The Development of a Sample Preparation Technique for the Analysis of Trace Elements in Mine Impacted Waters containing High Levels of Iron

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Abstract

Inductively coupled plasma optical emission spectroscopy (ICP-OES) and mass spectrometry (ICP-MS) are suitable techniques for trace multiple-element analysis but may have difficulty with these analyses when samples comprise complex matrices (due to spectral interference and matrix effects). High iron concentrations (>3 g/L) in acid mine drainage (AMD) necessitate large dilutions to render samples suitable for analysis. In these cases, trace element concentrations (0.2-5 mg/L) are reduced to method detection limits, where the uncertainty of measurement increases and precision decreases.

Selective ion-exchange (IX) resins, weak-based anion, weak-acid cation, chelating resins, and selective silica-based media were explored as an alternate method to precipitation techniques. The polyamine weak-based media, and the functionalised silica-based exchanger showed selective iron loading, thereby reducing concomitant trace metals losses by occlusion or adsorption, and reducing dilution requirements for instrumental analysis. Findings from this study suggest that IX and other adsorbers can potentially be used successfully to reduce interference and increase the accuracy of trace element analysis in AMD.

Keywords: Mine impacted water, ion exchange resin, inductively coupled plasma, iron removal

Introduction

Acid mine drainage (AMD) in South Africa is typically caused by the oxidation of pyrite resulting in an acidic ferrous sulfate solution. Valuable trace elements, such as Rare Earth Elements (REE), may also be present. Recovery of REEs from AMD would achieve a two-fold benefit of creating value from sale of the REEs, and remediation of the water as part of the value recovery process.

Quantification of low trace element concentrations is challenging owing to, the high ionic strength (due to the presence of protons and sulfate), and high iron (Fe) concentrations, which could be present in as much as four orders of magnitude higher than the trace elements of interest. Inductively coupled plasma optical emission spectroscopy (ICP-OES) and inductively coupled plasma mass spectroscopy (ICP-MS), are multi-element techniques suitable

for simultaneous analysis of several elements in samples comprising varied concentration levels. ICP-OES can tolerate higher total dissolved solids (TDS) concentrations and is fast and simple to operate, while ICP-MS has high sensitivity, can achieve lower detection limits, and has a wider dynamic range. ICP-OES suffers spectral overlap, while ICP-MS can be prone to isobaric interferences, is complex to operate, has slower analysis times, and higher set-up and operating costs (Agilent Technologies Inc., 2021). Dilution is required to reduce the complex sample matrix which also decreases the already low trace element concentrations to instrument and method detection limits, where the uncertainty of measurement is increased. ICP-MS is more suitable for analysis of analytes at low concentration, and atomic/isotope mass selection avoids spectral inter-element overlap, making it the preferable technique. If Fe could be removed, less dilution would be required, which would also limit the reduction of trace element concentrations and enable more accurate measurement of trace elements by ICP-OES. Analysis using ICP-OES has the advantage of being a more cost effective and robust method for trace element analysis that can provide fast turn-around to support rapid decision making for optimisation of upgrading testwork conditions.

Removal of Fe by precipitation (using pH adjustment) was considered in previous work, however significant quantities of REEs were co-precipitated using this approach. A pH alteration from 2.3 to 3.4 using lime addition and agitation, resulted in co-precipitation (likely due to occlusion) of multiple REEs ranging between 53 % (scandium) and 99 % (thorium) (Naidu et al., 2022).

An alternative method of Fe removal prior to analysis was therefore investigated using several specialised and commercially available ion exchange resins. Given that the aim of this work was to create a laboratory scale method, recovery and reuse of the resin media were not prioritised, and because of this it was possible to test some resins that have been reported to be extremely selective for Fe as to be irreversibly bound (Lee & Nicol, 2007).

Methods

The initial test work consisted of batch contact between the resins and the AMD solution. This is commonly known as an isotherm test. Seven resins were selected, Lewatit CNP80, Lewatit TP272, Lewatit TP308, Lewatit A365, Purolite MTS9570, PhosphonicS POH1, and Lewatit MonoPlus TP260 in both the hydrogen the monosodium forms. A strong acid cation resin Lewatit MonoPlus S108 was tested in previous work and showed a selectivity of REEs over Fe and so was not re-tested (Naidu et al., 2022).

Chelating resins with phosphonic groups are known to have a high selectivity for Fe (POH1, MTS9570 and TP260) (Fortin-Lecomte et al., 2022). This is also predicted by the hard and soft acids and bases (HSAB) theory. The POH1 is a functionalised silica media and has been recommended as a potential Fe removal sorbent.

Weak-based anion (WBA) resins have tertiary amine groups and can remove acidity and precipitate metal oxides. Polyamine WBA resins such as A365 may also have chelating effects (Amphlett et al., 2018; Ogden et al., 2017). Strong based anion (SBA) resins have a quaternary amine group that have a positive charge and are known to sorb acids by acid retardation and can also load metal anionic complexes (Yang et al., 2007). A solvent impregnated resin, TP272 was also tested.

Adsorption studies were conducted where fixed volume to volume ratios (1:10, 1:20, 1:50 and 1:100) of media to AMD were measured out for each resin tested and contacted for 4 hours at ambient temperature. The pH of the solution was measured after contact. The resin and any resulting precipitate were removed from the solution by gravity filtration, and the filtrates were submitted for ICP-OES and ICP-MS analysis. The resin was photographed under a Celestron 44308 Digital Handheld Pro Microscope at x100 magnification. The precipitates were not analysed as part of this work.

Samples were diluted x10 and x100 and made up to volume in 2 % nitric acid (HNO3) prior to submission to an external laboratory in South Africa, for ICP-MS analysis, where they were analysed using a Spectro, quadrupole mass spectrometer. An original AMD sample was also submitted

to the University of Copenhagen, Denmark, where concentrations of trace elements were determined by inductively coupled plasma mass spectroscopy (ICP-MS) (Agilent Technologies, Agilent 7500C). Polyatomic interferences were removed with an octupole reaction system (ORS) pressurized with He or H2. External calibration was applied, and drift corrected for by periodic recalibration. For all analysis categories repeated analyses of selected samples showed that the analytical uncertainties were acceptable.

ICP-OES analysis was conducted at CM-Solutions MetLab analytical laboratory facilities, using an Agilent 5800 VDV ICP-OES instrument. Measurement conditions were set to axial viewing, which allows the optical system to view the plasma end-on, facilitating increased sensitivity and lower detection limits.

Calibration standards were prepared from a 1000 mg/L Ultraspec multi-element certified reference standard, purchased from De Bruyn Spectroscopic Solutions, and traceable to NIST Standard Reference Materials. Calibration was performed prior to analysis, requiring regression coefficients (R2) of 0.999 for all elements analysed, and averaged results were reported from three replicate readings. Samples were analysed as received, at x10 and x100 dilutions. All dilutions were prepared in 2 % HNO3. ICP-OES analysis was carried out with and without automated addition of a 10 mg/L indium internal standard to account for non-spectral interferences. Internal standards are used to account for physical interferences such as viscosity effects, whereby the emission intensities of the internal standard in the calibration standards and samples are measured and ratioed to the initial emission intensity measured in the sample blank. This enables correction of intensity readings for all elements by this ratio and thereby improving the accuracy and the precision of results.

Results and discussion

ICP-OES and ICP-MS analysis for metal quantification of AMD

Samples from adsorption tests were analysed by both spectroscopic techniques, and results demonstrated effective removal of Fe. Comparison of data between the two methods indicated similar concentrations, with some variances noted for selected analytes. The concentration differences were attributed to spectral interferences encountered on the ICP-OES owing to the complex sample matrix (Gilleland *et al.*, 2022; Liu *et al.*, 2020; Michaud & Mermet, 1982). An original AMD sample was analysed, prior to IX testwork (Batch 0), and with each sample batch, as a control, and these data showed that concentration variations also occurred between batches for the individual techniques (Table 1).

Table 1 Comparison of data for the original acid mine drainage sample for elements of interest.

Instrument ICP-OES/ICP-MS	Analyte Analyte	Batch 0 mg/L	Batch 1 #1098 mg/L	Batch 2 #1110 mg/L	Batch 3 #1123 mg/L
ICP-OES	Ce	—*	4.62	3.66	4.42
ICP-MS	Ce	4.86	5.57	4.18	4.53
ICP-OES	Dy	—*	0.13	0.25	0.29
ICP-MS	Dy	0.26	0.33	0.26	0.27
ICP-OES	Fe	3186	3255	2742	2722
ICP-MS	Fe	3445	3062	2952	2593
ICP-OES	La	0.59	0.55	0.46	0.53
ICP-MS	La	0.64/0.61	0.70	0.47	0.57
ICP-OES	Nd	—*	1.11	1.04	1.26
ICP-MS	Nd	1.06	1.34	1.01	1.11
ICP-OES	Pr	—*	0.26	0.23	0.29
ICP-MS	Pr	0.23	0.27	0.21	0.23
ICP-OES	Y	—*	1.79	1.55	1.47
ICP-MS	Y	1.73	1.96	1.60	1.73

*Element/analyte not analysed

Optimisation of the ICP-OES method to achieve better agreement with ICP-MS data can be achieved using the method development tools available as part of Agilent ICP Expert operating software. An IntelliQuant analysis tool enables a semi-quantitative assessment of the relative elemental composition in an unknown sample, by collecting data between the 167 and 785 nm spectral range. Recommended wavelengths, with intensities, and possible interferences are provided by the software, and optimal wavelength selection is guided by selecting wavelengths that are least affected by spectral interferences from analytes identified by IntelliQuant analysis, and that have sufficient intensity to quantify the analyte of interest at the expected concentration level (Gilleland *et al.*, 2022; Liu *et al.*, 2020; Michaud & Mermet, 1982).

Not all interfering analytes, are mitigated by wavelength selection, and some spectral overlap may still be present. In this instance, several instrument software background correction options are available of which the Fast Automated Curve-fitting technique (FACT), is particularly suited to complex matrices, and uses spectral modelling to "mathematically deconvolute the analyte signal from the raw spectrum" (Agilent Technologies Inc., 2020).

As an example, Batch 1 ICP-MS data reported three times higher dysprosium (Dy) concentrations than ICP-OES. Review of the Dy 364.540 nm wavelength used for ICP-OES analysis indicated several immediate high–intensity, spectral interferences that could have affected this analysis outcome. The Dy 353.171 nm wavelength, was selected as an alternative wavelength, which offered higher intensity, and fewer, lower–intensity interferences. ICP-OES analysis data for batches 2 and 3 reported Dy concentrations that achieved better agreement with the ICP–MS concentrations. The method was subsequently modified to include FACT corrections for spectral interferences from cerium (Ce), manganese (Mn), thorium (Th), and sulfur (S) on dysprosium. Re-analysis of the original AMD sample with FACT correction reported a reduced concentration of 0.28 mg/L for both the x10 and x100 dilutions, compared with the 0.30 and 0.33 mg/L concentrations that would have been reported for these dilutions respectively, and which provided better agreement with ICP-MS data previously reported. Figure 1 shows the Dy analyte peak without and with FACT correction, where the Dy has been separated from the interfering analytes.
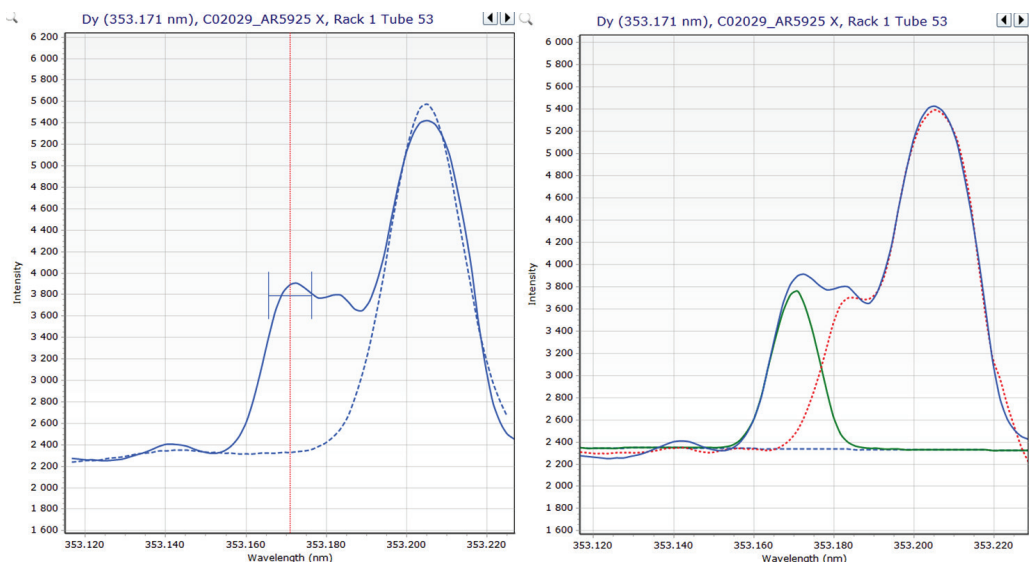
Method development is continuing, and

Figure 1 A screenshot of dysprosium peaks without and with FACT correction

seeks to quantify the effects of sample dilution, different internal standards, calibration using matrix matched standards, and the use of FACT, and/or other background correction tools, to further improve the method detection limits and reliability.

Ion Exchange Tests

Figure 2 shows the percentage removal of the REEs under investigation during this study, along side the removal of Fe from solution in the 1:20 ratio. The CNP80, TP272 and TP308 caused a loss of 2.7-3.3 % of the REEs analysed during treatment, but the Fe removal was low at 13 % for the TP272 ranging to 38 % Fe removal for the CNP80. Even at the highest solid to liquid ratios these resins did not show sufficient capacity for Fe to be useful for this application as a single step solution. Multiple contacts, or column tests might prove to be effective.

The TP260 performed poorly but has been reported to have a very high susceptibility to poisoning by Fe (III) in the metallurgical field, thus these results are expected (Arroyo-Torralvo *et al*., 2017). It was interesting to note that in this case the resin did not perform particularly favourably in either the hydrogen or monosodium forms compared

to the other resins evaluated. This could be due to kinetic effects, as the rate limiting step is likely to be particle diffusion and reaction between the Fe and the functional group. The MTS9570 was more effective at removing Fe, but also removed more of the REEs. This was unexpected as the dual functional groups should be more selective. The POH1 shows high Fe removal and low REE losses, and therefore shows promise for this application. In cases where the ion exchange caused a pH shift in the solution during contact a precipitation was observed and removed prior to analysis (Table 2). As this work did not include analysis of the solids, no distinction has been made to constituents loaded onto the resin, and those lost due to precipitation caused by the resin treatment. Tests on a larger scale would allow for a precipitate to be analysed to get a complete mass balance.

The A365 resin was able to remove the Fe quantitatively, while partially removing the REEs. This was the only resin able to remove Fe so that it was within an order of magnitude of the REEs. A mechanism proposed is that the resin is causing the Fe to precipitate with a very low level of supersaturation and thereby minimising coprecipitation. This contrasts with the conventional precipitation
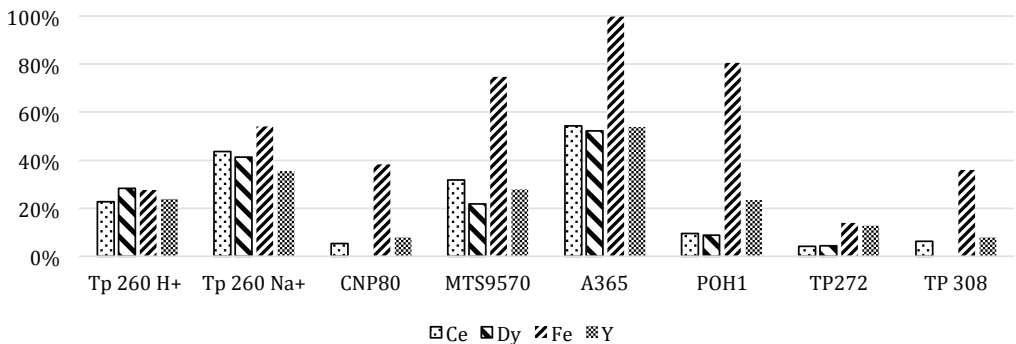

Figure 2 Percentage ion removal by resin at the 1:20 contact ratio

Table 2 Effect of resin on pH of the AMD solution after contact and resulting precipitation.

Resin	TP260 H+	TP260Na+	CNP80	MTS9570	A365	POH1	TP272	TP308
pH change		1.4	1.2	0.9	7.9	0.9	1.3	1.2
Precipitate	No	Slight		No	Yes	No		

techniques using the addition of a base containing reagent, such as the slag, caustic or lime work previously done (Naidu *et al.*, 2022). In the case of trivalent Fe $K_{sp} = [Fe^{3+}] \times [OH^-]^3 = 2 \times 10^{-39}$, which means that addition of base will result in supersaturation above a pH of 3. Typically, the precipitate is gelatinous, with a large surface area. The ferric oxide hydrate is amphoteric and can act as a cation exchange itself, loading the REEs and other cations onto its surface. Figure 3 shows one of the intermediate forms that the Fe can occur in, in the process of precipitation.

Conclusions

Adsorption test results demonstrated effective removal of Fe. Data comparison indicated similar results for Fe, with some variances noted for selected trace elements. ICP-MS isotope selection avoids inter-element overlap, making it the preferable technique, particularly when high dilutions are required.

Data showed that good agreement could be achieved between ICP-OES and ICP-MS data, and that ICP-OES can be reliably used for the analysis of trace elements, provided that samples are properly characterised to optimise wavelength selection and that the required inter-element interference corrections are applied.

The use of ion exchange and other adsorbers shows promise as an analytical technique to be developed further for the removal of Fe from complex solutions.

Acknowledgements

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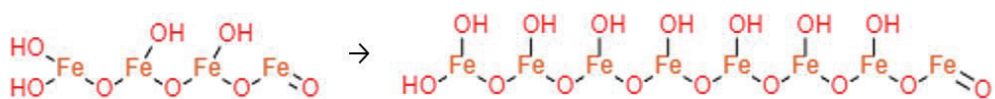

Figure 3 Depiction of Trivalent Fe (Kolthoff et al., 1969)

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