extraction procedure under 1. The mixture is shaken thoroughly until all the complex cupric salt is dissolved in the carbon tetrachloride and centrifuged. The carbon tetrachloride solution is then filtered and the extinction is determined as under 1.

3. *Application of the method.* The method was used to determine T.T.D. qualitatively and quantitatively in experiments on rabbit and man.

Rabbits were kept in metabolism cages and urine was sampled as a rule during 24 hours periods. T.T.D. in varying doses was given as a suspension by stomach tube. In one rabbit 0.3 g T.T.D. was given on three successive days. 27 per cent of the T.T.D. given was recovered in the urine in the reduced form while only traces of unaltered T.T.D. were found. In another rabbit, given 0.05 g T.T.D. in a single dose, 12 per cent of the dose given was recovered in the reduced form. 48 hours after the dosage practically no T.T.D. could be recovered in the urine. A third rabbit was given 0.1 g T.T.D. on three successive days and killed 6 hours after the last dosage. 3 per cent of the T.T.D. given was recovered in the urine in the reduced form. The unaltered form of T.T.D. was found in the contents of the digestive tract. No T.T.D. could be traced in the blood serum or in the liver.

Two healthy men were given T.T.D. per os during three days (1 + 0.5 + 0.5 g). On the third day urine and faeces were sampled. No T.T.D. could be traced in the urine. In the faeces 117 respectively 56 mg of unaltered T.T.D. were recovered and only minute amounts of the reduced form (0.5 and 0.2 mg respectively).

A closer study of the accuracy of the methods, their applicability under different conditions *etc.* is in progress.

The authors are indebted to Aktiebolaget Pharmacia for financial support.

A Simple "X-Ray Colorimeter"

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When performing a quantitative microchemical analysis often the problem of determining small amounts of an element with a high atomic number in the presence of elements with low atomic numbers arises. A typical case is that of a protein reacting with a heavy metal such as silver. By determining the amount of silver bound to a protein the number of the silverbinding groups in the protein can be calculated. In the example mentioned the quantitative estimation by ordinary methods of analysis of the small amounts of silver bound to the organic substance offers difficulties.

This paper describes a method permitting the rapid determination of a high atomic element bound to an organic compound. As the absorption of X-rays increases with the fourth power of the atomic number, an organic compound to which a small amount of a high atomic element is bound gives greater absorption of X-rays than the organic compound alone. This is the same principle as utilized in the determination of tetraethyl lead in gasoline¹.

The principle of the method can be seen from Figure 1. Primary X-rays are generated in the X-ray tube A. Philips' commercial diffraction unit was used as a source of X-rays. The voltage of the X-ray tube and the filtering of the X-rays may be

1. Hald, J., Jacobsen, E., Larsen, V., and collaborators, several papers in *Acta Pharmacol. Toxicol.* **4** (1948).
2. Fredga, A., *Rec. trav. chim.* **69** (1950). In the press.
3. Sandell, E. B., *Colorimetric determination of traces of metals*. New York (1944) p. 221.

Received December 27, 1949.

adjusted for different samples. The X-rays are filtered in B, collimated into two beams in C and pass through the two cuvettes 1 and 2 at D. The X-rays transmitted by the cuvettes strike the light proof fluorescent screen, F, which is attached to the photomultiplier G. By the shutter, E, (or a rotating sector) the radiation transmitted by the cuvette 1 or 2 can be cut off alternately. The photomultiplier used is a R.C. A 931 tube with a Patterson fluorescent screen. The high voltage for the multiplier tube is taken from the A.C.-line by means of the common stabilized D.C. power supply. The voltage on each dynode is 90 volts. The photocurrent from the anode is measured with a spot light galvanometer.

When adjusting the apparatus the two cuvettes, 1 and 2, are filled with the same solution, the untreated organic compound in its solution, which is used as a blank. The X-ray beams and the photomultiplier are then adjusted so that the X-rays transmitted by 1 give the same photocurrent as those transmitted by 2. This is checked by alternately cutting off the beams with the shutter E. To the contents of the cuvette 1 different amounts of the

Fig. 1. Schematic drawing of the experimental apparatus.

- A. Head of the X-ray diffraction unit.
- B. Filter.
- C. Pinhole diaphragm.
- D. Cuvettes 1 and 2.
- E. Shutter or rotating sector.
- F. Fluorescent screen.
- G. Photomultiplier tube.

high atomic element are added. The absorption of X-rays is greater in cuvette 1 and the difference between the intensities of the radiation transmitted by 1 and 2 is recorded by reading the galvanometer deflections. As an example, in Fig. 2, two curves for AgNO_3 and CuSO_4 as measured against water are reproduced. In that manner the apparatus is calibrated for the element or substance being determined.

Fig. 2. The difference in galvanometer deflection between the sample, d_s , and the blank, d_c , for solutions of silver nitrate and copper sulfate. The sensitivity of the galvanometer is not the same in the two cases.

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.