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Separation and quantitative analysis of polyhydric alcohol humectants in tobacco products

Several approaches have been used in the investigation of polyhydric alcohols present in tobacco products. Chromatographic approaches have included column[2], paper[5,6], and thin-layer[10] chromatography. FRIEDMAN AND RAAB[3] used gas chromatography techniques on cigarette tobacco, extracting it with acetone and purifying the extract before attempting a separation by gas chromatography.

BALAKHONTSEVA AND POLTININA[1], and HOLLIS[4] have examined a number of pure glycols by gas chromatography using different liquid phases.

The polyhydric alcohols are polar, high-boiling compounds. These factors make them relatively unsuitable for gas chromatographic analysis. Their conversion to relatively volatile, non-polar derivatives is therefore desirable. PUSCHMAN AND MILLER[7] prepared acetate derivatives from the extracted glycols prior to gas chromatographic separation. SUFFIS *et al.*[8] have employed the method of SWEELY *et al.*[9] to form the trimethylsilyl ether derivatives of partial esters of some polyhydric alcohols.

This paper describes a method for the qualitative and quantitative analyses of polyhydric alcohols in tobacco products. A minimum of sample handling is required as derivative formation is simple, rapid and quantitative. Conditions for the chromatographic separation are moderate and result in symmetrical peaks, good separation and excellent reproducibility. Glycols up to tetraethylene glycol are eluted in less than twelve minutes, with no interference from the sugars which may be present in the tobacco products.

Apparatus

A Beckman Model GC-5 gas chromatograph equipped with a thermal conductivity detector and temperature programming was used. The chromatographic columns were 6 ft. 1/8 in. O.D , stainless steel, filled with 3% SE-30 on 42/60 mesh Chromasorb G.

Chromatographic conditions were:

Carrier gas: helium

Flow rate: 60 ml/min at 65°

Column temperature: 65° for 2.5 min, then programmed to 180° at 13°/min

Detector temperature: 200°

Detector current: 300 mA

Inlet temperature: 200°

Line temperature: 300°

The trimethylsilylation reagent used was Tri-Sil, obtained from Pierce Chemical Company.

Approximately 4 g of the tobacco product was weighed to the nearest milligram in a tared extraction thimble. The sample was extracted in a Soxhlet apparatus with 250 ml of methanol for at least 5 h. The methanol solution was transferred quantitatively to a 250 ml volumetric flask and made up to volume. Five milliliters of this solution was pipetted into a glass vial, and the methanol evaporated by a dry nitrogen stream at room temperature. The vial was removed from contact with the nitrogen stream

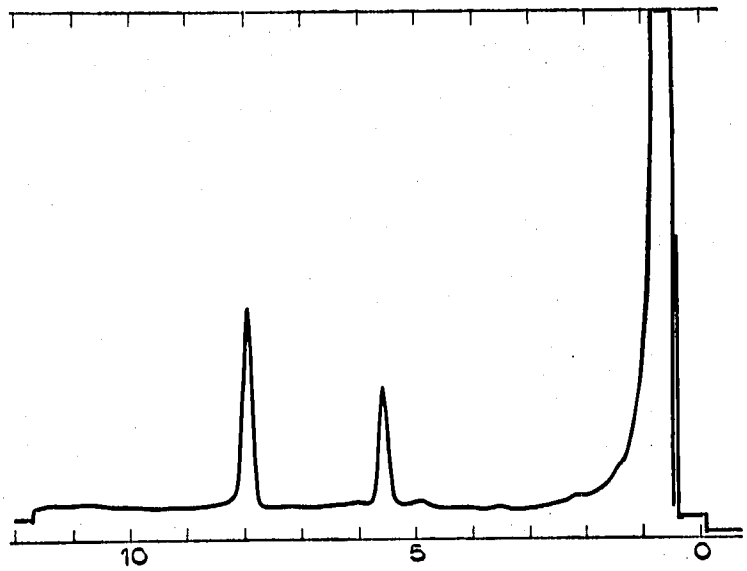

Fig. 1. Separation of trimethylsilyl ethers of glycols extracted from reconstituted tobacco sheet. Retention times: glycerine 5.5 min, triethylene glycol 8.0 min.

as soon as the evaporation was complete. One milliliter of the Tri-Sil reagent was added, the vial capped and shaken to disperse the contents.

Two microliters of this solution was injected into the gas chromatograph. Elution times were used for identification of the various glycol derivatives. The peak areas were measured by planimeter.

Results and discussion

A typical chromatograph of an extract, obtained from a commercial reconstituted tobacco sheet, is shown in Fig. 1. An example of the separation of glycol derivatives that can be made is shown in Fig. 2.

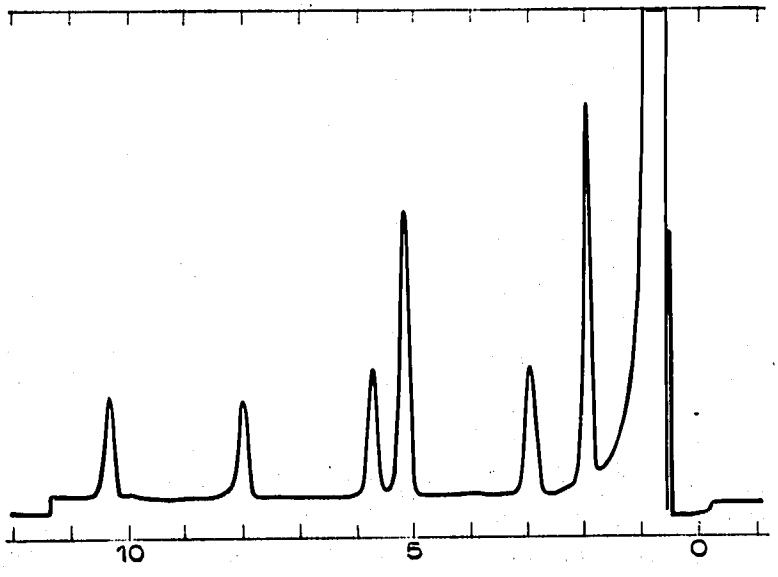

Fig. 2. Separation of trimethylsilyl ethers of pure glycols. Retention time (min): Propylene glycol, 2.0; 1,3-butylene glycol, 3.0; diethylene glycol, 5.0; glycerine, 5.5; triethylene glycol, 8.0; tetraethylene glycol, 10.5.

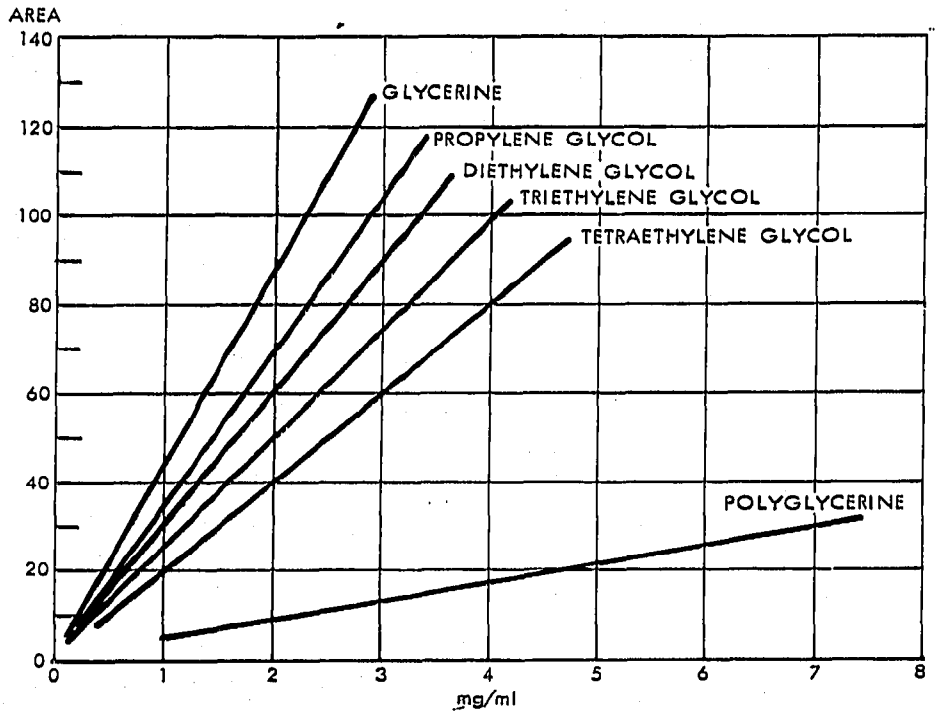

Fig. 3. Calibration curves of polyols. Concentration *versus* peak area.

Methanol solutions of pure polyhydric alcohols were prepared and then aliquots were evaporated, derivatized, and chromatographed. Calibration curves of polyol concentration *versus* peak area are shown in Fig. 3.

The reproducibility of the analysis was tested by examining ten samples of one type of commercial reconstituted tobacco sheet containing added tetraethylene glycol. The average value obtained for the tetraethylene glycol content was 4.98%. The highest value was 5.20%, the lowest 4.71%. The average deviation from the mean was $\pm$0.10 for these ten samples.

TABLE I

RECOVERY OF ADDED POLYOLS

Sample	*Tobacco sheet type*	*Dry wt.*	*Originally present (mg)*	*Humectant added*	*Added (mg)*	*Found (mg)*	*Recovery (%)*
11	A	4.06	203	TEG*	118	326	104
12	A	4.36	218	TEG	118	341	104
13	F	3.88	198	PG**	278	490	106
14	F	3.83	196	PG	278	490	106
15	A	4.00	—	Glycerine	114	108	95
16	A	4.22	—	Glycerine	114	112	98
17	A	4.13	—	TriEG***	132	138	104
18	A	4.03	—	TriEG	132	138	104

* TEG Tetraethylene glycol.
** PG = Polyglycerine.
*** TriEG = Triethylene glycol.

In order to test the completeness of the extraction, known amounts of polyols were added to the tobacco product, as well as to tobacco products containing no polyol or a different polyol than the original humectant. The recovery of added glycol varied from 95–106%. The data are shown in Table I.

Several control tobacco products (known to be free of added polyols) were also subjected to the procedure. No interfering bands appeared on the chromatograms.

Polyglycerine showed only two significant bands using this procedure. The major band was identified as glycerine, and this glycerine band was used for the quantitative estimation. The second peak was not identified, but eluted directly after the peak assigned to the tetraethylene glycol derivative.

Table II shows the results obtained from the analysis of cigarette tobacco, reconstituted cigar wrapper and cigar binder, and several other reconstituted tobacco products. Samples 19 and 20 were run on a smaller scale, dividing the tobacco from one

TABLE II

EXAMINATION OF COMMERCIAL PRODUCTS

Sample	*Tobacco type*	*Propylene glycol*	*Percentages found*			
			1,3-Butylene glycol	*Diethylene glycol*	*Glycerine*	*Triethylene glycol*
19	non-filter cigarette	1.15	—	—	2.36	1.09
20	non-filter cigarette	1.21	—	—	2.36	1.03
21	filter cigarette	1.13	—	—	1.38	1.26
22	filter cigarette	1.13	—	—	1.37	1.32
23	cigar wrapper	—	—	—	0.82	2.19
24	cigar binder	—	—	—	—	2.76
25	"B"	—	—	—	4.18	—
26	"B"	—	—	—	4.28	—
27	"C"	—	—	—	—	1.89
28	"C"	—	—	—	—	1.83
29	"D"	—	—	3.09	—	—
30	"D"	—	—	2.84	—	—
31	"D"	—	—	3.37	—	—
32	"E"	—	2.70	—	—	—
33	"E"	—	2.50	—	—	—

non-filter cigarette into two parts for extraction. This was repeated with the tobacco from a filter cigarette to obtain samples 21 and 22. Samples 23 and 24 were obtained by stripping the reconstituted wrapper and binder from commercially available cigars. Samples 25–33 are commercial reconstituted tobacco sheets containing various polyol humectants.

The small samples were extracted with a micro Soxhlet apparatus, diluting the final extracting medium to a volume proportional to the dilution specified previously.

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