

Detection and Measurement of Dissolved Metals in Mine Water Using Cation-Binding Resins and Field Portable XRF

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Abstract

The work presented demonstrates that Diffusive gradients in thin films (DGT) and similar passive sampling techniques that use cation-binding resins can be effectively combined with portable X-ray fluorescence (XRF) for reliable detection and monitoring of dissolved metals species in mine water. In this study, Chelex resin was used to capture metals from synthetic and real mine water through an ion exchange mechanism. Metal ions were detected on the resins after exposure to solutions containing low concentrations (ppb) of metals, and the amount of metals accumulated and detected on the binding layer was proportional to the deployment time. We present measurements of zinc, nickel and manganese ions in mine water using this technique which is in good agreement with ICP-MS results. In summary, the approach holds great promise for rapid and reliable detection and monitoring of metals in mine drainage and mine impacted water bodies.

Keywords: Metal detection, Mine water, DGT, Field portable XRF, Ion-exchange

Introduction

All around the world, mine water pollution is of serious concern and mine-derived contaminants have affected the environment. Passive samplers are becoming more widely used for monitoring metals and other organic pollutants in water. Diffusive gradients in thin films (DGT) passive sampler method can rectify the problems related to the distribution of metal which can change during sampling, storage, preservation, or through contamination (Buffle 2000, Batley 2004). Normally, the accumulated metal ions on DGT binding layer are eluted with acid after the deployment period and then measured by Inductively coupled plasma mass spectrometry (ICP-MS), Inductively coupled plasma optical emission spectrometry (ICP-OES), Atomic absorption spectroscopy (AAS) or other similarly analysis. These methods are costly in terms of technician time and consumables. To overcome this problem, portable XRF was used to detect the metal accumulated by the DGT. XRF is commonly used in the environmental studies

of metals. Portable XRF is a reliable method for on-site monitoring of metals in water and soil samples (Chou 2010, Kalnicky 2001). This study focuses on the development of a metal binding layer for the accumulation of Zn (as a key contaminant in UK metal mine waters), Ni and Mn, followed by measurement with a field portable XRF (cf. Chen 2013). The performance of the device in different pH and different time periods of deployment were assessed.

Materials and method

Chemicals and reagents

To prepare the binding layer for dissolved metal ions measurement, Chelex-100 resin, and acrylamide were purchased from Bio-Rad Laboratories, agarose from VWR chemicals, N, N, N', N'-tetramethyl ethylenediamine (TEMED) catalyst, Bismuth nitrate pentahydrate, and sodium hydrogen phosphate from Sigma Aldrich, and ammonium persulphate (APS) from Fisher Scientific. All metal standards were purchased from VWR chemicals. DGT

piston holders and Chelex/Metsorb binding layer-based DGT device was purchased from DGT Research Ltd. (Lancaster, U.K.). All chemicals utilized in this work were of analytical reagent grade.

Preparation of diffusive gel and binding gel

The gel solution was prepared with a mixture of acrylamide and agarose chemicals for the preparation of diffusive layer gel, in-house Chelex binding gel and BiPO_4 binding gel. In the diffusive layer preparation, gel solution mixed with 120 μL of 10% APS and 40 μL of TEMED. The obtained mixture gel solution undergoes casting at 45–48 °C for 1 h in between two glass plates with 0.8 mm thick spacers. For the in-house Chelex and BiPO_4 binding layer preparation, Chelex-100 resin (4g) and BiPO_4 (0.1g) was added with gel solution following same procedure separately by use of 0.4 mm thick spacer. Final cast gels were cut into discs and kept in 0.02 M NaNO_3 at 4 °C for storage before use. BiPO_4 was prepared by a hydrothermal method at 140 °C for 5 h using Bismuth nitrate pentahydrate and sodium hydrogen phosphate aqueous solution, which was washed and then dried at 100 °C for 12 h.

Measurement

In this study, the metal concentration was determined by S1 TITAN handheld XRF Bruker analyzer. Five elements, including Zn, Ni, Mn, Cd, and Pb were calibrated. The emission lines ($\text{K}\alpha_1$) of Zn (8.639 keV), Mn (5.90 keV), Ni (7.48 keV), and Cd (23.13 keV) were used for integrating the peak area. XRF measurement was focused on the exposure area of the top of the DGT device and using the GeoMining type and Oxide concentration method in XRF instrument. The recorded data was transferred to the system via a USB port. Then, all the data were collected through Bruker instrument tool software 1.8.0.136. After XRF measurement, the binding gel discs were removed from the housing unit and then eluted in 2 mL of 1 M HNO_3 for at least 24 h. The eluted metal ions were diluted and then measured by ICP-MS (NexION 300X, PerkinElmer). All the laboratory testing was conducted at 25 °C.

To validate the performance of the devices in real mine water samples, both devices with two different binding layers were deployed in mine water at a site in the S.West of England. Meanwhile, synthetic mine water samples were also prepared and tested using the commercial Chelex/ Metsorb DGT device.

Results and discussion

Blank and detection limit for the DGT device

The blank Zn concentrations of the Chelex/ Metsorb DGT and the in-house Chelex-binding layer device were estimated from the integrated peak area of Zn by the XRF detection method. The Chelex/Metsorb DGT device was assembled with the mixed binding gel (0.4 mm thick), APS diffusive gel (0.8 mm thick) and polyethersulphone filter membrane (0.14 mm thick) and deployed in buffer solution with Zn for 24 h. Similarly, the in-house BiPO_4 device was assembled with the BiPO_4 binding gel (0.4 mm thick) and polycarbonate membrane (0.4 μm pore size) and deployed in buffer solution with Zn for 24 h. The in-house Chelex device with Chelex binding gel (0.4 mm thick) and polycarbonate membrane was deployed in buffer solution with Zn for 72 h. Before deployment, the assembled DGT device didn't give any response peak for Zn. n-, indicating low-level contamination of Zn in the binding layer. In this XRF detection method, the Limit of detection so far determined for Zn using the in-house Chelex device (100 $\mu\text{g L}^{-1}$) is lower (5–30 times) than Chelex/Metsorb DGT (500 $\mu\text{g L}^{-1}$), and BiPO_4 binding layer (3 mg L^{-1}). This detection limit is lower than the permissible limit of Zn reported by the WHO guidelines for drinking water (WHO 2022). This suggested that the proposed device can provide useful data for the determination of Zn contaminants in the mine water environment. If the Zn concentration in natural sources is much lower than the detection limit determined above, a longer deployment period may improve the mass loading on the binding gel (or a reduction in the thickness of the diffusive gel when one is used) (Deng 2019). Increasing the XRF acquisition time will also help but that reduces the sample throughput in the field.



Metal analysis

The handheld XRF device was calibrated for Zn, Cd, Ni, Mn, and Pb with the standard solutions. The Chelex/Metsorb DGT device was deployed in the 2L solution (pH 5.8) with different concentrations (0.5 mg L⁻¹ to 10 mg L⁻¹) of Zn, Cd, Ni, Mn, and Pb ions for 24 h. The accumulated metal ions were detected and measured by XRF after the deployment period, which is presented in Fig.1 (A–D). Chelex/Metsorb DGT provides a good linear response for Zn (0.5 mg L⁻¹ to 5 mg L⁻¹), Ni (0.5 mg L⁻¹ to 10 mg L⁻¹), and Mn (3 mg L⁻¹ to 10 mg L⁻¹). Pb and Cd did not give expected results. XRF peak area for corresponding metal ions increases with the increasing solution concentration, which indicates the mass loading (or) metal accumulation enhances within the binding gel. XRF measurement on high concentration Zn solution (10 mg L⁻¹), observed a decrease in the peak area, possibly due to exceeding the adsorption capacities of the gel (Kunfu 2020). Similarly, the in-house Chelex gel provides a good linear response for Zn from 100 µg L⁻¹ to 3000 µg L⁻¹, as presented in Fig.1E.

Time-series accumulation

Zn accumulation on the in-house Chelex binding layer and BiPO₄ binding layer was monitored using the XRF after deployment for different periods of time (Fig. 2), which can be useful for validating the performance of the devices. For this study, the Chelex device was deployed over a time of 24 h, 48 h, and 72 h at pH 5.8 solution with 100 µg L⁻¹ Zn. A good linear response was observed over the period of Zn accumulation on Chelex (R² = 0.9987), which is compared with BiPO₄ gel (R² = 0.9884). These results proved that uptake of Zn by the Chelex gel is fast compared with BiPO₄ gel. The Zn accumulation over time for

BiPO₄ binding layers has not been reported previously.

Effect of pH

To determine the range of conditions under which the devices could be deployed, the performance of the in-house devices was tested at various pH values. The pH buffer solutions were adjusted by the solution of 1 M HNO₃ and 1 M NaOH. The in-house Chelex binding layer device was checked in pH solutions of 4.6, 5.8, and 7.0 with 100 µg L⁻¹ Zn by the deployment of the device in a 2L solution for 72 h. Fig. 3 clearly shows that the measured peak area for Zn accumulation on the gel at pH 7.0 was much lower than pH 5.8 and pH 4.6, indicating that the Chelex gel at pH 7 has a lower adsorption efficiency (Lin 1999). Normally, the Chelex gel adsorption mechanism for metal ions was based on the ion exchange method (Lin 1999). The detected Zn concentration at pH 7 was 27% lower than the expected concentration due to the pH-dependent ion exchange reaction that takes place between Chelex gel and Zn ions.

Detection and measurement in real mine water

To verify the efficacy of the Chelex devices, the in-house Chelex binding layer device and Chelex/Metsorb DGT devices were deployed in fresh mine water, located at the mine site in the South West of England. The results of the deployment are presented in Table 1, suggesting that measured Zn concentration from the XRF method showed good agreement with ICP-MS results. The performance of DGT was good over the week-long period. However, during the longer periods of deployment, the sensitivity of the analyte of the devices may be affected by biofouling or degradation of film.

Table 1 XRF-Chelex DGT detection of Zinc in mine water sample and comparison with ICP-MS results

Deployment period	DGT	Element	XRF results mg L ⁻¹	ICP-MS Results mg L ⁻¹
3 days	Chelex	Zn	1.24	1.50
3 days	Chelex	Zn	1.05	1.28
7 days	Chelex/Metsorb	Zn	1.18	1.06

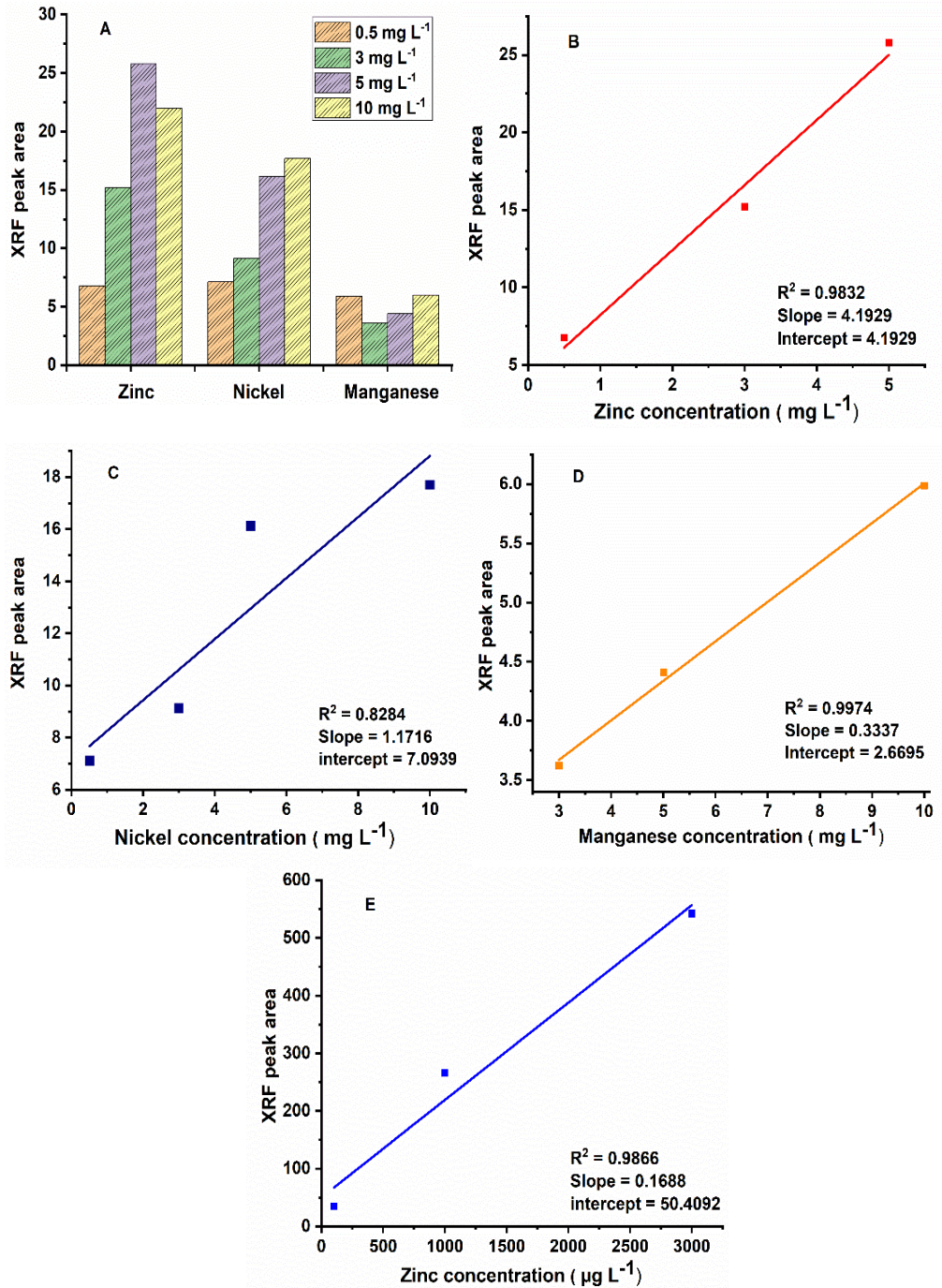


Figure 1 XRF peak area versus metal ions concentration in the measurement of trace metal ions present in synthetic mine water using Chelex/Metsorb DGT (24 h deployment time, 2L of pH 5.8 buffer) [A], the linear curve of XRF measured peak area versus corresponding Zn, Ni, and Mn concentrations while using Chelex/Metsorb DGT samplers [B, C, and D], the linear curve of XRF measured peak area versus Zn concentrations using the in-house Chelex sampler [E].

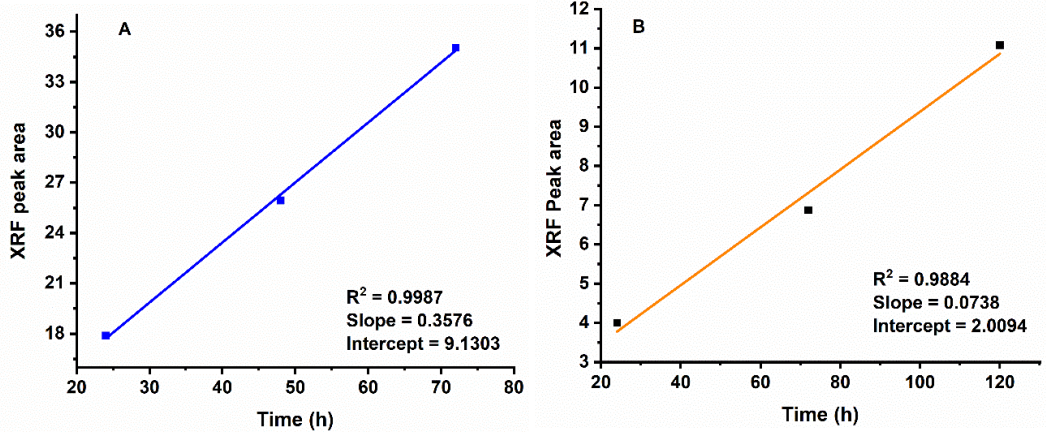


Figure 2 XRF measurement of Zn accumulation by the in-house Chelex-binding layer device placed in a solution containing $100 \mu\text{g L}^{-1}$ Zn, pH 5.8 for the different times from 24 to 72 h (A). XRF measurement of Zn accumulation by the in-house BiPO₄-binding layer device placed in a solution containing 3 mg L^{-1} Zn, pH 5.8 for different times from 24 to 120 h (B). Note the difference in the y-axis scales.

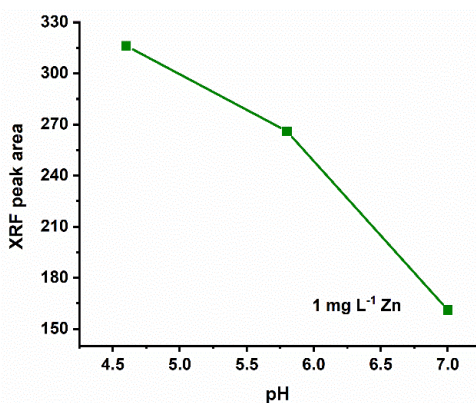


Figure 3 Effect of pH on measured Zn peak area by XRF-Chelex DGT sampler

Conclusion

This study demonstrates that it is feasible to detect and monitor metal species in mine water by using either commercially available DGT devices or in-house variants, followed by metal detection and quantification using field portable XRF. The in-house Chelex-based binding layer potentially provides a reliable method for measuring the dissolved Zn (and other metals) in mine water and was compared against the performance of a commercial Chelex/Metsorb DGT and an in-house BiPO₄-based binding layer device. From this method, we were able to detect and quantify (if the accumulation rate is known)

the low concentration of Zn down to $100 \mu\text{g L}^{-1}$. The developed binding-layer device performance is good in the pH range of 4.6-7.0 in the environmental water. This technology will simplify and make cheaper and quicker the application of passive samplers for in-situ monitoring of polluted waters.

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