

Th and Pb should be highlighted separately. For thorium (Th), the significance level ($p = 0.97$) indicates that exposure time has practically no effect on the results–the

Table 2: One-way ANOVA results for the effect of total analysis durationon on heavy metals concentration measurements (0–50 ppm range)

Variable	SS (Effect)	MS (Effect)	SS (Error)	MS (Error)	F	p
Mo	134.74	14.97	4.10	0.21	72.97	0.00
U	86.89	9.65	0.79	0.04	245.63	0.00
Th	12.35	1.37	91.10	4.55	0.30	0.97
Pb	46.64	5.18	50.66	2.53	2.05	0.09
As	142.61	15.85	21.33	1.07	14.85	0.00
Cu	1773.70	197.08	60.18	3.01	65.49	0.00
Sc	3725.54	413.95	43.40	2.17	190.78	0.00

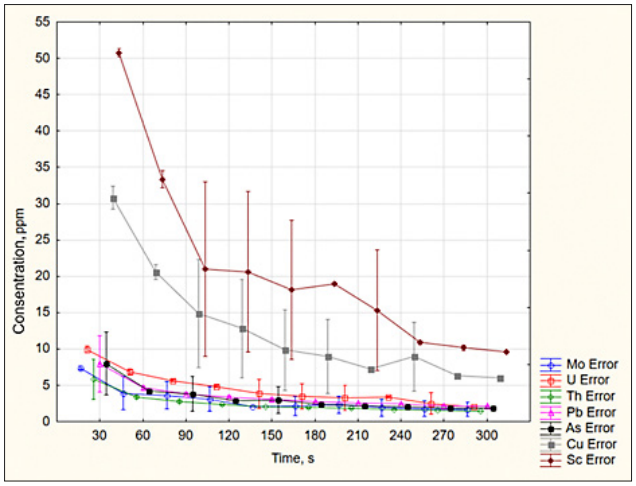


Figure 2: Dynamics of pXRF measurement instrument error as a function of total analysis duration for heavy metals (0–50 ppm range)

device consistently records its concentration from the very first seconds. For Pb (p = 0.09), the influence of time is also not critical at the 5% level, confirming the possibility of express analysis for this element within a short timeframe.

Figure 2 demonstrates a clear dependency: as the analysis time increases, the level of instrumental error rapidly decreases for all studied heavy metals. The highest error values were recorded at the initial stage (30 s), particularly for Sc (50.75 ppm) and Cu (30.79 ppm). Since these error values significantly exceed the actual concentration of the elements in the soil, the device naturally reports the result as LOD during short detection times.

The most active decline in the curves is observed during the first 120 seconds. Specifically, the error for Sc decreases from 50.75 to 20.60 ppm, and for Cu from 30.79 to 12.79 ppm. After 240 s of total analysis duration, the curves demonstrate a marked reduction in the rate of precision improvement, rather than reaching a full plateau. While the variability remains present, further increases in exposure time no longer yield the same magnitude of radical enhancement in data stability observed in the initial stages. For such heavy metals as Mo, U, Th, Pb, and As, the error stabilizes at minimal levels (1.5–2.5 ppm) after 270 seconds of measurement.

Statistical data processing using ANOVA demonstrated the absolute significance of exposure duration's impact on the level of instrumental error for all studied elements without exception (p = 0.000). This indicates that changing the measurement time does not merely adjust the results but fundamentally transforms the quality of the obtained data, moving it from the category of estimated to the category of reliable (see **Table 3**).

The highest F-test values were observed for U (F = 80.6), followed by Sc (F = 68.43) and Cu (F = 60.98). This is explained by the fact that at short exposures (30–60 s), the error for these elements is abnormally high, which statistically renders these measurements unsuitable for analysis. The sharp decrease in error with increasing time creates a colossal difference between groups, which ANOVA records as a high significance of the time factor.

It is important to note that even for Th and Pb, where the impact of time on the mean concentration was not as critical, the error level (p = 0.000) still demonstrates a significant dependence on the analysis duration. This means that although the device can "see" Pb in a short time, only prolonged exposure allows for a substantial narrowing of the confidence interval and ensures high reproducibility of the result.

Based on **Figure 3**, it can be stated that the group of heavy metals consisting of Sr, Rb, and Cr demonstrates a fundamentally different nature of dependence on detection time. The mean concentrations of Sr (84–87 ppm) and Rb (70–71 ppm) remain practically unchanged throughout the entire measurement interval from 30 to 300 seconds, indicating high reproducibility of results even at the minimum analysis duration. Cr exhibits slightly higher variability within the range of 54–63 ppm; however, the overall trend of its concentration shows no pronounced increase or decrease, suggesting that the accumulated signal is sufficient even during the initial scanning stages. The stability of mean indicators for elements whose content in the soil confidently exceeds 50 ppm (e.g. Sr, Rb, and Cr) suggests that higher concentrations play a decisive role in signal stabilization. While the reliability of Pb and Th measurements is primarily attributed to their high-energy fluorescence lines and superior signal-to-noise ratio, the precision ob-

Table 3: One-way ANOVA results for the effect of total analysis duration on pXRF measurement error for heavy metals (50–100 ppm range)

Variable	SS (Effect)	MS (Effect)	SS (Error)	MS (Error)	F	p
Mo Error	80.82	8.98	5.85	0.29	30.72	0.00
U Error	151.03	16.78	4.16	0.21	80.60	0.00
Th Error	46.79	5.20	2.52	0.13	41.20	0.00
Pb Error	83.70	9.30	4.97	0.25	37.41	0.00
As Error	93.07	10.34	9.00	0.45	22.97	0.00
Cu Error	1635.28	181.70	59.59	2.98	60.98	0.00
Sc Error	4295.60	477.29	139.50	6.97	68.43	0.00

served for Sr, Rb, and Cr is largely a function of their higher mass fractions in the matrix. In these cases, the sheer number of fluorescent X-ray photons reaching the detector is sufficient to overcome statistical fluctuations even without prolonged exposure.

Statistical data processing (see **Table 4**) revealed the absence of a statistically significant impact of detection duration on the measurement results for these heavy metals. The significance levels substantially exceed the critical threshold, indicating high stability of the analytical signal even at the initial stages of analysis. Low F-test values further confirm that the data variability within time groups is caused by random measurement error rather than the systematic influence of the time factor. Consequently, for the study of Sr, Rb, and Cr (with concentrations ranging from 50 to 100 ppm) in soil, the application of express modes with a duration of 60 seconds is entirely justified.

The error dynamics for the group of heavy metals mentioned above demonstrate a steady decline as exposure time increases (see **Figure 4**). Sr and Rb are characterized by high convergence of results: the highest level of uncertainty was recorded at the initial 30-second mark (approximately 5 ppm); however, after the first minute of scanning, the curves rapidly reach a plateau where error values stabilize at less than 2 ppm. Cr exhibits a significantly higher starting error threshold, exceeding 17 ppm at the 30th second, which is due to the spectral characteristics of its detection in a heavy loamy Chernozem matrix with a high Fe background. The high initial error for Cr is caused by the matrix effect of the soil. Since the soil has a high Fe content, the energy peaks of Fe and Cr overlap. This creates «noise» that interferes with the sensor, requiring a longer exposure time to obtain a stable and accurate reading. Nevertheless, it is for Cr that the most noticeable positive effect of prolonged signal accumulation is observed, as the level of instrumental error decreases to 5 ppm by the 300th second. Thus, while the analysis time does not significantly alter the mean concentration values of these metals, it plays a crucial role in narrowing the confidence intervals, ensuring a transition from estimated measurements to precision data.

Statistical data processing revealed an extremely high significance of the exposure duration's impact on the

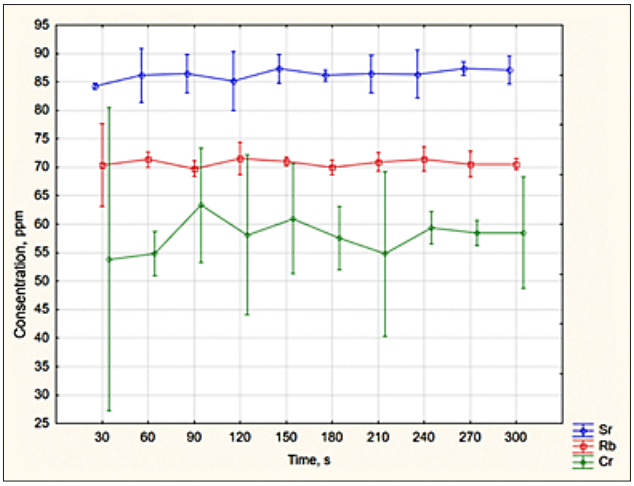


Figure 3: The relationship between the detection frequency of heavy metals (50–100 ppm range) and total analysis duration

level of instrumental error (see **Table 5**). Despite the previously established lack of significant influence of time on the mean concentration of heavy metals, the error indicators demonstrate the opposite picture ($p = 0.000$). The colossal F-test values indicate that changing the exposure time Pbs to a radical and systematic reduction in random data variability, which cannot be explained by chance factors. Such high statistical significance is attributed to the minimal within-group variance (MS Error). This indicates that the instrument operates very stably, and every additional second of measurement makes a clearly predictable contribution to improving the method's precision. For Cr, the MS Effect value (44.21) is substantially higher than for Sr and Rb, confirming its greater sensitivity to signal accumulation time.

The analysis results for heavy metals with concentration levels in the range of 100 to 500 ppm demonstrate a steady independence of mean values from exposure duration (see **Figure 5**). Zr exhibits the highest stability, maintaining a value of approximately 500 ppm with minimal data dispersion starting from the first 30 seconds of measurement, which is explained by the intensive energy response of this element. Mn and Ba also

Table 4: One-way ANOVA results for the effect of total analysis duration on Sr, Rb, and Cr concentration measurements (50–100 ppm range)

Variable	SS (Effect)	MS (Effect)	SS (Error)	MS (Error)	F	p
Sr	25.54	2.84	33.51	1.68	1.69	0.16
Rb	10.31	1.15	25.73	1.29	0.89	0.55
Cr	232.06	25.78	474.86	23.74	1.09	0.41

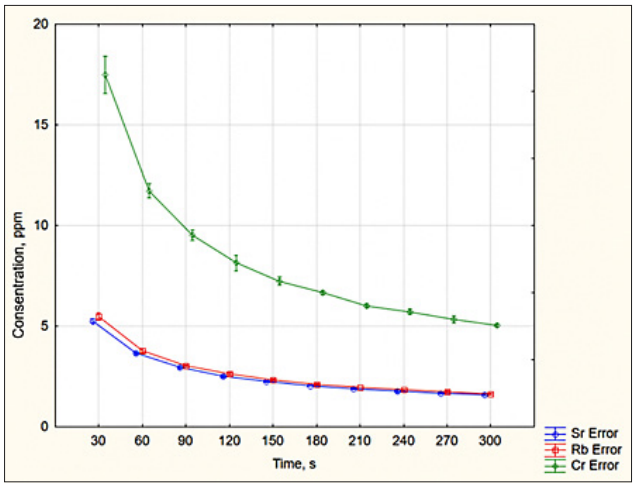


Figure 4: Instrumental error of pXRF measurements for Sr, Rb, and Cr as a function of total analysis duration (50–100 ppm range)

concentration in this group (around 100 ppm), demonstrates slightly wider confidence intervals at short exposures, but its mean value stabilizes very rapidly.

Statistical analysis confirmed the overall stability of the measurements, yet revealed specific characteristics for certain indicators (see **Table 6**). For Zr, V, and Ba, the p-level significantly exceeds the 0.05 threshold, mathematically proving the lack of substantial influence of exposure time on the determination of their mean concentrations. This suggests that at high concentrations of these metals in the soil, the Niton XL3t GOLDD device provides reliable results within the first seconds of analysis, and further signal accumulation does not alter the quantitative assessment. Special attention should be given to Mn, for which a statistically significant impact of measurement time was recorded (p = 0.012). High values of the sum of squares (SS Effect) and the F-test indicate the presence of certain fluctuations in mean values

Table 5: One-way ANOVA results for the total analysis duration on Sr, Rb, and Cr measurement error (50–100 ppm range)

Variable	SS (Effect)	MS (Effect)	SS (Error)	MS (Error)	F	p
Sr Error	35.55	3.95	0.01	0.00	7796.96	0.00
Rb Error	38.48	4.28	0.02	0.00	4933.02	0.00
Cr Error	397.93	44.21	0.42	0.02	2095.15	0.00

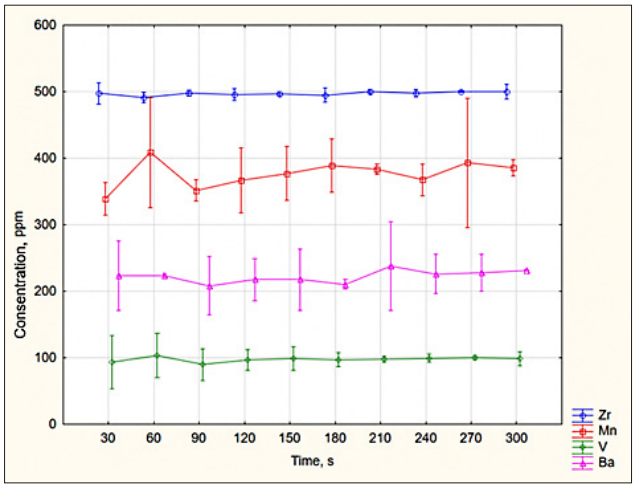


Figure 5: The relationship between the detection frequency of heavy metals (100-500 ppm range) and total analysis duration

show stable trends at levels of 350–400 ppm and 220 ppm, respectively; despite the presence of isolated fluctuations in mean values, these are not systemic and remain within the statistical norm. V, having the lowest

across different time intervals. This may be related to the complexity of signal stabilization for Mn in ferruginous or manganiferous soils, where spectral overlaps require slightly longer exposure to achieve final stability (**Magiera & Wawer-Liszka, 2025**). However, for practical applications, even these statistical deviations are not critical, as the overall concentration trend remains within the target range.

Analysis of the obtained graphical data confirms that for heavy metals with a content exceeding 100 ppm, exposure duration remains a decisive factor for minimizing instrumental error (see **Figure 6**). A classic exponential decay curve for measurement error is observed for all presented heavy metals, with the highest values recorded at the 30-second mark of the analysis. Mn demonstrates the most pronounced dependence, with its error reaching 90 ppm at the beginning of the measurement, which explains the statistical significance (p = 0.012) identified in the ANOVA for this element. Ba and V also show a substantial improvement in precision: their errors decrease from 58 ppm and 38 ppm, respectively, to their minimum levels upon reaching the 240–300 seconds mark of exposure. Zr remains the most stable, with

Table 6: One-way ANOVA results for the effect of total analysis duration on Zr, Mn, V, and Ba concentration measurements (100-500 ppm range)

Variable	SS (Effect)	MS (Effect)	SS (Error)	MS (Error)	F	p
Zr	191.40	21.27	228.88	11.44	1.86	0.12
Mn	11409.84	1267.76	7652.76	382.64	3.31	0.01
V	361.06	40.12	1354.31	67.72	0.59	0.79
Ba	2346.03	260.67	4515.32	225.77	1.15	0.37

its error being minimal from the first seconds (approximately 11 ppm) and gradually decreasing to 3 ppm, by the 300th second, which correlates with its ultra-high stability shown in the concentration plots.

The results of the analysis of variance (see **Table 7**) confirm the absolute statistical significance of the impact of detection duration on measurement precision. Although for most of these heavy metals (except Mn), time did not have a critical effect on the mean concentration, the time factor is decisive for instrumental error indicators. These statistical results are directly linked to the properties of the analyzed soil samples. The studied Typical Chernozem is characterized by a high Fe background and a significant Mn content. Such a 'ferruginous' matrix creates substantial spectral interference, where the intense Fe signals overlap with Mn peaks. The exceptionally high F-test values for Mn confirm that for this specific soil type, increasing exposure time is not just beneficial but essential to mathematically separate these overlapping signals and achieve stable readings. Extremely high F-test values, particularly for Zr (F = 16221.7) and Mn (F = 3407.3), indicate that the intergroup variability caused by the change in exposure time is thousands of times greater than the random measurement error. The minimal mean square error (MS Error) values, which for Zr practically tend toward zero, point to the ultra-high stability of the detector during signal accumulation for these elements. The SS Effect values for Mn (10467.12) and Ba (4452.57) emphasize that for these specific metals, increasing the exposure time yields the most tangible result in reducing measurement uncertainty. The high stability of Zr compared to V and Boron is explained by the physics of X-ray detection. Zr emits high-energy signals that easily pass through the soil matrix with minimal interference. In contrast, V is a lighter element with much lower emission energy, making its signal easily absorbed or hidden by «noise» from more abundant elements like Fe. As for Boron, it is too light for reliable detection by pXRF technology; therefore, any recorded values for B are highly unstable and represent instrumental noise rather than actual concentrations.

The analysis of the results revealed a clear correlation between the concentration of an heavy metals in the soil and the required detection duration to obtain reliable data. The conducted studies allow for the classification of the investigated metals into three functional groups based on their response to changes in measurement time.

The first group, comprising chemical elements with concentrations up to 50 ppm, demonstrated a critical dependence on the time factor. In the initial stages (30–90 s), high instrumental error levels, which often exceeded the actual metal content, led to unstable detection or results reported at the limit of detection. The statistical significance ($p < 0.05$), confirmed by ANOVA, indicates that for these heavy metals, signal accumulation 240-300 seconds is a mandatory requirement to overcome the detector's background noise.

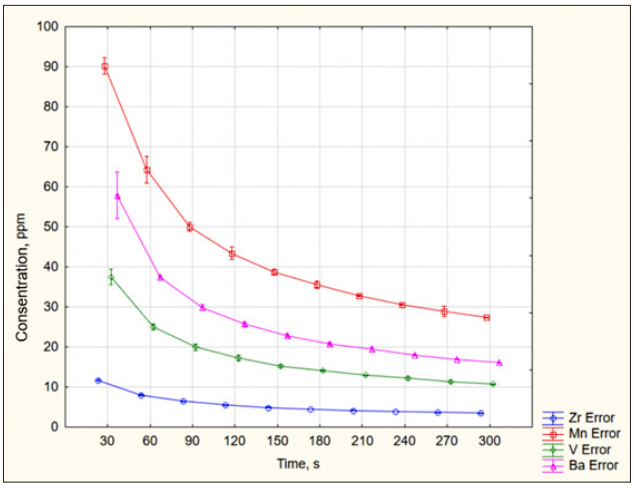


Figure 6: Dynamics of instrumental measurement error for Zr, Mn, V, and Ba as a function of total analysis duration (100-500 ppm range)

In contrast, heavy metals with concentrations of 50–100 ppm and those exceeding 100 ppm exhibited high stability of mean values from the very first seconds of analysis. The absence of a statistically significant impact of time on the mean concentration for most of these elements (except for Mn) suggests that their emission power is sufficient for identification by the Niton XL3t GOLDD analyser without prolonged signal accumulation, although the 240–300 seconds interval is still recommended for maximum precision.

Despite the stability of mean values for these groups, the analysis of instrumental error for most heavy metals timeshowed high significance ($p = 0.000$). This is a fundamental aspect of the discussion: detection duration does not always change the concentration of an heavy metals, but it always improves the precision of the obtained data.

An analysis of 84 scientific publications conducted by **Jenkins et al. (2025)** confirms that the pXRF method is a reliable alternative to laboratory methods for monitor-

Table 7: One-way ANOVA results for the effect of total analysis duration on Zr, Mn, V, and Ba measurement error (100-500 ppm range)

Variable	SS (Effect)	MS (Effect)	SS (Error)	MS (Error)	F	p
Zr	175.68	19.52	0.02	0.00	16221.70	0.00
Mn	10467.12	1163.01	6.83	0.34	3407.30	0.00
V	1837.74	204.19	2.03	0.10	2010.04	0.00
Ba	4452.57	494.73	11.68	0.58	847.17	0.00

ing heavy metals in urban soils, provided proper calibration using certified reference materials (CRM) is performed. Researchers note that while in situ measurements are more practical, laboratory conditions (ex situ) ensure higher precision due to controlled envFemental parameters.

Similar studies have been conducted previously, albeit using the Niton XL2 analyzer (**Yatsenko et al., 2025**). That study established that increasing pXRF analysis accuracy directly depends on the calibration of detection time, which should be at least 180–220 s for soil substrates and 140 s for sandy ones. Extending the measurement duration ensures the statistical reliability of the data, which is critical for the dependable detection of heavy metals such as Nickel and As.

While ultra-short detection (2 s) in field conditions is sufficient for assessing the physicochemical properties of soil (**Tavares et al., 2023**), the analysis of heavy metals presented in this work requires significantly more time to overcome instrumental error. This indicates that the strategy for selecting exposure time should be differentiated. At the same time, research on sites contaminated with heavy metals using in situ pXRF analysis revealed that over 95% of total measurement uncertainty is attributed to sampling error rather than instrumental error. This confirms that the ability to perform a large number of rapid measurements (even with a duration of 20 s) significantly enhances the characterization of a site and reduces the risk of territory misclassification compared to isolated laboratory analyses (**Rouillon et al., 2017**). The reliability of pXRF for rapid screening of key envFemental contaminants is further supported by comparative studies with Inductively Coupled Plasma Mass Spectrometry, which demonstrate no significant differences in concentrations for elements such as Mn, Ba, and Pb across diverse soil matrices. Research of **Alqattan et al. (2023)** has shown that while some elements like Fe may show statistical differences between methods, portable X-ray Fluorescence remains a robust and cost-effective tool for calculating pollution load indices and geo-accumulation indices. These findings align with our results, confirming that this method provides sufficient precision for soil monitoring and envFemental health assessments without the need for expensive laboratory-based 'gold standard' techniques. The effectiveness of portable X-ray Fluorescence for soil analysis depends on a systematic approach to addressing factors such as sample heterogeneity, instrumental drift, and detector resolution. Recent studies of **Ravansari et al. (2020)** emphasize that light elements, particularly those found in soil organic matter and water, can negatively affect measurements due to X-ray scattering and attenuation. Furthermore, for elements with lower characteristic fluorescence energy, the effective volume of analysis is reduced, meaning that careful optimization of instrumental settings and analysis times is essential to ensure that the results are representative of the whole sample.

While this study establishes an optimal exposure time for the analyzed Typical Chernozem using a Niton XL3t GOLDD+ analyzer, certain limitations regarding the generalization of these findings should be noted. The specific hardware configuration of the instrument, including its SDD detector and Ag anode X-ray tube, significantly influences the signal-to-noise ratio and detection limits. Therefore, while the observed trends in elemental stability are likely universal for high-energy analytes, the precise temporal thresholds may vary for other pXRF systems with different excitation geometries or detector efficiencies. Furthermore, the high Fe content and organic matter characteristic of Chernozems create a unique matrix effect; consequently, soils with substantially different mineralogical compositions (e.g. highly calcareous or ferralsolic soils) may require further calibration and adjusted exposure durations to achieve comparable precision.

4. Conclusions

The conducted study confirms that the effectiveness of pXRF analysis directly depends on elemental concentration and detection duration, which determine the qualitative transition of data from the "estimated" to the "reliable" category. It was established that for low-content heavy metals (below 50 ppm), such as Mo, U, As, Cu, and Sc, prolonged exposure 240-300 seconds is critically necessary to overcome background noise and stabilize the analytical signal. Conversely, for heavy metals with concentrations exceeding 50 ppm (Sr, Rb, Zr, Ba, V), mean values remain stable from the very first seconds of measurement, allowing for the application of express modes (60–90 s). However, the statistical indicator $p = 0.000$ for the instrumental error of all studied metals without exception proves that increasing exposure time is a universal tool for minimizing random variability and narrowing confidence intervals. Particular

attention should be paid to Mn, which, even at high concentrations, requires prolonged signal accumulation due to the specific nature of spectral overlaps. Thus, for reliable envFemental monitoring and precision soil studies, a differentiated approach is recommended: utilizing short cycles for elements with content above 50 ppm and extended intervals to guarantee the detection of heavy metals within the 0–50 ppm range.

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SAŽETAK

Optimizacija vremena izlaganja u pXRF protokolima radi visokopreciznoga geokemijskog kartiranja teških metala u tlu

Ova studija pruža znanstvenu potvrdu protokola za primjenu metode prijenosne rendgenske fluorescencijske (pXRF) spektrometrije za praćenje poljoprivrednih tala degradiranih uslijed antropogenoga utjecaja, s naglaskom na optimizaciju vremena izlaganja kako bi se povećala pouzdanost *in situ* određivanja koncentracija teških metala. Eksperimentalni rad proveden s Niton XL3t GOLDD uređajem na uzorcima tla, s vremenima izlaganja u rasponu od 30 do 300 sekundi i primjenom analize varijance (ANOVA), pokazao je da je za elemente s niskim koncentracijama (ispod 50 ppm), poput molibdena (Mo), urana (U), arsena (As), bakra (Cu) i skandija (Sc), trajanje vremena izlaganja dulje od 240 do 300 sekundi kritično za stabilizaciju signala iznad granice detekcije (LOD). Suprotno, za elemente s koncentracijama 50 – 100 ppm (stroncij (Sr), rubidij (Rb), cirkonij (Zr), barij (Ba) i vanadij (V)), stabilnost srednjih vrijednosti postiže se već nakon 60 sekundi iako povećanje vremena detekcije ostaje univerzalni alat za minimiziranje slučajne varijabilnosti i sužavanje intervala pouzdanosti. Na temelju dobivenih rezultata diferencirani pristup regulaciji provedbe pXRF analize znanstveno je opravdan: za brzi probir elemenata s koncentracijama iznad 50 ppm dovoljno je 60 – 90 sekundi, dok je za preciznije praćenje elemenata ispod navedene granične vrijednosti potrebno produljenje vremena izlaganja od 240 do 300 sekundi kako bi se osigurala pouzdanost podataka za naknadnu sanaciju zemljišta.

Ključne riječi:
antropogena degradacija, praćenje stanja okoliša, vrijeme izlaganja, instrumentalna pogreška, limit detekcije (LOD)

Author's contribution

Oksana Datsko (PhD in Agronomy): conceptualization, manuscript writing. **Ihor Kovalenko** (Dr., Prof.): methodology and supervision. **Yurii Spychak** (PhD in Agronomy): data curation and resources. **Vitalii Yatsenko** (PhD in Agronomy)**:** visualization and formal analysis. **Olha Bakumenko** (PhD in Agronomy, Associate Professor): writing – original draft and validation**. Olena Melnyk (**PhD in Ecology, Associate Professor): writing – review & editing and formal analysis**.**
All authors have read and agreed to the published version of the manuscript.