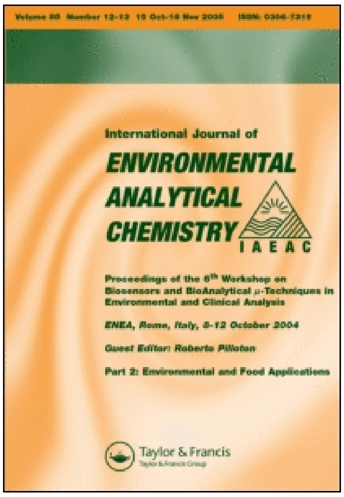

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Kinetic-fluorimetric Determination of Selenium in the Environment with Use of Methylene Blue

F. Grases[a]; G. Genestar[a]; R. Forteza[a]
[a] Department of Analytical Chemistry, Faculty of Sciences, University of Palma, Mallorca, Spain

To cite this Article Grases, F. , Genestar, G. and Forteza, R.(1986) 'Kinetic-fl uorimetric Determination of Selenium in the Environment with Use of Methylene Blue', International Journal of Environmental Analytical Chemistry, 23: 4, 321 — 329

To link to this Article: DOI: 10.1080/03067318608076453

URL: http://dx.doi.org/10.1080/03067318608076453

Intern. J. Environ. Anal. Chem., 1986, Vol. 23, pp. 321–329
0306-7319/86/2304-0321 $ 18.50/0

Kinetic-fluorimetric Determination of Selenium in the Environment with Use of Methylene Blue

F. GRASES, G. GENESTAR and R. FORTEZA

Department of Analytical Chemistry, Faculty of Sciences, University of Palma de Mallorca, Spain

(*Received April 12, 1985; in final form July 30, 1985*)

A kinetic-fluorimetric method for determination of traces of selenium (0.01–0.4 ppm) is described. It is based on the fact that the reducing power of alkali sulfides can be considerably enhanced by the addition of elemental selenium. The experimental variables and interferences have been studied. The selenium quantities are estimated in diverse environmental samples.

KEY WORDS: Kinetic analysis, spectrofluorimetry, selenium.

INTRODUCTION

No method for the kinetic determination of selenium based on the appearance of fluorescence is to be found in the literature. Some kinetic methods have been based on different techniques, thus, Bognar and Sarosi[1] recommended a Landolt reaction method based on the chlorate–chloride–hydrazine sulfate system by which 0.1 to 1 μg per 5 ml of selenium can be determined. Kawashima and Tanaka[2] have determined 0 to 0.15 μg amounts of selenium by the catalytic reduction of 1,4,6,11-tetra-azo-naphthacene with phosphorous acid in hydrochloric acid medium. The reaction has to be started at 50°C, and after a fixed time of 30 min the mixture is cooled to 0°C to stop the reaction. The extinction of the solution must be measured at 600 nm within 30 s. Another method, based on the oxidative coupling reaction of phenyl hydrazine *p*-sulfonic acid with 1-naphthylamine, has been reported.[3] The mixture should be kept at 50°C for 60 min, then the reaction can be stopped by cooling the system to 0°C, and the extinction of the solution is measured at 525 nm. The method of Markova and Kaplan[4] used the selenide or selenourea-catalyzed reduction of silver bromide in a photographic plate by *p*-methylaminophenol-hydroquinone developer. Klochkovskii and Neimysheva[5] based their catalytic method on the reduction of nitrate by iron(II)-EDTA, enhanced by SeO_3^{2-}. A sensitive catalytic method for determining selenium was proposed by Kawashima *et al.*[6] Selenium catalyzes the oxidation of *p*-hydrazinobenzenesulfonic acid to *p*-diazobenzenediazonium ion, which then is converted to a yellow azo dye by coupling with *m*-phenylenediamine. Selenium and tellurium have been determined by use of their ability to increase significantly the catalytic activity of colloidal gold in the reduction of a cobalt(III)-EDTA complex.[7] A variable-time procedure, potentiometric monitoring, is described, with a picrate ion selective electrode.[8]

The reaction between methylene blue and sulfide ion, enhanced by elemental selenium, has been adopted as a sensitive and selective test for the detection of selenium.[9,10] If selenium is present, decoloration occurs significantly more quickly. The smallest amount of the element which can be determined is 0.08 μg. West and Ramakrishna[11] recommended the use of the reduction of methylene blue with sodiumsulfide at pH 10.8 for the catalytic determination of selenium. The time for complete decolorization is measured visually for various concentrations of Se and is used to prepare the calibration curve. Between 0.1 and 1 μg of selenium can be determined by the method. In the present paper, a simple procedure is described for the kinetic fluorimetric determination of selenium based on the blue fluorescence that appears when the former reacts with methylene blue in presence of sodium sulfide. Selenium has been recognized as a natural toxicant since the 1930s when seleniferous vegetation was discovered. This vegetation contains concentrations up to 10 ppm of Se. Therefore, presence of selenium in food at concentrations below 3 ppm is beneficial for diverse animals. For this a periodic analysis allows one to detect deficiencies before appearance of pathologic symptoms and the interest in the development of simple procedures for selenium determination in environmental samples is understandable.

EXPERIMENTAL

Reagents and solutions

A methylene blue (Merck) solution 0.1% was prepared in ethanol. A standard solution of selenium(IV), 1.27×10^{-2} M was prepared from $Na_2SeO_3 . 5H_2O$ (Merck). Alkaline sodium sulfide solution (*ca.* 0.04 M) is prepared by dissolving 0.96 grams of sodium sulfide, an equal weight of sodium sulfite, and 1.6 grams of sodium hydroxide in 100 ml of deionized water. This solution is prepared and renewed daily. A 0.25 M solution of disodium ethylene diamine tetra acetate and a formaldehyde solution (35%) were also used.

Apparatus and measurement conditions

FIKA 55 MK II spectrofluorimeter. The intensity of fluorescence emitted-time curves have been obtained fixing the excitation and emission wavelengths and by constant movement of the needle of the recorder, whose speed was 60 s cm^{-1} for all the experiences done.

Procedure

In a cell of 4.5 × 1 cm, provided with a cover, are placed 1.6 ml of formaldehyde solution (35%), 0.5 ml of 0.25 M EDTA solution, 0.2 ml of 0.04 M alkaline sodium sulfide solution (0.4 M in NaOH, that provides a final pH of about 11), a volume of the solution of the analyte necessary for the final concentration of selenium to be between 0.01 and 0.4 ppm and 1 ml of 0.1% methylene blue solution. The final volume is adjusted to 4 ml, if necessary, by addition of deionized water before the addition of the reagent. Mix the contents of the stoppered cell well after addition of methylene blue solution. When 30 s have elapsed after the addition of the reagent, recording of the fluorescence intensity-time curve is started ($\lambda_{ex} = 360$ nm, $\lambda_{em} = 465$ nm), working at ~20°C. The duration of each measurement is *ca.* 12 min.

Determination of selenium in environmental samples

The determination of selenium in water was carried out without previous treatment of the sample and eliminating the cationic species by use of an Amberlite IR-120 resin. The determination of selenium in geological or biological samples was carried out from 0.1–1 g of dried sample digested by use of a pressure reactor PHAXE 2000 and with HF and HNO_3 for the geological samples or with HCl and HNO_3 for the biological ones. Under these conditions, selenium transforms into selenite and elimination of cationic species has been carried out using an Amberlite IR-120 resin.

RESULTS AND DISCUSSION

The reaction between methylene blue (MB) and sulfide ion occurs according to the equation:

$$2\,MB + S^{2-} + 2\,H_2O = 2\,HMB + 2\,OH^- + S$$

the selenium accelerates this reaction. The general nature of the "selenium effect" can be explained by the fact that when selenium is present, ions $[S\ldots Se]^{2-}$ are formed which react significantly more quickly than sulfide ions. The selenium set free again reacts with sulfide ion.

The reaction-rate can be monitored fluorimetrically, since the colorless compound obtained shows a blue fluorescence ($\lambda_{ex} = 360$ nm, $\lambda_{em} = 465$ nm). The oxidized form of methylene blue, blue in color, does not exhibit any fluorescence.

Studies on the variables affecting the fluorescence development

As has been shown by West *et al.*[11] the optimum pH values for the reduction to take place are comprised between 10.6 and 11.1.

A study of the influence of methylene blue concentration on fluorescence development has been carried out in the first place. It was found that the most pronounced changes in fluorescence were obtained at a reagent concentration around 7.8×10^{-4} M, which has been taken as the optimum value.

For this reagent concentration it was found that the reduction of methylene blue by sodium sulfide takes place too quickly to satisfactorily detect the catalytic effect of selenium. Two procedures may be followed in order to prevent fluorescence of the blank. One of them consists of accelerating the formation of elemental selenium (which accelerates the process), heating on a steam bath the mixture selenite–sodium sulfide, before adding the reagent. Study of this parameter leads to an optimum heating time of about 10 min when sodium sulfide concentration is 1×10^{-1} M.

The second procedure to obtain an effective measurement of selenium catalytic action consists in trying to stabilize the blank solution by addition of a water-miscible organic solvent. Studies carried out in this direction[11] prove that formaldehyde presents excellent characteristics to be used with this aim. Studying the influence of its concentration it was found that best results are obtained when this organic solvent is present with 12% at a sodium sulfide concentration of 2×10^{-3} M.

In both cases the optimum concentration of sodium sulfide has been chosen considering the stability of the blank as well as the speed of the reduction mechanism. The two mentioned concentrations were found to be ideal for control of the reaction. To attain reproducible measurements, it is convenient to use quartz cuvettes (1 cm in light path and 4.5 ml in volume), provided with teflon cover, being also useful to add methylene blue no later than 5 min after the rest of the reagents have been added.

The mentioned observations support the hypothesis according to which the catalytic action on the methylene blue reduction is due to elemental selenium. Thus, in the absence of formaldehyde it is necessary to heat before adding methylene blue to aid the reduction from the selenite to elemental selenium. In presence of formaldehyde, this compound makes the direct reduction of methylene blue by the sulfide difficult (the blank is stabilized) and leaves sufficient time for the reduction of selenite to elemental selenium to take place and its catalytic action can be revealed. The stabilizing action of the formaldehyde is probably based on a modification of the solvation sphere of the reagent slowing down the direct reduction action of the sulfide ion.

Finally, the convenience of waiting at most 5 min before adding the other reagents is probably a consequence of the formation of elemental selenium. This will occur in colloid form; hence, for long waiting times its coagulation or adsorbtion on the recipient's wall will begin and as a consequence of this the catalytic capacity will decrease.

Characteristics of the kinetic methods

The fluorescence–time curves for different amounts of selenium, in presence and absence of formaldehyde, have been obtained using optimum conditions (Figures 1 and 2).

Owing to the special shape of these curves only the induction period method and the tangent method have been applied to prepare the calibration graphs. The results obtained are summarized in Table I. Of the three methods obtaining kinetic data, the one presenting the best analytical characteristics, i.e. the smallest amount determinable and greatest precision, is the induction period method in the presence of formaldehyde, hence this method is recommended.

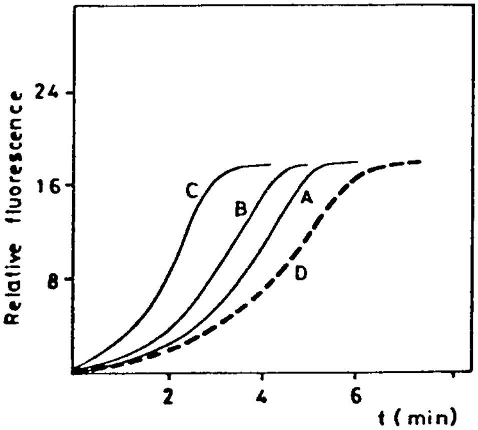

FIGURE 1 Fluorescence intensity–time curves for various cation concentrations (ppm) in absence of formaldehyde: (A) 0.1; (B) 0.2; (C) 0.4; (D) reagent blank. [Methylene blue] = 7.8×10^{-4} M. [S^{2-}] = 0.1 M λ_{ex} = 360 nm; λ_{em} = 465 nm.

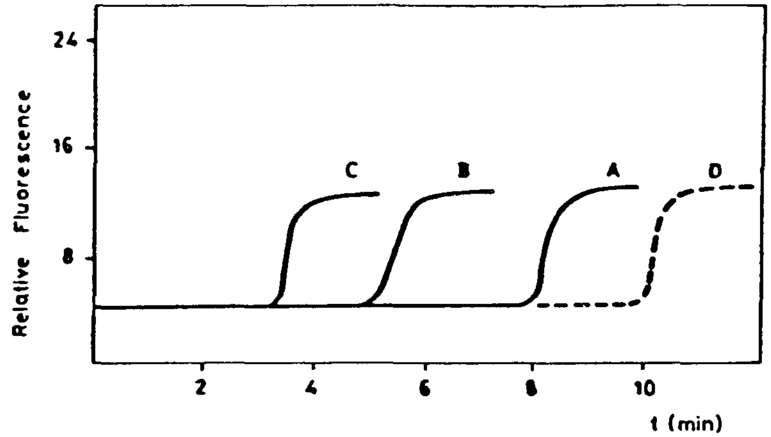

FIGURE 2 Fluorescence intensity–time curves for various cation concentrations (ppm) in presence of formaldehyde: (A) 0.02; (B) 0.2; (C) 0.4; (D) reagent blank; using the recommended procedure.

TABLE I

Characteristics of the kinetic methods

Method	Range of applicability (ppm)	Relative error[a]
Initial rate (in absence of formaldehyde)	0.1 –0.6	3.7
Induction period (in absence of formaldehyde)	0.1 –0.6	4.5
Induction period (in presence of formaldehyde)	0.01–0.1	5.6
	0.1 –0.4	3.3

[a] Relative error (100t(s.d.)/$\bar{x}n^{1/2}$, where t is Student's t-test for 95% confidence) for $n = 10$ measurements in all instances.

Selectivity of the methods was tested obtaining the intensity–time curves in the presence of several foreign ions under the recommended conditions and using EDTA as a general masking agent. It was found that the lowest level of interferences was given by the induction period method. As can be seen in Table II, only Co(II) interfere seriously.

TABLE II

Concentrations of foreign ions tolerated for 0.2 ppm selenium[a]

Ion	Amount tolerated (ppm)
Ca(II), Sr(II), Ba(II), Mg(II), Zn(II), Cd(II), Ni(II), Al(III), Cr(III), NO_3^-, SO_4^{2-}, Cl^-, AsO_4^{3-}	20[b]
ZrO^{2+}, Mo(VI), Be(II), Th(IV), UO_2^{2+}	10
V(V), Tl(III)	10 (max)
Mn(II), Hg(II), Bi(III)	2
Pd(II), Fe(III)	0.2
Cu(II)	0.2 (max)
Co(II)	<0.2

[a] Ions were considered as interferences when in their presence the error of the measurements was superior to the one obtained by application of the recommended procedure.

[b] Largest amount examined.

TABLE III

Selenium determination in environment samples

Sample	Se in sample (ppm)	Se added (ppm)	Percent standard deviation	Recovery (percent)
Sea water	—	0.09[a]	3.2	98
Spring water	—	0.08[a]	3.4	101
Soils	1.3[b]	2[b]	6.6[c]	95
Copper ore	7.1[b]	10[b]	4.1[c]	96
Lead–zinc ore	4.3[b]	6[b]	3.8[c]	97
Limonite	3.1[b]	5[b]	3.8[c]	99
Rice flour	—	1[b]	5.2[c]	102
Alfalfa	0.8[b]	1[b]	8.3[c]	96

[a] Ten separate determinations.

[b] Three separate determinations.

[c] Se in sample.

Determination of selenium in environmental samples

The data on the determination of selenium in water, biological and geological samples are given in Table III. In all instances, the standard addition method was employed. The results showed that the recovery of selenium was satisfactory.

References

1. J. Bognar and Sz. Sarosi, *Mikrochim. Acta* **361** (1969).
2. T. Kawashima and M. Tanaka, *Anal. Chim. Acta* **40,** 137 (1968).
3. T. Kawashima, S. Nakano and M. Tanaka, *Anal. Chim. Acta* **49,** 443 (1970).
4. L. V. Markova and M. L. Kaplan, *Zh. Anal. Khim.* **28,** 1018 (1973).
5. S. P. Klochkovskii and L. P. Neimysheva, *Zh. Anal. Khim.* **29,** 929 (1974).
6. T. Kawashima, J. Kai and S. Takashima, *Anal. Chim. Acta* **89,** 65 (1977).
7. S. P. Klochkovskii and G. D. Klochkovskaya, *Zh. Anal. Khim.* **32,** 736 (1977).
8. E. P. Diamandis and T. P. Hadjiioannou, *Anal. Chim. Acta* **123,** 143 (1981).
9. F. Feigl and P. West, *Anal. Chem.* **19,** 351 (1947).
10. H. Goto, T. Hirayma and S. Ikeda, *J. Chem. Soc. Japan* **73,** 652 (1952).
11. P. W. West and T. V. Ramakrishna, *Anal. Chem.* **40,** 966 (1968).