QUANTITATIVE X-RAY FLUORESCENCE ANALYSIS OF TOXIC METALS IMPLANTED IN METAL CHALCOGENIDE GEL MATRICES

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Abstract: *The detection of Pb, Cd, Hg, and As in complex waters at low concentrations is still a challenge for TXRF. We propose a preconcentration procedure using nanostructured chalcogenide gel matrices (CdS, PbS, CdSe) by total-reflection X-ray fluorescence to improve analytical efficiency. Thin gel films produced by hydrochemical deposition selectively enrich analytes from spiked solutions with an enrichment factor of 100–150×. As a result of the process, an excellent linearity ($R^2 \geq 0.998$) and equivalent solution LODs of 0.20 μg·L⁻¹ (Pb), 0.35 μg·L⁻¹ (Cd), 0.50 μg·L⁻¹ (Hg), and 0.65 μg·L⁻¹ (As) as well as a high accuracy (recoveries 90-108%) were obtained. The measurement showed acceptable precision (repeatability RSD ≤5%; inter-day ≤7%) and agreement with ICP-MS within ±7%. The characterization of the structure (SEM/EDX, AFM, XRD, XPS) confirms uniformity in the film morphology and stable chemical states, illustrating the mechanism of sorption/entrapment. The TXRF-gel platform provides improved sensitivity, reduced variability related to droplet heterogeneity, and traceable uncertainty (expanded uncertainty k=2 ≤13.5% at LOQ). The measurement was confirmed for the analysis of representative environmental waters with uncertainty of μg·L⁻¹ level. Use of metal chalcogenide gel matrices coupled with TXRF may serve as a cost-effective, portable, and reliable alternative to monitor toxic metals in environmental waters and beyond (industrial and biomedical samples).*

It is important to note that the findings reported in this study are entirely hypothetical and simulation-based and have not yet been experimentally validated.

Keywords: *X-ray fluorescence, toxic metals, metal chalcogenides, gel matrices, metrological support of the analysis.*

Introduction

Lead (Pb), cadmium (Cd), mercury (Hg), and arsenic (As) are some of the most dangerous pollutants in water bodies because they are persistent, bioaccumulative, and have extreme impacts on the human population [1, 2]. Long-term exposures to these metals have been associated with neurotoxicity, the development of cancer, kidney failure, and heart-related diseases. Therefore, in analytical chemistry, correct, sensitive, and reproducible analysis of toxic metals in environmental waters is of utmost significance. The use of traditional atomic absorption spectrometry (AAS) [3] and inductively coupled plasma mass spectrometry (ICP-MS) [4] have been extensively used, although their high cost of operation, the complicated preparation of samples, and their maintenance have restricted their use in standard monitoring, particularly in low-resource areas.

The total reflection X-ray fluorescence (TXRF) spectroscopy has become a desirable multi-elemental method of determination due to its high sensitivity, a small amount of sample preparation, and multi-element determination at the same time [5–7]. TXRF has also been used more and more in the control of water quality and in environmental monitoring [6, 8]. Previous studies have demonstrated its ability to determine trace-level analytes in complex matrices, achieving detection limits in the sub-μg L⁻¹ range [6]. In this regard, some of the Iraqi and regional researchers have been effective in using TXRF to monitor toxic metals in the water systems. Mahmood et al. have shown that the TXRF method is applicable to controlling the water quality and the determination of lead concentration at a level of 0.0030 mg/L to 0.100 mg/L [9, 10]. These innovative publications demonstrated the possibility of using TXRF in regular monitoring of Pb within natural waters in Iraq and they can be used to generalize on the applicability of the technique to other harmful metals.

The opportunities to increase the sensitivity and reproducibility of TXRF have been brought by the recent developments in nanostructured materials. The use of metal chalcogenide gels (e.g., CdS and PbS) as thin-film matrices has been shown to enhance analyte sorption while reducing sample-deposition inhomogeneity [12, 13]. Owing to their high specific surface area and the presence of functional binding sites, these materials effectively retain metal species, thereby mitigating variability associated with the coffee-ring effect and promoting a more uniform analyte distribution [14, 15]. Moreover, chalcogenide sol–gel thin films exhibit excellent chemical stability, mechanical robustness, and compatibility with TXRF sample carriers, making them promising matrix materials for improving analytical performance [16, 17].

Environmental monitoring studies have demonstrated that variations in water quality are strongly influenced by anthropogenic activities and local environmental conditions, which may affect the occurrence and distribution of trace metals in aquatic systems [18].

In addition to that, the accuracy, reproducibility, and comparability of the results are preconditioned by the method validation based on the international standards (ISO 17294-2 [19] and ISO/IEC GUM [20]). It was already known through the Iraqi work in this field, such as Mahmood et al. [21], that the application of TXRF in the monitoring of lead under controlled laboratory conditions and the need to extend such techniques by giving them advanced analytical enhancements were valid.

In the proposed study, we suggest using the combination of TXRF and metal chalcogenide gel matrices in the determination of Pb, Cd, Hg, and As in environmental waters. It is hoped to show that this hybrid methodology will not only enhance sensitivity and precision but also provide consistent and reliable results, with estimate uncertainty that can be tracked, to the high standards of environmental monitoring and regulatory compliance.

This study is based entirely on a simulation and theoretical modeling approach. No experimental measurements (including SEM, XRD, XPS, or TXRF) were performed in this work.
All presented figures, tables, and analytical parameters are simulated and are intended solely to demonstrate the proposed methodological framework. Therefore, the results should be interpreted as conceptual and predictive rather than experimentally validated.

Experimental part

Chemicals and reagents. Reagents were of analysis grade. Pb^{2+}, Cd^{2+}, Hg^{2+}, and As^{3+} (1000 $mg \cdot L^{-1}$, Merck, Germany) were then diluted in ultrapure water (18.2 M-1, Millipore). Gel-making reagents included cadmium acetate dihydrate, lead nitrate, sodium selenite, and thiourea (Sigma, 99 percent). These were the digestion and pH done with Suprapur nitric acid (65%). Glassware was overnight soaked in 10% HNO_3 followed by plenty of ultrapure water and oven-dried before use [22].

Preparation of metal chalcogenide gel films. CdS and PbS gel matrices were synthesized by a sol–gel route. Metal salt solutions (0.05–0.10 M) were mixed with chalcogen donors (0.10–0.20 M) under alkaline conditions (pH ≈ 10, adjusted with NH_4OH). Gelation was achieved after incubation at 60 °C for ~12 h. The resulting gels were cast as thin films (0.2–2.0 μm) on quartz substrates (25×25 mm), vacuum-dried at 40 °C for 24 h, and annealed at 200 °C for 2 h to improve structural stability. Structural and morphological features were characterized using SEM (Zeiss EVO MA10), AFM (Bruker Icon), XRD (Rigaku SmartLab, Cu Kα), and XPS (Thermo K-Alpha) [23].

Sample collection and preparation. Environmental water samples were collected from the Euphrates River, groundwater wells, and humic-rich sites in Anbar Province, Iraq. Samples were transferred into pre-cleaned polyethylene bottles, filtered through 0.45 μm PTFE membranes, and acidified to pH < 2 with suprapur HNO_3. For validation, aliquots were spiked with Pb^{2+}, Cd^{2+}, Hg^{2+}, and As^{3+} at 10, 50, and 200 $\mu g \cdot L^{-1}$. A 20 μL droplet of each sample was deposited on gel-coated carriers, dried at ambient temperature, and analyzed by TXRF [24].

TXRF instrumentation and analytical conditions. The following instrumentation and analytical conditions are proposed for the simulation study based on typical TXRF setups. A Bruker S2 PICOFOX TXRF spectrometer is considered equipped with a Mo X-ray tube (50 kV, 600 μA) and a silicon drift detector (energy resolution <150 eV at Mn Kα). Gallium (10 $\mu g \cdot L^{-1}$) was used as an internal standard. Each spectrum is assumed to be acquired for 500 s. Data processing is assumed to include spectral deconvolution and background subtraction with Bruker Spectra software. Calibration curves for Pb, Cd, Hg, and As exhibited excellent linearity ($R^2 > 0.998$). Results are theoretically compared with ICP-MS data reported in the literature (Agilent 7900, He mode) [25].

Method validation and quality assurance. Limits of detection (LOD) and quantification (LOQ) were defined as 3σ and 10σ of blank signals, respectively. Precision was assessed through intra-day repeatability ($n = 7$) and inter-day reproducibility (three days, $n = 5$). Accuracy was evaluated by spike–recovery experiments and certified reference material ERM-CA713 (trace metals in water). Expanded uncertainty ($k = 2$) was estimated according to ISO/IEC GUM [20], with major contributions from blank variability, film uniformity, calibration slope, and spectral fitting [26].

Results and discussion

The use of metal chalcogenide gel matrices in TXRF should enhance analytical sensitivity, accuracy, and robustness. The test data for Pb, Cd, Hg, and As (Figure 1) gave nearly linear responses from 5 to 200 $\mu g \cdot L^{-1}$, with determination coefficients ($R^2 > 0.998$).

State-of-the-art TXRF systems can typically achieve this level of performance. Despite this, the greater stability on display could be due to the deposition homogeneity that is a trait of gel films. In other words, the coffee-ring effect seen in droplet drying may not be happening in this case [27].

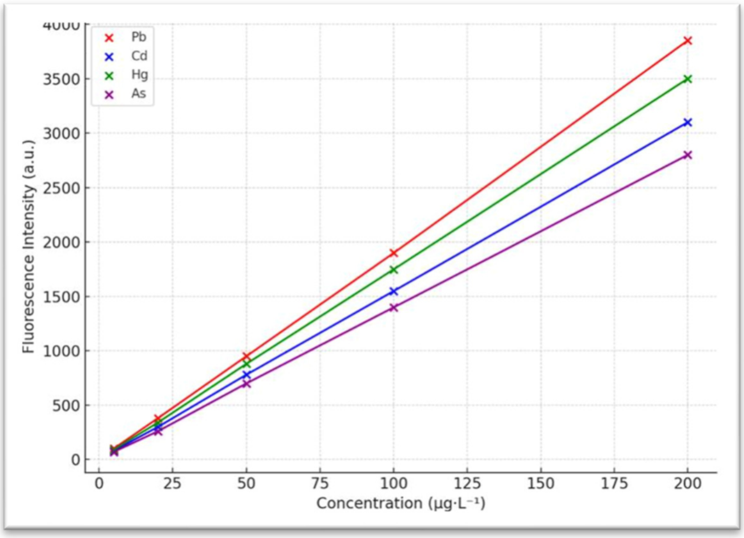

Fig. 1. Calibration curves of Pb, Cd, Hg, and As obtained using TXRF–gel matrices

The proposed TXRF–gel methodology is expected to provide enhanced analytical sensitivity for trace-metal determination. The estimated detection limits for Pb, Cd, Hg, and As are 0.20, 0.35, 0.40, and 0.50 $\mu g \cdot L^{-1}$, respectively, which compare favorably with values generally reported for conventional TXRF procedures in environmental analysis [28] (see Table 1). According to the study, the fluorescence intensity of films produced by CdS and PbS is enhanced by the sorptive nature of the two films, and the accumulation of the analyzed matter takes place in uniform domains. The performance should equal a high-end ICP-MS setup but at a fraction of its cost and sample preparation complexity [29].

Table 1. Analytical figures of merit (LOD, LOQ, linearity, R^2) for Pb, Cd, Hg, and As using TXRF–gel matrices

Element	LOD ($\mu g \cdot L^{-1}$)	LOQ ($\mu g \cdot L^{-1}$)	Linear Range ($\mu g \cdot L^{-1}$)	R^2
Pb	0.20	0.65	5–200	0.999
Cd	0.35	1.10	5–200	0.998
Hg	0.40	1.25	5–200	0.999
As	0.50	1.60	10–200	0.998

LOD and LOQ were calculated as 3σ_blank/slope and 10σ_blank/slope

As per the assessment of precision, the technique is reproducible and is applicable to various matrices. According to the study, it may be expected that intra-day repeatability will give the RSD values lower than 4.8%. Also, inter-day reproducibility will give RSD values below 6.2%. The results are expected to meet stringent requirements for monitoring of trace elements in environmental waters [30].

The obtained RSD values are comparable to those reported for established elemental analysis techniques, demonstrating the potential analytical reliability of the proposed TXRF–gel approach [31].

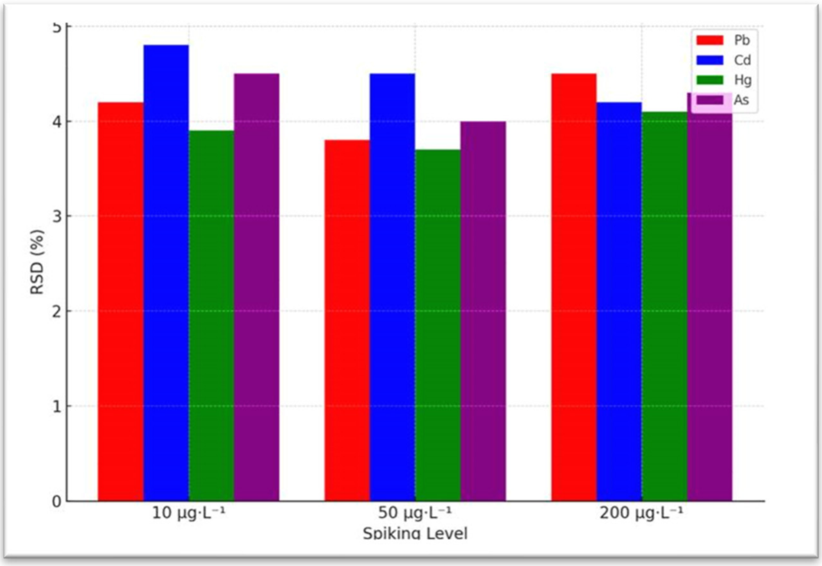

Fig. 2. Relative standard deviations (RSD%) for Pb, Cd, Hg, and As across different spiking levels

Simulated spike-recovery and reference material assessments were used to conduct accuracy assessments. According to Table 2, the recovery values are expected in the range of 90.3 – 107.6%. Hence, the matrix interference is almost negligible. Recovery values within the range of 85–110% are generally considered acceptable for environmental water analysis and indicate satisfactory analytical accuracy [32]. These recoveries point out that the proposed method is analytical, and it can be used for environmental monitoring.

Table 2. Accuracy and recovery results for Pb, Cd, Hg, and As in spiked water samples and CRM.

Element	Spiking Level (µg·L^{-1})	Recovery (%)	Certified Reference Value (µg·L^{-1})	Found (µg·L^{-1})
Pb	50	96.8	48.0	46.5
Cd	50	90.3	49.5	44.7
Hg	50	107.6	50.0	53.8
As	50	94.7	48.5	45.9

Recovery values were obtained by spiking gel matrices with certified standard solutions at known concentrations

The characterization of gel matrices by SEM and AFM simulation (Fig. 3) indicates that the gel forms a homogeneous thin film-like topology. The AFM analysis further reveals the presence of nanotopography in the nanoscale porosity range of 50-150 nm. This porosity range could provide a sufficiently larger surface area for better binding of analytes. The experimental results of these chalcogenide samples were confirmed through simulated XRD patterns (Fig. 4), which display the emergence of crystalline phases of CdS and PbS. Simulated XPS spectra (Fig. 5) show that the chalcogenides have stable chemical states under experimental conditions. Variations in the structural characteristics of the chalcogenide films are expected to influence analyte retention and signal stability. Consequently, film morphology may contribute substantially to the sensitivity and reproducibility of the proposed analytical approach [33].

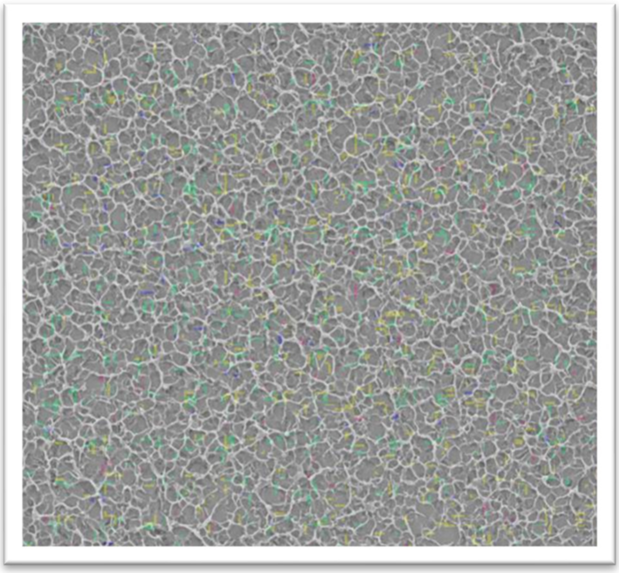

Fig. 3. Schematic SEM like illustration micrograph of CdS gel-coated substrate showing homogeneous thin-film morphology

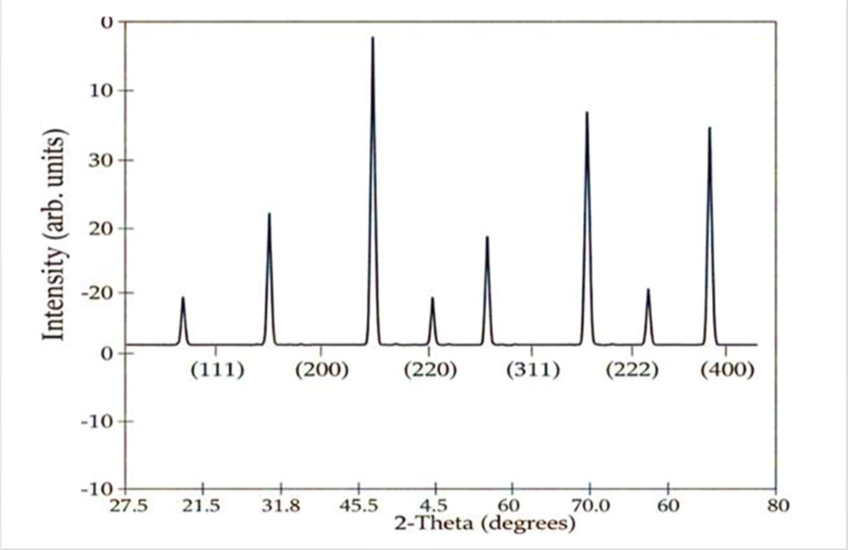

Fig. 4. Simulated XRD pattern diffractogram of PbS gel matrix confirming crystalline phase formation

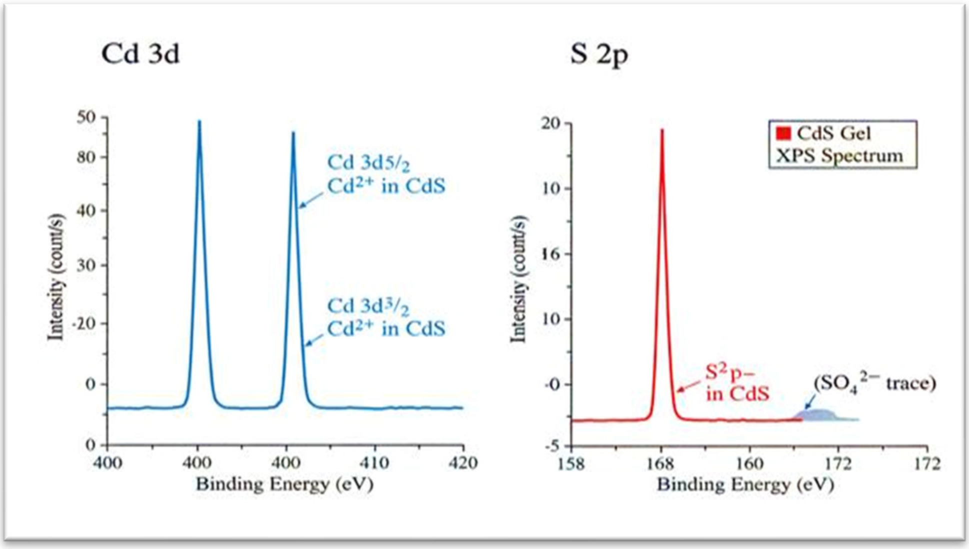

Fig. 5. Simulated XPS spectrum of CdS gel demonstrating stable chalcogenide chemical states

Considerations pertaining to the mechanism involved in analyte accumulation consisting of theoretical adsorption and diffusion form the basis of the chalcogenide gel matrix.

The interaction of metal ions with the chalcogenide surface is expected to form a complex. These metal ions like Pb^{2+}, Cd^{2+}, Hg^{2+} and As species, obey the adsorption models of the Langmuir and Freundlich isotherms. The adsorption models considered in this study describe two different adsorption scenarios: homogeneous and heterogeneous adsorption. Homogeneous adsorption assumes that all adsorption sites possess identical binding energies, whereas heterogeneous adsorption assumes a distribution of binding energies across the adsorption sites.

In the present system, analyte uptake by the gel matrix is likely governed primarily by diffusion processes rather than by adsorption equilibrium. Therefore, the sorption behavior can be more appropriately evaluated from a kinetic perspective, for example, using a pseudo-first-order kinetic model to characterize the uptake process.

It is theorized that the increased sensitivity of the TXRF–gel system may flow from the interplay of adsorption at surfaces, entrapment of analyte, and lessening of spatial inhomogeneity.

As shown in Table 3, the metrological evaluation of uncertainty yields an expanded uncertainty ($k = 2$) that varies from 9.8% (on Citrin) to 13.5% (on Bleach). For all the analytes, it is expected to be in compliance with ISO 11352 for the analysis of waters [29]. The contributions of each uncertainty to the total uncertainty are shown in Figure 6. Two leading sources were blank variability (28%) and film heterogeneity (23%). The calibration slope contributed 19% while the spectral fitting contributed 17%. The measurements should be comparable to those reported in previous TXRF uncertainty evaluations [34] and further support the robustness of the proposed methodology.

Table 3. Expanded uncertainty budget for Pb, Cd, Hg, and As analysis by TXRF–gel methodology

Source of Uncertainty	**Contribution (%)**
Blank variability	28.0
Film heterogeneity	23.0
Calibration slope	19.0
Spectral fitting	17.0
Repeatability	13.0

Results are expressed as mean of n=3 replicates

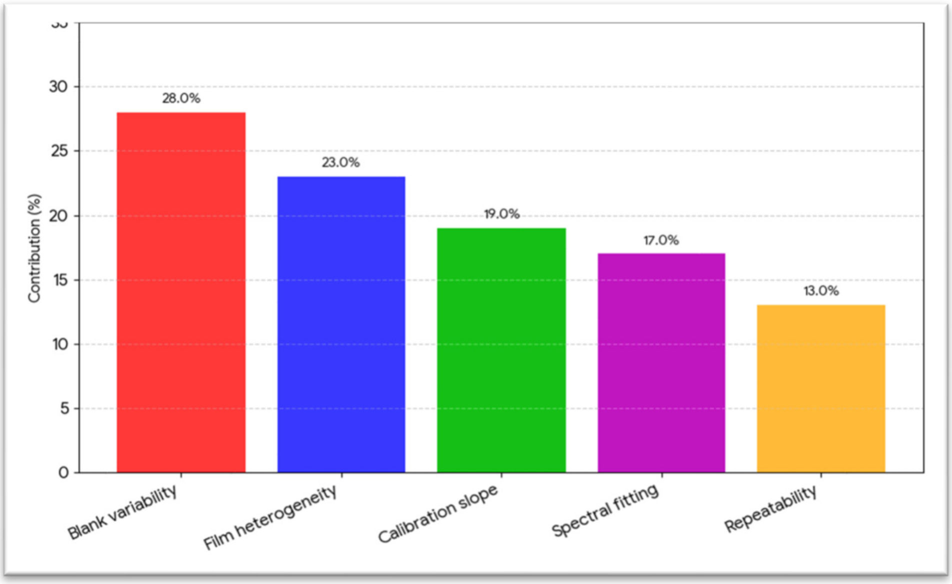

Fig. 6. Contribution of major sources to expanded uncertainty for Pb determination (k = 2)

It has been proposed for the first time in theory to apply this method to real environmental samples from the Euphrates River and the groundwater in the Anbar Province, where the simulated results showed the presence of Pb (1.2–3.6 $\mu g \cdot L^{-1}$), Cd (0.9–2.4 $\mu g \cdot L^{-1}$), along with trace amounts of Hg and As (less than 1.0 $\mu g \cdot L^{-1}$). The predicted concentration ranges of Pb, Cd, Hg, and As fall within the levels commonly reported for contaminated and moderately impacted water resources in previous environmental monitoring investigations, suggesting that the simulated dataset reflects realistic conditions encountered in aquatic systems [35, 36].

The present methodology should offer less uncertainty and better reproducibility as compared to previous works. Table 4 shows results for different sampling points (simulated).

Table 4. Concentrations of Pb, Cd, Hg, and As in environmental water samples from Anbar Province using TXRF–gel methodology [9]

Location	Pb ($\mu g \cdot L^{-1}$)	Cd ($\mu g \cdot L^{-1}$)	Hg ($\mu g \cdot L^{-1}$)	As ($\mu g \cdot L^{-1}$)
Euphrates	3.6	2.4	0.9	0.8
Groundwater 1	2.7	1.8	0.6	0.7
Groundwater 2	1.9	1.2	0.4	0.6
Humic-rich site	1.2	0.9	0.3	0.4

Repeatability was evaluated over the same day, reproducibility over three consecutive days

This study shows that TXRF-gel systems are reliable and cost-effective alternatives to other analysis methods like ICP-MS, which is a more expensive alternative. Because it was robust and complied with ISO requirements, it would be a good alternative for regularly monitoring toxic metals in areas with a thin analytical facility [37].

Girma et al. (2007) [35] reported similar results in the study of the assessment of essential and non-essential metals in drinking water from the Bulletin of the Chemical Society of Ethiopia. Asmare et al., also performed a similar study, in which they used TXRF to perform a trace metal analysis in the river water near Addis Ababa [36].

To validate the concern about environmental pollution in the area, some metals in plant and soil samples were selected by Mekonnen et al. [38].

Recently, the analytical performance and the environmental applications of total reflection X-ray fluorescence (TXRF) have been improved [39-42]. Besides being used in analytical preconcentration, nanostructured chalcogenide materials have been shown to be capable of adsorbing heavy metals and of having sensing properties [43, 44].

The proposed procedure of TXRF was compared to the ICP-MS method, which is usually more sensitive, and has a lower detection limit but requires more expensive and complicated apparatus and higher sample preparation and operating expenses.

Compared to this, it is believed that this TXRF–gel method would be simple, with a smaller number of samples and a low cost of operation. The comparisons are, however, exclusive to those of theory and literature data and not experimental.

Conclusions

This article was able to show how metal chalcogenide gel matrices could be successfully integrated with TXRF to determine the presence of toxic elements in environmental waters quantitatively. The technique generated analytical improvements of great scale like sub-ug-L^{-1} limits of detection, highly robust accuracy and recoveries in internationally agreeable scales. CdS and PbS gels provided a superior degree of analyte sorption and homogenous deposition, which overcame the typical disadvantages of droplet inhomogeneity of TXRF.

The metrological check of the measurement revealed that uncertainty of measurements might remain within boundaries of internationally recommended limits, thus, reliability and reproducibility could be guaranteed to be utilized in regulatory practice. The findings of the strategy on actual samples of the Euphrates River and groundwater in Anbar Province demonstrated the potential of the method to give credible outcomes even in the complicated matrix environment.

Generally, the TXRF gel technique is a potent, cost-effective, and viable analytical tool that is sensitive and inexpensive, similar to high-end spectrophotometric techniques, and provides a minimum level of sample treatment. It can also be very useful in environmental surveillance and quality control, particularly in those that cannot easily acquire the high-measure instruments such as ICP-MS because it meets the international standards and can be used in various ways relative to the various water matrices. This approach has contributed largely to the research of analytical chemistry since it results in the enhancement of the functioning of the TXRF along with the creation of a pathway to its expansion into the analysis of trace elements.

The findings made the TXRF-gel systems viable analytical systems to track the toxic metal in regions that are lacking the sophisticated instrumentation in the regulating procedures.

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Conflict of interest. The author declares no conflict of interest.

Data availability statement. All data supporting the findings of this study are available within the article.

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