PHOTO-CHEMICAL ANALYSIS.

PART II.

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In a previous communication Gopala Rao and Ramacharlu (1942) have reported the development of a new technique for quantitative chemical analysis. The photo-chemical reaction between mercuric chloride and sodium oxalate has been employed as the basis of a method for the quantitative estimation of mercuric chloride. This reaction takes place rather slowly when the reaction mixture is exposed to sunlight in glass vessels, hence they employed uranyl nitrate as a photo-sensitiser to accelerate the reaction. In this way, the reduction of the mercuric chloride to mercurous chloride can be made to occur quantitatively in sunlight or in the light of the quartz mercury vapour lamp under conditions specified in the paper. It was, however, noticed that with uranyl nitrate as photo-sensitiser the reaction does not take place rapidly enough in the light from a 1,000 watt tungsten filament lamp. Many laboratories may not afford an ultraviolet ray equipment; moreover, uranium salts are costly. We, therefore, attempted to use a cheaper photo-sensitiser which will permit exposures from a 1,000 watt tungsten filament lamp. We found that ferric chloride answers the purpose at very low concentrations. In this paper we describe the conditions under which a quantitative reduction of mercuric chloride by oxalate can be effected with ferric chloride as photo-sensitiser with different types of illumination.

EXPERIMENTAL.

A mixture of the requisite quantities of mercuric chloride, sodium oxalate, and the photo-sensitiser was exposed to light and after the reaction was over the mixture was treated with an excess of a solution of iodine in potassium iodide as in the previous work. The iodine reacted with the precipitated mercurous chloride, and the unreacted iodine was titrated with a solution of standard sodium thiosulphate. From the amount of iodine consumed one could calculate the amount of mercuric chloride originally taken.

From a large number of trials it was found that the use of ferric chloride at high concentrations results in the further reduction of mercurous chloride to metallic mercury even in short exposures. A solution of M/100 ferric chloride in M/100 hydrochloric acid was prepared and preserved in a stoppered brown

Jena bottle. The presence of hydrochloric acid and the mode of preservation prevented the hydrolysis of ferric chloride for a considerable time. From this stock solution was prepared by dilution with distilled water the M/10,000 solution of ferric chloride just before it was required for use as photo-sensitiser. Otherwise solutions of this dilution undergo marked hydrolysis very rapidly. It was noticed by us that solutions containing hydrolysed ferric chloride do not exhibit marked photo-sensitisation. It must also be remembered that the concentration of hydrochloric acid cannot be kept too high because the reduction of mercuric chloride is inhibited by a high hydrogen ion concentration. A few typical results from out of the many obtained in sunlight are given in the table below.

TABLE I.

X ml. of M/20 $HgCl_2$+X ml. of N/5 $Na_2C_2O_4$+X/5 ml. of M/10,000 $FeCl_3$ exposed for one hour to sunlight in 100 ml. Monax conical flasks.

Milliliters of $HgCl_2$ solution taken.	Milligrams of mercury taken.	Milligrams of mercury found.
1	10·03	10·11
2	20·06	20·05
5	50·15	50·13
7	70·21	70·21
10	100·30	100·2
15	150·45	149·9

Ferric chloride at this dilution does not liberate iodine from potassium iodide in amounts detectable even by starch. Hence its presence will not vitiate the iodometric estimation of mercurous chloride.

Experiments in the light of a quartz mercury vapour lamp.

The mixture of mercuric chloride, sodium oxalate and ferric chloride was exposed in a conical flask kept underneath the arc. It was found necessary to employ a higher concentration of ferric chloride, namely M/3,000.

TABLE II.

X ml. of M/20 $HgCl_2$+X ml. of N/5 $Na_2C_2O_4$+X/5 ml. of M/3,000 $FeCl_3$ exposed for one hour.

Milliliters of $HgCl_2$ solution taken.	Milligrams of mercury taken.	Milligrams of mercury found.
1	10·03	10·04
2	20·06	20·08
5	50·15	50·12
7	70·21	70·16
10	100·30	100·1

The mercury arc was of the Hereaus type worked on 220 volts D.C. at 3·5 amps.

Experiments in the light from a 1,000 watt tungsten filament lamp.

The mixture was exposed in a 100 ml. conical flask kept underneath the electric bulb. The lamp was worked on the 220 volts A.C. mains at 4 amps. It was found necessary to use a high concentration of ferric chloride of the order of M/50. Ferric chloride at this concentration liberates iodine from potassium iodide, but in the presence of excess of oxalate it does not do so. Hence, even this high concentration of ferric chloride will not interfere with the iodometric estimation under these conditions.

TABLE III.

X ml. of M/20 $HgCl_2$+X ml. of N/5 $Na_2C_2O_4$+X/5 ml. of M/50 $FeCl_3$ exposed for two hours.

Milliliters of $HgCl_2$ solution taken.	Milligrams of Hg taken.	Milligrams of Hg found.
1	10·03	10·05
2	20·06	20·12
5	50·15	50·22
7	70·21	70·04

We also found that much smaller quantities of mercury can be estimated than those indicated in the tables. We refrain from giving the results for lack of space.

SUMMARY.

1. From the results presented in this paper it is evident that ferric chloride, at suitable concentrations, serves as a good photo-sensitiser for the quantitative reduction of mercuric chloride by oxalate in sunlight. Moreover, the use of ferric chloride enables us to work with a cheap source of artificial light, namely, a 1,000 watt tungsten filament lamp.

2. Our experiments showed further that with ferric chloride as photo-sensitiser one can carry out the reaction in sunlight in brown glass bottles. With brown glass bottles the danger of reduction of mercurous chloride to metallic mercury due to unduly long exposures is entirely eliminated. Under these conditions one can also use with safety higher concentrations of ferric chloride than have been indicated in Table I.

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REFERENCE.

Gopala Rao, G. and Ramacharlu, P. T., (1942). Photo-chemical Analysis. Part I. *Proc. Nat. Inst. Sci. Ind.*, **8**, 383–388.