# COULOMETRIC DETERMINATION OF SULPHUR COMPOUNDS USING THE INDUCED IODINE-AZIDE REACTION

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The review summarizes application of coulometry for determination of the sulphur compounds that induce the iodine-azide reaction. The article discusses advantages of the coulometric method. The influence of potassium iodide on induction coefficients is also described. Moreover, determination ranges of several inductors are presented and sensitivities of determination by different methods are compared.
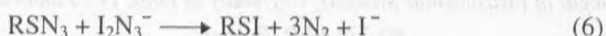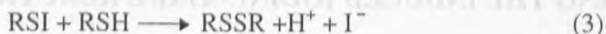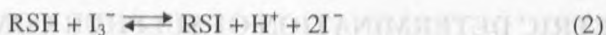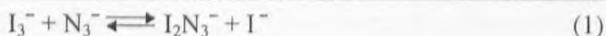
**Key words**: iodine-azide reaction, coulometric determination, sulphur compounds.

## 1. Introduction

Iodine-azide reaction induced by sulphur compounds was described by Raschig [1] and introduced to analytical chemistry by Feigl [2]. All inorganic divalent sulphur compounds as well as elementary sulphur after cleavage of the $S_8$ ring have inducing activity. Among organic compounds the following are inductors of iodine-azide reaction: compounds containing thiol or thione groups, compounds with P=S and PSH groups, disulphides (e.g. cystine), sulphur heterocycles (e.g. vitamin $B_1$).

Inorganic inductors and thiol and thione compounds induce the iodine-azide reaction quickly (in optimal conditions the reaction time ranges between less than one minute to several minutes). The rate of the reaction induced by organic disulphides, sulphur heterocycles and elementary sulphur is considerably slower.

The iodine-azide reaction proceeds as follows:

$$I_3^- + N_3^- \rightleftharpoons I_2N_3^- + I^- \tag{1}$$

$$RSH + I_3^- \rightleftharpoons RSI + H^+ + 2I^- \tag{2}$$

$$RSI + RSH \longrightarrow RSSR + H^+ + I^- \tag{3}$$

$$RSSR + I_2N_3^- \rightleftharpoons RSI + RSN_3 + I^- \tag{4}$$

$$RSI + N_3^- \rightleftharpoons RSN_3 + I^- \tag{5}$$

$$RSN_3 + I_2N_3^- \longrightarrow RSI + 3N_2 + I^- \tag{6}$$

$$RSI + 2I_3^- + 3H_2O \longrightarrow RSO_3H + 7I^- + 5H^+ \tag{7}$$

$$RSN_3 + 2I_3^- + 3H_2O \longrightarrow RSO_3H + 6I^- + N_3^- + H^+ \tag{8}$$

In specified conditions, the consumption of iodine, the amount of nitrogen evolved during the reaction and the heat emitted are linearly dependent on the amount of the inductor and this is the reason why the reaction in question has found numerous applications for determination of sulphur compounds. The sensitivity of determinations heavily depends on the induction coefficient, which is defined by the formula:

$$F_i = \frac{n_I}{n_{RSH}}$$

where $n_I$ is moles of iodine consumed in the induced reaction and $n_{RSH}$ is moles of the inductor.

The higher the induction coefficient, the more sensitive the determination of a given inductor.

## 2. Coulometric Titration

Coulometric titration with the use of iodine-azide reaction was first applied by Press and Murray [3] who determined sulphide ions in the range of 0.01-0.08 ppm in a 70 ml sample.

Further applications of coulometry for determination of inductors of the iodine-azide reaction were then presented by Jędrzejewski and Ciesielski [4-13].

Coulometric titration with the anodically-generated iodine can be applied for determination of all sulphur compounds that quickly induce the iodine-azide reaction. Inductors of a long induction time can be determined by kinetic methods with anodically generated iodine. These are described in the subsequent section.

In the coulometric method the content of inductors is calculated from the calibration graph showing the dependency of electric charge needed to generate iodine necessary for the induced reaction on the amount of the inductor. In this procedure it is not possible to calculate the content of sulphur compounds using Faraday laws. This method enables to determine very small amounts of inductors with a considerable accuracy. Another advantage is that it requires no standard solutions. The end-point is detected biamperometrically.

Table 1 shows determination ranges of iodine-azide reaction inductors for which coulometric determination methods were elaborated. In the case of certain compounds – diethyldithiocarbamate, dithiophosphates, organothiophosphorous compounds, thioguanine and carbimazole – the delay time has to be set at 30 s in order to complete the titration.

Table 2 compares thioguanine induction coefficients in the following methods: coulometric, spectrophotometric and volumetric back-titration.

It was found that increasing iodide ions concentration causes the decrease of the rate of the thioguanine, induced iodine-azide reaction. If iodine is introduced slowly and gradually, as it is the case in coulometric titration, the iodine consumption does not depend on the concentration of iodide. When iodine is added quickly and is in excess in the reaction solution (in the spectrophotometric and volumetric back-titration methods) the iodine consumption and thus the induction coefficient increases with the increase of iodide concentration. At high concentrations of iodine in the volumetric back-titration method, the induction coefficient is lower when compared with the spectrophotometric method which is due to faster destruction of the inductor caused by oxidation by iodine (reactions 7 and 8).

In the case of many inductors the increase of iodide ions concentration causes the increase of the induction coefficient. In the case of diethyldithiocarbamate at the potassium iodide concentration of $3 \cdot 10^{-2}$ mol/l the induction coefficient in the coulometric method [8] reaches 1970, which is nine times higher than in the case of volumetric back-titration [14].

Table 3 compares induction coefficients of diethyldithiocarbamate for various iodide concentrations and two different currents. The induction coefficient depends on the rate of iodine introduction. When the concentration of iodide increases, the inductor is active for a longer period of time and as a consequence the induction coefficients are higher. This is due to decreasing

iodine potential in the presence of iodide ions. As a result, the level of inductor deactivation becomes lower and the inductor can take part in a greater number of cyclical stages of the induced reaction (reactions 5 and 6). At low iodide concentration, when the rate of iodine introduction is increased (at greater current), the iodine consumption decreases, which is due to faster inductor deactivation. This phenomenon, however, is not observed at higher iodide concentrations. Increasing the iodide concentration above $3 \cdot 10^{-2}$ mol/l causes further increase of the induction coefficient but the use of such solutions appears to be unfavourable because the rate of the induced reaction becomes too slow for coulometric titration.

Mojski and Murawski [15] applied the iodine-azide reaction to coulometric determination of sulphur ($0.2 - 20$ µg) in organic solvents and liquid fuels. The analysed samples were first transformed to oxides and then to hydrogen sulphide. The titration end-point was detected potentiometrically.

In the coulometric determination of inductors discussed here, constant current should be maintained since the electric charge depends on the current. This phenomenon does not occur in commonly used coulometric titration methods.

## 3. Kinetic Methods in Coulometry

Ciesielski used kinetic methods for determination of sulphur compounds of a long induction time. The amounts of inductors were determined based on the induced reaction rate. The measurements were made in open systems in which during the reaction course a substrate (iodine) is introduced.

Kinetic methods of analysis are commonly used in determinations of compounds that act as catalysts [16]. Since at the beginning the rate of the iodine-azide reaction does not change in the presence of vitamin $B_1$ and cystine – these compounds act like catalysts – they may be determined by means of kinetic methods.

In earlier kinetic determinations in open systems the substrate was added into the reaction solution in the form of the standard solution using the automatic burette [17,18].

Ciesielski described anode iodine generation in steady-state determination of cystine [19] and stat determination of cystine and vitamin $B_1$ [20]. In the steady-state method, iodine was generated at the constant current, in the solution containing azide and iodide ions and cystine. In this system a stationary condition is reached in which iodine is added at the same rate as it is being consumed in the iodine azide reaction.

The stationary concentration of iodine is measured biamperometrically. Linear dependence between the reciprocal of the indicator current in biamperometric current and cystine concentration is used as a calibration curve. In the stat method, the current in the generating circuit was proportional to the concentration of the catalyst – vitamin $B_1$ or cystine, which enables to plot a calibration curve. The concentration of the indicator substance – iodine – was controlled biamperometrically and maintained at constant level. In the described methods inductors of a short induction time do not cause interference as they are oxidised during the initial stage of determination.

The advantage of the discussed kinetic determination in the open system is short analysis time and the fact that standard solutions are not required.

The methods described above were used to determine vitamin $B_1$ in drugs and cystine in wool and hair.

## 4. Conclusions

The coulometric methods discussed here can be said to be ones of the most sensitive and accurate methods of analysis of these sulphur compounds which induce the iodine-azide reaction. In Table 4 the sensitivity of the determination of thiourea by means of different methods – with application of iodine-azide reaction – is presented.

Iodine consumption in the induced iodine-azide reaction for a given sulphur compound depends on reaction conditions i.e. concentrations of azide, iodide, iodine, pH of the solution as well as on the rate of iodine introduction. The increase of iodide ions concentration decreases the rate of the induced reaction since the concentration of $I_2N_3^-$ produced in the reversible reaction decreases:

$$I_3^- + N_3^- \rightleftharpoons I_2N_3^- + I^-$$

At the same time, the rate of inductor oxidation becomes lower and thus the inductor takes part in the reaction for a longer period of time. As a result, in the case of majority of sulphur compounds the iodine consumption increases. In most cases, at low iodine concentration, which is observed during coulometric determination of inductors, the rate of inductor destruction decreases. Therefore, the induction coefficients are higher when compared to those in other methods, in which the iodine concentration is higher.

In the proposed procedures coulometric titration is not an absolute method and thus the standard curve has to be used, but it shares all other advantages with other coulometric methods.

Table 1. Determination ranges of sulphur compounds for which coulometric determination methods were elaborated.

| Compound | Determination range | References |
|---|---|---|
| Thiocyanate | 1- 7 µg | 4 |
| Sulphide | 20 – 1000 ng | 5, 9 |
| Thiosulphate | 50 – 7000 ng | 5, 9 |
| Thiourea | 10 – 3000 ng | 4, 9 |
| Cysteine | 50 – 400 ng | 6 |
| Glutathione | 50 – 6000 ng | 6, 9 |
| Dithiooxamide | 1 – 6 µg | 7 |
| Sodium diethyldithiocarbamate | 20 – 200 ng | 8 |
| Thioguanine | 10 – 200 ng | 10 |
| Dithiophosphates | 1 – 20 nmol | 11 |
| Organothiophosphorus compounds | 1 – 20 nmol | 12 |
| Carbimazole | 2 – 20 nmol | 13 |

Table 2. Induction coefficients for thioguanine.

| C (KI) mol/l | Coulometric method | Spectrophotometric method | Volumetric back-titration method |
|---|---|---|---|
| $3 \cdot 10^{-3}$ | 2630 | 2080 | 1840 |
| $3 \cdot 10^{-2}$ | 2630 | 2430 | 2260 |

Table 3. Induction coefficients for diethyldithiocarbamate.

| C (KI) mol/l | I = 1mA | I = 5mA |
|---|---|---|
| $3 \cdot 10^{-3}$ | 1520 | 1080 |
| $1 \cdot 10^{-2}$ | 1850 | 1460 |
| $3 \cdot 10^{-2}$ | 1970 | 1920 |

Table 4. Sensitivity of the determination of thiourea by different methods.

| Method | Sensitivity according given procedure | Accuracy | References |
|---|---|---|---|
| Volumetric back-titration | 4500 ng/50 ml | ± 90 ng | 21 |
| Competitive reactions | 150 ng/15 ml | | 22 |
| Stat method | 180 ng/5 ml | ± 8 ng | 18 |
| Slow titration | 25 ng/15 ml | ± 5 ng | 23 |
| Flow injection analysis | 2 ng/10μl | ± 0.4 ng | 24 |
| Flow continuous analysis | 2 ng/1 ml | ± 1 ng | 25 |
| Spectrophotometric method | 20 ng/7 ml | | 26 |
| Coulometric titration | 10 ng/20 ml | ± 1 ng | 9 |

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