# 1,3,3-Trimethyl-2-[3-(1,3,3-trimethyl-1,3-dihydroindol-2-ylidene)propenyl]-3*H*-indolium Chloride, a Highly Sensitive Reagent for the Spectrophotometric Determination of Selenium

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A highly sensitive spectrophotometric method for the determination of selenium is reported. The method is based on the oxidation of iodide by selenium(IV) and the spectrophotometric detection of the liberated iodine in the form of an ion associate with 1,3,3-trimethyl-2-[3-(1,3,3-trimethyl-1,3-dihydroindol-2ylidene)propenyl]-3*H*-indolium chloride reagent. The appropriate reaction conditions have been established. The molar absorptivity is $2.4 \times 10^5$ dm$^3$ mol$^{-1}$ cm$^{-1}$ at 556 nm wavelength. The absorbance of the coloured extracts obeys the Beer's law in the range from 0.01 to 3.84 mg dm$^{-3}$ of Se(IV).

Spectrophotometric analysis based on the measuring of the absorbance of coloured complexes is frequently used in trace analysis of inorganics. The advantages of the spectrophotometric methods, such as rapidity and simplicity, are well known. Direct spectrophotometric methods are preferable. In this case, the element to be determined reacts with an organic reagent to form coloured products. The concentration of the element is then determined based on a calibration plot. Unfortunately, the determined element sometimes forms no coloured complexes. Therefore, using of indirect spectrophotometric methods is expedient. In spite of some of the shortcomings of the indirect methods, their application can in some cases be very advantageous. The indirect spectrophotometric methods for the determination of nitrite [1], tetrathionate [2], chromium(VI) [3—5], selenium [6—8], *etc.* were described. Application of the indirect methods extends the possibilities of the atomic absorption spectrometry for the determination of nonmetallic compounds, such as ascorbic acid [9].

Selenium is an essential element and has been widely used in semiconductor technology. Information about the distribution of selenium in monocrystals and semiconductor thin films is important for quality control of the final product. Selenium has unique properties intermediate between metals and nonmetals. Selenium(IV) is a relatively strong oxidation agent which oxidizes many organic and inorganic compounds. In consequence of this, many spectrophotometric methods for selenium determination based on the reaction of selenium(IV) with various reducing agents have been described. Iodide in an acidic medium is oxidized quantitatively by selenium(IV) to elemental iodine and determination is followed by spectrophotometric detection of the triiodide anion [6, 7] at 352 nm or in the form of the ion associate of triiodide with triphenylmethane dyes [10]. Another method is based on the reaction between selenite and Fe(II). The Fe(III) forms complexes with KSCN and determination is followed by the spectrophotometric detection at 480 nm [8].

Cyanine dyes are often used in analytical practice. The properties of some cyanine dyes were reported [11]. The advantages of these dyes are stability and high value of molar absorptivity [11]. We have previously reported the spectrophotometric methods for the determination of manganese [12], tellurium [13], and chromium [14] by using cyanine dye reagents.

Therefore, the aim of this work was to investigate the symmetric carbocyanine dye, 1,3,3-trimethyl-2-[3-(1,3,3-trimethyl-1,3-dihydroindol-2-ylidene)propenyl]-3*H*-indolium chloride (DIC) for the extractive spectrophotometric determination of selenium. The rea-



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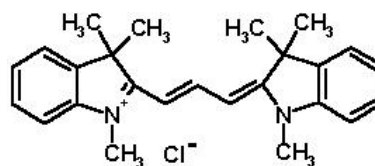
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gent is commercially available. The acid-base properties and main spectrophotometric characteristics of DIC were investigated [11].

## EXPERIMENTAL

All chemicals and solvents used were of analytical reagent grade. Double distilled water was used throughout. A stock 0.01 M solution of selenium(IV) was prepared by dissolution of sodium hydrogenselenite heptahydrate in water. Because of their lower stability, the working solutions of concentration range $10^{-5}$ to $10^{-4}$ mol dm$^{-3}$ were prepared by diluting the stock before use. The $10^{-3}$ mol dm$^{-3}$ aqueous solution of DIC was prepared from its chloride salt. The acidity of the solution was adjusted using sulfuric acid. The required concentration of iodide was reached using 0.05 mol dm$^{-3}$ sodium iodide. The necessary concentration of ligand was set by the addition of 0.1 mol dm$^{-3}$ potassium bromide. The following organic solvents were tested as extractants: hexane, heptane, benzene, toluene, amyl acetate, and butyl acetate.

An SF-10 double-beam UV VIS scanning spectrophotometer with matched quartz cells of 1 to 5 mm path length was used for recording complete absorption spectra. An ionometer EV-74 with a glass electrode was used for measuring the pH values of aqueous solutions.

### Procedure

1.58 $\mu$g of Se(IV) was added to the separation funnels. The volume was diluted with water and the required acidity of the solution and required iodide concentration were reached. The total volume of the aqueous phase was 5 cm$^3$. After the addition of each chemical, the solution was mixed. Next, the solution was left to stand for 5 min. The liberated elemental iodine was extracted by 5 cm$^3$ of organic solvent for 1 min. The organic phase was separated into the test tube containing the required concentration of bromide ligand and the dye reagent, and the formed ion associate was extracted for 30 s. All procedures were realized at room temperature. After the phase separation, the absorbance of organic phase was measured. At the same time, measurement of the blank test was realized.

## RESULTS AND DISCUSSION

The preliminary experiments show that selenium forms no extractable ion associate with the tested dye. Nevertheless, the indirect determination of selenium based on the oxidation of iodide by selenium(IV) and spectrophotometric detection of the formed iodine in the form of an ion associate with investigated dye is possible. We have previously reported the similar spectrophotometric methods for the determination of selenium by using 2-(4-dimethylaminostyryl)-1,3,3-
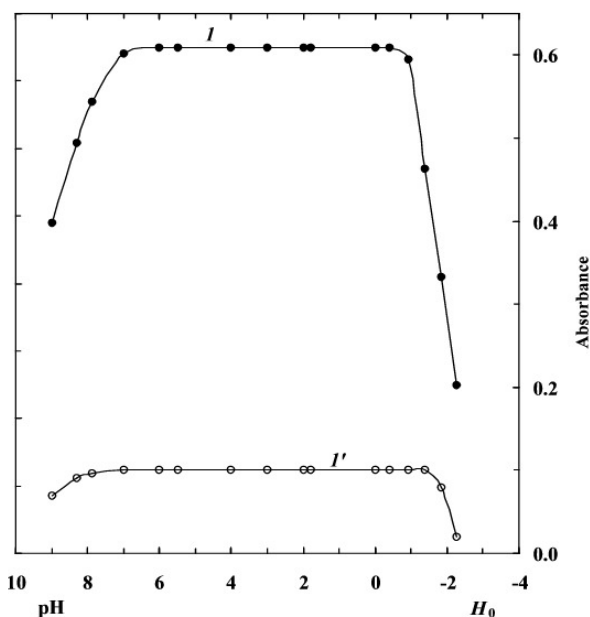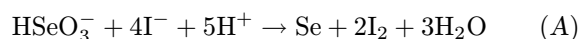


**Fig. 1.** Influence of the aqueous phase acidity on the extraction of $[I_2Br]^-R^+$ ion associates (*1*) by toluene. $4 \times 10^{-6}$ M-Se(IV); 0.01 M-KBr; $8 \times 10^{-5}$ M-DIC; $l = 0.5$ cm. *1'* – blank test.

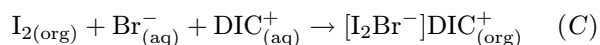trimethyl-2,3-dihydroindole [15] and $N,N'$-dimethylindoldicarbocyanine [16].

The selenite reacts with iodide to form iodine

$$HSeO_3^- + 4I^- + 5H^+ \rightarrow Se + 2I_2 + 3H_2O \qquad (A)$$

We used the similar experimental conditions for the redox reaction as described [15]: 0.5 mol dm$^{-3}$ sulfuric acid and 0.01 mol dm$^{-3}$ KI, reaction time 5 min. The solution must be protected from light and kept in the dark. The liberated iodine is extracted into toluene

$$I_{2(aq)} \rightarrow I_{2(org)} \qquad (B)$$

The ion associate is formed and extracted

$$I_{2(org)} + Br^-_{(aq)} + DIC^+_{(aq)} \rightarrow [I_2Br^-]DIC^+_{(org)} \qquad (C)$$

In order to find optimum conditions for complex formation and extraction, the influence of medium acidity, the concentration of bromide ions and dye reagents, and the nature of the extractant on absorbance of coloured extracts were all investigated.

The optimum conditions for the extraction of $[I_2Br^-]$ ion associate with DIC were determined: the acidity of the solution ranges from 2.2 mol dm$^{-3}$ H$_2$SO$_4$ to pH 7 (Fig. 1) and the concentration of ligand ranges from 0.006 to 0.0016 mol dm$^{-3}$. For a strongly acidic medium we used Hammett's function $H_0$ [17]. Benzene and toluene showed to be the best extractants. The results are similar for benzene and toluene,

**Table 1.** Determination of Selenium in Semiconductor Materials ($w_i/\%$)

| Material | Evaluated method | Given content | $s_r$ | Recovery/% |
|---|---|---|---|---|
| TlPSe$_2$ | $38.8 \pm 1.0$ | 37.90 | 0.021 | 102.4 |
| In$_3$PSe$_3$ | $40.4 \pm 2.2$ | 38.52 | 0.043 | 104.9 |

thus in Fig. 1 only the results for toluene are presented. Due to lower toxicity, toluene was used for further experiments.

The equilibrium of extracted coloured ion associates is established within 30 s and the colour is stable for several hours. The molar absorptivity is $2.4 \times 10^5$ dm$^3$ mol$^{-1}$ cm$^{-1}$ at 556 nm wavelength. The absorbance of the coloured extracts obeys the Beer's law in the range from 0.01 to 3.84 mg dm$^{-3}$ of Se(IV).

The determination of selenium does not interfere with alkali metals, Cl$^-$, PO$_4^{3-}$, SO$_4^{2-}$, 200-fold quantities of Te(IV), Ni(II), Co(II), Mn(II), Zn(II), 40-fold quantities of Pb(II), Ge(IV), and 10-fold quantities of As. The suggested method was applied to the determination of selenium in semiconductor materials with satisfactory results (Table 1). The positive error is probably caused by the presence of binary impurities in the samples, for example In$_2$Se$_3$.

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