Selenium measurement in sulphides by hydride generation high-resolution inductively coupled plasma mass spectrometry

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ABSTRACT: Selenium concentrations of transition metal sulphides, albeit low, may be an important tool in exploration for economic ore deposits. These low concentrations necessitate the use of hydride generation for sample introduction, a very sensitive means of pre-concentration that results in low interference. However, transition metals interfere with the production of selenium hydride so that their removal from solutions made from dissolution of transition metal sulphides is necessary for hydride generation of selenium to be effective. We have devised a two-step process for the determination of Se concentrations in small samples (c. 50 mg) of sulphide minerals wherein dissolved transition metals are removed by precipitation as metal hydroxides under alkaline conditions (pH c. 12) to prevent sorption of Se, followed by further metal removal by chelating resin. Determinations made by hydride generation inductively coupled plasma mass spectrometry on the CCU-1c certified reference material (copper concentrate) and concentration standards showed quantitative recoveries (100 ± 5%) of Se. Using this technique we find that sulphide minerals from the Horne volcanic-hosted massive sulphide deposit give high Se concentrations ranging from 250 to 750 µg g⁻¹. Average precision, expressed as relative standard deviation, is 10% and the detection limit is 4 µg g⁻¹ of Se in a sulphide mineral. The procedure offers a method for Se determination of sulphides that is operationally simpler than many other methods.

KEYWORDS: selenium, sulphides, hydride generation, ICP-MS

Selenium concentrations of sulphide minerals may be used to distinguish the economic potential of sulphide bodies, thus serving as a vector to economic ore deposits (Cox & Singer 1992; Hinchee et al. 2005). To date, only high concentrations of Se in sulphides have been determined with sufficient precision because of high detection limits or problems with interferences. With the advent of high-resolution inductively coupled plasma mass spectrometers (HR-ICP-MS), many mass interferences are resolvable but with a diminishment of signal response. As argon dimer interferences with the two most abundant Se isotopes (78Se, 80Se) are not resolvable, even at the resolution of HR-ICP-MS, the less abundant Se isotopes are measured. The resulting decrease in signal response raises the detection limit above a useful value for solutions resulting from the simple dissolution of sulphides. Coupling a hydride generator to the HR-ICP-MS effectively concentrates the sample Se prior to introduction to the ICP-MS so that signal response is improved and detection limits are lowered (down to 4 ng g⁻¹). In addition to pre-concentrating Se, the hydride generator simplifies the matrix so that only the gaseous hydride components reach the plasma.

Hydride generation is a common means of introduction for the measurement of elements that form stable hydrides such as As, Se, Sb, Pb, Sn, Ge and Bi, and there are a variety of hydride generation techniques (Dedina & Tsalev 1995; Tsalev 1999). Hydride generation is most commonly used with atomic absorption spectroscopy (AAS) (Dedina & Tsalev 1995; Tsalev 1999), atomic fluorescence spectroscopy (AFS) (Wallischlager & Bloom 2001; García et al. 2005; Qiu et al. 2006), and ICP-MS (González Lafuente et al. 1998; Menegário & Giné 2000). The choice of ICP-MS detection rather than AAS or AFS in the present study is based on operational flexibility and lower instrumental detection limits for ICP-MS.

Many transition metals inhibit Se hydride production (Dedina & Tsalev 1995; Tsalev 1999), making determination of Se in sulphides difficult regardless of the analytical detector. We have developed a two-step method for sample preparation that partially removes transition metals by metal hydroxide precipitation followed by further transition metal removal by an iminodiacetic acid chelating resin. Each step, if used alone, does not remove sufficient transition metals to allow for quantitative production of Se hydride. The removal of metals by metal hydroxide precipitation is limited by the solubility of the metal hydroxides and the use of the chelating resin requires a pH at which metal hydroxide precipitation will occur.

A typical hydride generation reaction involves the reduction of the oxidized analyte by mixing a reagent solution of sodium borohydride and sodium hydroxide with an acidified sample (Dedina & Tsalev 1995; Tsalev 1999). Borohydride is unstable in acidic to neutral solution so the presence of sodium...
hydroxide is necessary to maintain borohydride in solution. The commonly employed hydride generation reaction (1) is specific to the Se(IV) state such that Se(VI) does not participate, so pre-reduction is necessary in order to ensure that all Se is Se(IV). Hydrochloric acid reduces Se(VI) to Se(IV) quantitatively (Bye & Lund 1988). The alkalinity present in the sodium borohydride/sodium hydroxide solution is neutralized by the acdity present in the sample allowing the hydride generation reaction for Se as follows:

\[ 3H^+ + 3BH_4^- + 4H_2SeO_3 = 4H_2Se + 3H_2O + 3H_3BO_3 \]  

(Dedina & Tsalev 1995; Tsalev 1999). Se(IV) is reduced to Se(-II) which forms gaseous Se hydride (H\textsubscript{2}Se).

The presence of transition metals in solution significantly impairs the hydride generation process due to both direct and indirect effects. One direct effect is the formation of insoluble transition metal selenides that precipitate in the hydride generator, removing Se from solution (Welz & Schubert-Jacobs 1986). Indirect effects are anti-catalytic in nature. Transition metals accelerate the decomposition of borohydride prior to selenium hydride formation and transition metal borides, formed as a side reaction, decompose Se hydride (Smith 1975; Kirkbright & Taddia 1978; Agterdenbos & Bax 1986; Bye 1986a, Hershey & Kelih 1986). Some transition metals have particularly strong effects: the presence of Cu impedes hydride generation due to the formation of sparingly soluble copper selenides (Welz & Schubert-Jacobs 1986). The similarly strong inhibiting effects of Fe are not fully understood because Fe(III) can also increase tolerance levels of Ni and Cu under certain conditions whereas Fe(II) is itself an inhibitor of hydride generation (Welz & Melcher 1984a, b; Bye 1986b, 1987; Halicz & Russell 1986). The direct and indirect effects are such that both the concentration of transition metals and the ratio of transition metals to Se are of concern. In samples with low transition metal content (e.g. waters, biological materials, silicates) the inhibitory effects of transition metals can be reduced by complexation and by kinetic modification of the hydride generation reactions (Vijan & Leung 1980; Bye et al. 1983; Bye 1985, 1986b, 1987; Halicz & Russell 1986).

The high contents of transition metals in many sulphides and corresponding high metal to Se ratios require that, following dissolution of the sulphide, the metals must be removed from solution prior to the hydride generation reaction. Removal of transition metals and pre-concentration of Se has been achieved with varying degrees of success by a number of techniques but are limited to samples of low transition metal content. Co-precipitation of Se on lanthanum hydroxide has been used for both ICP-MS and AAS analysis (Maher 1983; Ebdon & Wilkinson 1987; Hall & Peclat 1997a, b), but as lanthanum hydroxide also co-precipitates Cu and Fe (Reichel & Bleakley 1974) it is not effective for the analysis of samples with high transition metal/Se ratios.

Ion-exchange resins, both anion and cation, for pre-concentration of Se and removal of transition metals are effective, but over a limited pH range (Hershey & Kelih 1989; Itoh et al. 1989; Offley et al. 1991; Ornemark & Olin 1994). Recent refinement of a thiol carbon fibre technique (TCF) for Se capture (Shan & Hu 1985; Marin et al. 2003; Layton-Matthews et al. 2006) is effective for Se pre-concentration but does not necessarily ensure separation from transition metals. The TCF technique also captures potential interferents Pt, Pd, Au, Te, As, Hg, Bi, Sn, Ag, Cu, In, Pb, Cd, Zn, Co, Ni and Ti (Yu et al. 1983, 2001, 2002), so that Se must be liberated from the TCF without liberating these transition metals. The most recent work ascribes 100% Se recovery from reference materials, despite a lack of concentration measurements, on the basis of no significant isotope fractionation occurring during both pre-concentration and hydride generation (Layton-Matthews et al. 2006). However, the certified reference material containing high transition metal content (CCRMP WMS-1) does not have prior isotope data available for a basis of comparison so 100% Se recovery has not been established for samples of high transition metal content. There remains a need for a technique that can remove transition metals from samples of high content while retaining and pre-concentrating Se. The technique presented here provides this capability.

**Experimental**

**Reagents**

All reagent and sample preparation was done in a Class 100 clean laboratory. Deionized water (>18.2 MΩ) is used in all reagent preparation. All solid reagents are of ACS certified grade or better. Stock solution of 1N sodium hydroxide is prepared from solid pellets (Fisher Scientific, Ottawa). The analysis of the sodium hydroxide pellets shows significant concentrations of transition metals so the sodium hydroxide solution is purified by passing it through a column of Chelex\textsuperscript{®} 100 iminodiacetic acid resin (100–200 mesh, Bio-Rad Ltd, Hercules, California) to remove transition metals. A sufficient quantity (generally 1 litre) of 0.5% sodium borohydride in 1M sodium hydroxide solution is prepared on a daily basis by adding powdered sodium borohydride to the previously prepared 1M sodium hydroxide stock solution. It was found that the sodium borohydride dissolved completely and no filtration was necessary. Dilute nitric and hydrochloric acids are prepared from reagent grade acids that have been purified by sub-boiling Teflon\textsuperscript{™}-still distillation. Calibration solutions for a multi-point least square regression linear calibration are prepared daily by serial dilution of nominal 1000 mg L\textsuperscript{-1} Se standard (Spe ClertiPrep, Metuchen, NJ). Copper-selenium standards are prepared using a nominal 1000 mg L\textsuperscript{-1} Cu standard (Spe ClertiPrep, Metuchen, New Jersey) and the Se standard. All standards are prepared in hydrochloric acid solutions because nitric acid is reported to have detrimental effects on hydride generation (Cutter 1983).

**Chelating resin columns**

The choice of Chelex\textsuperscript{®} 100 resin for use in the columns is based on the selectivity of the resin for transition metals. Chelating iminodiacetic acid resin has a ten times greater selectivity for divalent transition metals than the commonly employed and less selective sulphonic acid cation-exchange resins (Bio-Rad Ltd; Chelex 100 and Chelex 20 Chelating Ion Exchange Resin Instruction Manual; Instruction Manual, AG 50W and AG MP-50 Cation Exchange Resins, Rev B). In contrast, anions, such as Se, pass through an iminodiacetic acid resin column unhindered (Jones et al. 1982; Hershey & Kelih 1989). The iminodiacetic acid resin is effective for transition metal capture above a pH of 4 (Narasaki 1988), allowing a broad pH range where transition metals can be separated from Se.

The columns contain 12 ml of Chelex\textsuperscript{®} 100 loaded as resin–water slurry into acid cleaned 20-ml polypropylene columns (17 mm × 120 mm) with glass frits. The quantity of resin is optimized such that the milliequivalents of active sites on the resin are eight times greater than the total milliequivalents of the transition metals in 50 mg of chalcopyrite (CuFeS\textsubscript{2}). Washing and regeneration of the columns follows the manufacturer’s recommendations. The column scheme is shown in Table 1 with the initial cleaning represented by steps 1 and 2.
Reference materials

The choice of CCU-1c (CCRM, NRCan, Ottawa) as a reference material is based on its similarity to the sulphides measured in this study and the lack of other suitable certified reference materials (Salley et al. 2000). The CCRM WMS-1 reference material shares similar Se and transition metal concentrations to CCU-1c but has only an informational value for Se concentration. The CCU-1c reference material contains: 107 ± 15 μg g⁻¹ Se, 25.62 ± 0.05 wt% Cu, and 29.34 ± 0.28 wt% Fe. These concentrations produce the ratios: Se/Cu = 0.418 ± 0.062 × 10⁻³ and Se/Fe = 0.363 ± 0.054 × 10⁻³, the lowest ratios in certified or standard reference materials.

Sample preparation

Portions of discretely identifiable sulphide minerals, from hand samples previously collected from ore deposits, were separated using a dental drill and placed in clean containers. The ore deposits are: the Horne volcanic-hosted massive sulphide deposit (Rouyn-Noranda, Quebec) (Barrett et al. 1991; Gibson et al. 2000); the Gaspe Cu porphyry deposit (Murdochville, Quebec) (Allcock 1982); and the Bingham Canyon Cu porphyry deposits (Bingham Canyon, Utah) (Lanier et al. 1978). Selenium concentrations in the Horne deposit have been measured previously by other methods and provide a comparison in order to assess this preparation and measurement method (Hawley & Nichol 1959; Barrett et al. 1991). CCU-1c reference material is supplied as a powder and is used directly. Samples and reference materials prepared more than once from powder are referred to as ‘sample replicates’ and repeat analysis of the same sample solutions are referred to as ‘analytical replicates’.

A 50-mg portion of sample or reference material is placed in a 5-ml PFA screw-top beaker (Savillex Corp.), to which 1 g of 2M nitric acid is added to dissolve the sample. A procedure blank and one or more sample replicates of CCU-1c reference material are included in each batch of ten samples. The batch of containers are sealed and heated at 60 to 70°C for a period of 72 hours to dissolve the sulphides. The contents of the containers are transferred to 15-ml centrifuge tubes using deionized water to flush the vial and centrifuged at 10 000 rpm for 10 min to separate any undissolved silicates and other refractory phases that may be present in the samples. Following centrifuging, the solutions are decanted into 30-ml centrifuge tubes, the residue washed with deionized water, and the solution centrifuged and added to the original decant. Some 1M NaOH is added to the sample solutions drop-wise to adjust the pH to 12 ± 0.2, resulting in the precipitation of metal hydroxides. The samples are left for 24 hours at room temperature to allow desorption of Se from the hydroxides. Following desorption, samples are centrifuged for 10 min at 10 000 rpm to remove the metal hydroxide precipitates from solution. The solution is decanted into 60-ml HDPE bottles and the centrifuged solids washed three times with water to remove all Se from solids. This results in a range of sample volumes of 6 to 8 ml. Precipitates were dissolved by nitric acid to test for the presence of Cu and Fe.

Sample batches were collected to test for the presence of Cu and Fe in order to establish the presence of the metals in the sample prior to ion exchange. The time required for sample preparation (except pre-reduction) is five days.

Solutions containing Se are pre-reduced to ensure that all Se is in the Se(IV) state by the addition of 1 g of concentrated hydrochloric acid and subsequent heating at 60 to 70°C for three hours followed by an hour of cooling at room temperature prior to introduction to the hydride generation apparatus. The pre-reduction stage is performed on the day of analysis during the period of instrument start-up and tuning. The calibration standards were prepared identically.

Instrumentation

An Element™ (Finnigan MAT) HR-ICP-MS and a LI-2 Advanced Membrane Cold-Vapor and Hydride Generation System (Fig. 1; further referenced as LI-2; Klause, B.; User’s Manual LI-2 Advanced Membrane Cold Vapour and Hydride Generation System; Klause & Blum 1999) are used with typical operating parameters listed in Table 2.

Flow rates of the sample, acid, reductant and waste are manually controlled by a four-channel peristaltic pump and variable pump tubing diameters. The hydride generation process produces only a gaseous sample stream to the ICP-MS so that samples with total dissolved solid contents above the recommended limit of 0.1% for the ICP-MS can be introduced into the hydride generator with no adverse effects on the ICP-MS. The choice of concentration parameters for hydride generation is made based on HG-AAS literature (Dedina & Tsalev 1995; Tsalev 1999), with limitation of reagent consumption and maximum transition metal tolerance the goals. The choice of a 0.5% m V⁻¹ concentration of NaBH₄ is on the low end of literature values. A low concentration, while restricting signal response, has benefits in its improved tolerance to metal interferences, reduced hydrogen gas production, and reduced
build-up of NaNO₃ and Na₂BO₃ in the LI-2. The acidity level is chosen for similar reasons.

On a daily basis, lens and gas flow parameters of the ICP-MS are adjusted to maximize sensitivity and maintain resolution. Tuning at high mass resolution of c. 9300 (m/Δm⁻¹ at 5% peak height) is accomplished using hydride generation and a Se solution (200–250 ng g⁻¹). The use of an internal standard for Se measurement by hydride generation is precluded by the need for the internal standard to be similarly converted to a hydride. Indium, in common use as an internal standard for ICP-MS, generates hydride in an inconsistent and non-quantitative fashion (Liao & Li 1993) and so is unsuitable for use. Other hydride-generating elements, with predictable behaviour, can be present in significant concentrations in the transition metal sulphides and so do not meet the requirements of an internal standard.

There are six stable isotopes of Se (Table 3); however, the two of highest abundance (⁷⁰Se, ⁷⁸Se) are subject to isobaric interferences by argon dimers that require mass resolutions greater than that achievable by the Element™ for separation. Of the remaining isotopes, ⁷²Se is the optimal isotope for measurement; ⁷⁴Se cannot be resolved from ⁷⁶Ge and has low abundance, and the potential isobaric interferences on ⁷⁷Se (³⁶Ar⁴⁰Ar) and ⁸²Se (⁸²Kr) are irresolvable. Although the abundance of krypton in the argon gas is low, a simple blank subtraction to correct the ⁸²Se signal for ⁸²Kr is not possible so that the instrument cannot be run at the medium resolution setting to measure ⁸²Se. As a poor ionizer, the ionization efficiency of ⁸²Kr is subject to matrix influence and so the ⁸²Kr signal will be inconsistent between blank and samples.

All isotope signals, except ⁷⁰Se, are recorded as the additional data serve as indicators of the state of hydride generation and plasma conditions. Iron and Cu in the dissolved precipitates and column washes are measured at a medium resolution setting (m/Δm⁻¹ at 5% peak height: 4000) using a conventional Scott spray chamber and Teflon™ microflow concentric nebulizer (Elemental Scientific Inc).

### RESULTS AND DISCUSSION

The effects of pH adjustment, co-precipitation, and tolerence levels

The addition of sodium hydroxide to both pyrite and chalcopyrite sample solutions to raise pH and to precipitate metal hydroxides during sample preparation produced orange-brown precipitates containing Fe. Green precipitates, suggestive of Cu or Fe(II) (oxy)hydroxides, were not observed, although Cu was detected by conventional HR-ICP-MS analysis of the orange-brown precipitates from chalcopyrite samples, indicating either mixed Fe–Cu hydroxides or sorption of Cu to the precipitates. In some pH ranges, co-precipitation of both transition metals and Se can occur (Benjamin & Leckie 1981a, b). Indeed, co-precipitation of Se on Fe hydroxide has been used as a means of pre-concentration for Se (Ohta & Suzuki 1975), but as this technique does not remove transition metals it is not suitable in the present case.

The influence of pH on the sorption behaviour of Se on Fe hydroxides is opposite to that of transition metal cations. Thus, the pH ranges of co-precipitation for Se and transition metals are not identical (Fig. 2). Selenium sorption decreases with increasing pH from maximum sorption of Se(IV) in acidic conditions to a minimum at a pH of 10. Se(VI) is sorbed only at low pH whereas cation sorption increases with increasing pH (Davis & Leckie 1980; Leckie et al. 1980; Hayes et al. 1988). A high pH results in the removal of transition metals with Se remaining in solution. A practical upper limit of pH is dictated by the solubility of Fe hydroxide; increased solubility of Fe and other hydroxides at high pH results in less effective removal of transition metals, particularly Fe (Fig. 2). At pH 12, some transition metals remain in solution but a partial separation of Se from the transition metals is achieved. During the adjustment of sample solutions to pH 12, precipitation of hydroxides begins at pH 3 and continues as pH is increased. It is not possible for samples to be adjusted upwards to the minimum pH of 4 needed for the chelating resin to be effective in capturing transition metals without hydroxide precipitation resulting in sorption and co-precipitation of Se. The precipitation of the hydroxides in the operating pH range of the chelating resin prevents the use of the chelating resin alone.

Copper and Fe were detected in the sample solutions after hydroxide precipitation, but prior to passing through the resin columns. Hydride generator extraction of Se from sample solutions after metal hydroxide precipitation, but prior to the use of the chelating resin, resulted in Se signal intensities up to...
Effect of pH on sorption of Se and Cu ionic species and solubility of Ca and Fe hydroxides. Percentage sorption of 7.9 µg ml⁻¹ Se or 635 µg ml⁻¹ Cu(II) (Schultz et al. 1987; Hayes et al. 1988) solutions onto 0.1 g ml⁻¹ ferrihydrite (amorphous iron hydroxide): —, Se(IV); ——, Se(VI); ••••, Cu(II). Solubility at 25°C (Stumm & Morgan 1996): — —, Fe(OH)₃; ••••, Cu(OH)₂

80% below expected values and precipitation of a silvery-grey substance in the hydride generator, most likely an Fe precipitate. The detrimental effect of transition metals on hydride generation is persistent; the Se signal of transition metal-free solutions passed through the hydride generator was greatly reduced if they followed solutions containing transition metals. The presence of the aforementioned silvery-grey substance, possibly acting as an anti-catalyst for hydride generation, may be the direct cause of the diminished signal. Although the bulk of the transition metals (>99%) contained in the sample solutions are removed by co-precipitation of the hydroxides, it is evident that a single step of co-precipitation is inadequate to reduce transition metals to levels tolerable for hydride generation. The maximum concentration of metals in the unexchanged sample solutions can be taken as conservative tolerance limits by simple dilution would require an approximately 70 000-fold dilution. This dilution level would bring all but the highest concentrations of Se below the instrumental detection limit so that simple dilution is not adequate for sample preparation for hydride generation.

Following desorption of Se from the Fe hydroxides at a pH of 12 and the physical removal of Fe hydroxide precipitates, the sample solutions were passed through the ion exchange columns. As previously noted, precipitation of hydroxides begins at a pH of 3, well outside of the effective range of the resin, so that co-precipitation is necessary prior to the use of the chelating resin. Removal of Cu and Fe remaining in solution following hydroxide precipitation was indicated by a change in colour of the resin, to orange-brown for pyrite sample solutions and to green for chalcopyrite sample solutions, and by the detection of Fe and Cu in the washes of the resin columns.

Calibrations, detection limits and method blank
Calibrations are linear in the range of 5 to 250 ng g⁻¹ with a limit of detection of 4 ng g⁻¹. Method blanks have Se concentrations below the limit of detection for the ICP-MS. Typical precisions on a single analysis of calibration standards, expressed as relative standard deviations, are less than 10%. Precisions from analytical replicates (three) of calibration solutions are further improved with typically relative standard deviations of 5%, similar to that previously reported for other HG-ICP-MS methods (Heitkemper & Caruso 1990; Hall & Pelchat 1997a, b; Gonzalez Lafuente et al. 1998; Menegátor & Giné 2000). Using our procedure for preparing the natural samples, which results in a 1000-fold dilution, in conjunction with the detection limit of 4 ng g⁻¹ using the hydride generator and ICP-MS, the detection limit for Se in a sulphide mineral is 4 µg g⁻¹. The dilution factor is the result of the 20-fold dilution of acid digestion and the lesser dilutions from the washing stages of the sample preparation (three- to four-fold dilution). Some reduction of dilution factor might be possible with a decrease of the volume of nitric acid used for digestion, but this might increase digestion time.

Analysis of standards and reference materials
Recovery of Se from synthetic solutions prepared from Se and Cu concentration standards, in varying proportions, followed by our separation procedure gives recoveries of 100 ± 10% (Table 4). Furthermore, Cu has been reduced to a concentration below which inhibition of hydride generation occurs, otherwise low recoveries of Se would result. Concentrations measured for sample replicates of Se standards individually passed through the ion exchange columns show variation.
concentrations between 350 and 1000 µg g⁻¹ and distributions reported previously (Table 6). Measured Se phides from the Horne deposit are consistent with the values (Sindeeva 1964). Selenium concentrations measured in sulphides show the capacity of the method to measure smaller concentrations of sulphides from the Gaspe and Bingham deposits‡ as compared to chalcopyrite and the large differences in concentration than analytical replicates (2%), probably due to imprecision and inaccuracy is removed.

**Analysis of natural sulphides**

Sample replicates of a sulphide show larger variation (8%) in concentration than analytical replicates (2%), probably due to the natural variation of Se concentration in natural sulphides (Sindeeva 1964). Selenium concentrations measured in sulphides from the Horne deposit are consistent with the values and distributions reported previously (Table 6). Measured Se concentrations between 350 and 1000 µg g⁻¹ are similar to the high values reported by Hawley & Nichol (1959) and Barrett et al. (1991). The higher measured concentrations of Se in pyrite as compared to chalcopyrite and the large differences in measured concentrations between samples of pyrite are consistent with prior data from the Horne ore deposit (Table 6) and reflect higher temperatures of formation of pyrite, an interpretation supported by experimental studies and thermodynamic data (Franz 1971; Simon & Essene 1996; Hannington et al. 1999). It is important to note that the Se concentrations in the Horne ore deposit are anomalously high compared to other ore deposits (Table 6). Other ore deposits of the same type from the Noranda district, near the Horne ore deposit, have much lower Se concentrations (Table 6). The measured Se concentrations of sulphides from the Gaspe and Bingham Canyon show the capacity of the method to measure smaller concentrations of Se in sulphides and are consistent with the low concentrations generally found in porphyry Cu deposits (Karamyan 1962; Chitaeva 1965, Filimonova 1972).

### Table 4. Selenium recovery in selenium and copper standards.

<table>
<thead>
<tr>
<th>Standard</th>
<th>Se (ng g⁻¹)</th>
<th>Cu (ng g⁻¹)</th>
<th>Se/Cu × 10⁻⁵</th>
<th>Measured Se (ng g⁻¹)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu/Se 1</td>
<td>81.3 ± 0.7</td>
<td>0.969 ± 0.13</td>
<td></td>
<td>83.9 ± 1.1</td>
<td>99 ± 16</td>
</tr>
<tr>
<td>Cu/Se 2</td>
<td>80.7 ± 0.7</td>
<td>6.36 ± 0.04</td>
<td></td>
<td>83.6 ± 10.4</td>
<td>104 ± 14</td>
</tr>
<tr>
<td>Cu/Se 3</td>
<td>73.3 ± 0.6</td>
<td>98.9 ± 0.5</td>
<td>0.741 ± 0.001</td>
<td>71.5 ± 15.0</td>
<td>98 ± 24</td>
</tr>
<tr>
<td>Se standard</td>
<td>187 ± 1</td>
<td>n/a</td>
<td></td>
<td>185 ± 20.0</td>
<td>99 ± 11</td>
</tr>
<tr>
<td>Mean of sample replicates</td>
<td>96 ± 9</td>
<td>n/a</td>
<td></td>
<td>98 ± 7.4</td>
<td></td>
</tr>
</tbody>
</table>

### Table 5. Determination of selenium in five measurements of reference material CCu-1c.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Se concentration (µg g⁻¹)</th>
<th>Difference from certified value (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Certified value*</td>
<td>107 ± 15</td>
<td>–</td>
</tr>
<tr>
<td>1</td>
<td>109 ± 11</td>
<td>1.9</td>
</tr>
<tr>
<td>2</td>
<td>99 ± 23</td>
<td>7.4</td>
</tr>
<tr>
<td>3</td>
<td>94 ± 27</td>
<td>12.2</td>
</tr>
<tr>
<td>4</td>
<td>90 ± 22</td>
<td>16.2</td>
</tr>
<tr>
<td>5</td>
<td>87 ± 25</td>
<td>18.2</td>
</tr>
<tr>
<td>Mean of sample replicates</td>
<td>96 ± 9</td>
<td>10.2</td>
</tr>
</tbody>
</table>

* Salley et al. (2000)

### Table 6. Concentration of selenium in sulphides from the Horne and other ore deposits.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Concentration (µg g⁻¹)</th>
<th>Replicates (3 analytical replicates except as noted)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrite: range of previous studies</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Noranda District VHMS*</td>
<td>&lt;15 to 320</td>
<td>mostly pyrite n = 66</td>
</tr>
<tr>
<td>Russian copper porphyry deposits‡</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chalcopyrite: present study</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Noranda District VHMS*</td>
<td>23 to 280</td>
<td>n = 12</td>
</tr>
<tr>
<td>Chalcopyrite: range of previous studies</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Noranda District VHMS*</td>
<td>360 to 535</td>
<td>n = 7</td>
</tr>
</tbody>
</table>

* Hawley & Nichol (1959), X-ray spectrography
† Barrett et al. (1991), NAA
‡ Karamyan (1962), Chitaeva (1965), Filimonova (1972), method unknown

The relative standard deviation of the measurements of simple Se solutions of known concentration and that of CCu-1c might be considered high in the context of modern instrumental analysis but is not much larger than that observed for single analyses of the single-element calibration standards and can be attributed to non-systematic and temporal variations in hydride generation and plasma conditions. In the absence of an internal standard, such variations cannot be corrected. The relative standard deviation of the measurements are consistent with previous Se analysis by HG-ICP-MS where internal standards have not been used (Heitikemper & Caruso 1990; Hall & Pelchat 1997a, b; González Lafuente et al. 1998; Menegário & Giné 2000). One can surmise that the separatory technique by itself does not introduce imprecision, nor alter accuracy by loss or gain of Se, and, by removing transition metals, a source of both imprecision and inaccuracy is removed.
CONCLUSIONS

Removal of transition metals that interfere with Se determination by HG-ICP-MS of solutions prepared from sulphide minerals has been accomplished by raising the pH of sample solutions to 12 causing co-precipitation of Fe hydroxides and other metals, followed by further separation of Se from remaining transition metals via chelating ion-exchange resin. Both precipitation and chelating ion-exchange resin steps are required to achieve sufficient transition metal removal. This method of Se purification in conjunction with HG-ICP-MS detection results in analytical accuracies and precisions for Se similar to those for previously reported methods using hydride generation for samples with low transition metal contents. The method proved useful for determining Se concentrations of natural sulphides.

This study, conducted at the Queen’s Facility for Isotope Research, forms part of the PhD thesis work of the first author. The study is financially supported by the Natural Science and Engineering Research Council (NSERC), the Ontario Innovation Trust and the Canadian Foundation for Innovation. The manuscript was significantly improved by comments from the reviewers.

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