

On-site mine water analysis: application note for the PDV6000plus

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Abstract This study presents a matrix-removal system for metals that interfere with the determination of arsenic with a voltammetric instrument capable of on-site use. A three-step sample pre-treatment system was developed to remove Fe, Cu and Zn: filtration, adjustment of pH (pH 5.5) and column-extraction of interfering metals using chelating resin. This set-up allowed the direct and accurate determination of As in mine waters containing up to 1500 $\mu\text{g L}^{-1}$ Cu and 500 $\mu\text{g L}^{-1}$ Zn and confirmed interferences at higher concentrations. Column optimisation and method adaptation for rapid on-site use are discussed.

Key Words mine water analysis, arsenic, voltammetry, in situ, matrix removal, chelating resin

Introduction

Metal mining operations, associated waste piles and drainage are continuous sources of arsenic, metals, sulfate and acidity arising from the microbially-mediated oxidative dissolution of arsenic-bearing metal sulfides (Mayes et al. 2009). Acid mine drainage (AMD) is among the most hazardous type of water pollution, due to its complex composition, persistence and high cost of remediation (Grande et al. 2010). Reported arsenic concentrations in AMD span five orders of magnitude, with highest levels observed at Iron Mountain Mine, California (850 mg L^{-1} As, Nordstrom et al, 1999). Regulatory requirements and the drive to a more sustainable water use (Madin 2008) make the quantification of As in AMD a regular activity of mining companies and government bodies. While advanced spectrometric methods, such as inductively coupled plasma mass spectrometry (ICP-MS) offer detection limits better than 1 $\mu\text{g L}^{-1}$, the rapid, on-site determination of arsenic offers clear advantages over the transport of samples to a laboratory for analysis. The voltammeter PDV6000plus (Cogent Environmental Ltd., Cambridge, UK) is capable of on-site analysis of several metals and metalloids. However, elements regularly present in arsenic-rich mine waters (e.g. Cu, Zn, Fe) interfere with As quantification. The aim of this study was to develop a sample pre-treatment system that removes interfering metals ahead of As analysis with the PDV.

Methods

Ultra pure water (UPW, 18 $\text{M}\Omega\text{ cm}^{-1}$) was used for the preparation of all aqueous solutions. Reagents for voltammetric analysis were supplied by Cogent Environmental Ltd. All other reagents were of Aristar grade or better and purchased from Sigma Aldrich or Merck Chemicals. Standard solutions for ICP-MS analysis were prepared from Spectrosol stock by serial dilution and acidified (1% HNO_3). All laboratory ware was acid washed (1.5 mol L^{-1} HNO_3 , >24 h), rinsed with UPW and dried (filtered laminar air flow). Toyopearl AF-Chelate-650 resin slurry (Tosoh Bioscience, Germany) was packed into a micro column (Perspex™, 1.5 mm i.d., 30 mm length) and enclosed by HDPE frits (pore range 22–27 μm). Toyopearl resin contains NTA-type (nitrilotriacetic acid) chelating groups immobilised onto semi-rigid gel spheres, is highly porous, hydrophilic (Tosoh 2010) and shows no sign of swelling over a wide pH range. The conditional stability constants for complexes between metals (Fe, Co, Zn, Pb, Cu, Zn) and NTA cover a wide range (e.g. $\text{FeOH}[\text{NTA}]^{2-}$: $\log K = -1.06$; $\text{Fe}[\text{NTA}]_2^{3-}$: $\log K = 25.9$; under standard conditions), whereas oxyanions, such as those formed by arsenic, are not retained. The resin column was connected to a peristaltic pump (pump tubing: PVC) using PTFE tubing and cleaned in-line (flow rate 1.06 mL min^{-1}) with HCl (pH 1.5, 20 mL) followed by MQ water (50 mL). The performance of the resin column was tested using two synthetic solutions (pH 5.5): A: 200 $\mu\text{g L}^{-1}$ Cu and 150 $\mu\text{g L}^{-1}$ As and B: 4000 $\mu\text{g L}^{-1}$ Cu and 150 $\mu\text{g L}^{-1}$ As, pumped across the pre-cleaned column at a flow rate of 1.06 mL min^{-1} . The column efflux was captured in aliquots of 3.0 mL in individual containers (Fig. 1), until backpressure built up, indicating that the column became blocked.

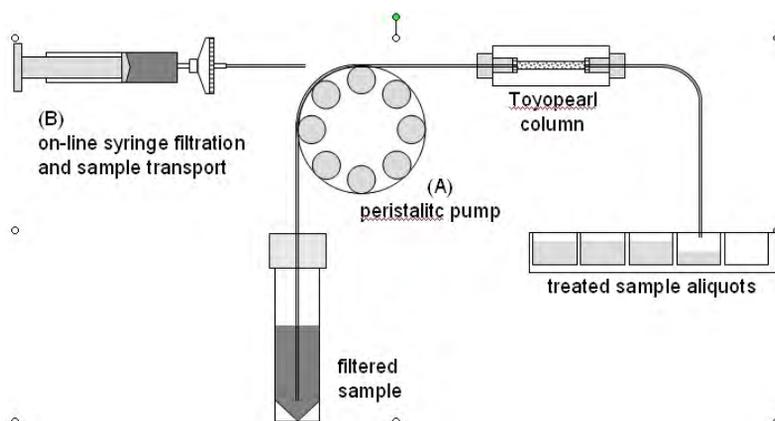


Figure 1 Interference removal from synthetic or natural mine water samples through cation removal with Toyopearl resin contained in Perspex™ column. Sample pH adjusted to 5.5. Sample transport via peristaltic pump in the laboratory (A) or via syringe and on-line filtration during in-field applications (B)

The PDV600oplus is a portable instrument for the analysis of a range of elements (e.g. As, Cd, Cr, Cu, Hg, Mn, Ni, Pb and Zn) by anodic stripping voltammetry (ASV). The instrument is based on a three-electrode electrochemical cell and is described in detail in Cogent (2010). In this study, the PDV was prepared and operated according to standard methods for analysis of total dissolved arsenic concentrations with a solid gold working electrode (Cogent 2009). Briefly, the gold working electrode was polished for 60 s and immersed in 5.0 mol L⁻¹ HCl for 5 min. The reference electrode (Ag/AgCl) solution (1 mol L⁻¹ KCl) was renewed and all three electrodes (including platinum counter electrode) were rinsed in UPW, assembled into the cell and connected to the control handset and PC. The working electrode was conditioned in arsenic electrolyte solution (10.0 mL acetic acid, 10.0 mL MQ, 0.5 mg L⁻¹ As) using the standard arsenic analysis programme (15 s deposition time) also employed for blank and sample analysis: pre-concentration of the analyte at a deposition potential of -900 mV (15–120 s), linear sweep ASV (-200 to +600 mV, sweep rate 500 mV s⁻¹) and measurement of current between -50 and +400 mV, followed by electrode cleaning at +500 mV (10 s) (Cogent 2009). Hereby, 10.0 mL of supporting electrolyte (1.2 mol L⁻¹ CH₃COOH in 0.63 mol L⁻¹ HNO₃) was mixed with varying volumes of UPW water and sample solution, affording different degrees of dilution. The analyte was quantified by the standard addition method.

AMD samples were taken from four abandoned mine workings in the Gunnislake/Calstock mining district in southwest England: Wheal Fanny (WF) adit and Blanchdown (BD) drain in the Devon Great Consols Mine complex, Bedford United Mine (BU) adit and Gunnislake Clitters (GC) Mine adit. Samples were syringe-filtered (0.45 µm pore size, Whatmann Nuclepore) on-site. pH was determined in-situ using a calibrated (pH4 and 7) portable instrument (Hanna H9025). In the laboratory, sub-samples (20 mL) were pH-adjusted (5.5) using NaOH (0.1–1.0 mol L⁻¹) where necessary and 13 mL of each sample were pumped through the column (1.06 mL min⁻¹). The first 3 mL were discarded in order to allow for the conditioning of the column and 10 mL were collected for analysis by ICP-MS and PDV. Between samples, the column was cleaned in reverse flow mode. AMD samples, column treated AMD and synthetic solutions (all acidified, pH1.0, HNO₃) and a certified reference material (SLRS-4) were spiked with internal standard (50 µg L⁻¹ In) and analysed on the ICP-MS (Thermo Scientific XSeries2) using a collision cell (7% H₂ in He, gas flow rate 3 mL min⁻¹) to allow multi-element analysis including Fe and As. The analysis of the CRM returned satisfactory results.

Results and Discussion

Copper loaded onto the column in test solution A was retained on the column, with efflux concentrations of <2.0 µg L⁻¹ Cu (Fig. 2) and 148±4.5 µg L⁻¹ As. Backpressure in the column built up after treatment of 192 mL solution, equivalent to the retention of 38 µg Cu. Using test solution B,

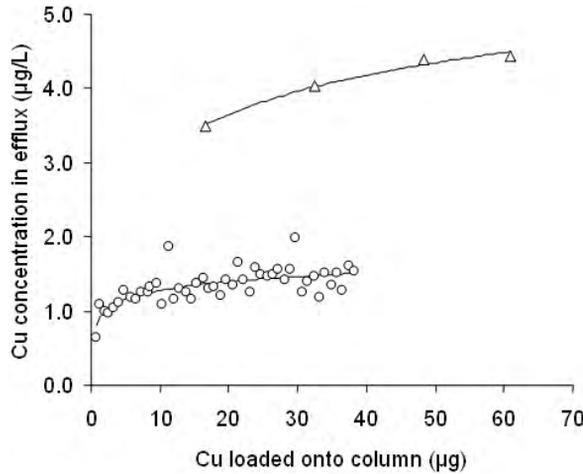


Figure 2 Copper concentrations in column efflux versus the amount of Cu loaded onto the column synthetic solutions. Symbol *š*, solution A: 200 µg L⁻¹ Cu, 150 µg L⁻¹ As; symbol *r*:solution B: 4000 µg L⁻¹ Cu, 150 µg L⁻¹ As. Solid lines are logarithmic functions fitted for illustration purposes only

61 µg Cu were retained before development of back pressure and less than <5 µg L⁻¹ Cu were observed in the column efflux. The results show that solutions containing AMD-relevant concentrations of As and Cu can be treated with a small (53 µL) Toyopearl resin column, with less than 1.5% As retained in the column. The build-up of backpressure may have arisen from Cu precipitation within the column once the complexing capacity of the resin was exhausted and this merits further investigation. Reverse-flow cleaning of the column between samples is required in the laboratory, while several columns can be taken into the field to reduce on-site reagent handling.

Mine waters collected at the four locations varied in pH (3.1–6.2) and concentrations of As (22–82 µg L⁻¹), Cu (100–2600 µg L⁻¹), Fe (4.0–1900 µg L⁻¹) and Zn (47–530 µg L⁻¹; Fig. 3). Lead and silver concentrations were more than one order of magnitude below that of arsenic in all samples. Toyopearl treatment was effective for samples containing 50 µg L⁻¹ Fe, 1500 µg L⁻¹ Cu

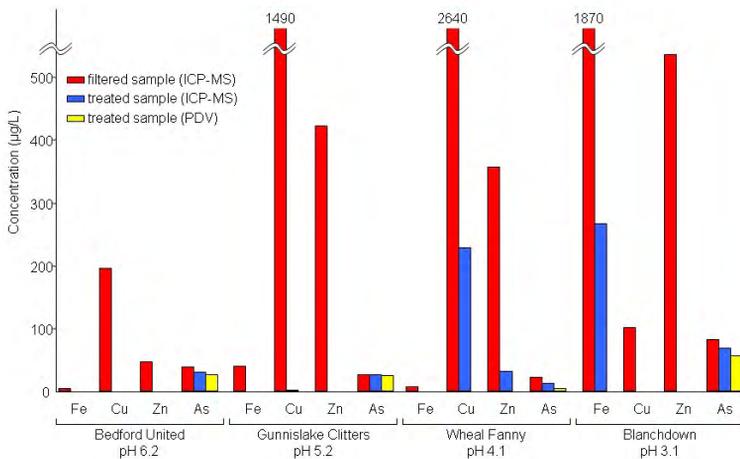


Figure 3 Comparison of Fe, Cu, Zn and As concentrations in mine water samples. Red: concentrations in filtered, otherwise untreated samples, blue: concentrations in samples treated with the Toyopearl column, both analysed by ICP-MS. Yellow: As analysis of column treated samples using the PDV600oplus. The numbers on top of the bars indicate the concentration of Cu and Fe beyond the scale of the graph. In-situ pH values

and $500 \mu\text{g L}^{-1}$ Zn, while allowing passage of arsenic. However, some limitations are also evident (Fig. 3). Column breakthrough occurred at higher concentrations of Fe ($>500 \mu\text{g L}^{-1}$) and Cu ($>2500 \mu\text{g L}^{-1}$), which can be readily avoided by increasing the chelating capacity (i.e. resin volume) of the column. Arsenic was partially retained on the column of samples that caused Fe breakthrough. In this case, the mechanism of retention may be co-precipitation or co-adsorption of As with Fe phases (Courtin-Nomade et al. 2005) within the column, rather than direct chelation by the resin. To avoid this, samples high in Fe concentrations could be diluted prior to column treatment and in the same context, the effect of presenting a higher cross-sectional area (i.e. larger column diameter) to the sample flow could be investigated. Arsenic analysis of column treated sample with the PDV suffered interference from Cu and Fe in samples from WF and BD, respectively, that contained Fe, Cu or Zn at concentrations known to cause interference with As analysis (in samples containing $50 \mu\text{g L}^{-1}$ As, concentrations of $50 \mu\text{g L}^{-1}$ Cu or $2000 \mu\text{g L}^{-1}$ Fe causes a 20% drop in signal intensity, Cogent 2009). However, results from the PDV and ICP-MS were comparable, with a mean recovery of $93 \pm 9.5\%$ As by PDV, in sample aliquots in which matrix removal was successful (BU and GC, Fig.3). Although a more accurate result might be desirable, the advantages of a rapid screening tool for arsenic in the field over time-consuming and costly sample analysis in contract laboratories may outweigh this shortcoming. Furthermore, method optimisation may improve analytical performance. Finally, the critical step of pH adjustment prior to column treatment requires further investigation, as the use of NaOH could be cumbersome in the field. Buffers (e.g. ammonium acetate) may offer convenient alternatives.

Conclusions and Further Work

The PDV6000plus has proven to be suitable for rapid on-site analysis of arsenic in mine waters after removal of interfering metals from the sample matrix using Toyopearl resin. The low sample volume required (2–5 mL per aliquot) allows for the adaptation of the column treatment to manual operation, while columns with larger chelating capacity should be trialled to optimise the system for on-site applications. Further on-site applications can be developed through use of resin columns in pre-concentration mode to improve the analytical capability of the instrument in the detection of some of the highly toxic metals often present at low concentrations, including Cr, Hg and Cd.

Acknowledgements

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