The Determination of Propylene Glycol in Tobacco by Cellulose-column Chromatography

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The cellulose - carbon column method for the quantitative determination of glycerol in tobacco has been extended to the determination of propylene glycol, which is occasionally found in tobacco, either as the sole humectant or in small amounts associated with added glycerol. Glycerol and propylene glycol can both be accurately determinated in the presence of each other, in a single experiment.

In an earlier paper,[1] procedures were described for the qualitative and quantitative determination of glycerol in tobacco. In the course of the qualitative detection of glycerol, the presence of propylene glycol was occasionally clearly indicated, and in this paper an extension of the column method is described, so that propylene glycol detected by the paper-chromatographic procedure[1] can be accurately determined. In this paper, only modifications of the earlier procedure[1] will be described in any detail.

The first portion of eluate from the cellulose - carbon column contains all the propylene glycol, accompanied by a small portion of the glycerol (see Fig. 1).

The method developed is for determining propylene glycol and glycerol based on collection of the eluate in two portions; the propylene glycol and some of the glycerol are determined in the first portion, and the remainder of the glycerol in the second. When attempts to determine glycerol and propylene glycol in a single 500 ml of eluate were made, interference in the estimation of propylene glycol arose from the material responsible for the "apparent glycerol" blank value of the tobacco. In the proposed method, however, this interference becomes significant only in the second fraction, containing glycerol alone, and the added glycerol may be calculated by subtracting the appropriate "apparent glycerol" blank value for the unmanufactured tobacco; some experimentally determined blank values are listed in Table II of the earlier paper.[1] In addition, inaccuracies arose when a suitable portion of a single 500 ml of eluate was analysed for a small quantity of propylene glycol in the presence of a large excess of glycerol, since the determination of propylene glycol depended on a small difference between two larger titrations; this possible error is minimised when the first part of the eluate, containing a relatively small proportion of glycerol, is analysed separately for propylene glycol.

Experimental

Experiment has shown that the optimum conditions for accuracy require the collection of an initial 200 ml of eluate, followed by a further 400 ml. The glycerol content of the 200-ml portion increases with temperature; for example, it is approximately 10 per cent. of the total glycerol present at 15° C and 20 per cent. at 25° C.

The glycerol is determined in the 200-ml portion of the eluate in the presence of the propylene glycol, by making use of the fact that when glycerol is oxidised with periodate it yields formic acid (which can be titrated with alkali) and formaldehyde, but propylene glycol only yields aldehydes.[2,3] The propylene glycol content is determined by measuring the total periodate consumed, less that required to oxidise the glycerol; the glyercol in the 400-ml portion of eluate is most readily determined by measuring the total periodate used.

It is necessary to remove all the solvent from the eluate before oxidising the glycerol and subsequently determining the formic acid. The titration cannot be carried out in the presence of ether, which removes the indicator from the aqueous layer, and in the presence of alcohol low results are obtained. The solvents are most conveniently removed by evaporation on a steam-bath; no loss of glycerol occurs, and propylene glycol, which may be lost to some extent, is determined on a separate portion of eluate without removal of the solvent.

None of the many methods available[4 to 10] for determining glycerol by acidimetric titration of the formic acid produced by periodate oxidation proved entirely suitable; most were designed for amounts of glycerol greater than the milligram or less present in the eluate, and, for simplicity, a titration in which an indicator was used was preferred to an electrometric end-point measurement. Potassium periodate was used as the oxidant, and the amount of sulphuric acid added when preparing the solution was kept to a minimum to keep the blank value of the acidimetric titration as low as possible; this modification gave satisfactory results in the procedure for determining total periodate used. It is better

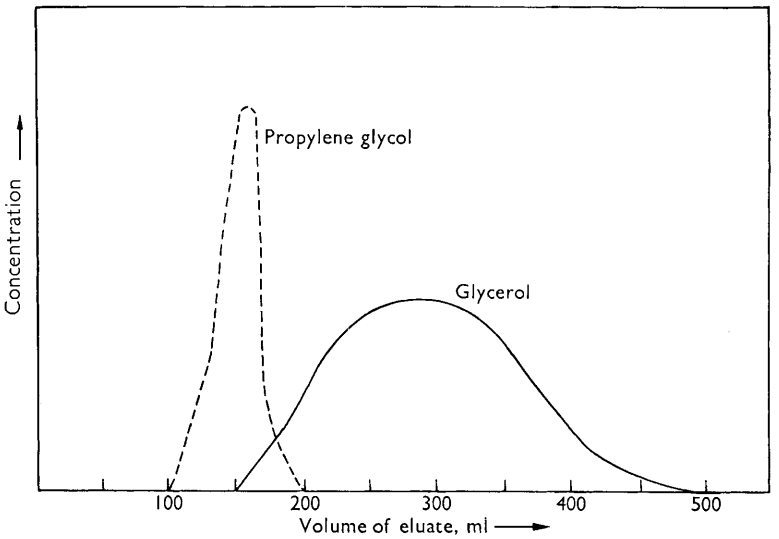

Fig. 1. Curve illustrating the recovery of propylene glycol and glycerol. (Column temperature, 17° C)

not to oxidise with neutral solutions as recommended by Neuburger and Bruening,[8] since neutral solutions prepared with the reagent we used (analytical-reagent grade potassium periodate) gave an inconvenient negative blank value. We tried bromocresol purple,[8] bromothymol blue,[5] phenol red[7] and methyl red[3] as indicators, and preferred bromocresol purple. The excess of periodate was destroyed with ethylene glycol, as recommended by Erskine, Strouts, Walley and Lazarus.[7]

Method

The preparation of the column, extraction of the sample and its transfer to the column are described in the previous paper.[1]

Additional reagents—

Potassium periodate solution—Dissolve 1·15 g of analytical-reagent grade potassium periodate in about 600 ml of hot water that has been boiled to expel carbon dioxide, cool, add 7 ml of 0·1 N sulphuric acid and dilute to 1 litre with carbon-dioxide-free water.

Sodium hydroxide solution, approximately 0·02 N—Prepare in carbon-dioxide-free water.
Sulphuric acid, 0·02 N.
Bromocresol purple solution, 0·1 *per cent. w/v in* 95 *per cent. ethanol.*
Ethylene glycol solution, approximately 10 *per cent. v/v, aqueous.*

Collection of the eluate from the column—

Collect the first 200 ml of eluate into a 200-ml graduated flask, and the next 400 ml of eluate into a 500-ml graduated flask containing initially 100 ml of solvent mixture.

Analysis of the first 200 ml of eluate—

To make the maximum use of this eluate, transfer by means of a pipette a further 2 ml of solvent mixture into the graduated flask, and thoroughly shake the flask. This facilitates duplicate determinations on 50-ml portions.

Determination of total periodate used—Transfer 50 ml of the eluate to a 500-ml conical flask fitted with a ground-glass socket, and proceed as directed under "Procedure for oxidising glycerol with periodate" in the earlier paper.[1] A sufficient excess of potassium periodate must be maintained; if the difference in titre between blank value and sample exceeds 4 ml, the oxidation should be repeated using a smaller portion of eluate.

Determination of glycerol—By pipette transfer 50 ml of the eluate (or a smaller portion, if this was necessary for determining the total periodate used) into a 250-ml beaker, add 70 ml of water, and evaporate on the steam-bath until approximately 25 ml of solution remain. Cool and transfer, with the aid of distilled water, to a 500-ml conical flask, fitted with a ground-glass socket, so that the final volume is approximately 100 ml. Add 1 ml of 0·02 N sulphuric acid, boil for 5 minutes, close the flask with a rubber stopper carrying a soda-lime guard tube and cool to room temperature. Add 0·2 ml of bromocresol purple solution, titrate with 0·02 N sodium hydroxide until the first distinct purple colour appears and add 25 ml of the potassium periodate solution from a pipette. Mix, close the flask with a glass stopper, and set aside in the dark at room temperature for 40 minutes. Add 0·5 ml of 10 per cent. ethylene glycol, mix, set aside for a further 20 minutes, and titrate with 0·02 N sodium hydroxide until the same distinct purple colour appears. Carry out a blank determination, at the same time, on 100 ml of water.

The sodium hydroxide solution should be standardised by titrating it against 0·02 N sulphuric acid with bromocresol purple as indicator.

If necessary, rinse down the flask during the titration with carbon-dioxide-free water that has been titrated with the sodium hydroxide solution until the first distinct purple colour appeared.

NOTES—

1. The solution obtained by simple evaporation of the eluate may occasionally be so cloudy that the end-point of the titration is obscured; this can be avoided by separating off the ether layer before evaporation: 50 ml of the eluate should be shaken with 50 ml of water, and then a further 15 ml of water, and the combined aqueous layers transferred to the 250-ml beaker and evaporated on a steam-bath before oxidation as described above.

2. The purple colour of the end-point changes fairly rapidly to a bluish-grey colour. A lasting purple end-point colour can be obtained, if preferred, by passing nitrogen into the flask during the titration; duplicate determinations, made in the presence and absence of nitrogen, were satisfactory, and detection of the end-point in the absence of nitrogen was not difficult.

ANALYSIS OF THE FINAL 400 ml OF ELUATE—

The glycerol in this solution is most conveniently determined on a 50-ml portion by the iodimetric procedure referred to above for determining total periodate used.

Calculation of glycerol and propylene glycol—

1 ml of 0·02 N sodium hydroxide ≡ 1·84 mg of glycerol.
1 ml of 0·05 N sodium thiosulphate ≡ 1·90 mg of propylene glycol or 1·15 mg of glycerol.

Example—

Determination made on 1 g of tobacco.

If V is the sodium hydroxide titre for 50 ml of the 200 ml eluate (diluted to 202 ml)

$$\text{Glycerol content} = 1{\cdot}84 \times \frac{202}{50} V \text{ mg in the 202 ml}$$

and sodium thiosulphate equivalent of the glycerol content of the 50 ml eluate $= \frac{1{\cdot}84}{1{\cdot}15} \times V$.

If v_1 is the sodium thiosulphate titre (blank titre *minus* sample titre) for 50 ml of the 202-ml eluate, the sodium thiosulphate equivalent of propylene glycol content in the 50 ml aliquot is given by—

$$v_1 - \frac{1{\cdot}84}{1{\cdot}15} \times V$$

$$\text{Propylene glycol content} = \left(v_1 - \frac{1{\cdot}84}{1{\cdot}15} V\right) \times 1{\cdot}90 \times \frac{202}{50} \times \frac{1}{10} \text{ per cent.}$$

If v_2 is the sodium thiosulphate titre (blank value) for 50 ml of the 400 ml eluate (diluted to 500 ml)—

$$\text{Glycerol content} = 1{\cdot}15\, v_2 \times 10 \text{ mg in the 500 ml}$$

$$\text{and} \quad \text{Total glycerol} = \left(11{\cdot}5\, v_2 + 1{\cdot}84 \times \frac{202}{50} V\right) \times \frac{1}{10} \text{ per cent.}$$

Added glycerol = total glycerol (per cent.) $- x$, where x is the blank value determined on unmanufactured tobacco of similar origin (see earlier paper[1]).

RECOVERY OF GLYCEROL AND PROPYLENE GLYCOL FROM TOBACCO—

Recovery experiments were carried out as described in the previous paper.[1] Accurately measured volumes of propylene glycol and glycerol solutions were added to 1 g of tobacco sample, and the glycerol and propylene glycol contents of the solutions were determined. The recoveries are shown in Table I.

TABLE I

RECOVERY OF GLYCEROL AND PROPYLENE GLYCOL FROM 1 g OF TOBACCO

Glycerol added, mg	Propylene glycol added, mg	Glycerol recovered,* mg	Propylene glycol recovered, mg
20	10	19	10
20	5	19	5
—	15	0	15
38	—	37	0
—	39	0	39

* Corrected by subtraction of the apparent glycerol blank value ≡ 2 mg

We thank the Government Chemist and the Department of Scientific and Industrial Research for permission to publish this paper.

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Received *June 5th*, 1963