Spectrophotometric Determination of Selenium in the Presence of Copper and Tellurium. Application to Anodic Slimes

Güler SOMER† and Güler EKMEKÇI

Department of Chemistry, Gazi University, 06500 Ankara, Turkey

Selenite reacts with iodide ion quantitatively in acidic solution forming selenium and iodine. The iodine formed is extracted into chloroform phase and its absorbance is measured at 509 nm. With this method $10^{-2}-5\times10^{-6}$ M selenium could be determined. The interference of copper is removed by the precipitation of its hydroxide at pH 6–6.5 and 10^{-4} M selenite could be determined with 1–4% relative error in the presence of 10^{-2} M copper and tellurium. This method is applied to anodic slime samples. The results are in accordance with the results obtained with different methods.

Keywords Selenium determination, anodic slime, spectrophotometry, copper, tellurium

Selenium is an important element because of its use in plenty of areas such as in the production of redressors and photocells, in glass, rubber, steel and chemical industries. There are no natural minerals from which selenium can be produced efficiently. The highest selenium and tellurium reserves are copper zinc pyrites. They contain about $10^{-3}-10^{-5}$% selenium and tellurium. The most important source for selenium is anodic slime which is obtained during the electropurification of copper. In the United States 90% selenium is obtained from this source. A simple, rapid and accurate method for determining the amount of selenite is therefore desirable. Atomic absorption spectrometry[1,2], neutron activation[3] and anodic stripping voltammetry[4,5] are used for the determination of trace amounts of selenium. Anodic slime contains Se, Te, Cu, Au, Ag, Pb, As and Sb. The level of selenium is between 8 and 20%, copper is between 20 and 40%, and tellurium is between 0.3 and 3%. After dissolution of such samples the selenium concentration is expected to be $10^{-3}-10^{-2}$ M. Thus there is no need to use fancy and expensive instruments. This level of selenium has been determined by gravimetric[6–8], titrimetric[9,10], polarographic[11,12] and spectrophotometric[13–16] methods. In nearly all selenium determination methods copper and tellurium seem to be the most serious interfering elements, because their oxidation-reduction properties are very similar to those of selenium. There are many investigations in which spectrophotometry has been used for the determination of selenium. But even though very specific and expensive reagents have been used, there are still many interference problems and they need long and tedious separation procedures. The aim of this work is to propose a simple and inexpensive method for the determination of selenite in anodic slime and in some samples resembling in constitution to anodic slimes.

† To whom correspondence should be addressed.

Experimental

Apparatus

Absorption spectra and absorbances were recorded using a Bausch and Lomb, Spectronic 2000, Double Beam UV-Visible Spectrophotometer.

Reagents

All reagents used were of analytical-reagent grade. Triply distilled water was used throughout. By dissolving 1.109 g of SeO_2 in 100 ml of triply distilled water 0.1 M selenite solution was prepared. Buffer solution of pH=5 was prepared by using potassium hydrogenphtalate and buffer solutions of pH=6 to 7.5 were prepared from KH_2PO_4.

Procedure

About 0.5 g of anodic slime was digested[9] in HNO_3 and HCl. The solution was boiled after addition of about 1 g of urea and it was diluted into 100.0 ml. An aliquot of 2.0 ml was taken, pH was adjusted to about 5 with NaOH and then pH=6–6.5 buffer was added. The precipitate was filtered and washed with water for several times. The filtrate was diluted to 25.0 ml and 2.0 ml of it was taken, pH was adjusted to one or two and 1–2 ml of 0.1 M KI was added. The iodine formed was extracted with 2.0 ml portions of chloroform until the organic phase was colorless. The extracts were collected and the solution was diluted with chloroform to 25.0 ml. The absorbance of the solution was measured at 509 nm. Using the extinction coefficient of ε=870 l mol^{-1} cm^{-1}, the concentration of iodine formed in the

Table 1 Determination of iodine formed after the reaction with known amounts of selenite

Initial selenite concentration/M	Number of samples	Iodine expected/ M	Iodine determined/ M	Standard deviation/M	$\bar{X}\pm ts/\sqrt{N}$	Relative error, %
4.75×10^{-4}	5	3.80×10^{-5}	3.76×10^{-5}	0.09×10^{-5}	$(3.76\pm0.11)\times10^{-5}$	2.6 - 3.4
1.90×10^{-4}	5	1.52×10^{-5}	1.51×10^{-5}	0.10×10^{-5}	$(1.51\pm0.12)\times10^{-5}$	2.1 - 9.2
9.50×10^{-5}	5	7.62×10^{-6}	7.79×10^{-6}	0.06×10^{-6}	$(7.79\pm0.07)\times10^{-6}$	5.1 - 9.3

t: 95% confidence interval.

reaction with selenite which is present in the solution was calculated. The selenite content was calculated from the relation between selenite and iodine.

Results and Discussion

We found experimentally that selenite reacted with iodide quantitatively in acidic solution forming elemental selenium and iodine. This reaction was used[9] for the titrimetric determination of 0.1 M selenite. In this method the iodine formed was titrated with standard thiosulfate solution. In the present work we used the reaction between selenite and iodide and we determined the selenite concentration by an indirect method. Here, the iodine formed is determined spectrophotometrically after extracting it into an organic phase. With this method it was possible to determine $10^{-2}-5\times10^{-6}$ M selenite concentrations, a value which could hardly be reached with spectrophotometric methods.

Preliminary experiments

pH of medium. For the reaction between selenite and iodide given below, the pH should be as low as possible

$$SeO_3^{2-} + 4I^- + 6H^+ \rightleftharpoons 2I_2 + Se + 3H_2O$$

Since the iodide ion can be oxidized easily with air in acidic solution, according to the reaction

$$2I^- + 1/2O_2 + 2H^+ \rightleftharpoons I_2 + H_2O$$

the pH of the solution should not be too low. Otherwise iodide ion would be oxidized in air and this would lead to wrong results. Since at acidities higher than 0.4 M the oxidation rate of iodide ion increases greatly, the acid concentration should be lower than 0.4 M. According to our investigations the reaction between selenite and iodide ion would reach completion in the pH interval 1 - 2.

Iodide ion concentration. The iodide ion concentration is also very important because of its oxidation in air as stated before. It was found that its concentration could be 10 - 15 times of selenite concentration without giving any problem.

Spectrophotometric determination

In the proposed method the quantity of selenite ion is determined indirectly from the concentration of iodine formed. Iodine concentration was determined spectrophotometrically. In order to eliminate the interference of red colored elemental selenium, the iodine was extracted first into chloroform phase. This solution had a maximum absorption at 509 nm. A plot of iodine concentration *versus* absorbance showed a linear relationship in the concentration range of $10^{-6}-10^{-3}$ M iodine in chloroform with an extinction coefficient of ε=870 l mol^{-1} cm^{-1}.

Extraction efficiency

Preliminary experiments were performend to obtain the extraction efficiency. First aqueous 0.1 M iodine solution was prepared using KI and it was standardized against As_2O_3. A known volume (*e.g.* 0.25 ml) was taken into a separatory funnel and with 2.0 ml portions of chloroform it was extracted until the chloroform phase was colorless. This solution was diluted to 25.0 ml and the absorbances were measured. For a 1.156×10^{-3} M iodine solution after four extractions a value of $(1.159\pm 0.003)\times10^{-3}$ M was obtained. This value fell into 95% confidence limit.

Procedure for the determination of selenite

The working conditions obtained in the preliminary experiments were applied to various selenite solutions. To achieve this, about 1 ml of a 0.1 M KI solution was added to various selenite solutions. This selenite solutions were prepared from 1 - 5 ml of $10^{-3}-10^{-4}$ M selenite solutions (KI concentration has to be 10 - 15 times of selenite concentration). Hydrochloric acid was added dropwise until the pH was about one or two. The reaction tube was immediately closed with a cork or glass stopper. It was stored in a dark place for about 3 - 4 min. One milliliter from this solution was taken and the iodine formed was extracted with 2.0 ml portions of chloroform as quickly as possible. The extracts were collected in a volumetric flask and the solution was diluted with chloroform to 25.0 ml. The absorbance of the solution was measured at 509 nm. The results are given in Table 1, with the errors made in the determination of iodine concentration.

It should be borne in mind that with the initial concentration of selenite at 10^{-4} M, the expected iodine concentration was 2×10^{-4} M. But since after extraction the solution was diluted 25 times, the iodine concentration and the corresponding selenite concentrations

Table 2 Determination of selenite, after precipitation of copper at different pH values

pH	Number of samples	$[SeO_3^{2-}]$ expected/M	$[SeO_3^{2-}]$ determined/M	Standard deviation/M	$\bar{X}\pm ts/\sqrt{N}$	Relative error, %
6.0	4	4.03×10^{-5}	4.17×10^{-5}	0.09×10^{-5}	$(4.17\pm0.14)\times10^{-5}$	+3.47
6.5	4	4.03×10^{-5}	3.62×10^{-5}	0.13×10^{-5}	$(3.62\pm0.21)\times10^{-5}$	−10.17
7.0	4	4.03×10^{-5}	4.61×10^{-5}	0.15×10^{-5}	$(4.61\pm0.23)\times10^{-5}$	+14.39
7.5	4	4.03×10^{-5}	4.51×10^{-5}	0.03×10^{-5}	$(4.51\pm0.05)\times10^{-5}$	+11.91

t: 95% confidence interval.

Table 3 Determination of selenite, after precipitation of copper at different pH values in anodic slime

pH	Number of samples	$[SeO_3^{2-}]$ found/M	Standard deviation/M	$\bar{X}\pm ts/\sqrt{N}$	Average (%) Se
6.0	8	8.50×10^{-5}	0.34×10^{-5}	$(8.50\pm0.23)\times10^{-5}$	10.52
6.5	4	8.05×10^{-5}	0.19×10^{-5}	$(8.05\pm0.30)\times10^{-5}$	9.97
7.0	4	9.43×10^{-5}	0.52×10^{-5}	$(9.43\pm0.52)\times10^{-5}$	11.60
7.5	4	10.63×10^{-5}	0.22×10^{-5}	$(10.63\pm0.35)\times10^{-5}$	13.02

t: 95% confidence interval.

would be 8×10^{-6} M and 4×10^{-6} M, respectively. This is the concentration of iodine measured spectrophotometrically.

Interferences

In nearly all selenium determination methods, copper and tellurium are the main interfering ions and therefore long and tedious separation procedures or expensive reagents have to be applied. Selenium is mostly found together with copper and tellurium. In the above given procedure selenite reacts with iodide ion and the iodine formed is determined. Tellurite reacts with iodide ion forming a complex, but since iodine is not formed, interference of tellurium is eliminated. On the other hand copper(II) reacts with iodide forming iodine. To remove copper ion from the solution some complexing and precipitating agents can be tried. However since the reaction between selenite and iodide is taking place at pH one or two, most of the complexing agents do not form complexes with the interfering ions at this pH value. Therefore complexation can not be used to eliminate the interferences. Copper can be quantitatively precipitated as $Cu(OH)_2$ at pH 5.5. At higher pH values $CuSeO_3$ can precipitate also. Considering that $K_{sp}=2.1\times10^{-8}$ for $CuSeO_3$ and $K_{sp}=2.2\times10^{-19}$ for $Cu(OH)_2$ copper ion can be precipitated only as $Cu(OH)_2$, by the adjustment of pH. To illustrate this, solutions which contain 5×10^{-2} M Cu^{2+} and 1×10^{-2} M SeO_3^{2-} were prepared, 2.0-ml portions were taken, and pH was adjusted to 5.5, 6.0, 6.5 and 7.0 with buffer solutions. The precipitate was filtered, washed and the filtrate was diluted to 25.0 ml. The filtrate was controlled for Cu^{2+} with a few drops of 0.1 M $K_4Fe(CN)_2$ which gives a red color with 10^{-4} M Cu^{2+} ion. For lower concentrations of copper ion, ammonium mercury(II) thiocyanate is used which gives violet color with 2×10^{-5} M Cu^{2+}. It is found that after precipitation at pH=5.5 copper ion concentration in the filtrate was larger than 10^{-4} M. At pH=6 and pH=6.5 however copper concentration was lover than 2×10^{-5} M. But when pH was larger than 7.0 copper concentration in the filtrate was larger than 10^{-4} M which means that with excess hydroxide ion $Cu(OH)_2$ has formed complex ions.

Table 4 Percentage of Se in anodic slime determined with four different methods

Method	Se in anodic slime, %
This work	10±1
Volumetric[9]	10±1
Spectrophotometric[15]	10±1
Polarographic[11]	10±1

A synthetic sample which contained 6.3×10^{-3} M selenite, 2×10^{-3} M tellurite and 1.26×10^{-2} M copper was prepared (such composition is taken to resemble anodic slime solution). A 2-ml sample was taken and the pH was adjusted to 6. The precipitate was filtered, washed and the filtrate was diluted to 25.0 ml. An 2.0 ml aliquot was taken, the pH was adjusted to one or two and 1 - 2 ml of 0.1 M KI solution was added. The iodine formed was extracted with chloroform and the absorbance was measured. The same procedure was applied for 10^{-3} M selenite solution at different pH values. The results obtained are given in Table 2.

Application to anodic slime

This method was also applied to anodic slime samples, which contained selenium, tellurium, copper, lead, arsenic, antimony, silver and gold. In such samples the copper concentration was 2 - 4 times larger than selenium. For this purpose about 0.5 g of anodic slime was digested in HNO_3 and HCl.[9] The solution was filtered and washed with dilute HCl solution. Nitric acid was

removed by urea and the solution was diluted into 100.0 ml. The presence of nitrate ion was controlled with iron(III) sulfate reagent since excess nitrate ion may react with iodide ion. The selenite concentration in this solution was about 10^{-2} M. An aliquot of 2.0 ml of it was taken, pH was adjusted to about 5 with NaOH whereafter the solutions were buffered at different pH values. These solutions were used in order to find the most convenient pH for separation. The precipitate was filtered and washed with water for several times. The filtrate was diluted to 25.0 ml and the above given procedure was applied. The results are given in Table 3. It can be observed that the pH must be between 6 – 6.5 for separation. To check the validity of the method, the same anodic slime was analyzed by volumetric[9], spectrophotometric[15] and polarographic[11] methods (Table 4). It can be seen that the results obtained with the proposed method are consistent with those given by the other methods.

The reaction between selenite and iodide is proposed for the determination of selenium in the presence of copper, tellurium, lead, silver, gold, arsenic and antimony. Optimum pH and iodide concentrations are given for the reaction. It was possible to determine a wide range ($10^{-2} - 5\times10^{-6}$ M) of selenite concentrations in the presence of large amounts of copper precisely. There is no need for fancy instruments and long and tedious separation precedures. The reagents used are very cheap and common substances. Since selenium is always found in nature next to large quantities of copper, the proposed method can be applied safely for such samples.

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