*Chem. Anal. (Warsaw)*, **41**, 77 (1996)

# Determination of Iodine and Ozone by Iodine–Azide Reaction Induced by Thioammeline

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**Key words:** iodine, ozone, iodine–azide reaction, thioammeline

The iodine–azide reaction induced by thioammeline is applied for the determination of nanogram amounts of iodine in aqueous solution. The method is based on the measurement of thioammeline amount oxidized by iodine to a compound non-inducing the iodine–azide reaction. A very high inducing activity of thioammeline makes possible to determine 10–200 ng of iodine in a 5-ml sample and 4–25 ng in a 10-ml sample depending on the technique applied for carrying out the induced reaction. The measurement of iodine amount produced in the reaction $O_3 + 2I^- + H_2O \rightarrow O_2 + 2OH^- + I_2$ enables the determination of ozone in the ranges 10–200 ng and 2–15 ng, respectively, after passing a sample of air through 25 ml of absorbing solution (10 g $l^{-1}$ of KI in phosphate buffer of pH 7.1).

Reakcję azydku sodu z jodem indukowaną tioammeliną zastosowano do oznaczania nanogramowych ilości jodu w roztworach wodnych. Metoda polega na oznaczeniu ilości tioammeliny utlenionej przez jod. Produkt utlenienia nie indukuje reakcji jodo-azydkowej. Bardzo wysoka aktywność indukcyjna tioammeliny umożliwia oznaczanie 10–200 ng jodu w 5 ml roztworu lub 4–25 ng w 10 ml roztworu w zależności od techniki prowadzenia reakcji indukowanej. Pomiar ilości jodu wydzielonego w reakcji $O_3 + 2I^- + H_2O \rightarrow O_2 + 2OH^- + I_2$ umożliwia oznaczanie ozonu w zakresach 10–200 ng lub 2–15 ng po pochłonięciu próbki powietrza w 25 ml roztworu absorbującego (10 g $l^{-1}$ KI w buforze fosforanowym o pH 7,1).

There are number of methods for the determination of iodine. The most important in terms of extensive practical use is the titration of iodine with the standard sodium thiosulphate solution in the presence of starch. Titration in the micro scale makes possible to determine the iodine at the concentration level $10^{-4}$ mol $l^{-1}$. The photometric methods enable the determination of iodine as $I_3^-$ or complex starch–$I_3^-$ at 350 nm or 575 nm respectively, from $10^{-3}$ mol $l^{-1}$ to $10^{-7}$ mol $l^{-1}$ [1]. By means of the potentiometric method it is possible to determine iodine in the concentration range $1\times10^{-1} - 2.5\times10^{-8}$ mol $l^{-1}$ [2]. The most sensitive procedures in which the catalytic property of $I_2/I_3^-$ is used allow the determination of both species at the level $10^{-8} - 10^{-14}$ mol $l^{-1}$ but these methods do not differentiate iodine from iodide [3].

Iodine can be determined by the measurement of the amount of thiol compound oxidised in the reaction

$$2RSH + I_2 \longrightarrow RSSR + 2HI \tag{1}$$

Spectrofluorimetric method based on this reaction with application of naphthalene-2-thiol has been described [4].

The amount of thiol compound consumed by iodine can also be estimated by the iodine–azide reaction

$$2N_3^- + I_3^- \xrightarrow{S^{2-}} 3I^- + 3N_2 \tag{2}$$

This reaction is selectively induced by sulphur(II) compounds. The decrease in the inducing activity of a solution containing a known initial amount of thiol compound is proportional to the amount of iodine present in the sample provided that RSSR produced in the reaction (1) does not induce the iodine–azide reaction.

## EXPERIMENTAL

### Reagents

A 0.01 mol $l^{-1}$ stock solution of iodine containing 4 g $l^{-1}$ of potassium iodide was standardised by titration with 0.01 mol $l^{-1}$ sodium arsenate(III) solution. A standard solution of iodine containing 1 mg $l^{-1}$ in 1% KI solution was freshly prepared from stock solution containing 100 mg $l^{-1}$ in 1% KI before measurements. A stock solution of sodium azide contained 200 g $l^{-1}$. The required pH of the solution was obtained by addition of a suitable amount of 0.01 mol $l^{-1}$ hydrochloric acid; an internal $HN_3$–$NaN_3$ buffer system is formed and no additional buffer is needed. A $10^{-3}$ mol $l^{-1}$ stock solution of thioammeline was prepared by dissolving 14.3 mg of thioammeline in 5 ml of 0.1 mol $l^{-1}$ sodium hydroxide solution adjusted to pH 5.0 with 0.1 mol $l^{-1}$ HCl and diluted with water to 100 ml. Thioammeline was synthesised from dicyanamide and ammonium thiocyanate [5]. Phosphate buffer of pH 7.1 containing 10 g $l^{-1}$ of KI was used as ozone absorbing solution.

### Equipment

Microtitrator type 322 (Unipan, Poland).

The assembly for titration at a constant and known rate consisted of automatic burette SBU 1a (Radiometer) and polarograph OH 102 (Radelkis).

The determination of the end point of the titration was done amperometrically with two polarised platinum electrodes of the surface 10 mm$^2$ each [6].

Ozonator OG-31 ( Zelmech, Poland)

Spectrophotometer Beckman DU-7500

Sulphur(II) compounds have different inducing activity in the iodine–azide reaction. The higher the inducing activity the lower amount of inductor and then iodine can be determined. For iodine determination thioammeline (2-thio-4,6-diamino-1,3,5-triazine) has been chosen for its very high inducing activity what enables the determination of nanogram changes in its concentration and nanogram amounts of iodine. In 1% KI solution thioammeline consumes in the induced reaction about 7000 times more iodine than in the iodometric reaction.

Two procedures for the determination of *iodine** were evaluated and the optimum conditions were established. The determination of *iodine* was based on the measurement of the amount of iodine consumed in the iodine–azide reaction induced by a known amount of thioammeline (blank sample), and in the reaction induced by the remaining amount of thioammeline that has not reacted with *the determined iodine.* The difference in the inducing activity is proportional to the amount of *determined iodine* in the sample. The bigger the difference the more *iodine* is present in a sample. In both procedures an excess of thioammeline in relation to *the determined iodine* was taken.

### Procedure 1

Back-titration of an excess of unreacted iodine:

20 μl of $10^{-4}$ mol $l^{-1}$ thioammeline solution (286 ng of thioammeline) was introduced into a 5-ml sample containing 10–200 ng of *determined iodine* in 1 % KI solution. Solution was mixed and then 1 ml of $NaN_3$ solution (0.2 g) and 2 ml 0.1 mol $l^{-1}$ HCl (pH 5.6±0.1) was added. The content of the vessel was stirred vigorously with a magnetic stirrer, 1000 μl of 0.01 mol $l^{-1}$ iodine solution was added and the time was measured from this moment. After 20 min the excess of unreacted iodine was back-titrated with 0.01 mol $l^{-1}$ sodium arsenate(III) solution using starch as indicator and the amount of iodine consumed was measured. In the absence of *determined iodine* the added amount of thioammeline consumes in the induced reaction 695±5 μl of iodine.

Continuous, automatic adding of diluted iodine solution to the sample containing azide and sulphur(II) compound and recording the end point of titration by amperometry with two polarised platinum electrodes enables determination of inductors at the nanogram level [6]. The measurement of changes in thioammeline amount in the sample by means of this technique enables the determination of *iodine* at nanogram level.

### Procedure 2

Automatic titration with iodine solution:

To an electroanalytical cell equipped with a mechanical stirrer and two platinum electrodes a 10-ml sample containing 4–25 ng of *iodine* in 1 % KI was introduced followed by 250 μl of $10^{-6}$ mol $l^{-1}$ thioammeline solution (36 ng of thioammeline). Then 1 ml of $NaN_3$ solution (0.2 g) and 2 ml 0.1 mol $l^{-1}$ HCl were added. The potential difference 25 mV at platinum electrodes was fixed and from the automatic burette 0.0025 mol $l^{-1}$ iodine solution was introduced at the rate of 10 μl $min^{-1}$. The end point of titration was marked by the increase of recorded current. In the absence of *determined iodine* in the sample 36 ng of thioammeline consumes 380±15 μl of iodine solution.

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* Remark. In order to avoid misunderstanding and clearly distinguish the iodine which is the reagent in the iodine–azide reaction from the iodine which is determined, the *determined iodine* is written in *italics* where necessary.

## RESULTS AND DISCUSSION

Spectrophotometric investigations pointed out that thioammeline at concentrations $10^{-3}$–$10^{-7}$ mol $l^{-1}$ reacts with iodine quantitatively and the only product of oxidation is disulphide which does not show inducing activity in the iodine–azide reaction during 20 min of induction. Only 40-fold excess of disulphide in relation to thioammeline causes noticeable increase in measurements, but under the conditions applied for the determination of iodine such excess is not possible.

The influence of iodide ions on the course of the oxidation reaction and the induced reaction was investigated. It was important because an excess of iodide ions can have a significant influence on the equilibrium of the reaction of sulphur(II) compounds with iodine [7] and activity of inductors [8]. The excess of iodide ions in the analyte is necessary because these ions stabilise the free iodine in water solution. It has been experimentally verified that at pH 4,5–7.5 potassium iodide at concentration from 0.001 % to 1.0 % does not shift the equilibrium of the oxidation reaction. When the induction reaction is carried out in 1 % solution of KI the inducing activity of thioammeline increases and the sensitivity of the determination of thioammeline and iodine also enhances (Fig. 1, plot I and II).

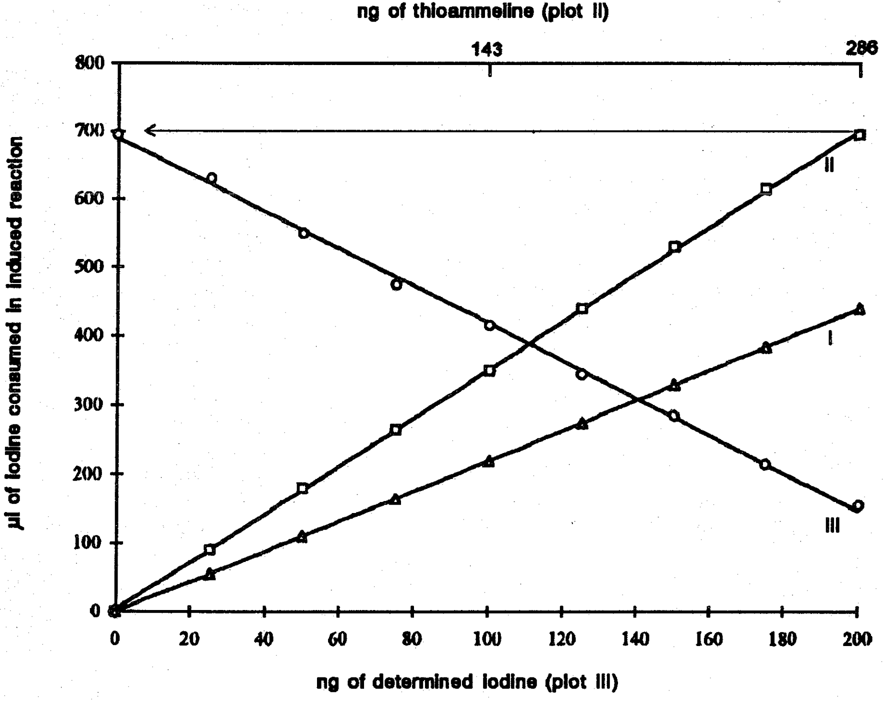

**Figure 1.** Back-titration method. Iodine consumption in the iodine–azide reaction induced by increasing amounts of thioammeline without KI (I) and in 1% KI solution (II); decrease in iodine consumption with increasing amounts of *determined iodine* in a sample containing 20 µl of $1\times10^{-4}$ mol $l^{-1}$ thioammeline solution (286 ng thioammeline) (III)

By means of procedure 1 it is possible to determine iodine in the range 0.01–0.2 μg in a 5-ml sample what corresponds to the concentration $8\times10^{-9}$ –$1.6\times10^{-7}$ mol $l^{-1}$. The set of results is presented in Table 1. The standard deviation for 6 independent determinations is ±0.004 μg at the level 0.1 μg of iodine and 0.007 μg at the level 0.2 μg of iodine in the sample. Application of procedure 2 makes possible to determine 4–25 ng of iodine in a 10-ml sample what corresponds to $0.15\times10^{-8}$ –$1\times10^{-8}$ mol $l^{-1}$ with an accuracy ±2 ng. The greater amounts of iodine can be determined provided that the greater amount of thioammeline is added to the sample. This procedure enables to determine iodine with the sensitivity about five times better than by procedure 1.

**Table 1.** Determination of iodine by procedure 1 in the presence of 286 ng of thioammeline and by procedure 2 in the presence of 36 ng of thioammeline

| Procedure 1 | | Procedure 2 | |
|---|---|---|---|
| ng of $I_2$ in a 5-ml sample | μl of 0.01 mol $l^{-1}$ $I_2$ consumed in the induced reaction* | ng of $I_2$ in a 10-ml sample | μl of 0.0025 mol $l^{-1}$ $I_2$ consumed in the induced reaction** |
| 0 | 695 | 0 | 380 |
| 25 | 630 | 5 | 310 |
| 50 | 550 | 10 | 275 |
| 75 | 475 | 15 | 190 |
| 100 | 415 | 20 | 155 |
| 125 | 345 | 25 | 85 |
| 150 | 285 | | |
| 175 | 215 | | |
| 200 | 155 | | |

* Accuracy of the determination ±5 μl.
** Accuracy of the determination ±15 μl.

Metals do not interfere with the determination because metal chelates of thioammeline are not stable in a solution containing an excess of the azide ions. Thiocyanate ions do not interfere because theirs inducing properties are blocked in the presence of an excess of iodide. Occurrence of simple thiols, sulphides and thiosulphate is precluded in the presence of iodine. However, it is recommended to check whether the sample alone induces the iodine–azide reaction. Anions do not influence the course of the induced reaction.

The proposed method is worth to be recommended thanks to its simplicity and sensitivity higher than the potentiometric or photometric method. The method can be applied for the determination of all oxidants which release iodine from iodide solution. The determination of ozone as an example is presented.

## Determination of ozone

Majority of the methods for ozone determination are based on the reaction between ozone and iodide ions and measurement of produced iodine. The iodine quantity released is determined by photometry [1], potentiometry [2] or spectrofluorimetry [3]. Seidelmann compared photometric and potentiometric methods [9]. By means of these methods ozone can determined at the level $10^{-7}$ mol $l^{-1}$.

In the first approach the reaction of thioammeline alone with oxygen and ozone was investigated by spectrophotometry and by the iodine–azide reaction. Air and ozone-loaded air was sucked with a flow rate 0.1 l $min^{-1}$ through $10^{-4}$–$10^{-6}$ mol $l^{-1}$ thioammeline solutions for 5–60 min. No changes in thioammeline concentration even during 60 min of sampling were observed. It was found that ozone reacts with thioammeline instantly and the decrease in thioammeline concentration is proportional to the amount of introduced ozone. However, the oxidation reaction proceeds beyond or omits the disulphide stage. On the UV-spectra the decrease of absorption of thioammeline at $\lambda_{max}$. 279 nm does not result in appearance of disulphide spectrum. When ozone is introduced to the solution of thioammeline disulphide the decrease in disulphide concentration is recorded. Products of the oxidation reaction do not induce the iodine–azide reaction even after a long induction time what proves that the sulphur(II) compounds do not occur in the solution. Due to this mechanism the thioammeline concentration does not depend linearly on the amount of introduced ozone when more than 30% of thioammeline is oxidised. In the first stage only thioammeline reacts with ozone and afterwards also the intermediate products of the oxidation reaction consume ozone. This excludes the determination of ozone on the base of the reaction of thioammeline with ozone. The use of the intermediate system $O_3 + 2I^- + H_2O \rightarrow O_2 + 2OH^- + I_2$ is necessary.

The dry air was pumped with a flow rate 5 or 10 l $h^{-1}$ through ozonator and by a tube filled with glass wool coated with chromic acid solution in order to remove $SO_2$. A gas-washing bottle was placed close to the ozone source. In order to obtain stable operating conditions the whole system was running 1 hour before the measurements were carried out. Then the ozone-loaded air was passed through a gas-washing bottle with a known volume of a buffered 1 % potassium iodide solution. Efficiency of ozonization was estimated by titration of produced iodine with a standard sodium thiosulphate solution after passing of a known volume of ozone-loaded air.

Then the defined volumes of ozone-loaded air were sucked through a 25 ml of absorbing solution. The produced iodine was determined by means of procedure 1 in the 5-ml portions and by procedure 2 in the 10-ml portions. An example of the obtained results is presented in Table 2.

**Table 2.** The results of ozone determination

| $O_3$ introduced into 25 ml of absorbing solution, ng ±10% | $O_3$ determined, ng |
|---|---|
| 4 | 2.5–5* |
| 9 | 7.5–10* |
| 17 | 15–20** |
| 34 | 35–40** |
| 68 | 60–70** |
| 135 | 135–150** |

* By procedure 2 from 2 parallel determinations.
** By procedure 1 from 4 parallel determinations.

The detection limit for a sample taken to the iodine–azide reaction is 2 ng of ozone by procedure 1 and 1 ng of ozone by procedure 2. This corresponds to 4 ppb and 1 ppb(V/V) in a 1 l sample of air, respectively. The ranges of ozone determination are 10–200 ng and 2–15 ng.

The method can be applied to the determination of ozone in air samples. The interference from $SO_2$ is eliminated by $CrO_3$ based filters [4,10] and there is no interference from $NO_2$ at concentration lower than 0.4 ppm(V/V) in 1% KI solution used as an absorbent solution [4].

**Acknowledgement**

*The authors wish to acknowledge financial support for this work by the State Committee for Scientific Research (Project No. KBN BS-31-443).*

## REFERENCES

1. Gottardi W., *Fresenius Z. Anal. Chem.*, **313**, 217 (1982).
2. Gottardi W., *Mikrochim. Acta (Wien)*, **I**, 371 (1982).
3. Williams W.J., *Handbook of Anion Determination*, (Polish ed) by PWN, Warszawa 1985, p. 474.
4. Sakai T. and Nishikawa H., *Analyst*, **117**, 1339 (1992).
5. *Houben Weyl Methoden der Organischen Chemie*, vol.8, p.239, Thieme, Stuttgart 1955.
6. Kurzawa J. and Kurzawa Z., *Chem. Anal.(Warsaw)*, **31**, 45 (1986).
7. Kurzawa J. and Janowicz K., *Acta Chim. Hung.*, **125**, 147 (1988).
8. Kurzawa J., *Chem. Anal. (Warsaw)*, **32**, 875 (1987).
9. Seidelmann U., *Fresenius J. Anal. Chem.*, **345**, 537 (1993).
10. Zygmunt B., Chrzanowski W., Janicki W. and Namieśnik J., *Chem. Anal. (Warsaw)*, **37**, 719 (1992).

*Received April 1995*
*Accepted August 1995*