

On-Site XRF Analysis of Metal Concentrations of Natural Waters

Tommi Tiihonen¹, Tuomo Nissinen², Joakim Riikonen¹, Pertti Sarala³, Vesa-Pekka Lehto¹,
Bruno Lemièrè⁴

¹*Dept. of Applied Physics, University of Eastern Finland, FI-70210 Kuopio, Finland, joakim.riikonen@uef.fi*

²*AWater Oy, FI-70210, Kuopio, Finland, tuomo@3awater.com*

³*Geological Survey of Finland, FI-96101 Rovaniemi, Finland, pertti.sarala@gtk.fi*

⁴*BRGM, F-45060, Orléans, France, brunole45@orange.fr, ORCID 0000-0002-8907-1280*

Abstract

Real-time and on-site analysis of metals in waters is not routinely carried out for environmental monitoring. Laboratory analyses are used instead, which require sampling on-site, shipping to a laboratory and analysis making them expensive and slow. A novel analytical technique based on nanotechnology enhanced preconcentration and portable X-ray fluorescence was developed in this study. The analysis system was calibrated for Mn, Ni, Cu and Zn between concentrations of 50 µg/L and 10 mg/L and fast on-site analysis was demonstrated for two mining related sites.

Keywords: On-Site Analysis, Pxf, Runoff, Hydrogeochemical Exploration, Compliance Analyses

Introduction

Trace element analyses of water are used at all stages of mining projects, for both commodity and environmental purposes. This includes exploration stage (hydrogeochemical exploration, Kidder *et al.* 2020), mine development and exploitation stages (Li *et al.* 2020), ore processing (Ghorbani *et al.* 2017), mine closure stage and modelling (Nordstrom *et al.* 2015; Cánovas *et al.* 2018), as well as post-closure environmental monitoring (Wheeler *et al.* 2021). The analyses are also used in environmental impact assessment and monitoring of any industrial activities or environmental projects.

While metal analyses of solid media are increasingly done on-site (Lemièrè & Uvarova 2020), allowing sample screening and dynamic sampling plans, most water analyses are still performed in the laboratory. This involves high costs for sample shipping and analyses, and delays for results ranging from days to months depending on site and laboratory location. Most of the time, this precludes any possibility of taking results into account for sample selection, sampling plan adaptation or site management decisions.

Economic reasons may be involved in choosing on-site techniques, by reducing

laboratory costs or by increasing the number of analysed samples for a given budget. But the most important expected benefit is to improve the quality of the data set: Better investigations of the anomalies identified on site, a better representativity of samples selected for laboratory analyses, and denser data sets. Denser map grids can be obtained for exploration or impact mapping. Denser time series can be applied for process or runoff monitoring.

Field analysis techniques used for solids, especially portable X-ray fluorescence (pXRF), are not directly usable for water due to the low volumic concentration of analytes. Electrochemical water analysis techniques proved to be more sensitive (Yehia *et al.* 2019) but they require longer operations and highly skilled personnel.

A novel analytical system, Multimetal Water Analysis System (MWAS), developed by 3AWater for sensitive and robust on-site analysis of metal contents of water, without the challenges of electrochemical techniques. The technology is based on concentrating metals from a water sample in a composite filter containing thermally carbonised nanoporous silicon with bisphosphonate functionalised surface (Thapa *et al.* 2020).

Metals can be concentrated up to 200 times in the filter, which allows analysis with a fast and inexpensive portable X-ray fluorescence spectrometer (pXRF). Empirical calibrations for Mn, Ni, Cu and Zn were used to convert the measured pXRF intensities to the metal concentration of the original water sample.

Experimental

The MWAS system consisting of filter, filter holder, adapter, syringe pump and a pXRF is presented in Figure 1.

The metal collecting composite filters used in the analytical technique were prepared by coating a thin cellulose filter paper with a slurry. The slurry consisted of bisphosphonate functionalised thermally carbonised porous silicon (BP-TCPSi) particles, with median particle size of 15 μm and specific surface area of 230 $\text{m}^2 \text{g}^{-1}$, polyacrylic acid (PAA) and carboxymethyl cellulose (CMC) in aqueous solution. The weight ratio of these components in the final slurry was 80% BP-TCPSi, 10% PAA and 10% CMC. To lower the viscosity for easy pipetting of the slurry, 1.9 mL of deionised water and 1 mL of isopropyl alcohol was added per 1 g of BP-TCPSi. 130 μl of the slurry was pipetted on a circular cellulose filter paper with 15 mm diameter. The filters were first dried at RT for 45 min and then in 150 $^{\circ}\text{C}$ vacuum oven for 2

h for the PAA and CMC to form a crosslinked structure binding the BP-TCPSi particles on the filter surface. The mass of the BP-TCPSi was 20 mg per filter.

A specific holder for the filters was designed enabling easy utilization of the method in field conditions. The holder pieces were 3D printed with SLS technique from polyamide 12 and two additional O-rings were used to ensure leak free operation. Schematic design and photographs of the holder with metal collecting filter is presented in Figure 2. A compatible adapter was also designed to be used with Hitachi X-MET8000 pXRF. The adapter was attached on the light radiation shield of the X-MET8000 device, and the holder could be attached there by first removing the top piece from the holder and using the threads of the middle piece to fasten it on the adapter. The size of the holder opening was optimised for the X-ray window geometry of X-MET8000.

The MWAS system was calibrated for four metals Mn, Ni, Cu and Zn. Empirical calibrations were made with water samples prepared by spiking lake water with known amounts of metals. The metal concentrations of the calibration samples varied between 50 $\mu\text{g L}^{-1}$ and 10 mg L^{-1} and the pH was adjusted to 7. 10 mL of the water sample was pumped through the metal collecting filter with flow



Figure 1 The 3A Water Multimetal Water Analysis System (MWAS, prototype 2.1): A) Battery operated syringe pump, B) consumable filters including a 0.45 μm prefilter and the metal collecting filter inside a filter holder, C) handheld XRF spectrometer, D) adapter on the spectrometer with the filter holder inserted and E) image of the screen of the spectrometer showing results from an on-site analysis (not specific to the present pilots).

rate of 1 mL min^{-1} and the adsorbed metals were analysed with pXRF. The initial concentrations of the water samples analysed with ICP-MS were plotted with the XRF intensities to create calibration curves optimised for natural water samples with pH close to neutral. Hitachi X-MET8000 Control software (SW version: 4.1.0.222) was utilised to create empirical calibration to X-MET8000 from the data set.

On-site experiments were performed in Finland on two mining sites during spring 2020. The sampling included five groundwater samples from Site 1 and five surface water samples from site 2. pH and electric conductivity (EC) were measured with handheld YSI Professional Plus multimeter on-site in both cases. The MWAS by 3AWater was utilised to analyse dissolved metal concentrations of the samples on-site. Following steps were performed for the MWAS analyses on-site:

1. Approximately 11 mL of water sample was taken into a 20 mL syringe.
2. Battery operated syringe pump was used to pump 10 mL of water sample from syringe through a $0.45 \mu\text{m}$ prefilter and a metal collecting filter with a 1 mL min^{-1} flow rate.
3. After the filtration, water was flushed out from the holder by manually pushing air

through the holder using a syringe.

4. The filter holder was opened and attached to an adapter on a handheld X-ray fluorescence spectrometer (pXRF, Hitachi X-MET8000 Expert).
5. Metals were analysed from the filter with the pXRF. The metal concentrations in the initial sample were determined using predetermined calibrations. The concentrations were read from the display of the pXRF device.

The pumping took 10 min, flushing and transferring the holder from the pump to the pXRF 1 min and the pXRF analysis 2 min. Therefore, results were obtained within 15 minutes from the sampling.

Reference samples were collected, filtrated through $0.45 \mu\text{m}$ syringe filter and acidified on-site with ultrapure nitric acid to prevent precipitation and then delivered for ICP-OES analysis to the University of Oulu.

Results

The 3D printed filter holders were designed to protect the filter from mechanical wear and chemical contamination. It allows also easy transfer and attachment of the filter to measurement position of pXRF with the designed adapter. The XRF emission peaks

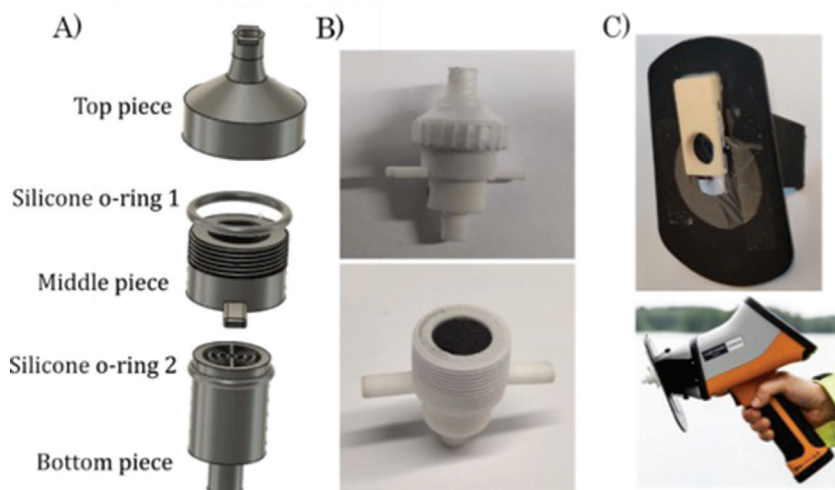


Figure 2 Filter holder used in the study. A) An exploded view of the design of the 3D printed parts with two additional silicone O-rings. B) Photographs of the holder. The top photograph shows the holder with all parts assembled and the bottom photograph shows the holder with top piece removed showing the surface of the filter, from which metal signals are measured with pXRF. C) Adapter used to attach the filter and holder to pXRF measurement position.

originating from the metals adsorbed in the metal collecting filter in the calibration experiments correlated well with metal concentrations of the water samples analysed by ICP-MS. A regression analysis was utilised successfully to create metal specific empirical calibration curves (presented in Supplementary Material Figure S1.) for the X-MET8000.

The first site (Site 1) was a mine and analyses were done in environmental monitoring purposes during routine sampling from the groundwater bore holes. The next site (Site 2) was closed mine and sampling was performed on the natural waters surrounding the old tailings pond again on monitoring purposes. The results of the MWAS measurements compared to the laboratory are presented in Table 1 and 2. Among the four metals calibrated in the system, Mn was most often found in the samples, and notable Zn concentration were present in the samples 5 and 8. Notable Ni concentration was also found in the sample 8.

Similar results were obtained from the on-site analyses and the reference ICP-OES analyses for the samples from both sites. Mn results obtained on-site with MWAS follow ICP-OES results accurately in all samples except the Sample 10, showing slightly higher, 36%, difference between the analyses as seen

in the Figure 3. The correlation coefficient for the Mn results is 0.83 and if the sample 10 is removed the correlation coefficient is 0.99. The MWAS gave higher concentration for Zn in the Sample 5 compared with ICP-OES with concentration close to the detection limit of the system. Lower concentrations for Ni and Zn were obtained in the Sample 8.

A blank sample for ICP-OES was made by filtrating, acidifying, and storing the DI water similarly as the samples and analysed together with actual samples. The blank sample showed slightly elevated Zn concentration of about 37 µg/l. It seems that small Zn contamination is originated from the bottles or from the acid for reference samples. These higher Zn levels can be seen at least in the ICP-OES analyses of samples 6 – 10. The blank DI water analysis for MWAS did not show any signals from the calibrated metals.

Discussion

Analytical capabilities of the new technology are limited by (a) the analyser and (b) properties of the concentrating media (the filter) (c) the precision of the pXRF and (d) the accuracy of the reference method. Element range of pXRF currently spans from Si to U, excluding light elements and most precious metals, for analyzing solid concentrations between a few mg/kg and a few percents

Table 1 Results of Site 1 on-site analyses with the MWAS system compared with reference analyses (LAB). Concentrations above the detection limit of the MWAS system (50 µg l⁻¹) are marked with a bold font.

Sample (Site 1)	pH	Temp (°C)	EC (µS/cm)	Mn (µg l ⁻¹)		Ni (µg l ⁻¹)		Cu (µg l ⁻¹)		Zn (µg l ⁻¹)	
				MWAS	LAB	MWAS	LAB	MWAS	LAB	MWAS	LAB
Sample 1	5.3	4.4	99	< 50	< 30	< 50	< 20	< 50	41	< 50	16
Sample 2	6.4	4.6	136	347	356	< 50	36	< 50	< 20	< 50	32
Sample 3	6.0	4.0	101	348	365	< 50	33	< 50	< 20	< 50	30
Sample 4	6.4	6.4	134	490	479	< 50	42	< 50	< 20	< 50	27
Sample 5	5.0	4.6	32	< 50	< 30	< 50	< 20	< 50	< 20	64	35

Table 2 Results of Site 2 on-site analyses with the MWAS system compared with reference analyses (LAB). Concentrations above the detection limit of the MWAS system (50 µg l⁻¹) are marked with a bold font.

Sample (Site 2)	pH	Temp (°C)	EC (µS/cm)	Mn (µg l ⁻¹)		Ni (µg l ⁻¹)		Cu (µg l ⁻¹)		Zn (µg l ⁻¹)	
				MWAS	LAB	MWAS	LAB	MWAS	LAB	MWAS	LAB
Sample 6	5.8	12.9	115	162	153	< 50	< 20	< 50	< 20	< 50	59
Sample 7	6.3	13.2	138	376	379	< 50	30	< 50	< 20	< 50	58
Sample 8	6.3	11.8	339	< 50	< 30	78	172	< 50	< 20	190	326
Sample 9	6.1	12.8	300	60	79	< 50	< 20	< 50	< 20	< 50	47
Sample 10	6.5	14.4	479	291	457	< 50	37	< 50	< 20	< 50	48

(Lemière and Uvarova 2020). Filters are currently able to concentrate cationic species – the metals, *sensu stricto*. In addition to four metals calibrated, proof of concept study has been performed for U and Pb. These metals already cover the regulatory needs of some mines (coal, iron and transition elements, base metals, phosphate) have been calibrated on the system, but the system's capabilities are not limited to these metals. Additional elements that would not require developments beyond specific calibration include Fe, Co, Ti and Sr. Elements that may be detected if their abundance is high include Cd, Ag, V and Cr.

However, anionic species such as As, Sb or Se cannot be currently analysed. Arsenic is a major issue for mining applications, and a topic of future development. Gold and platinum group elements are beyond the reach of predictable elements and have to be addressed through tracers or proxies. Lithium is also out of reach of pXRF unless indirect approaches are used. Based on the calibration curves MWAS can analyse concentrations ranging about from $50 \mu\text{g L}^{-1}$ to 10mg L^{-1} and the range can be sifted to even lower concentrations by utilizing larger volumes for the filtration.

With solid samples, most of the differences between pXRF and laboratory results are systematic biases caused by differences in calibration and on-site samples and a slightly

higher dispersion of the on-site analyses compared with the laboratory analyses (Young *et al.* 2016). These can be incorporated in higher reporting uncertainties for safety, but it also is possible to use raw pXRF results reliably for sample ranking and classification purposes (Lemière 2018; Lemière and Uvarova 2020). A bias may also be observed for water analyses between pXRF and laboratory results, but in most cases, there is a good correlation between them for a given matrix type. Samples will therefore be accurately ranked from low to high concentrations for each element, and inter-element ratios will be conserved. Empirical correction factors can be defined for a given matrix type and applied at a given site.

Decisions can therefore be made on-site without waiting for the laboratory results if pXRF results are significantly above or below thresholds or action levels. With the developed system, large gains are possible, in terms of both costs (sampling and analysis) and quality of data sets, because of better sample selection. At the present stage, the results can be used for screening purposes, to detect anomalies, time series variations and therefore efficiently select the samples to be sent to the laboratory. Usability and accuracy of the system are being constantly improved by optimizing the design and calibrations.

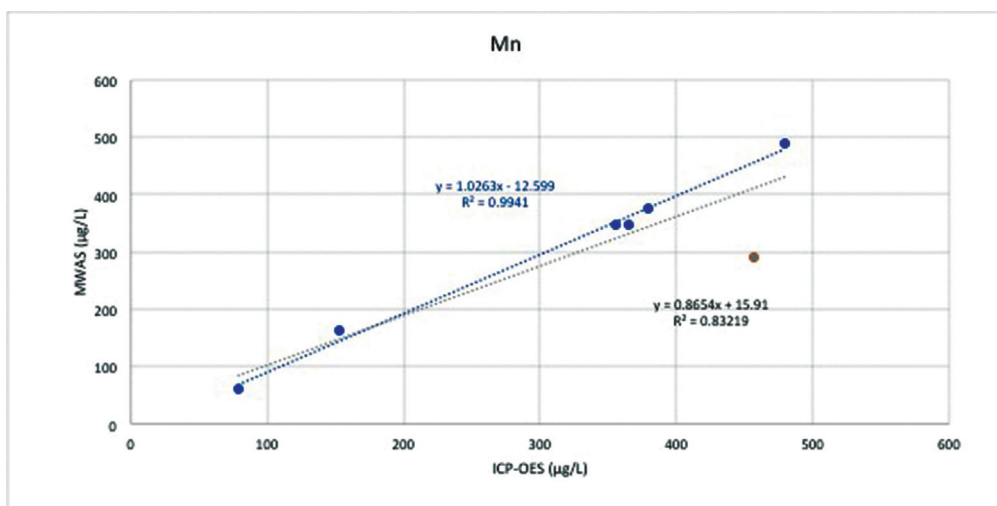


Figure 3 Correlation between Mn concentrations obtained with laboratory ICP-OES and MWAS on-site analysis system. The grey data point is Sample 10 that differs from the rest of the set. The grey fit line includes the data point and the blue one does not.

Conclusions

The results show that the current MWAS prototype can be used on-site to screen metal concentrations of environmental waters related to mining. The results correlated especially well with ICP-OES results with Mn. There was more variation between MWAS and ICP-OES results with Zn and Ni. It should be noted that these analyses were the first tests of the prototype and further improvements are being made to improve the precision and accuracy of the system. The results highlight a major advantage of the system. The MWAS on-site analyses do not suffer from possible changes of the sample during storage and transport.

The potential applications of this novel technology are many. At the exploration stage, it would facilitate hydrogeochemical prospecting by allowing on-site analysis, and therefore dynamic sampling. The lower analytical limits may be too high for some elements, but the technique is a simultaneous multielement one. This allows tracking pathfinder elements or favourable matrixes. During mine exploitation and after closure, the technique allows a much more frequent monitoring of discharged water than laboratory analyses. At a processing plant, it allows monitoring the quality of input and output water, and internal loops. It facilitates runoff water reuse and allows immediate operational decisions on water management.

Acknowledgements

This work was supported by the Maj and Tor Nessling Foundation, EIT RawMaterials, Academy of Finland (project no. 292601) and Business Finland (project GWW - Green Sensor for Water and Waste Monitoring). Hitachi High-Tech Analytical Science Oy is acknowledged for providing the pXRF device.

References

- Cánovas CR, Macías, F, Olías M (2018) Hydrogeochemical behavior of an anthropogenic mine aquifer: Implications for potential remediation measures. *Science of The Total Environment* 636:85-93, <https://doi.org/10.1016/j.scitotenv.2018.04.270>
- Ghorbani Y, Fitzpatrick R, Kinchington M, Rollinson G and Hegarty P (2017) A Process Mineralogy Approach to Gravity Concentration of Tantalum Bearing Minerals. *Minerals* 7:194; doi:10.3390/min7100194
- Kidder JA, Leybourne MI, Layton-Matthews D, Bowell RJ, Rissmann CFW (2020) A review of hydrogeochemical mineral exploration in the Atacama Desert, Chile. *Ore Geology Reviews* 124:103562, <https://doi.org/10.1016/j.oregeorev.2020.103562>
- Lemière, B. (2018) A review of applications of pXRF (field portable X-ray fluorescence) for applied geochemistry. *Journal of Geochemical Exploration*, 188: 350–363.
- Lemière, B. and Uvarova, Y.A. (2020) New developments in field portable geochemical techniques and on-site technologies and their place in mineral exploration. *Geochemistry: Exploration, Environment, Analysis*. Published Online <https://doi.org/10.1144/geochem2019-044>.
- Li G, Klein B, Sun C, Kou J (2020) Applying Receiver-Operating-Characteristic (ROC) to bulk ore sorting using XRF. *Minerals Engineering* 146:106117, <https://doi.org/10.1016/j.mineng.2019.106117>
- Nordstrom DK, Blowes DW, Ptacek CJ (2015) Hydrogeochemistry and microbiology of mine drainage: An update. *Applied Geochemistry* 57:3–16, <http://dx.doi.org/10.1016/j.apgeochem.2015.02.008>
- Rinez Thapa, Tuomo Nissinen, Petri Turhanen, Juha Määttä, Jouko Vepsäläinen, Vesa-Pekka Lehto, Joakim Riikonen, Bisphosphonate modified mesoporous silicon for scandium adsorption, *Microporous and Mesoporous Materials* 296:109980, <https://doi.org/10.1016/j.micromeso.2019.109980>
- Young, K.E., Evans, C.A., Hodges, K.V., Bleacher, J.E. and Graff, T.G. (2016). A review of the handheld X-ray fluorescence spectrometer as a tool for field geologic investigations on Earth and in planetary surface exploration. *Applied Geochemistry*, 72: 77-87.
- Wheeler S, Henry T, Murray J, McDermott F, Morrison L (2021) Utilising CoDA methods for the spatio-temporal geochemical characterisation of groundwater; a case study from Lisheen Mine, south central Ireland. *Applied Geochemistry* 127:104912, <https://doi.org/10.1016/j.apgeochem.2021.104912>
- Yehia R, Heberlein DR, Lett RE (2019) Rapid Hydrogeochemistry: A summary of two field studies from central and southern interior British Columbia, Canada using a photometer and voltammeter to measure trace elements in water. *Explore* 184:1-17.

Supplementary Materials

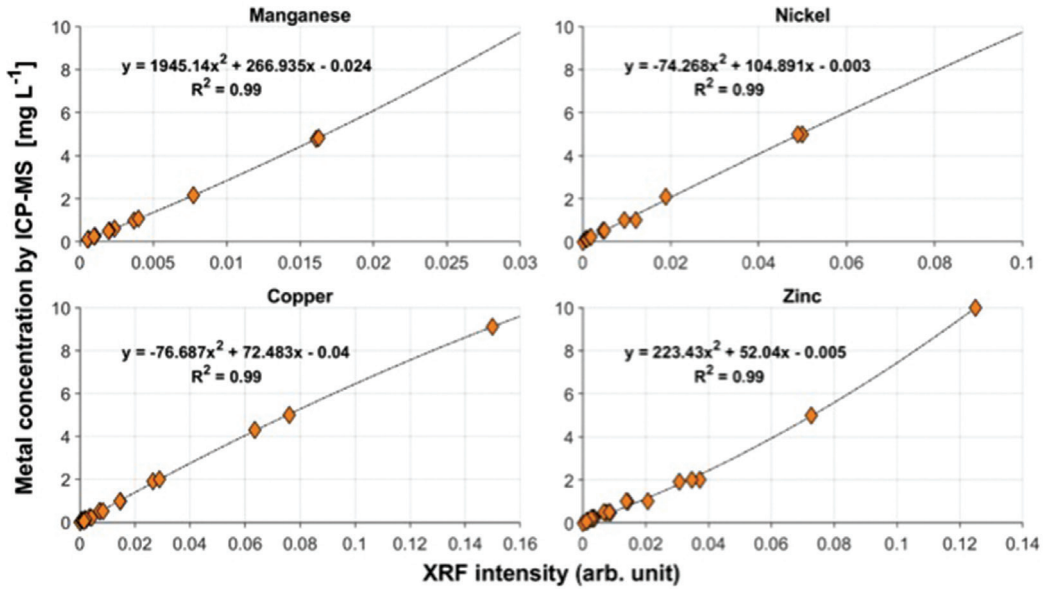


Figure 1 Empirical calibration curves for Mn, Ni, Cu and Zn created with Hitachi X-MET8000 Control software (SW version: 4.1.0.222) for the X-MET8000 pXRF.