

Quecksilber durch Zementation mit Kupferpulver angereichert werden. Die Zementation gelingt aus schwach sauren, auch salpetersäurehaltigen Lösungen praktisch vollständig, wenn 3 Std gerührt wird und etwa in der Lösung vorhandene oxydierende Substanzen zuvor mit SO_2 reduziert werden. Zur Zementation gut geeignetes Kupferpulver ist durch Ausfällen mit Zinkpulver aus schwach saurer Kupfersulfatlösung zu gewinnen. Das Zementat, Kupferpulver mit anhaftendem Quecksilber, wird nach Filtration in Salpetersäure gelöst und die Lösung dann direkt colorimetriert. Bei Einwaagen von etwa 10 g Probesubstanz können nach der beschriebenen Methode noch Gehalte von 2–5 ppm Hg mit einem Fehler von $\pm 10\%$ bestimmt werden.

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Interference of Certain Ions with the Catalytic Action of Iodine in the Sandell-Kolthoff Reaction

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With 3 Figures in the Text

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The oxidation-reduction reaction between Ce^{IV} and As^{III} , when catalysed by iodine, may be disturbed by several substances which also have a catalytic effect on this reaction or act as oxidising or reducing agents. SANDELL and KOLTHOFF⁵ found that osmium and ruthenium catalyse this reaction in the same manner as iodine, while manganese

and permanganate do so in the presence of bromides. Among substances reducing Ce^{IV} they listed nitrite, thiocyanate and ferrous ions, while bromate and permanganate were classed by them as oxidising As^{III} . These authors also pointed out that certain substances, such as fluoride, form compounds with Ce^{IV} , giving a stable complex; silver, cyanide and mercury salts react with iodide.

CHANEY³, KLEIN⁴ and ACLAND¹, who investigated this problem more recently, observed the inhibitory action of sodium, sulphuric acid and zinc on this reaction, while BARKER² recommended the addition of chlorides, which help to stimulate the reaction.

The purpose of the present study was to work out a universal ultra-micro method for the iodine determination in biological material. To this end, the influence of various ions on the catalytic effect of iodine was examined. This effect was investigated under optimal conditions, specially determined for this particular reaction^{6,7}.

Experimental

Reagents. 1. *Iodide Standard.* 0.020 μg of I^- per 1 ml. 100 ml of the solution contain 66.0 ml of 2N sodium carbonate.

2. *Acid Mixture.* 1.0 M NaCl and 0.1 N As_2O_3 in 4.5 N sulphuric acid. 120.5 ml of conc. sulphuric acid are added into 500 ml of redistilled water. 58.45 g of sodium chloride are dissolved in 200 ml of water and this together with 4.9455 g of As_2O_3 , previously dissolved in 20.0 ml of 70% potassium hydroxide solution, is added into diluted sulphuric acid and the whole brought to 1000 ml with water.

3. *Ceric Ammonium Sulphate, 0.005 M in 3.0 N Sulphuric Acid.* 3.165 g of ceric salt is suspended in 500 ml of water and 80.4 ml of conc. sulphuric acid are added under constant stirring. When the salt is dissolved, the whole is brought to 1000 ml with water.

4. *1% Brucin Acetate Solution.* 5 g of the base are dissolved in 200 ml of water and 6.0 ml of ice-cold acetic acid. The whole is filtered and the volume made up to 500 ml with water.

5. *Solutions* of the substance being studied.

Working Procedure. 1.0 ml of the substance under observation and 2.0 ml of the acid mixture, are added into 1.0 ml of iodide standard. The samples are cooled for 10 min in an ice bath ($+ 4.0^\circ\text{C}$). 2.0 ml of an equally cooled solution of cerium are added and the samples are placed in a warm bath ($40.0 \pm 0.1^\circ\text{C}$). After 5, 10, 15 and 20 min, these are transferred in batches back into the ice bath ($+ 4.0^\circ\text{C}$) for another period of 10 min, after which, 0.5 ml of brucin is added. The samples are then incubated for 15 min in a thermostat at 100.0°C , cooled down to room temperature and their extinction values are measured at 430 nm by means of a Zeiss spectrophotometer.

The values for the rate constant of individual concentrations of the substance may be calculated from the results obtained from the equation

$$K = \frac{2.303}{t} \log \frac{a}{a-x}$$

which is valid for reactions of the first order¹, and where a = the initial and $a - x$ = the final concentration of Ce^{IV} in the time t .

Results

Any concentration of any substance in the reacting medium, causing a change in the rate constant equivalent to ± 5 percent, was considered, in the present study, to be an interfering agent. This change corresponds to $\pm 0.001 \mu\text{g}$ of I^- .

The effect of various concentrations of NaCl , NaF , KH_2PO_4 , ZnSO_4 , KCl , MgSO_4 , KBr and of CuSO_4 was also studied. Tables 1 and 2 list the

Table 1. *Substances with Inhibitory Effects on the Catalytic Reaction*

| NaF | | KH_2PO_4 | | KCl | | ZnSO_4 | |
|---------------|--------------------------|--------------------------|--------------------------|-----|--------------------------|-----------------|--------------------------|
| μg | Percent of change of „K“ | mg | Percent of change of „K“ | mg | Percent of change of „K“ | mg | Percent of change of „K“ |
| 0 | 100.0 | 0.0 | 100.0 | 0 | 100.0 | 0.0 | 100.0 |
| 10 | 100.0 | 0.25 | 98.5 | 5 | 100.0 | 0.002 | 100.0 |
| 20 | 98.9 | 0.50 | 97.7 | 10 | 97.9 | 0.016 | 97.9 |
| 40 | 95.3 | 1.0 | 94.5 | 20 | 99.2 | 0.13 | 97.3 |
| 80 | 92.8 | 2.0 | 92.7 | 40 | 95.0 | 1.0 | 96.7 |
| 160 | 84.5 | 25.0 | 84.3 | 80 | 89.7 | 8.0 | 95.8 |
| 320 | 72.2 | 50.0 | 73.1 | 160 | 78.5 | 65.0 | 94.0 |
| 640 | 56.3 | 100.0 | 52.3 | 266 | 64.7 | 524.0 | 71.9 |
| 1280 | 40.8 | 200.0 | 27.5 | | | | |

Table 2. *Substances Stimulating the Catalytic Effect of Iodine*

| KBr | | CuSO_4 | | MgSO_4 | | NaCl | |
|---------------|--------------------------|-----------------|--------------------------|-----------------|--------------------------|------|--------------------------|
| μg | Percent of change of „K“ | mg | Percent of change of „K“ | mg | Percent of change of „K“ | mg | Percent of change of „K“ |
| 0 | 100.0 | 0.00 | 100.0 | 0 | 100.0 | 0 | 100.0 |
| 3 | 100.0 | 0.25 | 100.0 | 1 | 100.0 | 5 | 100.0 |
| 7 | 102.2 | 0.50 | 101.5 | 2 | 98.3 | 10 | 100.0 |
| 18 | 103.9 | 1.00 | 105.0 | 4 | 102.9 | 20 | 102.7 |
| 47 | 104.1 | 2.00 | 110.4 | 8 | 108.1 | 40 | 103.9 |
| 117 | 104.8 | 4.00 | 122.1 | 16 | 123.5 | 80 | 107.5 |
| 293 | 104.3 | 8.00 | 146.1 | 32 | 154.0 | 160 | 110.3 |
| 732 | 106.5 | 16.00 | 184.3 | 64 | 200.6 | 266 | 113.0 |

concentration of the various substances and their effect on the rate constant, expressed as percentage, and Fig. 1, 2 and 3 indicate the correlation between the value of the rate constant on various concentrations of sodium fluoride, manganous sulphate and sodium, respectively.

The substances studied may be grouped into two categories, i. e. reaction inhibiting and reaction stimulating agents. A decrease amounting to 5 percent in the rate constant corresponding to $0.001 \mu\text{g}$ of I^- was observed with more than 0.04 mg of NaF , 1.0 mg of KH_2PO_4 , 40.0 mg of KCl and 65.0 mg of ZnSO_4 in the reagent solution. An increase of 5 per-

cent in the rate constant value was noted with more than 0.3 mg of KBr, 1.0 mg of CuSO_4 , 4.0 mg of MgSO_4 and 40.0 mg of NaCl. The effect of sodium on the rate constant forms an inverse ratio and a change of

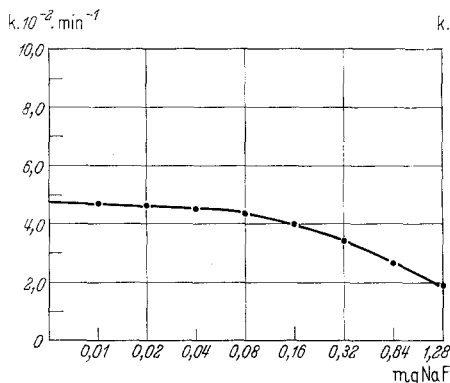


Fig. 1. Effect of NaF on the rate constant value

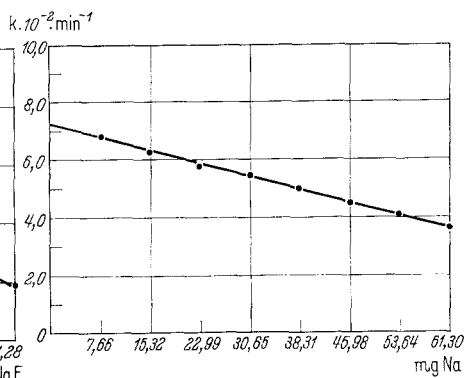


Fig. 3. Effect of Na on the rate constant value

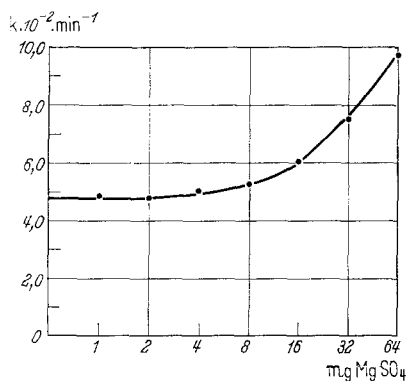
Fig. 2. Effect of MgSO_4 on the rate constant value

Table 3. Relation of Sodium and other Substances on the Catalytic Effect of Iodine

| Inhibitory Substances | Substances Relation | Stimulating Substances | Substances Relation |
|--------------------------|---------------------|------------------------|---------------------|
| Na^+ | 1.00 | Na^+ | 1.00 |
| NaF | 125.00 | KBr | 17.06 |
| KH_2PO_4 | 5.00 | CuSO_4 | 5.00 |
| KCl | 0.13 | MgSO_4 | 1.25 |
| ZnSO_4 | 0.07 | NaCl | 0.13 |

± 5.0 mg of Na^+ in the reagent solution causes an increase or a decrease of the resulting value of iodine by $0.001 \mu\text{g}$.

Table 3 gives the total effect of the concentrations of the substances in relation to the sodium effect, as this is the only element studied, in which the rate constant value is in a linear correlation with its concentrations.

Discussion

The present results agree with the findings of certain authors^{1,3} concerning the inhibitory effect of sodium and zinc on the reaction catalyzed by iodine. Similarly, the findings of SANDELL and KOLTHOFF⁵ that bromides stimulate the reaction more than chlorides, while fluoride inhibits it, have also been confirmed.

According to literary data, the interfering concentrations of the substances studied, are far in excess of their normal values in biological

material. The concentrations referred to are those added directly to the colorimetric solution. Since our method^{6,7} requires only one-third or less of the supernatant into which iodide had been extracted following the ashing of the biological material, the interfering substances would be present in this amount of the supernatant, and therefore their actual concentration in the biological material should be three times higher or more. Only water soluble substances are to be considered here, as in this method, the iodine from the ashed material is extracted by redistilled water in which carbonates of metals are not readily soluble. The interfering effect may also be avoided by estimating iodine in a smaller amount of biological material, where the concentration of the agent is not sufficient to affect the reaction. It should be pointed out here, that biological material, even from pathological states, does not contain concentrations high enough to cause interference under our optimal conditions. These facts bring out the universal character of our method and enable it to be employed for iodine assay in various biological materials.

Summary

On the basis of changes in the rate constant values in the Sandell-Kolthoff reaction, amounting to ± 5 percent, the concentrations of agents, responsible for these changes and equivalent to $\pm 0.001 \mu\text{g}$ of I^- , were determined. It was found that these substances, in the amounts given, stimulate the reaction, viz.: KBr 0.3 mg; CuSO_4 1.0 mg; MgSO_4 4.0 mg; NaCl 40.0 mg, while the following cause a lowering of the iodine value by $0.001 \mu\text{g}$: NaF 0.04 mg; KH_2PO_4 1.0 mg; Na^+ 5 mg; KCl 40.0 mg and ZnSO_4 65.0 mg.

Zusammenfassung

Es werden die Störungen bei der katalytischen Beschleunigungswirkung von Jodid auf die Reaktion zwischen Cer(IV) und Arsen(III) (nach SANDELL u. KOLTHOFF) untersucht. Als störend wird jede Veränderung der Geschwindigkeitskonstanten um $\pm 5\%$ (entsprechend $\pm 0.001 \mu\text{g I}^-$) betrachtet. Mehr als 0,3 mg KBr , 1,0 mg CuSO_4 , 4,0 mg MgSO_4 oder 40,0 mg NaCl verursachen eine Änderung um $+5\%$, während mehr als 0,04 mg NaF , 1,0 mg KH_2PO_4 , 5 mg Na^+ , 40,0 mg KCl oder 65,0 mg ZnSO_4 eine solche von -5% verursachen.

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Photometrische Bestimmung kleinster Mengen von Anilin, o-Toluidin, m-Toluidin und p-Toluidin

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Mit 3 Textabbildungen

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Die meist angewandten Verfahren zur Bestimmung kleiner Mengen von Anilin und seinen Homologen, des o-, m- und p-Toluidins beruhen auf der Diazotierung dieser Amine und auf der Kupplung der gebildeten Diazoniumsalze z. B. mit H-Säure³ in Hydrogencarbonatlösung, Phenyl-I-Säure in Soda¹⁵ - oder Hydrogencarbonatlösung⁹ oder mit R-Salz⁷ in schwach alkalischem Medium. Zur Bestimmung kleiner Anilinnengen sind auch die Indophenolreaktion^{6,14} und die Indaminreaktion¹³ geeignet. RIEHL u. HAGER¹⁶ schlugen die Farbreaktion mit Furfurol zur schnellen Bestimmung von 5–150 ppm Anilin vor. Die Lauthsche Reaktion¹² benützten JAN, KOLŠEK u. PERPAR⁵ zur photometrischen Bestimmung von Anilin, Monomethyl-, Dimethyl- und Diäthylanilin. Von AFANASIEV⁴ wurde zur colorimetrischen Bestimmung des Anilins, der Toluidine, sowie des p-Phenylendiamins und des p-Aminophenols die Farbreaktion dieser Amine mit Chloramin T angewendet.

Diese angeführten Methoden sind zur Bestimmung kleinster Mengen und Spuren von Anilin und den Toluidinen in der Atmosphäre wegen zu kleiner Empfindlichkeit und beschränkter Haltbarkeit der entwickelten Färbung wenig geeignet. In dieser Arbeit wird deshalb zur Kupplung der diazotierten primären aromatischen Amine als Kupplungskomponente das Hydrochlorid des N-Äthyl-1-naphthylamins vorgeschlagen. Die Kupplung wird in äthanolisch-wäßrigem Milieu nach vorheriger Beseitigung der überschüssigen salpetrigen Säure durch Amidosulfonsäure ausgeführt.

Aus der Literatur¹⁷ ist bekannt, daß die Reaktivität der gebildeten Benzol- und Toluol-diazoniumchloride sehr gering ist. Deshalb verläuft