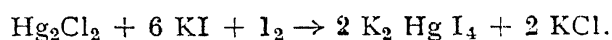


PHOTOCHEMICAL ANALYSIS

SEVERAL methods¹ have been proposed for the estimation of mercuric chloride, but they are not satisfactory either on account of (1) cumbersomeness, involving considerable time, etc., or (2) lack of sufficient accuracy or (3) the use of costly reagents. In our method we made use of the photochemical reaction between mercuric chloride and potassium oxalate in aqueous solution. At laboratory temperatures, in the dark, there is no appreciable reaction, but on exposure to light of suitable wave-length there is copious precipitation of mercurous chloride. Working with Monax or Pyrex glass conical flasks in sunlight, we found that the reaction goes to quantitative completion in about 30 to 60 minutes, in the presence of a minute concentration of uranyl nitrate, which acts as the photosensitizer. After exposure to light for the requisite time, the mixture is treated without filtration with a known excess of standard solution of iodine in potassium iodide. The precipitated mercurous chloride dissolves readily according to the following reaction



After adding the iodine solution, the flask is stoppered and allowed to stand for a few minutes with occasional agitation, until complete solution takes place. The residual iodine is titrated with standard sodium thiosulphate solution with starch as the indicator. From the volume of the standard iodine solution consumed in the oxidation of the mercurous to mercuric ion, we can calculate the amount of mercurous chloride formed in the photochemical reaction, and hence that of the mercuric chloride originally taken.

In the absence of the uranyl nitrate, the reaction takes place only very slowly. The uranyl nitrate does not interfere with the reaction or with the iodometric estimation in any manner, under the conditions described. The following table embodies typical results.

X ml. of M/20 HgCl_2 + X ml. of M/5 sodium oxalate + $\frac{X}{5}$ ml. of M/50 uranyl nitrate solution, exposed to bright sunlight for 45 minutes.

If the exposure to light is unduly prolonged,

Volume of HgCl_2 solution (x)	Milligrams of Hg taken	Milligrams of Hg found	Error per cent.
15 ml.	150.45	150.14	0.2
10 ml.	100.30	100.00	0.3
5 ml.	50.15	50.03	0.24
2 ml.	20.06	19.55	0.55
1 ml.	10.03	9.09	0.40

the mercurous chloride formed tends to decompose further into mercury. The appearance of a slight incipient grey colour is an indication that the reaction is complete. While working with concentrations of mercury chloride lower than M/100, the concentration of oxalate should be reduced, as otherwise the mercurous chloride undergoes further decomposition to metallic mercury. The uranyl nitrate concentration is however, retained at the usual value. Working with M/200 solution of mercuric chloride, we used M/50 solution of sodium oxalate with good results. We found that even one milligram of mercury in the form of mercuric chloride can be estimated with ease and considerable accuracy.

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¹ (a) Rupp and Müller, *Z. anal. Chem.*, 1925, **67**, 20; *Analyst*, 1925, **51**, 579.

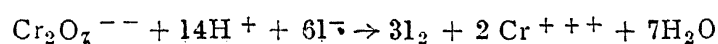
(b) Hillebrand and Lundell, *Applied Inorganic Analysis*, 1929, 172 (John Wiley & Son), 1929.

(c) Moser and Niessner, *Z. anal. Chem.*, 1928, **74**, 200.

(d) Robinson, *Analyst*, 1929, **52**, 146.

CATALYSIS OF DICHROMATE-HYDRIODIC ACID REACTION BY THE OXALATE ION

THE use of potassium dichromate as a primary standard in iodimetry is based on the following reaction.



The main features of this reaction are (1) increase in the speed of the reaction with increase in the concentration of iodide, dichromate and H⁺ ion, and (2) the interference of the autoxidation of hydriodic acid by atmospheric oxygen, which becomes appreciable at high concentrations of acid and of iodide, and in the presence of light. In spite of suitable precautions taken to overcome the difficulties encountered, the titration of weak solutions of dichromate (0.01 to 0.001 N) gives uncertain results. I. M. Kolthoff¹ has endeavoured to find suitable positive catalysts for this reaction, in order to improve the method, but without success. During the course of some other work, we accidentally discovered that oxalate ion exerts a marked catalytic effect on the reaction between dichromate and hydriodic acid. As this result is of great analytical and theoretical significance, we investigated the phenomenon in some detail.

The following table embodies some typical results.

5 ml of 0.001 N K₂Cr₂O₇ solution + 1 ml of 2 N HCl + 1 ml of 0.5 N KI + 2 ml of 1 per cent. starch + oxalate solution + distilled water, to make up to 20 ml.

Concentration of oxalate	Amount of iodine liberated in ml hypo solution instantaneously	Amount of iodine liberated in ml hypo solution in two minutes	Amount of iodine in ml hypo solution theoretical
Nil	3.77	4.56	5.40
0.00125 N	5.21	5.30	5.40
0.00250 N	5.30	5.36	5.40
0.00500 N	5.32	5.38	5.40
0.01000 N	5.37	5.38	5.40
0.01000 N	5.35	5.38	5.40

It will be seen from the above table that less than the theoretical quantity of iodine is liberated in the absence of oxalate, even when two minutes were allowed for the reaction. If an instantaneous titration is desired, Kolthoff recommends at least 20 ml of 4 N HCl per 100 ml of the reaction mixture. But it is the general consensus of opinion (cf. W. C. Vosburgh²) that at this high acid concentration the error due to air oxidation of hydriodic acid becomes appreciable,

From our results it is also evident that with a suitable concentration of oxalate, the quantitative liberation of iodine takes place almost instantaneously even at low hydrogen ion concentration, enabling the titration to be finished quickly. Control experiments have shown that, under our conditions, the reaction between oxalate and iodine and the reaction between oxalate and chromic acid do not interfere.

Oxalates of potassium, sodium and ammonium have been studied with almost identical results, so that we can conclude that it is the oxalate ion that exerts the catalytic effect. We also found that citrate and tartrate ions exert a positive catalytic influence, though to a lower degree than the oxalate ion. Succinate has no effect.

Fuller details will be published elsewhere.

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¹ I. M. Kolthoff, *Z. anal. Chem.*, 1920 **53**, 4041; *Volumetric Analysis*, 1929, 369 (John Wiley and Son).

² W. C. Vosburgh, *J. Amer. Chem. Soc.*, 1922, **4**, 2120.

2-N¹-SULPHANILAMIDO-4-n-PROPYL-THIAZOLE

In a recent publication,¹ we have described the synthesis of a series of 5-alkyl derivatives of 2-sulphanilamidothiazole. As a sequel to this, we undertook to synthesise a series of 4-alkyl derivatives, of which only the methyl and ethyl² derivatives are known so far. 2-Sulphanil-amido-4-n-propylthiazole has been synthesised as follows:

Butyrylchloride condensed with diazomethane in ethereal solution to yield the diazoketone (I) which on treatment with dry hydrogen chloride in ether solution yielded the corresponding chloroketone (II). On condensing the latter, with thiourea according to the usual procedure, 2-amino-4-n-propylthiazole (III) (picrate, m.p. 192° C.) was obtained. Treatment of this with acetsulphanilylchloride in pyridine solution furnished 2-acetsulphanilamido-4-n-propylthiazole (m.p. 202°) which on hydrolysis with