Analytica Chimica Acta, 123 (1981) 143–150

CATALYTIC DETERMINATION OF SELENIUM WITH A PICRATE-SELECTIVE ELECTRODE

E. P. DIAMANDIS and T. P. HADJIIOANNOU*

Laboratory of Analytical Chemistry, University of Athens, Athens (Greece)

(Received 9th July 1980)

SUMMARY

A method is described for the determination of selenium, based on its catalytic effect on the picrate—sulfide reaction. The determination involves a variable-time kinetic procedure using potentiometric monitoring with a picrate-selective electrode and automatic measurement of the time required for the potential to change by a preselected amount (5.0 mV). Selenium in the range 3—30 μg was determined with an average error of about 4% and relative standard deviations of about 2%. The reaction can also be followed spectrophotometrically.

The physiological role of selenium as a trace element is not well established. Selenium has been reported as having carcinogenic properties; other authorities have presented evidence that, at low levels, selenium is an essential element in the diet [1], while at higher concentrations it is toxic. A protective role of selenium against malignant disease has also been reported [2].

The most commonly used methods for the determination of selenium are based on the measurement, spectrophotometric or fluorimetric, of the piazselenols formed when selenium(IV) reacts with aromatic *o*-diamines such as 3,3′-diaminobenzidine or 2,3-diaminonaphthalene [3—6]. These methods are time-consuming and the reagents required are toxic and relatively unstable. The determination of selenium by atomic absorption spectrometry has also been reported [7—9]. The catalytic effect of selenium in redox reactions has been used to determine traces of selenium [10—13].

Recently, a new picrate-selective membrane electrode [14] and its applications to potentiometric titrations [15] and kinetic determinations [16] have been reported. In this paper, an automated kinetic potentiometric method is described for the determination of selenium, based on the catalytic effect of selenium in the reduction of picrate by sodium sulfide in alkaline media. The reaction is monitored with a picrate-selective electrode; the time required for the potential to change by a preselected amount (5.0 mV) is measured automatically with a window comparator [17] and related directly to the selenium concentration. Amounts of selenium in the range 3—30 μg in a sample volume of 15.00 ml can be determined with good accuracy and precision.

EXPERIMENTAL

Instrumentation

Electrodes. The picrate-selective membrane electrode was constructed as previously described [14] but with a teflon membrane [16]. A double-junction silver—silver chloride electrode (Orion model 90-02-00) served as the reference electrode with its outer compartment filled with equitransferent Orion 90-00-01 solution. The electrode potential was measured with an Orion Ionalyzer, Model 801.

Reaction cell. A double-walled 50-ml beaker was used as reaction cell. Water was circulated continuously through the reaction cell jacket with a thermostatted pump. The reaction mixtures were stirred with the aid of a magnetic stirrer.

Recording and measurement system. The recording and measurement system was the same as previously described [17]. The Window Comparator was used for automatic measurement of the time, Δt, required for the recorder pen to cross preselected positions in the chart corresponding to $(E_0 + 2.0)$ mV and $(E_0 + 7.0)$ mV, where E_0 is the initial electrode potential.

Reagents

All solutions were prepared with deionized—distilled water from reagent-grade materials (Merck except where specified).

Sodium picrate solution, 0.0100 M. Neutralize a suitable picric acid solution with sodium hydroxide solution to a pH about 6. No standardization is required. The solution should be kept in an amber bottle. The picric acid used was Fluka purum.

Composite solution A, 5% Na_2EDTA (w/v)—3.0 × 10^{-4} M Fe(III). Dissolve 0.0080 g of $FeCl_3 \cdot 6H_2O$ in about 80 ml of water, add 5.0 g of Na_2EDTA in small portions, adjust the pH to 7.0 with sodium hydroxide and dilute to 100 ml.

Composite buffer solution B, 0.25 M Na_2S—1.00 M $NaHCO_3$, pH 10.8. Dissolve 6.0 g of $Na_2S \cdot 9H_2O$ in about 80 ml of water, add 8.4 g of sodium hydrogencarbonate in small portions, adjust the pH to 10.8 with sodium hydroxide and dilute to 100 ml. The solution is kept in a refrigerator when not in use.

Stock selenium solution, 500 ppm. Dissolve 0.5000 g of pure selenium in a few drops of concentrated nitric acid, boil gently to expel brown fumes and dilute to 1 l with water. Standard working solutions (0.2, 0.5, 1, 2 ppm) were prepared by appropriate dilution.

During measurements all solutions are thermostatted at 60 ± 0.2°C.

Procedure

Transfer 15.00 ml of the selenium standard or sample solution, 3.00 ml of composite solution A and 2.00 ml of composite solution B to the reaction

cell, thermostatted at 60°C (final pH 10.1). Immerse the electrodes in the solution and start stirring at the maximum speed at which air bubbles are not formed. After about 1 min, inject rapidly 1.00 ml of 0.01 M sodium picrate solution, immediately start the recorder and record the potential change for a few minutes. For automatic measurements, after injecting the sodium picrate solution, press the Start button of the Universal Digital Instrument. The analysis is completed automatically and the number on the digital readout (time in hundredths of a second) is recorded. Press the Reset button, empty the cell with suction, rinse the electrodes and the cell with water and dry them with suction. The amount of selenium present is obtained from a calibration curve constructed by plotting Δt^{-1} (s^{-1}) vs. ppm Se.

RESULTS AND DISCUSSION

Effect of pH

The effect of pH on the rate of the selenium-catalyzed picrate—sulfide reaction was studied by carrying out the reaction at various pH values and various selenium concentrations. The composite buffer solution B did not contain hydrogencarbonate, and the pH was adjusted to the desired value with sodium hydroxide or hydrochloric acid. Figure 1 shows calibration curves for selenium at various pH values. The pH chosen, 10.1, is a compromise to ensure small blanks and relatively short measurement times. At lower pH values the blank is smaller but the measurements are less precise.

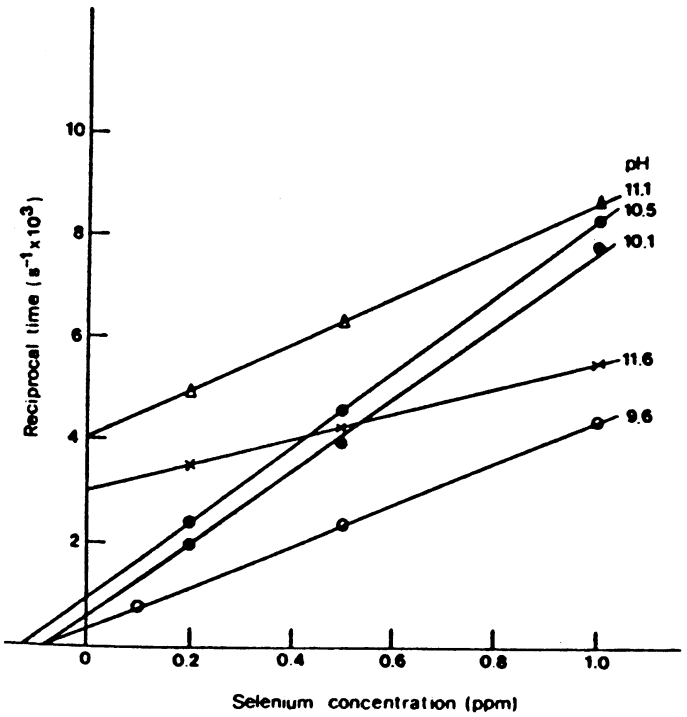

Fig. 1. Calibration curves for selenium at various pH values.

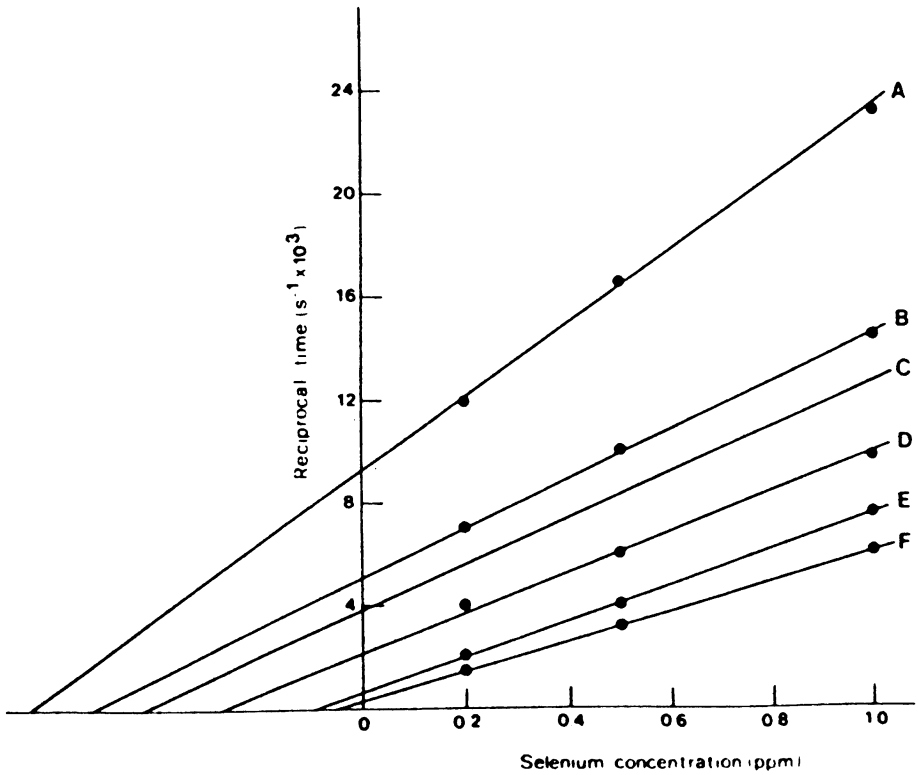

Fig. 2. Calibration curves for selenium at various initial iron concentrations (M): (A) 1.6×10^{-3}; (B) 7.4×10^{-4}; (C) 3.7×10^{-4}; (D) 8.5×10^{-5}; (E) 4.2×10^{-5}; (F) 2.1×10^{-5}. Other conditions as under Procedure.

Effect of iron concentration

It was observed that iron(III) in the presence of EDTA activates strongly the catalytic effect of selenium. This observation parallels earlier observations of West and Ramakrishna with the selenium-catalyzed methylene blue–sodium sulfide reaction [12]. In order to establish the optimum concentration of iron essential to accelerate the reaction, experiments were done as in the recommended procedure but with various concentrations of iron. Figure 2 shows a series of calibration curves obtained with various iron concentrations. As the iron concentration increases, the measurement times decrease but the blank increases. An initial concentration of 4.2×10^{-5} M (curve E) was chosen for the recommended procedure as a compromise between the reaction rate and blank effects.

Effect of picrate and sulfide concentrations

To study the effect of picrate concentration on the selenium-catalyzed picrate–sulfide reaction in the presence of the iron–EDTA complex and a large excess of sulfide [18], the concentration of the picrate solutions used in the recommended procedure was varied in the range 0.01–0.1 M. It was found that the initial rate of potential change is independent of the initial picrate concentration.

The effect of sulfide concentration on the rate of the selenium-catalyzed reaction was studied in the absence of iron for various sulfide and selenium

concentrations. The reaction rate increases with increasing sulfide concentration up to an initial sodium sulfide concentration of about 0.048 M, but remains practically constant at higher concentrations. An initial sulfide concentration of 0.0238 M (0.25 M Na_2S in composite solution B) was chosen to ensure short measurement times and small blanks. Composite buffer solution B is relatively stable when stored in a refrigerator. Over a period of a week the blank increased gradually but the detection limit was unaffected.

Effects of temperature and standing time

The rate of the reaction increases with increasing temperature in the range 30—60°C (Fig. 3). A temperature of 60°C was chosen, to ensure small measurement times without endangering the operation of the electrode. Under these conditions, the electrode response was unaffected for more than two months.

In order to study the effect of standing time, series of solutions containing 0.5 ppm of selenium were treated with all reagents except picrate as described in the recommended procedure. The solutions were allowed to stand for different periods of time (0.5—11 min) before the addition of picrate. It was found that the rate of the reaction is unaffected by standing time.

Interference studies

To investigate the effect of various ions that might interfere in the determination of selenium, measurement times for solutions containing 1 ppm of selenium and 50 ppm of the ion being investigated were compared with

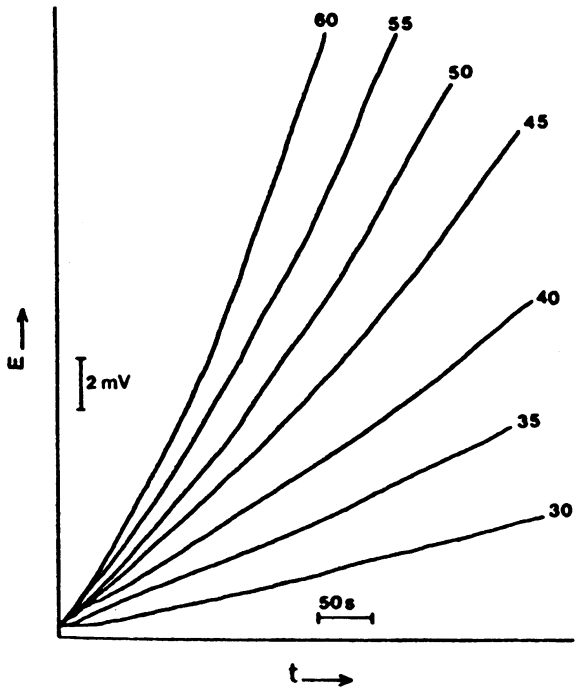

Fig. 3. Recorded curves of the cell voltage vs. time for the picrate—sulfide reaction at various temperatures (°C). Se = 1 ppm, other conditions as under Procedure.

those for a 1 ppm selenium solution (n = 7). The following cations did not interfere: Li^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Pb^{2+}, Al^{3+}, Cr^{3+}, Zr^{4+} (from the respective chloride or nitrate salts) and Te^{4+} (Na_2TeO_3). Hg^{2+} and Sn^{2+} ions (as their chloride salts) did not interfere at the 10 and 5 ppm level, respectively. Ag^+ ($AgNO_3$) and Cu^{2+} ($CuCl_2 \cdot 2H_2O$) ions interfered even at concentrations below 5 ppm. All interfering ions but Cu^{2+} caused negative errors.

Accuracy and precision

The voltage interval of 5.0 mV was chosen so that the measurement error is small in comparison. Figure 4 shows typical recorded curves and the corresponding calibration curve for the selenium-catalyzed reaction. The accuracy and precision of the method were tested by analyzing solutions containing known amounts of selenium. Results are shown in Table 1.

Spectrophotometric studies

The selenium-catalyzed picrate—sulfide reaction can also be followed by measuring the absorbance of the reaction product at 490 nm. Absorbances were measured with a Heath Model 701 recording spectrophotometer. The cell compartment was modified to accept a 10-ml thermostatted cuvette, with a pathlength of 1.3 cm, and a magnetic stirrer. The following procedure is suitable. An aliquot (5.00 ml) of the selenium standard or sample solution (0.1—1.4 ppm) followed by 1.00 ml of composite solution A and 0.700 ml of composite solution B are transferred to the cuvette and thermostatted at

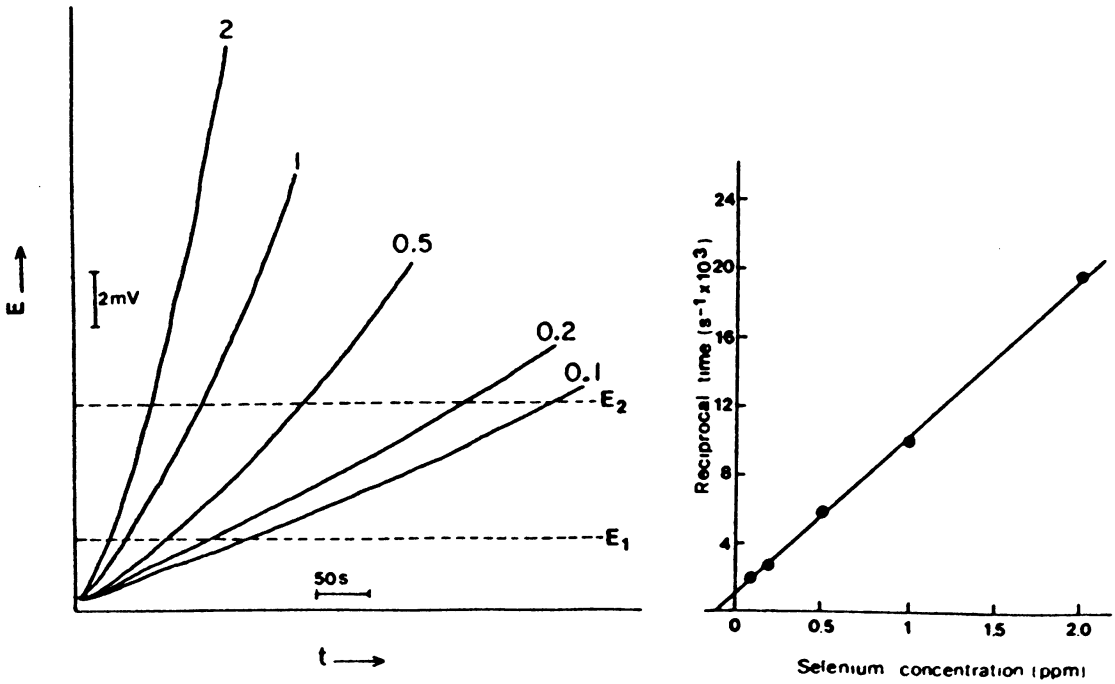

Fig. 4. Recorded curves of the cell voltage vs. time for the picrate—sulfide reaction in the presence of selenium, and the corresponding calibration curve. The numbers on the curves correspond to ppm Se. Other conditions as under Procedure.

TABLE 1

Results for the determination of selenium in aqueous solutions

Taken (ppm)	Found (ppm)[a]	Error (%)	R.s.d. (%)[b]
0.200	0.174	−13	—
0.500	0.479	−4	2.1
1.00	1.02	+2	1.7
2.00	1.99	−0.5	—

[a]Average of two measurements. [b]$n = 8$.

60°C. The stirrer is started and, after 2 min, 1.00 ml of 3×10^{-3} M sodium picrate solution is added rapidly. Immediately the recorder is started and the absorbance change is measured for about 4 min (at 490 nm). The amount of selenium present is obtained from a calibration curve constructed by plotting ΔA values ($A_{3\ \mathrm{min}} - A_{0.5\ \mathrm{min}}$) vs. ppm Se (Fig. 5).

The accuracy of the spectrophotometric procedure was checked by analyzing solutions containing known amounts of selenium in the range 0.1—1.4 ppm. The relative error ranged from 0.3 to 6.7% with an average of 3.2%.

In conclusion, the selenium-catalyzed picrate—sulfide reaction can be used

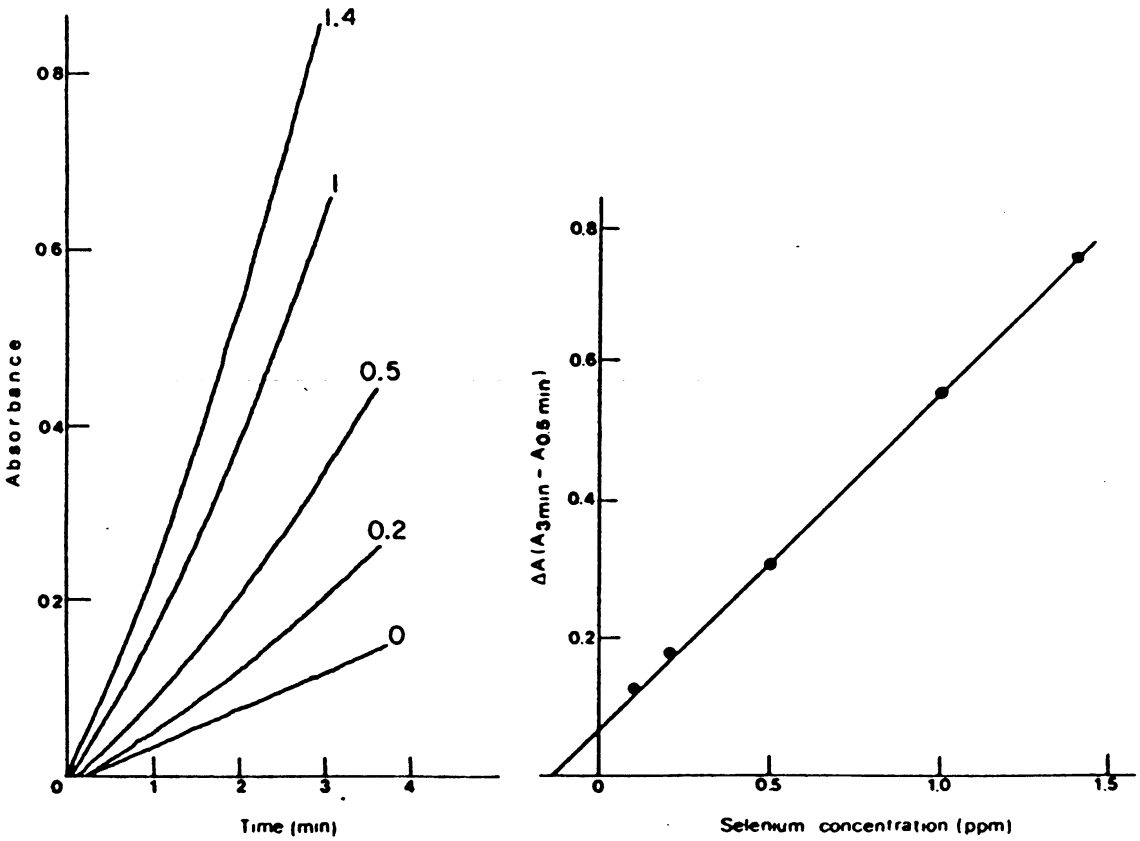

Fig. 5. Recorded curves of the absorbance vs. time for the picrate—sulfide reaction in the presence of selenium, and the corresponding calibration curve. The numbers on the curves correspond to ppm Se. Other conditions as under Procedure.

for analytical purposes to determine selenium in the range 0.1—2 ppm by a potentiometric or spectrophotometric technique.

The authors thank C. E. Efstathiou for stimulating discussions, and C. Athanassopoulou and Z. Nanou for technical assistance.

REFERENCES

1 M. Jacobs, Cancer, 40 (1977) 2557.
2 W. R. Wolf, Anal. Chem., 50 (1978) 190A.
3 R. J. Hall and P. L. Gupta, Analyst, 94 (1969) 292.
4 M. W. Brown and J. H. Watkinson, Anal. Chim. Acta, 89 (1977) 29.
5 N. D. Michie, E. J. Dixon and N. G. Bunton, J. Assoc. Off. Anal. Chem., 61 (1978) 48.
6 Y. Shimoishi and K. Tôei, Anal. Chim. Acta, 100 (1978) 65.
7 K. G. Brodie, Am. Lab., 9 (1977) 73.
8 M. Ihnat and H. J. Miller, J. Assoc. Off. Anal. Chem., 60 (1977) 813.
9 F. D. Pierce and H. R. Brown, Anal. Chem., 49 (1977) 1417.
10 T. Kawashima, S. Kai and S. Takashima, Anal. Chim. Acta, 89 (1977) 65.
11 F. Feigl and P. W. West, Anal. Chem., 19 (1947) 351.
12 P. W. West and T. V. Ramakrishna, Anal. Chem., 40 (1968) 966.
13 J. H. Tzeng and H. Zeitlin, Anal. Chim. Acta, 101 (1978) 71.
14 T. P. Hadjiioannou and E. P. Diamandis, Anal. Chim. Acta, 94 (1977) 443.
15 E. P. Diamandis and T. P. Hadjiioannou, Mikrochim. Acta (Wien), II (1977) 225.
16 E. P. Diamandis, M. A. Koupparis and T. P. Hadjiioannou, Microchem. J., 22 (1977) 498.
17 C. E. Efstathiou and T. P. Hadjiioannou, Anal. Chim. Acta, 89 (1977) 55.
18 T. S. West, Analyst, 17 (1962) 630.