Letters to the Editor

On Tobacco Smoke

Mario Domingues de Campos has published a paper (*An. Fac. farm. odontol. Univ. São Paulo,* 1939–40, **1**, 15) on this subject which came to my attention only recently (*Chem. Abstr.,* 1945, **39**, 5395). He reports, apparently as his discovery, that pyrrole, pyridine, hydrocyanic acid, carbon monoxide, and carbon dioxide were found in tobacco smoke but that he has been unable to detect nicotine. These are statements which need some comment, for the presence of all these compounds, including nicotine, in tobacco smoke was detected a long time ago; in fact, quantitative determinations have already been made in all cases. Out of the long list of nicotine determinations in tobacco smoke only the paper by Barta and Toole (*Angew. Chem.,* 1932, **45**, 671) may be mentioned. They confirmed Lehmann's earlier findings (*Arch. Hig.,* 1909, **68**, 319) that, on the average, 93 per cent of the nicotine appears in the smoke while the rest suffers decomposition. Also, the quantity of hydrocyanic acid in the smoke has been determined repeatedly. Waser and Stähli (*Z. Unters. Lebensm.,* 1934, **67**, 280) confirmed Lehmann's earlier work, finding 0.020–0.0034 per cent of the tobacco weight as hydrocyanic acid in the main (interior) flow of smoke. It is worth noticing that the tobacco itself is free of hydrocyanic acid and that the quantity of the acid formed is independent of the nicotine content. Lehmann has also shown that tobacco smoke contains pyrrole. The writer (*Oesterr. Chem. Ztg.,* 1937, **40**, 434) has performed a series of quantitative determinations of pyrrole in tobacco smoke showing that the main flow contains 20–80 mg. per cent pyrrole. The quantity varies with the speed of smoking and increases with the humidity and the N-content of the tobacco but is independent of its nicotine content. This indicates clearly that pyrrole is not a decomposition product of the nicotine. It was concluded that it is formed by the thermal decomposition of the proteins of the tobacco, as Schützenberger and Bourgeois (*Bul. Soc. chim.,* 1876, 289) had observed this reaction in the case of the destructive distillation of isolated proteins. Also, the determination of pyridine bases in tobacco smoke has been dealt with in several papers; Preiss (*Pharm. Zentralhalle,* 1936, **29**, 437) has given a list of references.

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A Method for the Quantitative Estimation of DDT in Plant and/or Sulfur-containing Materials

The original dehydrohalogenation method (F. A. Gunther. *Ind. eng. Chem.* (Anal. ed.), 1945, **17**, 149–150) for DDT estimation may involve blanks considerably higher than the expected DDT residues and attributable to chloride-contaminated reagents and filter paper and to secondary effects of saponification, *i.e.* fatty acids responding to the silver titration. Sulfur also interferes, and since DDT-sulfur may become an important insecticide, this disadvantage may be serious.

If halogen-free reagents, removable by volatilization or by phase separation, could replace alcoholic potassium hydroxide, nitric acid, barium nitrate, etc., both the reagent and saponification blanks could be reduced. Reduction of reagent blank from 2 mg. to 0 mg. of DDT has been accomplished by substituting 4.5 N ammoniacal methanol as the dehydrohalogenating reagent, which eliminates the necessity for barium precipitation, reduces the amount of nitric acid for neutralization, and usually eliminates the problem of saponification products.

The procedure is adaptable to the determination of DDT in mixtures containing as much as 90 per cent sulfur.

Procedure. Weigh sufficient dry sample to contain 1 or more mg. of DDT, cover with measured amount of benzol, and set overnight. Pour off the extract through a double thickness of "Shark Skin" filter paper, measure the volume, transfer to an Erlenmeyer flask, and evaporate just to dryness as described by Gunther. Add 3 ml. of benzol to the residue with shaking, then 25 ml. of 4.5 N anhydrous ammoniacal methanol solution (for 125-ml. flask; use 50 ml. of reagent if flask is 500-ml. size), cap the flask with a collapsed finger stall, and hold for 16 hours in a 45° C. incubator.

Add 10 ml. of 3 per cent hydrogen peroxide solution and evaporate the ammonia and methanol, on a hot plate, with the aid of a jet of air. To residue add 40 ml. of distilled water and 1 ml. of 2 N nitric acid.

Remove sulfur not reacted with the ammonia solution by filtration (chloride-free paper). If noticeable oily material is present, transfer the sample to a separatory funnel and extract with 35 ml. of diethyl ether. Discard ether extract, and re-extract the aqueous layer with 35-ml. portions of petroleum ether until no more color is extracted.

Titrate chloride ion in the sample with 0.01 N silver nitrate and 0.01 N thiocyanate, according to Gunther, or by his procedure using the Leitz G & D Electro-titrator with 0.05 milliequivalent added sodium chloride present and deducted prior to the calculation which follows:

Each milliequivalent silver nitrate = 0.3545 grams of DDT.

Therefore:

(1) $[(\text{ml. } AgNO_3 \times N) - (\text{ml. KSCN} \times N)] \times 0.3545 =$ grams of DDT (gross)

(2) grams of DDT (gross) − blank (if present) = grams of DDT (net)

(3) $$\frac{\text{grams of DDT (net)} \times \text{total benzol volume} \times 10^6}{\text{volume filtered extract} \times \text{grams of sample}} =$$ DDT in ppm.

Known quantities from 0.002 to 0.184 gram of DDT, with or without sulfur present, carried through the entire procedure gave recoveries of 91–96 per cent, technical