

A METHOD FOR RAPID DETERMINATION OF TRACE AMOUNTS OF SELENIUM IN ROCKS AND SOILS

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ABSTRACT

The classical method of determining very minor amounts of selenium in rocks and soils utilized a tedious distillation technique with hydrobromic acid in an all-glass apparatus. A rapid method using 3, 3'-diaminobenzidine has been used successfully on Cretaceous rocks where the selenium content is on the order of 1-100 p. p. m. Diphenylpiaszelenol is formed which can be quantitatively extracted by toluene. Absorbance at 420 $m\mu$ is then measured. Ferric iron and other commonly associated metal ions have been adequately masked by E. D. T. A. No special separations are needed to remove other elements.

INTRODUCTION

Work in our laboratory on the geochemistry of selenium led to search for a method of chemical analysis that would be more rapid and more sensitive than the classical reduction procedures. K. L. Cheng (1956a, 1956b) devised a spectrophotometric method for determining trace amounts of selenium in stainless steels and copper using the reagent 3, 3'-diaminobenzidine. Pien *et al* (1937) first described the reaction of 3, 3'-diaminobenzidine (DAB) with selenium with the formation of a yellow diphenylpiaszelenol. The reaction is discussed thoroughly by Cheng (1956a).

Interference by other ions, particularly oxidizing agents has complicated selenium analyses. Hoste (1948) found methods to eliminate interference of all agents examined except vanadium (+5). The investigations of Cheng (1956a, 1956b) led to the discovery that the disodium salt of ethylenedinitrilotetraacetic acid (EDTA), in addition to preventing interference from the polyvalent metals (except V) did not inhibit the formation of the piaszelenol in acidic media.

With some minor modifications, Cheng's method has been successfully used on over 300 samples of minerals, rocks, and soils to determine trace amounts of selenium where the selenium content of the sample is less than 100 p.p.m. Further modifications would be necessary for use with highly seleniferous rocks and minerals

such as some ore deposits and many pyrites. The use of this method in uranium deposits or other ore deposits with high vanadium content is highly questionable.

The results of analysis by this method in our laboratory compare favorably with an analysis performed on the same sample by the classical distillation and reduction method in another laboratory.

PROPERTIES OF 3, 3'-DIAMINOBENZIDINE

This compound is secured as the hydrochloride salt. It is a soluble base which rapidly darkens and deteriorates in air at room temperature when dissolved in water for use in this method. In our experience the aqueous solution of DAB may be kept in usable condition for about three days if stored in a refrigerator. It is possible to keep the solution stable indefinitely by passing nitrogen gas through it (K. L. Cheng, personal communication). However, it is advisable to prepare only the amount of solution needed for a three-day period because of the high cost of the reagent and its instability in aqueous solution.

Although the yellow piaszelenol formed in the reaction of DAB with Se(+4) can be extracted by a number of organic reagents at various pH levels this method uses toluene to quantitatively extract the piaszelenol at the pH range 2 to 3 where the EDTA is an effective masking agent. In most rocks and soils the chief interfering ion will be ferric iron. The amount of ferric iron in the sample should be roughly known and only a slight excess of EDTA necessary (approximately 0.2 ml. of 0.1 molar EDTA per mg. of Fe) to mask the iron should be added. The addition of large excesses of EDTA apparently interferes with the extraction or the maximum development of the color with the result that final readings on the colorimeter or spectrophotometer always give results that are too low.

REAGENTS AND STANDARDS

A standard selenium solution can be made by dissolving 1.6335 grams of reagent grade selenous acid (H_2SeO_3) in one liter of water. This gives a ratio of 1 mg. Se per ml. H_2O . From this solution a 10 p.p.m. selenium solution may be made by diluting 10 ml. to one liter. Other standard solutions should be made up to allow construction of a standard curve for selenium (equivalent of up to 100 p.p.m. in the original sample or 100 micrograms of selenium per determination). The standard curve used in our work was determined from aliquots with 5, 10, 20, 30, 50, 70, and 90 micrograms of selenium. Plotted on semilogarithm paper with micrograms of Se plotted against the log per cent transmittancy a straight line relationship will result.

A 0.1 molar solution of EDTA may be made by dissolving 37.2 grams of reagent grade disodium EDTA dihydrate in one liter of water.

As needed 0.5% aqueous solutions of DAB should be made. In addition, 2.5 molar formic acid, concentrated nitric and hydrochloric acids, 70% perchloric acid, 7 molar aqueous ammonium hydroxide, and C.P. toluene are needed.

PROCEDURE

Place a 1-gram sample of the unknown, containing not more than 100 micrograms of selenium, in a 400-ml. beaker and add 2.5 ml. of concentrated nitric acid. Cover with a watch glass and heat gently on a hot plate for about 15 minutes to allow organic materials in the sample to be digested. Remove, cool, and add 2.5 ml. of 70% perchloric acid. Replace on the hot plate and continue gentle heating to near dryness. The digest should be colorless before heating is discontinued. Cool and wash the inside of the beaker with 10-20 ml. of hot distilled water. Add 20 ml. of 0.1% EDTA solution. A greater quantity may be required if large amounts of interfering elements are present.

Adjust the pH of the solution to the range 2.5-3 with 7-molar ammonium hydroxide. Add 2 ml. of 2.5 molar formic acid. Follow with 2 ml. of 0.5% aqueous diaminobenzidine and allow to stand for at least 30 minutes.

Adjust the pH of the solution to the range 6-7 with 7-molar ammonium hydroxide. Transfer to a 250 ml. separatory funnel, add 10 ml. of toluene, and shake vigorously for at least 30 seconds, 3 times. Separate the toluene layer, by a centrifuge, and determine its optical density at a 420 millimicron wavelength, using a 1-cm. cell and a reagent blank as reference fluid. Find the selenium content from the standard curve.

DISCUSSION

To insure reproducible and accurate results, the volume of the liquid should be carefully controlled. There should be no more than 100 ml. of liquid per sample at any time, and multiple shaking with the toluene is recommended if the volume exceeds 50 ml.

As shown by Cheng (1956a), the hydrogen ion concentration has important effects upon the formation of the piaszelenol and its extraction by the toluene. Therefore, pH control must be carefully maintained at the prescribed points in the procedure.

Interference from the polyvalent metal ions may cause precipitates to form in the solution. Samples exhibiting this phenomenon should be rerun using additional EDTA.

CONCLUSION

With proper technique this method should prove satisfactory for minerals, rocks and soils containing less than 100 micrograms of Se per gram of sample (100 p.p.m. Se). It is particularly useful when a large number of chemically similar samples (e.g. we ran over 200 samples of the Cretaceous Niobrara formation - a chalky shale) are being analysed. Analysis of forty samples per day (in duplicate) is attainable.

REFERENCES

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