

After the calibration the contents of the cuvette 1 are replaced by the organic compound which has combined with the high atomic element. The difference in absorption is recorded and the amount of the substance or element to be analyzed can be taken from the calibration curve. When the organic compound is an aqueous solution of low protein content the blank may be water without affecting the analytical results.

To simplify the technique a modification was introduced. The shutter E was designed as a rotating sector which alternately cut off the beams transmitted by 1 and 2. The sector was driven by a synchronous motor allowing for equal time period of transmission of the rays from 1 and 2. The photocurrents from 1 and 2 were amplified and connected with an oscillograph. The apparatus was adjusted with the same solutions, *e. g.* water, in the two cuvettes so that the oscillograph beam was balanced. When the contents of 1 were replaced by a substance with slightly higher absorption capacity the balance previously observed on the oscillographic screen was disturbed. With a microburette or pipette the solution in 2 was titrated with the same element as in 1 until balance was observed again. The amount of high atomic substance added to 2 was equal to the amount of the same substance present in 1. The end point of the titration is easily seen and if too much high atomic element is added in 2 the balanced oscillographic beam is disturbed but in the opposite direction to what would be observed before starting the titration. Balance can then be obtained again by "back titration" in cuvette 1. To get the correct amount of substance to be added the amount added to 1 is subtracted from that added to 2.

The method described has been used to determine the amount of silver that under certain experimental conditions is bound to a protein. It is obvious that the method

A Mercurimetric Modification of Zacherl and Krainick's Micro Halogen Determination Method

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In the course of synthetic work involving halogenated paraffin compounds the necessity arose of having at hand a rapid, simple and accurate method for the routine micro-determination of halogen in such compounds. A number of well established and generally adopted micro methods for the determination of chlorine and bromine are described in the standard literature^{1, 2}.

For our purposes titrimetric methods appeared to be most suitable because quick information was one of the features aimed at. Among the titrimetric methods the one first described by Zacherl and Krainick³ was chosen because firstly, it apparently requires no particular experi-

can be applied only in such cases where there are no high atomic substances present in the sample except the one being analyzed. Where the method can be used it is a rapid tool for the quantitative determination of small amounts of an element or substance. An optically inhomogeneous solution can be analyzed as well as a homogeneous one. The chemical combination of the high atomic element is unimportant for the determination, as the absorption of X-rays takes part in the electron shells close to the atomic nucleus. The method is also applicable to solids, gases, powders etc. when the sample containers are properly designed.

1. Doxey, G. A. *Electronics*. (1949) p. 87.
The instrument manual 1949. London (1949) p. 95.

ence, and secondly, it avoids such expensive and elaborate apparatus as are in general only used by specialized micro-analytical laboratories. In several runs using tetrabromostearic acid as a test substance, however, that method gave unsatisfactory results in our hands. In considering possible sources of error, it was thought that an acidimetric-alkalimetric system in such high dilutions might in itself be too susceptible for use in the ordinary organic laboratory, particularly because even traces of acidic or basic combustion products from substances containing sulphur or nitrogen might cause very serious errors. We therefore replaced the indirect alkalimetric by a direct mercurimetric procedure which allows to use one titrimetric solution only instead of two, and which avoids any steaming of flasks and boiling of the solutions to be titrated.

It will be seen in the experimental part that with halogenated hydrocarbons and fatty acids, as well as with nitrogenous substances such as arginine hydrochloride, the proposed method gave correct values within the usual limits of error. With the sulphur containing substance, S-benzylthiuronium chloride, however, the results were quite unsatisfactory under the conditions tried as yet.

Alicino *et al.*⁴ very recently published an excellent iodometric procedure for the microdetermination of bromine; but since by mercurimetry both chlorine and bromine can be determined with the same equipment the present method might in many instances still represent a welcome supplement with the limitations mentioned.

Experimental. The mercurimetric titrations were carried out essentially according to Kolthoff⁵, using diphenylcarbazide as an indicator. The mercuric nitrate solution was 0.01 *N* and was standardized against NaCl (C. P., dried and ignited). Samples corresponding to 2–5 ml of

0.01 *N* solution were taken for each analysis. After combustion and draining, 1 ml of 7 *N* HNO₃ and 4 drops of indicator (1 % alcoholic solution) were added to the halide solution (usually about 20 ml) which was then titrated with mercuric nitrate to a bright violet colour. Sharp end-points were always obtained in this way. The method was first tried with analytically pure tetrabromostearic acid as test substance. Some typical results follow.

Substance	Sample mg	ml Hg(NO ₃) ₂ 0.01 <i>N</i> <i>f</i> = 1.009	% hal. found	% hal. calc.
Tetrabromo- stearic acid	6.53	4.31	53.20	53.28 Br
	5.59	3.69	53.20	
	6.39	4.21	53.07	
	6.47	4.27	53.19	
	6.10	4.03	53.24	
Tetrabromo- stearic acid methylester ¹	5.33	3.44	52.02	52.05 Br
	5.26	3.41	52.32	
	4.93	3.18	52.17	
Pentabromo- heptadecane ²	7.18	5.60	62.87	62.93 Br
	5.85	4.22	62.63	
Arginine mo- nohydrochlo- ride ³	7.22	3.38	16.76	16.83 Cl
	4.35	2.03	16.69	
	6.99	3.23	16.52	
	6.60	3.11	16.89	

¹ Gravimetrically found 52.24 % Br (by Mr. Grossmann, Copenhagen).

² Gravimetric analysis gave 62.94 % (Grossmann).

³ Merck preparation, analyzed.

When this work was completed, a paper by Kirsten⁶ on a similar titration procedure came to our notice. This author recommends the use of an alcoholic solution of mercuric nitrate which, however, is unstable and must be freshly prepared every day. Our aqueous 0.01 *N* solutions, in contrast can be used directly and are fairly stable (in the course of one month the factor dropped from 1.015 to 0.99). It is only necessary to check the titer against standard NaCl.