CCCLXXXI.—*The Estimation of Nicotine.*

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Many methods have been proposed from time to time for the estimation of nicotine in tobacco and tobacco extracts, of which only two, *viz.*, those of Kissling (*Z. anal. Chem.*, 1882, **21**, 64, 383; 1895, **34**, 413; 1896, **35**, 309, 731) and of Bertrand and Javillier (*Bull. Soc. chim.*, 1909, **5**, 241; *Ann. Chim. Anal.*, 1911, **16**, 251), appear to have been used at all extensively.

In Kissling's method the nicotine, liberated from the dried and powdered tobacco by alcoholic sodium hydroxide, is extracted by ether and the amount present is estimated, after removal of the ether and steam-distillation, by titration with sulphuric acid.

In Chapin's modification (U.S. Dept. Agric., Bull. 133 of 1911) of Bertrand and Javillier's method, the nicotine is extracted as in Kissling's process and then precipitated as the silicotungstate by addition of a 12% solution of silicotungstic acid to a solution of the nicotine acidified with dilute hydrochloric acid.

The estimation of nicotine has acquired an increasing importance of late years owing to the extensive use of preparations containing nicotine as insecticides, and also owing to the importance of a knowledge of the nicotine content of smoking tobaccos.

As a consequence, an inquiry into methods for the estimation of nicotine was instituted by the United States Department of Agriculture in 1910 (U.S. Dept. Agric., Chem. Div., Bull. No. 101 of

1910), as a result of which the procedure described by Kissling was recommended for adoption.

A very careful critical examination of all methods proposed up to that time was carried out by Rasmussen (*Z. anal. Chem.*, 1916, **55**, 81), who recommended as the best method precipitation by silicotungstic acid as in Bertrand and Javillier's method, but with a modified procedure for extraction.* Of other methods investigated, he concluded that only those of Kissling and of Koenig (*Chem. Ztg.*, 1911, **35**, 521, 1047) were trustworthy. Koenig's method, a polarimetric one, is only applicable to the estimation of nicotine in liquid extracts.

Kissling's method suffers from two main objections. First, any ammonia present in the tobacco, and any pyridine bases (frequently added to extracts as an adulterant) are estimated as nicotine; and secondly, the method sometimes fails to furnish concordant results in the hands of different chemists. Its chief advantage is that it can be carried out quickly.

Bertrand and Javillier's method gives uniformly accurate results, but is tedious to carry out, since the precipitated silicotungstate requires 10 or 12 hours to settle in a filterable condition.

The authors have recently shown (this vol., p. 1314) that nicotine readily yields a beautifully crystalline, stable and sparingly soluble tetrachloroiodide. By means of it nicotine can be easily and accurately estimated, since in presence of a large excess of hydrogen chloride it separates practically quantitatively, even from dilute solutions, as a heavy, bright yellow precipitate which can be collected on a Gooch crucible and dried without loss. Alternatively, the precipitate collected on the Gooch crucible may be added to an excess of a warm concentrated solution of potassium iodide acidified with acetic acid, and the iodine liberated estimated by sodium thiosulphate. Eight atoms of iodine are liberated by each molecule of nicotine tetrachloroiodide decomposed.

By means of the tetrachloroiodide nicotine can just be detected when present to the extent of only 1 part in 100,000 parts of water. It can be estimated accurately in solutions containing 1 part of nicotine in 5,000 parts of water, and with a very fair degree of accuracy in solutions containing 1 part in 10,000.

In this method the presence of ammonia is of no consequence,

* Bertrand and Javillier extracted the nicotine by heating the tobacco four times with ten times its weight of 5% hydrochloric acid at 100°. In Rasmussen's method of extraction the tobacco is mixed with a solution of sodium hydroxide in aqueous alcohol, ether and light petroleum, the flask being closed and shaken at intervals for about 5 hours. After filtration the extract is shaken with 1% hydrochloric acid, and the acid layer separated and treated with silicotungstic acid.

as ammonium tetrachloroiodide is soluble in water; and pyridine, if present, can be removed by a preliminary steam distillation of the tobacco extract after addition of acetic acid, the nicotine being completely retained by the acid (compare Rasmussen, *loc. cit.*).

EXPERIMENTAL.

For the estimation of nicotine in tobacco the following procedure gives accurate results.

The dried and powdered tobacco (20 g.) is ground with 10 c.c. of 55% alcohol containing 0·6 g. of sodium hydroxide, and extracted with ether in a Soxhlet apparatus until exhausted. The solvent is distilled off and the residue is mixed with 50 c.c. of 0·4% aqueous sodium hydroxide and steam-distilled, until about 400 c.c. have come over, or until the distillate no longer gives a precipitate with a solution of iodine trichloride in hydrochloric acid. The distillate is saturated with hydrogen chloride and cooled. To it is then added a solution made by saturating with chlorine a suspension of 2 g. of powdered iodine in 20 c.c. of hydrochloric acid. Nicotine tetrachloroiodide separates as a yellow microcrystalline powder which settles rapidly. A slow stream of chlorine is then passed through the mixture for a few minutes to saturate the solution with chlorine. This ensures the complete conversion of the nicotine into tetrachloroiodide. The precipitated nicotine tetrachloroiodide is collected on a tared Gooch crucible, washed with a little concentrated hydrochloric acid, and dried, until the weight is constant, in a vacuum desiccator over phosphoric oxide in presence of a few lumps of lime to absorb the hydrogen chloride adhering to the damp precipitate. Nicotine tetrachloroiodide contains 23·077% of nicotine.

The accuracy of the method may be judged from the following results.

0·0720 G. of nicotine, dissolved in 100 c.c. of concentrated hydrochloric acid (1 part in 1400 parts approx.) and treated with tetrachloroiodic acid made from 0·5 g. of iodine, yielded 0·3120 g. of nicotine tetrachloroiodide, corresponding to 0·0720 g. of nicotine.

0·2365 G. of nicotine, dissolved in 2½ litres of concentrated hydrochloric acid (1 part in 10,000 parts approx.) and treated with tetrachloroiodic acid made from 1 g. of iodine, yielded 1·2135 g. of nicotine tetrachloroiodide, corresponding to 0·2357 g. of nicotine.

To compare the accuracy of this method with that using silicotungstic acid, the percentage of nicotine in a sample of tobacco was determined by both, the following results being obtained: by silicotungstic acid, 2·28%; by tetrachloroiodic acid, 2·23%.

Estimation of Nicotine in Presence of Ammonia and Pyridine.—A solution was made containing 0·6180 g. of nicotine, 0·5 g. of

pyridine, and 1 c.c. of concentrated ammonia solution (*d* 0·880). This was mixed with 50 c.c. of 15% acetic acid and steam was blown through the mixture until a drop of the distillate after saturation with hydrogen chloride gave no precipitate with tetrachloroiodic acid solution, showing that all the pyridine had distilled over. By this time about 200 c.c. of distillate had been obtained. The contents of the distillation flask retaining the nicotine and ammonia were then saturated with hydrogen chloride and the nicotine was precipitated as previously described; 2·6810 g. of nicotine tetrachloroiodide were thus obtained, corresponding to 0·6190 g. of nicotine.

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