Analytical Validation of 3AWater MWAS, a Fast On-site Analysis Tool of Dissolved Metals in Water

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Abstract

3AWater has commercialised a Multimetal Water Analysis System (MWAS) that analyses six dissolved metals (Mn, Ni, Cu, Zn, Pb and U) in the field conditions in less than ten minutes. The performance and usability of the system was validated for actual mine and environmental waters. The results of MWAS analysis were compared to laboratory results and system was found reliable and easy to use by environmental professionals. The real-time water quality results provide and enable fast decision making on-site that can make managing metal containing mine waters more effective and safer than the current standard of laboratory analysis.

Keywords: Water analysis, dissolved metals, on-site analysis methods

Introduction

Currently, the standard way of analysing dissolved metals from water is to send a sample to a laboratory for analysis with AAS, ICP-MS or ICP-OES techniques. The delay between sampling and obtaining the results can be considerably long because of logistics of delivering the sample to the laboratory. An onsite laboratory typically produces results within 4 to 24 hours while results from an external laboratory can take a few days or even several weeks. Therefore, the real-time information on dissolved metals in waters is not available.

Real time data on dissolved metals is essential to rapid decision making in mine water management such as optimising water treatment processes, determining leakages, and assessing environmental impacts. Ability to obtain such data quickly is also essential when fast reaction to water quality issues is needed e.g. after such incidents as storms, power outtakes, or dam failures.

3AWater has developed a measurement technology for analysis of low levels of dissolved metals in water. The Multimetal Water Analysis System (MWAS, Figure 1) is a portable system that gives almost real-time results on-site. The core of the technology is a metal collector made of a proprietary nanomaterial. A water sample is pumped through the metal collector, which gathers the metal ions from the solution. The metals are concentrated up to 200 times in the collector compared to the original water sample. Concentrating the metals into the collector, enables the metals to be analysed with a small and relatively affordable handheld X-ray fluorescence spectrometer (hXRF), which is too insensitive for measuring the water samples as such. The original metal concentrations in the analysed water samples are calculated and shown on screen of hXRF. Everything needed for the analysis are packed in an accessory kit backpack. The principle and an early prototype of the system were previously published by Tiihonen *et al.* (2022).

Method

In this study, the MWAS was used with a Hitachi X-MET8000 Expert hXRF. The analysis procedure for the study involved taking a water sample and measuring pH and conductivity on-site. 10 ml of sample was filtrated subsequently through 0.45 µm syringe filter and 3AWater metal collector with syringe pump (2 ml/min). The metal collector was flushed with 20 ml of air to

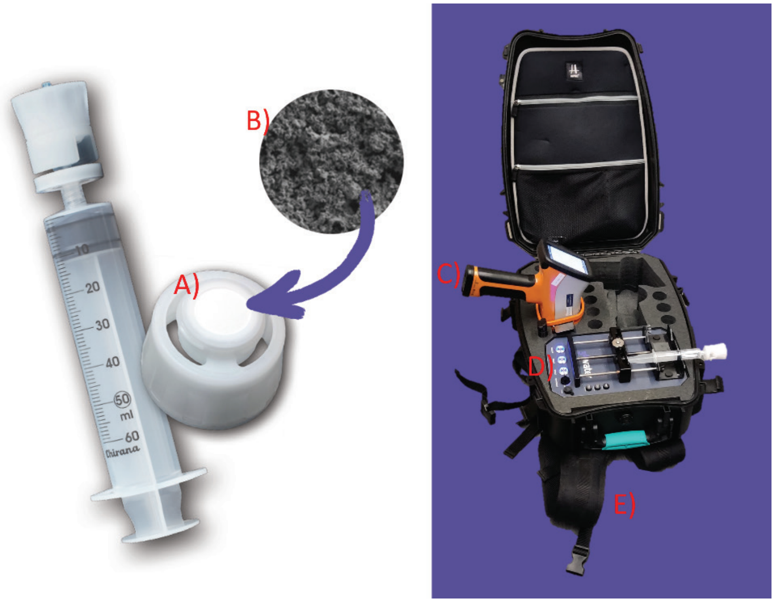

Figure 1 *3AWater Multimetal Water Analysis System: A) metal collector made of a B) proprietary nanomaterial, C) handheld X-ray fluorescence (hXRF), D) Syringe pump and E) Accessory Kit backpack containing the everything needed for the analysis.*

remove excess water. The metal collector was opened, and the metal concentrations were measured with help of sample adapter in the radiation shield. The analysis was performed with hXRF for two minutes.

The default calibrations made by 3Awater were used to analyse eighteen mine and environmental water samples. Each sample was analysed ten times with MWAS and reference samples were analysed by ICP-MS in two independent commercial laboratories. Five samples were spiked with some extra metals to create more variable set of samples. The calibration used for the analysis was selected from the default calibrations integrated in hXRF, depending on sample pH and electric conductivity (EC) listed in Table 1. The default calibration limits the conditions of the sample: pH needed to be 3.5–7.7 and EC <1000 µS/cm. All the experiments related to validation were done by personnel of a consultancy, Ramboll Finland, with assistance of 3AWater.

When the specifications of the pH range or conductivity were deseeded or exceeded, matrix specific calibrations can be created. This was demonstrated with two water samples, A and B, which were obtained from different locations of an active mining site. The samples had EC slightly over 2500 µS/cm and pH from 7.3 and 7.6. The calibration samples were created with sample A by spiking the water with 0-1.1 mg/L of Ni, Cu, Zn, Pb and U. Linear calibration equations were created based on the MWAS and ICP-MS analyses from the calibration samples. To test the performance of the matrix specific calibrations, the sample B as such and spiked with 1.1 mg/L of Ni, Cu, Zn, Pb and U were measured with MWAS in the field and with ICP-MS in the laboratory.

The effect of pH and EC on the MWAS results determined with the matrix specific calibrations were studied in a water matrix that was a 1:1 mixture of the samples A and

Table 1 *MWAS default calibration selection according to pH and electric conductivity.*

Electric conductivity (µS/cm)	pH	
	3.5 – 5	5 – 7.5
0 – 299	A1	B1
300 – 549	A2	B2
550 – 799	A3	B3
800 – 1000	A4	B4

B. The water was first spiked with 1 mg/L of Ni, 0.65 mg/L of Cu, Zn and Pb, and 0.5 mg/L of U. The pH was adjusted back to the original 7.7 after spiking. The spiked water sample was then split into three aliquots. The first one was measured as such. The second aliquot was used to test the effect of EC change. Its EC was increased from 3300 to 3800 µS/cm by adding a solution with 360 mg/L of Ca and 1140 mg/L of Mg. The sample was then measured with MWAS. The pH of the third aliquot was decreased from 7.7 to 7.2 by adding HCl before measurement with MWAS. All experiments done with matrix specific calibration were done by 3AWater and University of Eastern Finland.

Results and discussion

The on-site results obtained with default calibrations were compared to the standard dissolved metal analysis results obtained from the commercial laboratories (Figure 2). The limits of detection for the default calibrations are presented in Appendix and the results below these values are not reported. The results of MWAS analysis were mostly within ±30% limits compared to the laboratory results and all the results were within ±50% limits. This can be considered as a good result for a fast field analysis from an environmental expert's perspective. The MWAS system was found to be easy to use in the field. Less than an hour of training was needed for the trainee at Ramboll to perform the measurements reliably.

Matrix specific calibration was studied by determining the limits of detection for each metal (Ni, Cu, Zn, Pb and U) according to the equation LOD = I + S($1.645\sigma_{blank}$ + $1.645\sigma_{sample}$). The limits of detection of the matrix specific calibrations varied greatly between the metals (Table 2). For Cu, Pb and

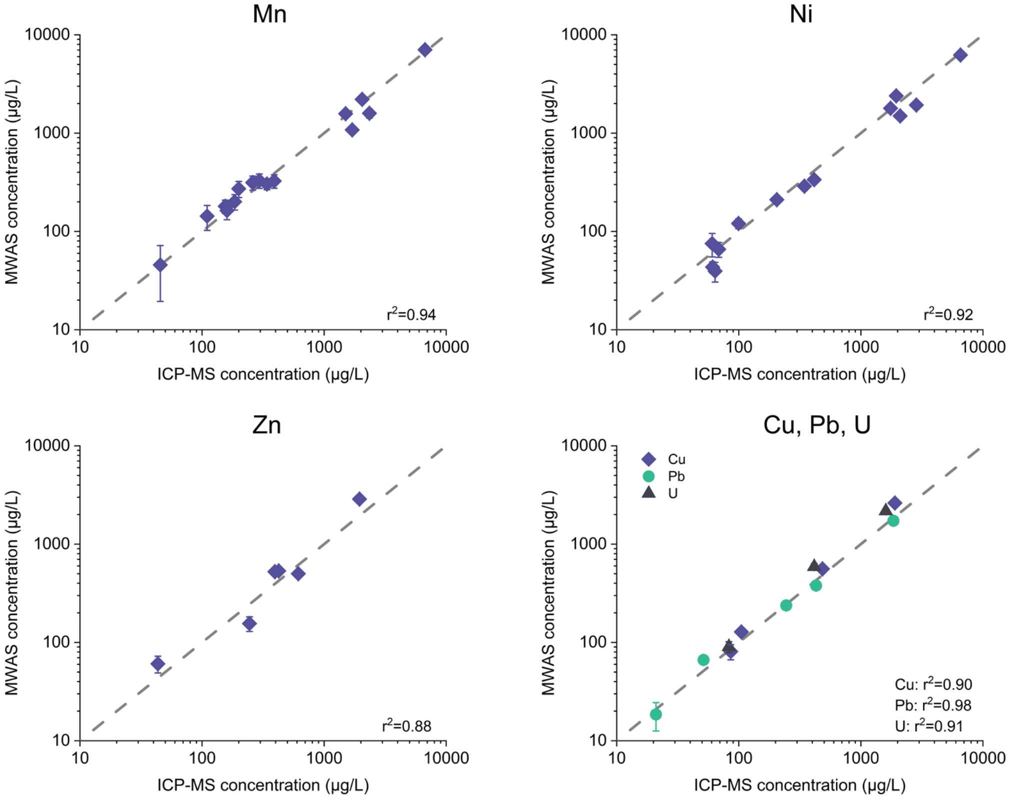

Figure 2 3AWater on-site MWAS analysis (N=10 with std) was compared to average of two commercial laboratories.

Table 2 Limits of detection (LoD) in the matrix specific calibrations.

Element	Ni	Cu	Zn	Pb	U
LoD (µg/L)	110	20	110	10	20

U the detection limits were between 10 and 20 µg/L whereas for Ni and Zn the detection limits were 110 µg/L. The detection limits for Ni and Zn increased, whereas Cu, Pb and U decreased compared to the limits of detection for default calibration in Appendix. This can be due to industrial water being more complex matrix, when the pH and conductivity are different from default calibration.

The sample B was measured as such and spiked with Ni, Cu, Zn, Pb, and U using the matrix specific calibrations. The results are shown in Figure 3. All the MWAS results were within ±26% of the ICP-MS results, when considering the results of metal concentrations above the LoDs.

The effect of changes in pH and EC on the accuracy of the matrix specific calibrations was studied by either decreasing the pH or increasing the conductivity and observing how the results of the MWAS change. The increase in conductivity of 500 µS/cm did not have significant effect on determined U concentrations but caused a decrease in the concentrations of Ni, Cu, Zn and Pb of between 22-34%. The decrease in pH of half a unit did not cause a statistically significant changes in the results ($p>0.05$). As conclusion, the matrix specific calibrations had good accuracy, detection limits were relatively close to default calibrations and not very sensitive to slight changes in pH or conductivity.

Conclusions

The default calibrations were accurate against the commercial laboratory. According to environmental professionals, the system was found easy to use and learn. The water matrix specific calibrations were also found accurate and reliable to demonstrate the applicability of MWAS for more complex mining waters. The study highlights the usability of the MWAS in the different water conditions.

The main advantage of MWAS comes from the easy and fast analysis. The system requires minimal maintenance and no calibrations by the end- user within default

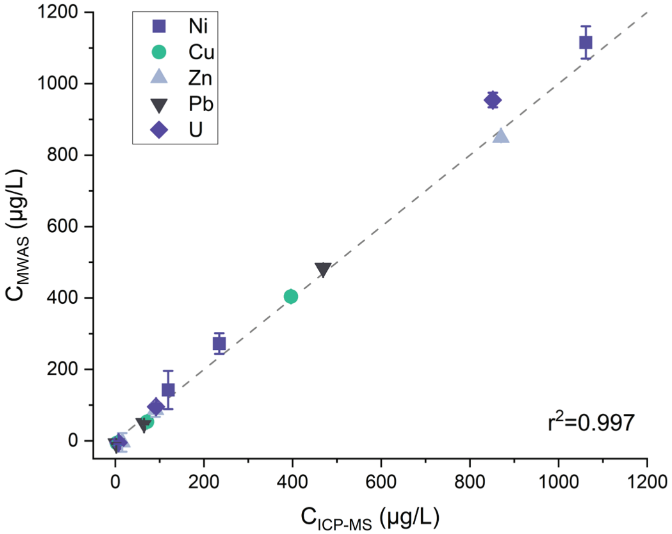

Figure 3 *Metal concentrations of sample B measured with MWAS using the matrix specific calibrations plotted against metal concentrations measured with ICP-MS. The dashed line represents the perfect correlation between MWAS and ICP-MS results.*

calibration conditions or after matrix specific calibrations are done. The almost real-time water quality data gives multiple advantages in the mining related water management operations. First optimisation of water treatment processes (such as metal removal) ensuring the compliance with regulation and savings in chemical and energy costs. Second, pinpointing leakages and other water quality issues and preventing further damage to the processes or the environment. Third, adaptive sampling i.e. pre-screening the water quality with the MWAS in order to select only relevant samples for further laboratory studies.

Acknowledgements

The authors thank Savonia University of Applied Sciences from collaboration and Centre for Economic Development, Transport and the Environment of Finland for financial support for this study.

References

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Appendix

Limit of detection in mg/L for the default calibrations for MWAS

			pH	
			3.5 - 5	5 - 7.5
Mn	EC [µS/cm]	0 - 299	0.150	0.050
		300 - 549	0.150	0.100
		550 - 799	0.300	0.200
		800 - 1000	2.000	0.300
Ni	EC [µS/cm]	0 - 299	0.060	0.060
		300 - 549	0.100	0.060
		550 - 799	0.100	0.100
		800 - 1000	0.200	0.100
Cu	EC [µS/cm]	0 - 299	0.025	0.025
		300 - 549	0.025	0.025
		550 - 799	0.025	0.025
		800 - 1000	0.025	0.025
Zn	EC [µS/cm]	0 - 299	0.040	0.040
		300 - 549	0.060	0.040
		550 - 799	0.060	0.040
		800 - 1000	0.060	0.040
Pb	EC [µS/cm]	0 - 299	0.025	0.025
		300 - 549	0.025	0.025
		550 - 799	0.025	0.025
		800 - 1000	0.025	0.025
U	EC [µS/cm]	0 - 299	0.050	0.080
		300 - 549	0.050	0.080
		550 - 799	0.050	0.080
		800 - 1000	0.050	0.080