Flow injection spectrophotometric determination of ultra trace amounts of selenium(IV)

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A flow injection spectrophotometric method has been described for determination of selenium(IV). The method is based on the catalytic effect of Se(IV) on the reduction of gallocyanine by sulphide. The decrease in absorbance of gallocyanine at 620 nm is proportional to the Se(IV) concentration in the range 2.5-500 ng/ml with a limit of detection of 1.0 ng/ml. The relative standard deviation for ten replicate measurements of 50 ng/ml of Se(IV) is 1.5%. Interference due to various ions has been studied.

In recent years, there has been an increasing interest in the estimation of Se(IV) due to its toxicological and physiological effect[1,2]. A number of methods have been reported for the determination of selenium(IV)[3-6]. Catalytic assays have also been applied for the determination of selenium[7-12]. But these methods suffer from problems like non-linear calibration[7], high limit of detection[8], many interfering ions[9-11] or time consuming procedure[10,12].

A few automatic flow techniques have been used for the determination of selenium[13-18]. But these methods have a high limit of detection (0.08 μg) and suffer from interference due to many ions. The present note describes a flow injection method for determination of Se(IV) based on its catalytic effect on the reduction of gallocyanine (GC) by sulphide ion.

Experimental

All chemicals were of AR grade and used as such. Doubly distilled water was used throughout.

Stock solution of selenium(IV) (500 μg/ml) was prepared by dissolving previously dried $Na_2SeO_3.5H_2O$ in water. Working solutions were prepared by appropriate dilution.

Stock solution of sulphide was prepared by dissolving $Na_2S.9H_2O$ in 50 ml of 0.001 M NaOH. The solution was diluted to 100 ml with water in a 100 ml volumetric flask and standardised by io-

dometric method. Working solutions were prepared daily from the stock solution by appropriate dilution with water.

Gallocyanine solution (5.0×10^{-4} M) was prepared by dissolving 0.0170 g of gallocyanine in 0.0001 M NaOH in a 100 ml volumetric flask.

Schematic diagram of the flow injection system is shown in Fig. 1. The twelve channel peristaltic pump (Desaga, PLG, 70 W) was fitted with three silicon rubber tubes (i.d., 1.0 mm). A Teflon mixing joint, and a quartz flow cell (1.0 cm light path, and 0.10 ml volume) were used. Silicon rubber tubing (i.d., 1.0 mm) was used for the mixing coil as well as for the connection. The thermostated water bath (GallenKamp Griffin, BGL) was kept at a temperature below $25 \pm 0.1°C$. The flow cell was set in the flow chamber of a Shimadzu Model 6A spectrophotometer. The change in absorbance of gallocyanine due to its reaction with sulphide in the presence of Se(IV) at 620 nm (maximum wavelength of GC) was recorded on a strip chart recorder (Varian, Model 9176). Samples were injected with a Rheodyne sample injector.

Recommended procedure

GC solution (Fig. 1, R_1) buffered at suitable pH, sulphide solution containing barium disodium ethylenediaminetetraacetate (Na_2BaY) (R_2) and water (R_3) were pumped at a flow rate of 0.5 ml/min. The sample solution was introduced with the help of an injection valve with a 100 μl loop in a H_2O carrier at joint M_2. The decrease in absorbance signal was recorded and the peak height measured. The concentration of Se(IV) was obtained by comparison with a calibration graph plotted with standard solutions. For general purpose (2.5-500 ng/ml Se(IV), the following optimum conditions are recommended: GC, 3.2×10^{-4} M; pH 7.0 (phosphate); S^{2-}, $5.5 \times 10^{-4}M$; sample loop volume, 250 μl; reaction coil length,
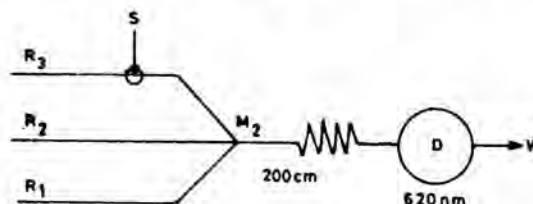

Fig. 1—Schematic diagram of the flow injection system

200 cm; pump flow rate for each of the solutions, 0.5 ml/min; λ_{max} 620 nm, and temperature of 30°C.

Results and discussion

The reaction between GC and sulphide ion occurs at a slow rate and is catalysed by selenium(IV). The accelerating effect of Se(IV) is due to the formation of $[SSe]^{2-}$ which reacts much faster with GC than with sulphide ion[17]. The reaction can be monitored spectrophotometrically at λ_{max} 620 nm.

The effect of pH on the catalyzed reaction between GC (2.8×10^{-4} M) and sulphide ion (5.6×10^{-4} M) was studied in the pH range 1-8 with 0.100 μg/ml of Se(IV) solution at 30°C. The results show that the sensitivity increases up to pH 7, above which sensitivity decreases. This indicates that at higher pH the uncatalysed reaction is fast. At pH < 7 the sulphide ion is deactivated due to its reaction with hydronium ion. Therefore, further studies were carried out at pH 7.0.

A study of the effect of concentration of GC with sulphide on the reaction shows that above 3.2×10^{-4} M, absorbance decreases. This effect may be due to the change of viscosity of the dye solution or change in reaction mechanism. Thus, 3.2×10^{-4} M GC solution was selected as optimum concentration for further studies.

The effect of sulphide concentration on the sensitivity (peak height) was studied at pH 7 in the presence of 3.2×10^{-4} M GC, and 0.100 μg/ml Se(IV) at 30°C. The results show that at above 5.5×10^{-4} M sulphide concentration, the peak height decreases. At high concentration of sulphide ions, the reduction of GC (uncatalysed reaction) is too fast to detect the catalytic effect of Se(IV) satisfactorily. Sulphide concentration of 5.5×10^{-4} M is recommended for further studies.

Increasing the temperature caused an increase in the rate of both the catalyzed and uncatalyzed reactions. But at > 35°C, the reproducibility of the peak height decreased. Thus all experiments were carried out at 30°C.

The selectivity of the method was greatly improved in the presence of EDTA due to complexation with interfering ions. Since photochemical reduction of the dyes by EDTA may also occur[17], the reaction was carried out in the presence of Ba(II)-EDTA. The low formation constant of the Ba(II)-EDTA complex permitted the complexation of most of the interfering ions through a displacement reaction.

The application of flow injection method based on catalytic kinetic reaction is dependent on the flow rate and the tube length. The effect of the flow rate on the peak height was studied over the range 0.25-0.75 ml/min in each stream. Lower flow rates gave higher peaks, but at flow rate of < 0.50 ml/min, the peak height reproducibility was poor and the peak broadened leading to lower sample throughput. On the other hand, the decrease in sensitivity was significant at a flow rate of 0.75 ml/min, hence a flow rate of 0.50 ml/min was selected as the best compromise between reproducibility, sensitivity, and sample throughput.

Reaction coil length of 130-300 cm were tested. Higher peaks were observed as the coil length was increased from 130 to 200 cm, because the longer residence time in the sample zone allowed more reaction to be complete. However peak broadening and tailing were observed with reaction coils > 300 cm. From the results, 200 cm was selected for further studies.

In flow injection measurements, the magnitude of the signal can generally be increased by in-
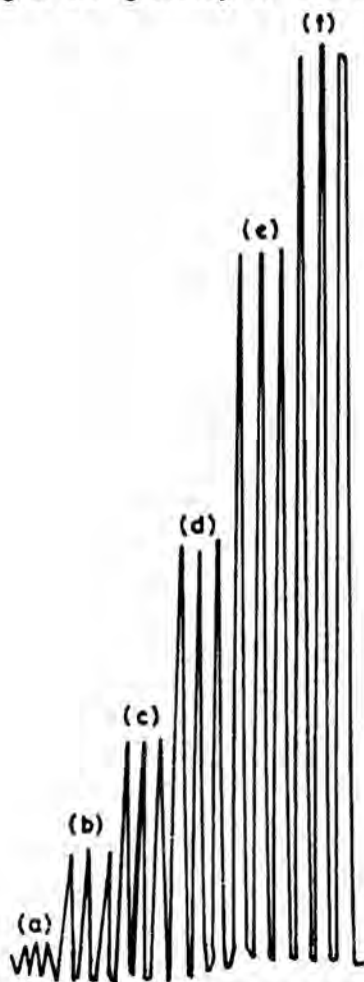

Fig. 2—Typical FIA response for the determination of Se(IV) [a, 2.5; b, 10; c, 20; d, 40; e, 60; and f, 80 ng/ml]

creasing the volume of the injected sample. The sensitivity increased by increasing the sample volume from 100 to 250 µl. However, injection of a larger sample volume into the water stream results in peak broadening and tailing. Therefore, 250 µl of sample volume was considered optimum.

Under the optimum conditions, the calibration graph was linear over the range 2.5-500 ng/ml of Se(IV) (0.62-125 ng in a 250 µl of the solution). The peak height increased linearly with Se(IV) concentraion (Fig. 2).

The relative standard deviation for ten replicate measurements of 0.010, 0.100, and 0.400 µg/ml of Se(IV) were 1.7, 1.4 and 1.2% respectively. A typical sampling rate of ca. 35 ± 5 samples/h was achieved.

The experimental limit of detection (three time of noise) (ref. 19) is equal to 1.0 ng/ml of Se(IV).

An ion was considered not to interfere if it caused a variation in the peak height of selenium (IV) of less than 2%. In the determination of 0.050 µg/ml Se(IV), Ca(II), Mg(II), Na(I), K(I), Th(IV), NO_3^-, Br^-, SO_4^{2-}, CO_3^{2-}, $C_2O_4^{2-}$, I^-, SCN^-, Cl^- ClO_4^-, SO_3^{2-}, Ba(II), Sr(II), ClO_3^-, Ba(II)-EDTA could be tolerated up to 1000 µg/ml, Rh(III), In(III), V(IV), Pd(II), Zr(IV), Pb(II), Zn(II), Mn(II), Al(III), Hg(II), Cd(II), As(III), Ni(II), La(III), Co(II), Cr(III), Ce(III) were tolerated up to 400 µg/ml and Ag(I), Cu(II) were tolerated up to 20 µg/ml. If two or more species were present at the maximum tolerance level the results remained unchanged.

The present method has been applied for the determination of selenium(IV) in ore, health-care product and in water (Table 1).

For analysis of the ore, the dried sample (0.50-2.00 g) was digested with HCl and HNO_3. Under these conditions, selenium(IV) is converted into selenite. Cationic species that are potential interferrants were removed by using a cation exchanger resin (an Amberlite IR-120) and water as eluant.

For the shampoo sample, 1.00 g of the sample was weighed into a 100-ml Kjeldahl flask[20]. Conc sulphuric acid (1.0 ml) was added and the mixture was heated to fuming for 15 min. The solution was allowed to cool and 5 ml of hydrogen peroxide (30% w/v) was added. The mixture was boiled vigorously to eliminate excess peroxide, and cooled and diluted to ca. 1.0 1 with doubly distilled water. The Se(IV) content was determined by the recommended procedure. The results are shown in Table 1.

A saturated solution of $Al(OH)_3$ (1 ml) was

Table 1—Determination of selenium (IV) in real samples

Sample	FIA Method µg/g (n = 4)	Piazselenol Method[29] µg/g (n = 4)
Lime stone	0.000	0.000
Lime stone + Se(IV) 0.115 µg/g	0.115 ± 0.006	0.116 ± 0.005
Iron ore	0.000	0.000
Iron ore + Se(IV) 0.076 µg/g	0.078 ± 0.004	0.076 ± 0.006
River water	0.00	0.00
River water + Se(IV) 0.100µg/g	0.101 ± 0.002	0.102 ± 0.003
Shampoo(I)	13.54 ± 0.22	13.56 ± 0.20
Shampoo (II)	8.25 ± 0.14	8.22 ± 0.11

added to 15 ml of river water to precipitate the through a 10-cm column containing cation exchanger resin. The column was washed with 2 ml changer resin. The column was washed with 2 ml distilled water three times, and the eluent was transferred into a 25-ml volumetric flask. The solution was diluted to the mark and Se(IV) content was determined by the recommended procedure.

References
1 Robberecht H & Van Grieken R, *Talanta*, 29 (1982) 823.
2 Robberecht H & Deelstra H, *Talanta* 31 (1984) 49.
3 Zong O, Xu P, Xiongand G & Liu Y, *Talanta*, 33 (1986) 443.
4 Khuhawar M Y, Bazdar R B & Babar M A, *Analyst*, 117 (1992) 1725.
5 Xunjlan L, Yefong T, Yang Z, Ling Z, Hslaoyan L, Hong Y, Yuanchen D & Rubel R, *Talanta*, 39 (1992) 207.
6 Hallog Y H, Gokmen I C, Aras N K & Gokmen A, *Analyst*, 117 (1992) 447.
7 Kawashina T & Tanaka M, *Anal chim Acta*, 40 (1968) 137.
8 Fiegl F & West P W, *Anal Chem*, 19 (1974) 351.
9 Hawkes W, *Anal chim Acta*, 183 (1986) 197.
10 Safavi A, Afkhami A & Massoumi A, *Anal chim Acta*, 232 (1990) 351.
11 Afkhami A, Safavi A & Massoumi A, *Talanta* 39 (1992) 993.
12 Ensafi A A & Bagherian Dehaghi G, *Anal Lett*, 28 (1995) 335.
13 Yamamoto M, Yasuda M & Yamamoto Y, *Anal Chem*, 57 (1985) 1382.
14 Chan C C Y, *Anal Chem*, 57 (1985) 1482.
15 Linares P, Luque de Castro M D & Valcarcel M, *Analyst*, 111 (1986) 1405.
16 Linares P, De Castro M L & Valcarcel M, *Analyst*, 111 (1986) 1405.
17 Lozano C M, Ruiz T P, Tomas V & Abellan C, *Analyst*, 114 (1989) 715.
18 Parham A & Shamsipur M, *Bull chem Soc Jpn*, 64 (1992) 3067.
19 Mottola H A, *Kinetic aspects of analytical chemistry vol 96 in Chemical analysis*, (John Wiley) 1988, Ch. 2.
20 Parker C A & Harvey L G, *Analyst*, 87 (1962) 558.