

PHOTOCHEMICAL ANALYSIS.

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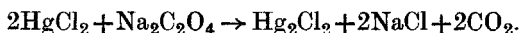
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It is well known that many chemical reactions are prompted by exposure to light of suitable wavelength. It therefore appeared to the authors that some of these photochemical reactions could be used as the basis of some interesting quantitative estimations, while still others might be used for qualitative detection.

The reaction which we have selected for experimental study is the photochemical reaction between mercuric chloride and sodium oxalate. It is our desire to make this reaction the basis for the volumetric estimation of mercuric chloride. Mercuric chloride cannot be titrated with standard thiocyanate solution by the Volhard's method. This method is very convenient for the estimation of mercuric nitrate solutions, but even here chlorides and bromides interfere. The estimation of mercuric chloride is of importance especially in connection with pharmaceutical preparations. Many analysts have applied themselves to this problem. Rupp (1906) and Rupp and Müller (1925) reduced mercuric chloride by formaldehyde in alkaline medium and determined the liberated mercury by the iodine thiosulphate titration. This method was employed by these workers for the estimation of corrosive sublimate in pharmaceutical preparations. This method has not been found altogether satisfactory and recourse was made to other reducing agents. Hillebrand and Lundell (1929) recommended reduction with phosphorous acid in hydrochloric acid solution and gravimetric estimation of the precipitated mercurous chloride after filtration and washing through Gooch crucible and drying at 100–105°C. This method has two drawbacks: (1) the reduction is slow and hence the solution must be allowed to stand for twelve hours or more before filtering; (2) mercurous chloride is appreciably soluble in water, especially in water containing chloride ions, giving too low results. Winkler (1924) and Moser and Niessner (1928) have investigated a method involving the reduction of mercuric salts to mercury by hypophosphorous acid in acid solution. Robinson (1929) studied the same method for the estimation of smaller quantities of mercury. We do not propose to discuss the numerous publications on the subject for the sake of brevity. It may, however, be said here that the several methods proposed till now are not satisfactory either on account of (1) lack

of sufficient accuracy, or (2) cumbrousness involving considerable time, filtration, etc., or (3) involving costly reagents.

Mercuric chloride and sodium oxalate do not interact in the dark at the ordinary temperatures. According to Dhar (1917) the dark reaction even at 80° is extremely slow. The light sensitiveness of this reaction was discovered by Planche (1815) and was utilised by Becquerel and Fremy (1868) and Eder (1879) for measuring the intensity of light. The photochemical reaction is represented by the equation:

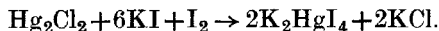


If this reaction were to be utilized for quantitative estimation it must be stoichiometric without interference by side reactions. We have, therefore, investigated this reaction carefully in order to establish conditions under which the mercurous chloride formed corresponds quantitatively to the mercuric chloride originally taken. Under these conditions, by estimating the mercurous chloride formed by the iodine thiosulphate titration, we can determine the amount of mercuric chloride originally taken.

Experimental.

The mercuric chloride and the sodium oxalate employed in our investigation are the Merck's analytical reagents.

Working with Monax or Pyrex glass conical flasks in sunlight, we found that the reaction is very slow. Hence, we used uranyl nitrate as a photosensitiser. After exposure to light for the requisite time the mixture is treated without filtration, with a known excess of a standard solution of iodine in potassium iodide. The M/20 solution of iodine must contain at least 50 grams of potassium iodide per litre. The precipitated mercurous chloride dissolves readily according to the following equation:—



After the addition of the iodine solution, the flask is stoppered and allowed to stand for a few minutes with occasional agitation, until complete solution has taken place. The residual iodine is titrated with standard sodium thio-sulphate solution with starch as the indicator. From the volume of the standard iodine solution consumed in the oxidation of 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. The uranyl nitrate does not interfere with the reaction or with the iodometric estimation in any other manner under the conditions described.

We made a large number of experiments varying the concentration of uranyl nitrate. Working with 5 ml. of M/20 mercuric chloride, the amount of uranyl nitrate solution (M/50) can be varied from 1 ml. to 6 ml. when quantitative reduction is obtained in about thirty minutes' exposure. With lower amounts of uranyl nitrate than 1 ml. the speed of the reaction is slower, necessitating unduly long exposures. With amounts of uranyl nitrate larger

than 6 ml. darkening of the precipitated mercurous chloride was observed due to the formation of mercury.

In another set of experiments the concentration of sodium oxalate was varied within wide limits (2 ml. to 20 ml. of N/5 oxalate for 5 ml. of M/20 mercuric chloride), without any noticeable difference in the results.

TABLE 1.

5 ml. of M/20 HgCl_2 + 5 ml. of N/2 $\text{Na}_2\text{C}_2\text{O}_4$ + 1 ml. of M/50 uranyl nitrate exposed to sunlight in 100 ml. Monax conical flasks (12 noon to 3 p.m.).
Mercury taken in each exposure = 50.15 mg.

Time of exposure in minutes.	Mercury found in mg.	Remarks.
5	46.03	
10	48.74	
20	49.72	
30	50.03	
40	50.03	
50	50.03	
60	50.03	
90	50.03	
120	50.47	Slightly darkens.
180	51.34	„

From the above table it will be noted that it is possible to reduce mercuric chloride to mercurous chloride easily and quantitatively; hence this photochemical reaction can be made the basis of a process for the estimation of mercuric chloride. We have made numerous estimations and we give below a few typical results to indicate the accuracy of our procedure.

TABLE 2.

Variation of Mercury taken.

X ml. of M/20 HgCl_2 + X ml. of N/5 $\text{Na}_2\text{C}_2\text{O}_4$ + X/5 ml. of M/50 uranyl nitrate exposed to sunlight for 45 minutes in 100 ml. Monax conical flasks.

X	Mercury taken in mg.	Mercury found in mg.	Error %.
1	10.03	9.99	0.40
2	20.06	19.95	0.55
5	50.15	50.03	0.24
10	100.30	100.00	0.30
15	150.45	150.14	0.20
20	200.60	200.06	0.27

Estimation of micro amounts of mercuric chloride.

We made experiments with varying volumes of M/200 mercuric chloride. We found that the concentration of oxalate has to be kept low if accurate

results are to be obtained. If the concentration of the oxalate is high there is a tendency for the mercurous chloride to undergo further reduction to metallic mercury. Moreover, a high concentration of oxalate will interfere in the subsequent iodometric estimation of mercurous chloride due to a slight reaction between the oxalate and iodine. The iodometric treatment was made with N/200 solution of iodine and the hypo solution employed was also N/200. Otherwise the details of the procedure are the same as those employed for the estimation of the more concentrated solution. The results given in the following table will show that the method is quite accurate even with solutions containing 1 mg. of mercury.

TABLE 3.

Variation of Mercury taken.

X ml. of M/200 HgCl_2 + X ml. of N/50 $\text{Na}_2\text{C}_2\text{O}_4$ + 0.2 X ml. of uranyl nitrate exposed to sunlight for 45 minutes in 100 ml. Monax conical flasks.

X	Mercury taken in mg.	Mercury found in mg.	Error %.
1	1.003	1.010	0.7
2	2.006	2.000	0.3
5	5.015	5.000	0.3
10	10.03	10.09	0.6
15	15.045	14.950	0.62

Experiments in artificial light.

As bright sunlight may not be available at all places, we thought it desirable to employ an artificial source of light in order to make this method one of common utility. The source of light employed by us was a Heraeus Quartz Mercury vapour lamp worked on 220 D.C. mains at 4 amps. The are was cooled by means of a fan.

Different types of exposure were tried. If the ultra-violet light from the quartz mercury vapour lamp was allowed to fall horizontally on the reaction mixture contained in a rectangular quartz stoppered cell, the mercurous chloride formed easily underwent further reduction to metallic mercury. It was found that the most satisfactory procedure was to expose the solution in an open glass conical flask directly under the arc. Under these conditions even long exposures did not produce metallic mercury, and mercurous chloride formed corresponded quantitatively to mercuric chloride taken, provided the time of exposure was at least thirty minutes. Exposure in conical flasks is convenient for another reason as well; the subsequent treatment with iodine and titration with thiosulphate could be done in the same vessel without transferring into another. Flat dishes for exposure are not convenient for this reason. The following table contains results of some of the experiments conducted in artificial light.

TABLE 4.

Mercury taken in mg.	Mercury found in mg.	Error %.
100.30	99.81	0.49
50.15	50.04	0.22
20.06	20.11	0.25
7.021	6.998	0.30
5.015	5.013	0.04
3.009	3.001	0.26
1.003	1.011	0.80

The concentration of oxalate and uranyl nitrate are the same as in the experiments with sunlight.

We also made experiments with 1,000 watt tungsten filament lamp under otherwise identical conditions, but the time required for complete reaction is unduly long.

From the results in Table 4 we find that even minute amounts of mercury can be estimated by our procedure with a considerable degree of accuracy.

When one compares the details of our procedure with those recommended by others, one finds that our method is more suitable. Simple laboratory ware and common reagents are sufficient for the work.

SUMMARY.

1. A new technique has now been introduced by us into analytical chemistry. We are the first to employ the photochemical action of light as an aid to quantitative chemical analysis.

2. Applying this technique we have shown that mercuric chloride can be estimated with a considerable degree of accuracy and rapidity. Our method is more rapid and suitable than the methods now in use.

3. A detailed study has been made of the conditions under which our photochemical method can be applied to the estimation of mercuric chloride under natural and artificial sources of illumination.

4. From our experience, we lay down the following criteria which must be satisfied if a photochemical reaction can be used for quantitative estimation : (1) the reaction must be sensitive to the action of the light employed, or must be capable of being made sensitive by the addition of a suitable photosensitiser; (2) the reaction selected must be capable of reaching completion without involving undesirable side reactions; and (3) the selected reaction must be fairly rapid, obviating unduly long exposures.

In conclusion we desire to place on record our deep debt of gratitude to Prof. N. R. Dhar, D.Sc. (Lond.), Dr.és Science (Paris), of Allahabad for his kind interest in this investigation. One of us (P. T. R.) desires to thank the authorities of the Andhra University, Waltair, for permitting him to join in this work.

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