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The Rapid Measurement and Monitoring of Selenite Concentration by Turbidimetry Following its Conversion to Colloidal State by Sulfite Reduction and Acidification

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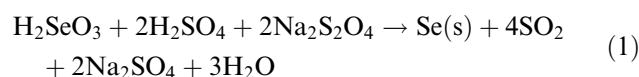
In this study, the rapid reduction of selenious ions using sulfite species at negative pH is described and its use as analytical technique in combination with turbidimetry is proposed. It was found that Se(IV) can be reduced quantitatively at ambient temperature via a combination of sulfite reduction and ultra-acidification with sulfuric acid to a colloidal form that can be determined using turbidimetry. The developed analytical procedure can accurately and reproducibly measure Se(IV) concentrations down to 1 mg/L. For concentrations above 20 mg/L dilution is necessary. Common transition metal ions such as iron(II), copper(II), or zinc(II) up to 10 g/L concentration were found not to have noticeable influence on the precision of the method. Finally the developed technique was shown to be equally effective with real Se(IV)-bearing industrial solutions generated in a zinc concentrate roasting operation, hence making the method particularly useful as a fast and simple process monitoring and control tool.

Keywords analytical; selenious acid; selenite; selenium; sulfur dioxide; turbidity

INTRODUCTION

Various extractive metallurgical industries generate dilute effluent sulfuric acid solutions coming from scrubber off-gases (1,2). These solutions generally contain small concentrations of various impurity elements and are also saturated with sulfur dioxide coming from the roasting process. One such impurity element is selenium, the removal of which from acidic effluents may be accomplished via a variety of technologies (3). For acidic effluents generated in the zinc industry selenium tends to be present as selenite in complex matrix solutions and at relatively high concentrations, more than 10 mg/L. For these types of solutions chemical reduction appears to be the preferred method to eliminate selenium (4).

One such industrial reduction process that is based on sodium dithionite (a powerful reducing agent) is employed by the Canadian Electrolytic Zinc Company (CEZinc, Valleyfield, Canada) (1,2). The chemistry of this process was described in a recent publication by the present authors (5). In this case, selenium(IV) is reduced to elemental form. The precipitate, once filtered, is disposed off while the weak acid solution is neutralized before being released in the environment. The selenium precipitation reaction can be summarized by:



While the dithionite reduction process for selenium-bearing acidic effluents has many advantages such as very fast reaction rates, high efficiency, and low toxicity, it also has a few drawbacks. The two main ones are the relatively high cost of sodium dithionite and the subsequent partial redissolution of the selenium precipitate. During an investigation on the later problem, the authors of this work discovered that the redissolution phenomenon is caused by dithionite decomposition by-products and that high concentrations of the reducing agent worsen the problem (6). In other words, if large excess dithionite is used (and this happens commonly because of the variable selenium loads), this constitutes significant economic losses but also complicates compliance with environmental regulations because of the ensued rapid selenium redissolution. In order to avoid these problems, the selenium concentration in the weak acid must be known before the dithionite treatment so the appropriate amount of dithionite reagent can be administered. This is accomplished currently via inefficient, relatively complex, and time consuming analysis using standard analytical methods such as atomic absorption spectroscopy (AAS). Because of this problem a project was launched into the development of a fast and simple technique to monitor the selenite concentration in weak acid solutions of industrial interest.

The first trials involved the use of ion selective electrodes, well known analytical tools that have been developed for the most common anions and cations. Two types of ion

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selective electrodes are commonly available. The first one, known as solid state electrodes, are commonly used to monitor the concentration of (uncomplexed) transition metal cations. The second type, known as membrane electrodes are generally used to monitor common anions such as perchlorates, nitrates, and carbonates (7). While commercial selenite electrodes were not available, the literature provided the description of several prototypes, of both the membrane and solid-state types (8–16). After thorough screening in the context of the intended application that involves a complex corrosive industrial weak acid, most of them were found unsuitable because of efficiency, durability, or interference issues. A potentially promising design involved the use of silver selenide and copper sulfide as the solid-state electrode (15). But despite following the same procedure to prepare the electrodes and consulting with the original authors (18), the obtained results were found to be extremely erratic and unreliable. Hence no further work with ion selective electrodes was pursued.

The other method selected for the evaluation was UV-Visible spectrophotometry involving the use of 3,3-diaminobenzidine and papaverine, two reagents known to react with selenious ions to produce colored complexes (orange and blue, respectively) (17–21). However, the complex nature of the industrial weak acid, especially the high amount of dissolved sulfur dioxide, caused interactions with both reagents, preventing the formation of colored complexes. Visible spectroscopy has also been used quantitatively on colloidal selenium precipitates formed by reduction by stannous chloride. However, it has been reported that the Beer-Lambert law was only followed for 1 to 10 mg/L selenium concentrations; a low and narrow range for industrial applications (22).

Interestingly, during these investigations, it was noticed that the industrial weak acid, when mixed with large amounts of concentrated mineral acids, formed also a red colloidal precipitate. Subsequent analysis showed that less than 0.5 mg/L of selenium remained in solution after the acid treatment and that the precipitate was too coarse to be measured directly with visible spectroscopy. However, the turbidity of the solution was found to vary linearly with the amount of selenium originally present in solution. It thus became possible to develop the present selenium determination method for industrial weak acid solutions using a simple turbidimeter.

EXPERIMENTAL

The majority of tests was performed with a synthetic weak sulfuric acid solution containing between 1.27×10^{-5} and 0.00633 mol/L (1 and 500 mg/L) of Se (IV) at pH 1.3 (adjusted with H_2SO_4). This range of concentration and pH were chosen as they represent typical conditions encountered in industrial zinc refinery acid effluent solutions (1). Reagent grade selenium dioxide from Sigma-Aldrich

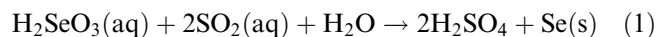
($\geq 99.5\%$ SeO_2) was used as the source of selenious species. Unless otherwise noted, all the experiments were performed at 23°C.

The turbidity of the final solution was measured using a HF Scientific Micro 1000 turbidimeter equipped with an infrared lamp. The pH of the solution was monitored using a Thermo Scientific Orion Sure-Flow pH glass electrode (EW-05718-55). The concentration of dissolved selenium in the samples was measured using regular atomic absorption spectrometry (AAS) with an air/acetylene flame. The precipitates were characterized using X-ray diffraction spectroscopy (Filips PW 1710, Cu anode, K-Alpha 1.54060 Å, scan rate: $2^\circ 2\theta/\text{min}$ and electron microscopy (Hitachi S-3000N FEG SEM).

RESULTS AND DISCUSSION

Background

As mentioned in the introduction, the ultra-acidification of the Se(IV)-bearing CEZinc weak acid solution resulted in the formation of colloidal selenium. The reducing agent involved here was apparently given the roasting gas origin of the acid, sulfur dioxide (SO_2). The latter is a well-known reducing agent with a standard reduction potential equal to 0.16 V. The relevant reduction reaction of selenium (IV) by SO_2 is given by Eq. 1. By employing the Nernst equation (Eq. 2) to the typical industrial solution parameters (25°C, $[H_2SO_4] = 0.1$ M, $[SO_2] = 0.1$ M, $[Se] = 0.003$ M (230 ppm)) it is determined that the above reduction reaction is thermodynamically feasible ($E = 0.54$ V).



$$\Delta E \cong \Delta E^\circ - \frac{RT}{nF} \ln \frac{[H_2SO_4]^2}{[H_2SeO_3][SO_2]^2} = 0.54 > 0.0 \quad (2)$$

However, in practice, the above reaction only occurs to a limited extent, this being so due to unfavorable kinetics. It has now been discovered that ultra-acidification accelerates the reaction leading to colloidal selenium formation, a phenomenon exploited in developing the analytical procedure described in this paper. Before the demonstration/application of this new procedure to the actual industrial solution (described section titled “Application to SO_2 - containing industrial solution”) results are presented involving synthetic solutions.

Results

The synthetic weak acid solution was composed of selenious ions 1.27×10^{-5} and 0.00633 mol/L (1 and 500 mg/L) of selenium and dilute sulfuric acid (pH 1.3). In this solution 0.156 M (10 g/L) of anhydrous sodium sulfite (Na_2SO_3) was added as reducing agent. Since this compound is very soluble in water (>2.5 kg/L of solution), its dissolution was fast and easy. Once the salt was totally

dissolved the solution was ultra-acidified with the addition of concentrated acid causing an immediate reaction. It was found that to obtain full and almost instantaneous reduction of Se(IV) to Se(0), a volume of concentrated mineral acid equal to that of the test solution was needed. Concentrated sulfuric (ACS grade, 98% w/w) and hydrochloric acid (ACS grade, >36% w/w) were both tested and found to be equally efficient to convert all the selenium(IV) in colloidal form. The colloidal Se produced with hydrochloric acid aggregated and settled faster than that produced with sulfuric acid (an hour or two hours as opposed to more than twelve). Thus, if hydrochloric acid is used, the turbidimetry measurements will need to be performed more quickly, since once the selenium precipitate has settled, no reliable turbidity measurement can be made.

Discussion

Here the beneficial effect of ultra-acidification in accelerating the reductive production of colloidal selenium precipitate is discussed on the basis of the relevant sulfur dioxide/sulfite/acid equilibrium expressed by Eq. (3).



Undissociated sulfurous acid (H_2SO_3) and sulfite ions (SO_3^{2-}) can be neglected from this analysis since the former species does not appear to exist in aqueous solutions and the latter is only present in negligible amounts because of the very low second dissociation constant of sulfurous acid (6.24×10^{-8}) (23). The equilibrium amount of aqueous sulfur dioxide can be determined using Eq. 4 (28). At 25°C the reaction constant (K) is equal to 1.28×10^2 . Moreover, according to literature, the constant decreases with temperature elevation due to the exothermic nature of the reaction (24).

$$K = \frac{\gamma[\text{HSO}_3^-] * \gamma[\text{H}_3\text{O}^+]}{([\text{Total dissolved SO}_2] - [\text{HSO}_3^-])} \quad (4)$$

Upon addition of sulfuric acid addition the $\text{SO}_2/\text{HSO}_3^-$ equilibrium (Eq. 3) shifts towards the formation of aqueous sulfur dioxide because of the combined effect of proton activity/concentration effect and temperature elevation. The sulfur dioxide can then react with the selenious ions to produce an elemental selenium precipitate and sulfuric acid (Eq. 1).

Colloidal Selenium Precipitate

In order to characterize the elemental selenium precipitate formed during the reduction reaction, 100 mL of a 1 g/L Se(IV) solution with 10 g/L (0.156 M) of dissolved sodium sulfite was mixed with 100 mL of concentrated (36% w/w) hydrochloric acid. The solution immediately turned brick red and the precipitate was separated (following its apparent aggregation) using a 0.2 μm filter. Interestingly,

some selenium colloidal nanoparticles remained in solution since the filtrate exhibited a light yellow-green color (25). The precipitate was then washed, dried and observed using scanning electron microscopy. The pictures shown in Fig. 1, reveal that the precipitate is made of spongy aggregates of sub-micron (200–300 nm) elongated primary particles. The as-produced precipitate was visibly composed of red amorphous selenium. This was confirmed (see XRD pattern in Fig. 2) via its recrystallization in boiling toluene solution (5,26).

Turbidimetry

Following the conversion of selenite to colloidal selenium via the combined action of sulfite reduction and ultra-acidification tests were performed to determine the optimum set of conditions for conducting the turbidity measurements. Among the parameters tested were the range of selenium concentration that provides a linear range of turbidity, the effect of sulfite concentration, and the possible interference by third ions.

Linear Concentration Range

It was found that for test solutions containing more than 12.5 mg/L of soluble selenite ions the turbidity to be rather high making the measurements prone to error (deviation

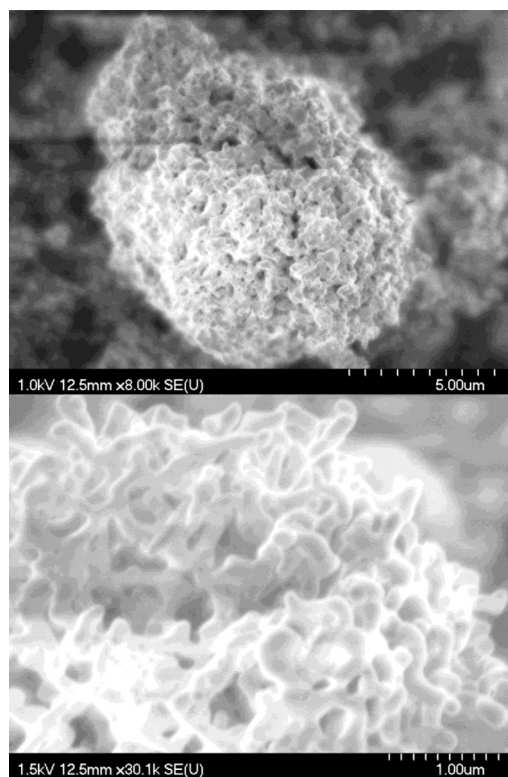


FIG. 1. Scanning electron microscope image of the colloidal selenium precipitate (following drying).

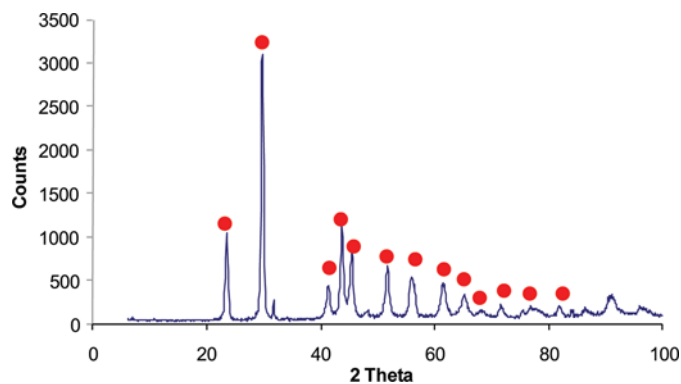


FIG. 2. XRD pattern of the selenium precipitate after toluene treatment, compared to that of hexagonal synthetic selenium (red dots, ICDS: 00-006-0362). (Color figure available online)

from linearity). It is thus necessary to dilute the solution, after the reduction procedure, in order to lower the selenium concentration within the linear range of turbidity measurements. For determining the most suitable dilution ratio (linear range), two sets of tests were performed. In these tests, 5 and 10 mL samples were mixed with the same volume of concentrated sulfuric acid and diluted to 100 mL using volumetric flasks. The results are shown in Figs. 3 and 4. Also in Fig. 5 a picture of the variable concentration colored solutions is provided.

As can be seen, both sets of results are linear up to a certain concentration (100 and 250 mg/L for the ten and twenty dilution factors, respectively) and start leveling off after that point. The upper limit of linear response is 15 mg/L Se. Thus, the dilution ratio has to be adjusted to lower the selenium concentration within the 1–15 mg/L linear range.

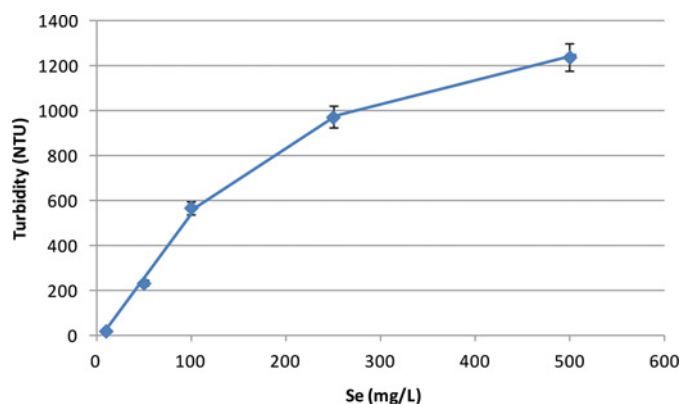


FIG. 3. Turbidity as function of initial selenium concentration for a dilution factor of ten (Conditions: 10 mL of sample, 0.1 g of Na_2SO_3 , 10 mL of 98% w/w sulfuric acid, mixed for a few seconds and diluted to 100 mL using deionized water, average of five tests). (Color figure available online)

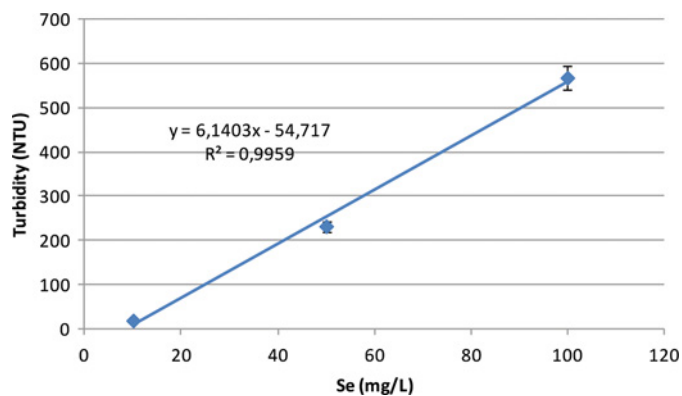


FIG. 4. Detail of Fig. 3 with linear regression. (Color figure available online)

Spectator-Ion Effects

Tests were also performed to evaluate possible interference effects from transition metal ions commonly found in industrial solutions, like Zn(II), Fe(II) and Cu(II). These metal ions were added into the solution at 1 g/L for cupric ions and 10 g/L for the ferrous and zinc ions (the maximum concentration encountered in industrial acid effluent solutions). No reaction between sulfite and these ions took place nor interference with the turbidity measurements was encountered. In addition, selenate-bearing solutions in lieu of selenite were tested but proved not suitable for application of the reduction/acidification/turbidimetry method because of selenate's resistance to reduction.

Sulfite Concentration Effect

To evaluate the effect of the sulfite/sulfur dioxide concentration on the turbidity results, 5 mL samples containing 100 mg/L of selenium (IV) and different concentrations

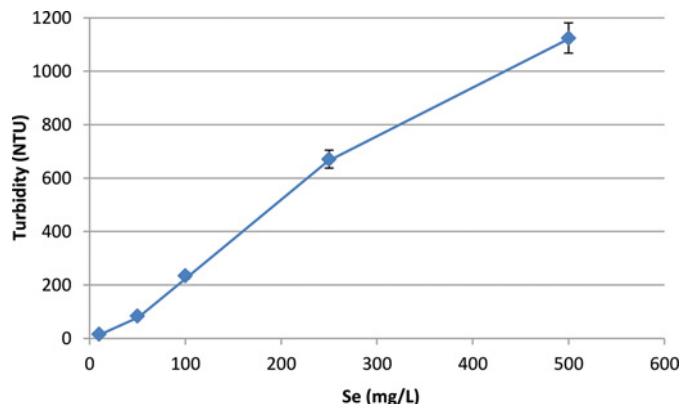


FIG. 5. Turbidity as function of initial selenium concentration for a dilution factor of twenty (Conditions: 5 mL of sample, 0.05 g of Na_2SO_3 , 5 mL of 98% w/w sulfuric acid, mixed for a few seconds and diluted to 100 mL using deionized water, average of five tests). (Color figure available online)

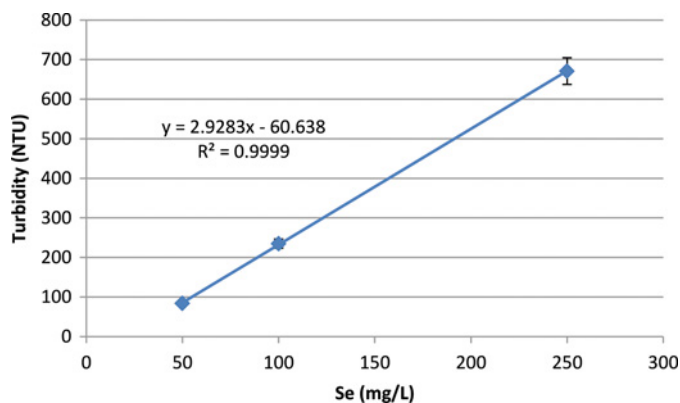


FIG. 6. Detail of Fig. 5 with linear regression. (Color figure available online)

of sodium sulfite were mixed with the same volume of concentrated sulfuric acid and diluted to 100 mL with deionized water. The results, shown in Fig. 6, indicate that sulfite concentration can have a significant effect on the turbidity of the final solution. While the exact phenomenon behind this effect is not totally clear, it appears to involve the formation of elemental selenium particles of slightly different morphologies, affecting the turbidity readings (in all cases less than 0.5 mg/L of selenium was left in solution). Thus, care should be taken to use the same sulfite concentration and preferably between 0.16 and 0.32 M (20 and 40 g/L) Na_2SO_3 to minimize any interference with selenium concentration determination.

Application to SO_2 - Containing Industrial Solution

Tests performed on industrial weak acid showed that the amount of dissolved sulfur dioxide (the method of determination is described in the Appendix) can vary widely according to various parameters, such as storage time and exposure to air, agitation, and temperature. It was determined generally to be between 5 and 25 g/L of the total dissolved SO_2 corresponding to 0.08 and 0.40 m sulfite. In order to compensate for this effect, it is possible to add sulfite ions or to use a higher dilution factor. For example, complex



FIG. 7. Color variation of solutions of different turbidity following 20 \times dilution (from left to right 50, 100, 250, and 500 mg/L initial selenium concentration).

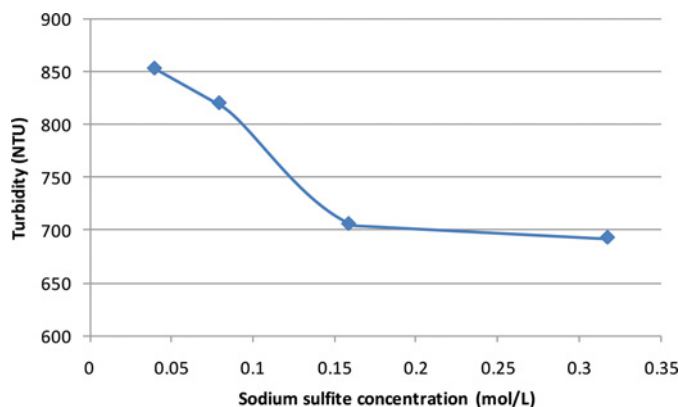


FIG. 8. Turbidity as function of sodium sulfite concentration for a dilution factor of twenty (Conditions: 5 mL of sample, 0.040, 0.079, 0.159, or 0.317 mol/L of Na_2SO_3 , 5 mL of 98% w/w sulfuric acid, mixed for a few seconds and diluted to 100 mL using deionized water). (Color figure available online)

industrial samples taken at several weeks interval were tested using the turbidimetry method. It was found that using a dilution factor of 40 compensated for variations in the sulfite effect and allowed accurate measurements to be performed. The obtained results are presented in Fig. 7.

Analytical Flowchart

Based on the work reported above, turbidimetry can be applied to selenium (IV) concentration analysis as per the flowchart of Fig. 8. Thus, typically sodium sulfite of at least 0.160 M concentration is added (if not already present) to the weak acid solution containing Se(IV) anywhere between a few to several hundreds mg/L of selenite. After that an equal volume of 98% sulfuric acid is added to produce the colloidal selenium. Prior to turbidity (T) measurement the appropriate dilution is required to operate within the linear turbidity vs concentration range.

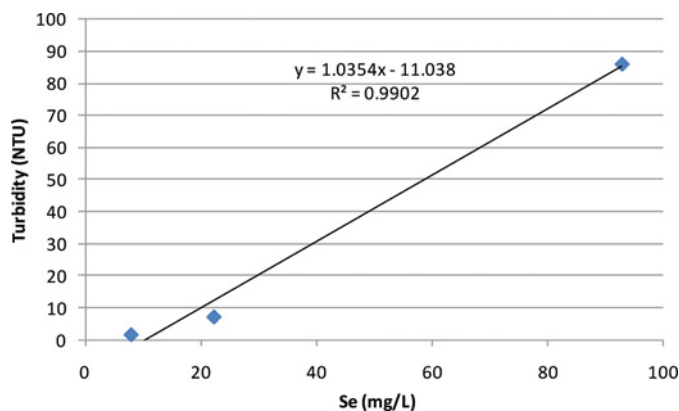


FIG. 9. Turbidity as function of initial selenium concentration for a dilution factor of forty (conditions: 5 mL of industrial weak acid sample, 5 mL of 98% w/w sulfuric acid, mixed for a few seconds and diluted to 200 mL using deionized water). (Color figure available online)

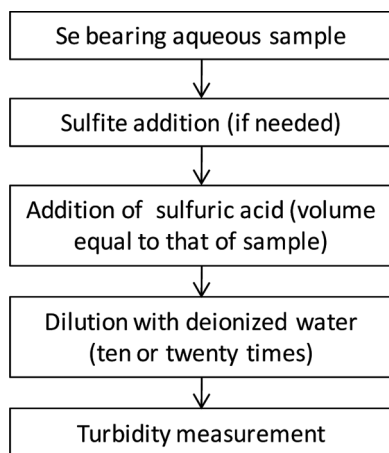


FIG. 10. Flowchart of the selenium(IV) measurement technique (in order to obtain a linear concentration range, dilution factor of ten should be used for selenium concentrations below 50 mg/L and twenty up to 250 mg/L. A sodium sulfite concentration above 0.160 mol/L is recommended in all cases).

CONCLUSION

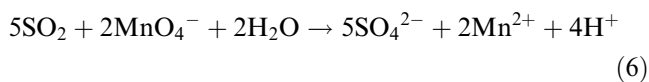
Selenite ions can be very rapidly reduced to a colloidal form using dissolved sulfur dioxide/sulfite salt (above 0.1 M of dissolved SO_2) if the solution is ultra-acidified using a strong mineral acid. The turbidity of the colloidal solution, once properly diluted, can be measured and related with excellent precision to the original selenium concentration. This analytical procedure is very fast, simple, and cost-effective making it highly suitable for industrial use. The method is free of interference effects by transition metal ions such as iron(II), copper(II), or zinc(II). The method is not applicable to selenate analysis.

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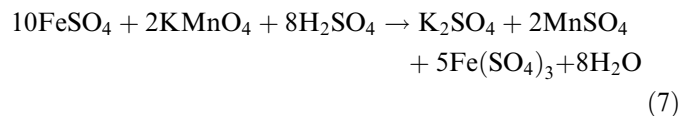
APPENDIX-DETERMINATION OF DISSOLVED SULFUR DIOXIDE

In order to measure the concentration of dissolved sulfur dioxide/sulfite in the industrial solution, sodium permanganate can be used according to:



The reaction can be monitored because of the color difference between Mn^{7+} (purple) and Mn^{2+} (light green) ions. When a slight purple color remains in solution for more

than a few seconds, the titration is complete, the volume of permanganate solution used is recorded, and the amount of dissolved sulfur dioxide is determined. A drawback of this technique is that the ferrous salts present in solution can also be oxidized by the permanganate ions according to:



If the concentration of ferrous ions is known, it is possible to account for it when calculating the dissolved sulfur dioxide concentration. Based on Eqs. 6 and 7, 0.57 g of dissolved sulfur dioxide is overestimated for every g/L of iron present in solution. While it is also possible to remove the iron using a cationic ion exchange resin (such as Dowex G-26H), experience has shown that a significant fraction of dissolved sulfur dioxide is lost when the acid is agitated and passed through the resin.

REFERENCES

1. Monteith, G.; Houlachi, G.; Pineau, M.; Laliberté, M. In: *Development, Testing and Full-Scale Operation of a New Treatment Method for Selenium Removal from Acidic Effluents*, Lead-Zinc 2000, Pittsburg, 2000; Dutrizac, J.E., Ed. TMS: Pittsburg, 2000; pp. 879–890.
2. Houlachi, G.; Monteith, G.; Rosato, L. Process for Removing Selenium and Mercury from Aqueous Solutions. 2412393, 2002.
3. Twidwell, L.; McCloskey, J.; Miranda, P.; Gale, M. (2000) Potential technologies for removing selenium from process and mine wastewater. In *Minor Elements 2000*; Young, C., Ed. Society for Mining Metallurgy & Exploration: Littleton, CO, 53–66.
4. Zingaro, R.A.; Cooper, W.C. (1974) *Selenium*; Editor Van Nostrand Reinhold: New York.
5. Geoffroy, N.; Demopoulos, G.P. (2009) Reductive Precipitation of elemental selenium from selenious acidic solutions using sodium dithionite. *Industrial & Engineering Chemistry Research*, 48 (23): 10240–10246.
6. Geoffroy, N.; Benguerel, E.; Demopoulos, G.P. (2008) In: *Precipitation of Selenium from Zinc Plant Weak Acidic Solutions using Sodium Dithionite and Sodium Sulphide*, COM 2008 - Lead Zinc 2008, Winnipeg, MetSoc: Winnipeg, 2008.
7. Vesely, J.; Weiss, D.; Stulik, K. *Analysis with Ion-Selective Electrodes*; E. Horwood, ed.; distributed by J. Wiley: Chichester; New York, Toronto, 1978.
8. Ansa-Asare, O.D.; Gadzekpo, V.P.Y. (1990) 4-Chloro-1,2-diaminobenzene as neutral carrier for selenium in selenium ion selective electrode. *Ghana Journal of Chemistry*, 1 (3): 172–175.
9. Stozhko, N.Y.; Morosanova, E.I.; Kolyadina, L.I.; Fomina, S.V. (2006) Ceramic composite electrode for the determination of selenium(IV) by stripping voltammetry. *Journal of Analytical Chemistry*, 61 (2): 158–165.
10. Kambo-Dorsa, J.; Gadzekpo, V.P.Y. (2003) Development of selenium ion - selective electrodes based on diamines. *Ghana Journal of Chemistry*, 5 (2): 124–139.
11. Mohsen, M.; Zareh, A.S.A.M.A.-A. (1995) New polycrystalline solid state responsive electrodes for the determination of the selenite ion. *Electroanalysis*, 7 (6): 587–590.
12. Ekmekçi, G.; Somer, G. (1999) A new selenite selective membrane electrode and its application. *Talanta*, 49 (1): 83–89.
13. Cai, Q.; Ji, Y.; Shi, W.; Li, Y. (1992) Preparation and application of selenite ion selective electrode. *Talanta*, 39 (10): 1269–1272.

14. Ashtamkar, S.M.; Thakkar, N.V. (2000) Preparation and study of selenium (IV) ion selective electrode using 1,8-diaminonaphthalene. *Transactions of the SAEST (Society for Advancement of Electrochemical Science and Technology)*, 35 (3-4): 107-111.
15. Ekmekçi, G.; Somer, G. (2000) Selenite-selective membrane electrodes based on ion exchangers and application to anodic slime. *Analytical Sciences*, 16 (3): 307-311.
16. Malone, T.L.; Christian, G.D. (1974) Selenium (IV) selective electrode. *Analytical Letters*, 7 (1): 33-39.
17. Sounderajan, S.; Kumar, G.K.; Udas, A.C. (2010) Cloud point extraction and electrothermal atomic absorption spectrometry of Se (IV)-3, 3'-Diaminobenzidine for the estimation of trace amounts of Se (IV) and Se (VI) in environmental water samples and total selenium in animal blood and fish tissue samples. *Journal of Hazardous Materials*, 175 (1-3): 666-672.
18. Masłowska, J.; Baranowski, J.B. (1982) Extraction-spectrophotometric method with 3,3'-diaminobenzidine for the determination of trace amounts of selenium in cosmetics. *Bromatologia i Chemia Toksykologiczna*, 15 (3): 173-178.
19. Sankalia, J.M.; Mashru, R.C.; Sankalia, M.G. (2005) Spectroscopic determination of trace amounts of selenium(IV) in multivitamin with multimineral formulations using 3,3'-diaminobenzidine hydrochloride. *Spectroscopy Letters*, 38 (1): 61-76.
20. Warren, L.E. (1915) A new color reaction for papaverine. *Journal of the American Chemical Society* 37 (10): 2402-2406.
21. P.T.; Taylor, E.P. (1950) A note on the oxidation of papaverine by selenium dioxide. *Journal of Pharmacy and Pharmacology*, 2 (5): 324.
22. Shakhov, A.; Shakhov (1945) Photocolorimetric determination of selenium and tellurium. *Zavodskâ laboratoriâ*, 11: 893.
23. Lide, D.R. (2005) *CRC Handbook of Chemistry and Physics*; CRC Press LLC: Boca Raton, FL.
24. Hocking, M.B.; Lee, G.W. (1977) Calculated sulfur dioxide equilibria at low concentrations between air and water. *Water, Air, and Soil Pollution*, 8 (3): 255-262.
25. Geoffroy, N.; Demopoulos, G.P. (2011) The elimination of selenium(IV) from aqueous solution by precipitation with sodium sulfide. *Journal of Hazardous Materials*, 185 (1): 148-154.
26. Becze, L.; Gomez, M.A.; Berre, J.F.L.E.; Pierre, B.; Demopoulos, G.R. (2009) Formation of massive gunningite-jarosite scale in an industrial zinc pressure leach autoclave: A characterization study. *Canadian Metallurgical Quarterly*, 48 (2): 99-108.