only is precipitated. By increasing the concentration of the acid the precipitate redissolves.

All the above acids, with the exception of oxanilic, give no precipitate with the rare earths in cold or hot neutral solutions.

New Hampshire College and Experiment Station.
Durham, New Hampshire.

NOTES.

A Modification of the Modified Winkler Method for the Determination of Sulphates in Water.—The Modified Winkler Method for the determination of sulphates in water colorimetrically consists in adding to the sample a small amount of barium chromate, acidifying with a few drops of concentrated hydrochloric acid, bringing to a boil, cooling, then adding sodium hydroxide solution (1 : 10) carefully until a tiny drop of the liquid placed upon red litmus paper produces a blue color; a greater excess of alkali must be avoided as the solubility of barium chromate varies greatly with the degree of alkalinity. After filtering, the color is compared in a colorimeter with that of a standard solution of potassium chromate. A correction must be made for the solubility of barium chromate. The SO_4 is equivalent to the CrO_4 found. It is a more or less tedious step in the procedure to neutralize the hydrochloric acid to just the right point. It occurred to the writer to modify the method at this point by changing the acidity from hydrochloric acid to acetic acid by the addition of sodium acetate. This seems to give good results and is easily carried out.

The process as modified is as follows: Measure into an Erlenmeyer flask 150 cc. of the sample. Add 10 drops of concentrated hydrochloric acid and sprinkle in 0.1 to 0.2 g. of pure barium chromate. Rapidly bring the contents of the flask just to a brisk boil. Cool at once and to the cooled liquid add 5 g. of sodium acetate. Filter, transfer 100 cc. of the clear filtrate to a colorimeter cylinder and make alkaline with sodium hydroxide. The standard for comparison should be made slightly stronger than this solution and should be made up to 100 cc. after adding sodium hydroxide to alkaline reaction. A blank determination must be made, using distilled water, to determine the correction to apply for the solubility of the barium chromate under the conditions of the experiment.

It requires but a moment to weigh out the sodium acetate (a close approximation is sufficient). This method gives duplicate results agreeing perfectly within one's ability to read the colors.

The following determinations were made by the method as described.

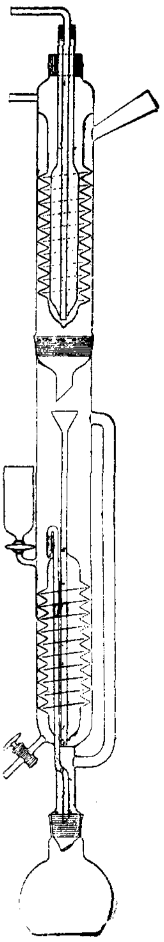
Different amounts of potassium sulphate were added to separate portions of distilled water and the SO_4 determined.

	Parts per million of SO_4 added.	Found (*a*).	Found (*b*).
1	27	22	22
2	54	53	52
3	108	105	104

4. In a water sample	SO_4 (parts per million).
Found by author's method	101.5
Found by Modified Winkler Method in the hands of another experimenter	101
Found by precipitation as $BaSO_4$	100

The correction applied for the solubility of the barium chromate used, under the conditions of the experiment, was 11 parts of SO_4 per million of water.

HOWARD W. BRUBAKER.



A New Apparatus for Extracting Liquids.—Hitherto all the usual types of apparatus for extraction of liquids have very fragile spirals, are difficult to clean and if a large quantity of liquid is to be extracted, the extraction must be interrupted by changing the liquid.

The following apparatus avoids these disadvantages. This apparatus differs from the usual Soxhlet apparatus for extracting solids only by the inner funnel-tube with a spiral-jacket, the inlet funnel and the higher opening of the siphon.

The use of the apparatus is as follows:

The apparatus is filled with the liquid up to near the siphon. Then by heating the flask filled with ether, etc., the ether vaporizes and the vapor goes through the vapor-tube to the condenser as in the ordinary Soxhlet apparatus. The condensate drops in the inner funnel-tube and rises in small drops following the thread of the funnel-jacket to the surface of the liquid. In this manner very good contact between the ether and the liquid to be extracted is obtained.[1] The ether accumulates above the surface of the liquid until it siphons over and the operation continues. Upon finishing the extraction, which can be ascertained by testing a small portion of the liquid drawn off through the cock, the liquid is removed and a new portion added through the funnel without taking the apparatus apart or interrupting the heating.

The condenser is a new return-condenser with the

---

[1] F. Friedrichs, "New Gas-washing Bottle," *Z. anal. Chem.*, **50**, 175–176; *C. A.*, **5**, 1694 (1911).

principle of counter-currents.[1] The essential feature of this condenser is the spiral cooling tube. The condensate between it and the outside-jacket forms a seal, compelling the vapor to travel a spiral distance of 4 feet up through the condenser.[2] To avoid heating the incoming cooling water by the outgoing warm water the outlet tube is insulated by an air-jacket. This jacket is enlarged so as to make the cooling water also take a spiral course exactly against the vapor.

This apparatus is manufactured by Greiner & Friedrichs, G. m. b. H, Stützerbach, Germany. FRITZ FRIEDRICHS.

ITHACA, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WASHINGTON.]

THE ACTION OF TETRABROMETHANE ON ORGANIC BASES.

BY WILLIAM M. DEHN.

Received December 18, 1911.

Tetrabromethane (acetylene tetrabromide) reacts with organic bases[3] with the greatest ease, yielding products in accordance with the equations:

$$\begin{aligned} RNH_2 &+ C_2H_2Br_4 \longrightarrow RNH_2.HBr + C_2HBr_3 \\ R_2NH &+ C_2H_2Br_4 \longrightarrow R_2NH.HBr + C_2HBr_3 \\ R_3N &+ C_2H_2Br_4 \longrightarrow R_3N.HBr + C_2HBr_3 \end{aligned}$$

The reactions were brought about in anhydrous ether, the salts of the respective bases being precipitated and the tribromethylene remaining in the ether solution. It was easily observed that the precipitations of the salts were accelerated by direct sunlight.[4] Solutions which remained clear in the dark were immediately precipitated by direct sunlight. These reactions were easy and quantitative and afford a convenient method of preparation not only of crystallized salts of the bases but also tribromethylene.[5]

In general aliphatic amines were more easily acted upon by tetrabromethane than the aromatic bases; primary amines were more easily acted upon than the secondary and the tertiary amines. Piperidine was almost instantaneously and quantitatively precipitated as the hydrobromide when treated with tetrabromethane, hence it is the most useful of all the bases to prepare tribromethylene from tetrabromethane.

Preparation of Tribromethylene.—A solution of tetrabromethane in dry ether is treated with piperidine as long as a precipitate forms. The

---

[1] *Chem. Z.*, **35**, 1125 (1911).

[2] *Z. angew. Chem.*, **23**, 2425–26. *C. A.*, **5**, 1347 (1911).

[3] Ells and Neuman studied the effect of ammonia, aniline and dimethyl aniline on tetrabromethane in alcoholic solution. They also obtained tribromethylane as the end-product. Ells, Neuman, *J. prakt. Chem.*, [2] **58**, 250.

[4] Compare Dehn and Dewey, THIS JOURNAL, **33**, 1588.

[5] See page 287. Also compare Lennox, *Ann.*, **122**, 125. Sabanejeu, *Ann.*, **178**, 122. Demole *Biol.*, **29**, 207. Dworkowitsch, *Ann.*, **216**, 280.