DIFFERENTIATION OF PEATED AND UNPEATED DISTILLING MALT BY G.L.C. ANALYSIS

By A. G. Taylor

(*Moray Firth Maltings Ltd., Elliot Industrial Estate, Arbroath*)

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Difficulty may occur in trying to distinguish unpeated malt from lightly peated malt by colourimetric analytical methods. This paper outlines a prospective method using gas chromatography following a selective extraction of volatiles from the malt. This method is discussed in relation to previous published methods used in the identification of peated export malts.

Key words: *Analysis, gas chromatography, malt, phenol.*

Introduction

Difficulty may be experienced when exporting peated distilling malt from Britain, due to delays in acceptance by some Overseas Departments of Customs and Excise. Analysis is carried out in these countries to verify that the malt is not liable for the duty payable on imported brewing malts Disputes can occur when the malt is only lightly peated and present colourimetric and gas chromatographic techniques cannot reliably distinguish between the peated and unpeated samples.

In the hope of speeding the passage of malt through these tariff restrictions, a system of gas chromatographic analysis has been investigated in accordance with the methods of Deki and Yashimura (2) and Deki (3) which are presently used by the Japanese Department of Customs and Excise. It was intended that a certified gas chromatogram of the malt phenols could then be despatched with the sealed malt cargo.

In carrying out this analytical procedure, a different interpretation of the results has arisen. These are discussed in this paper along with other methods which could form the basis of a suitable alternative procedure.

Experimental

Malt Samples.—All the samples of malt used in this work were production samples of unpeated malt and peated malt from Moray Firth Maltings Ltd.

Preparation of Malt Extract for Gas Chromatographic Analysis.—500g of malt was steam distilled under a stream of nitrogen gas. The distillate was collected at room temperature then saturated with 80 g of sodium chloride and extracted with 200 ml of diethyl ether. The ether layer was retained and extracted twice with 100 ml of 5% sodium bicarbonate solution. The ether layer was then washed twice more with 100 ml 2N hydrochloric acid.

The ether layer now freed of acids and bases, was extracted with two successive portions of 100 ml of 1N sodium hydroxide solution. The alkaline solution was separated and retained and the pH adjusted to <7·0 with 2N hydrochloric acid. 80g of sodium chloride were added and the solution extracted with 200 ml of diethyl ether. This ether solution of phenolic components was then concentrated by distillation at atmospheric pressure and 35°C till the residual volume of the ether was 1 ml.

Gas Liquid Chromatography:

A Perkin Elmer F33 programmable instrument, fitted with ¼" glass columns and flame ionization detectors, was used. The carrier gas was nitrogen.

The various columns used were:

(*a*) 5% polyethylene glycol 20M coated on 80–100 mesh chromasorb GAW.

(*b*) 5% Di—(3,3,5—trimethylcyclohexyl)—o-phthalate coated on chromasorb GAW DMCS, 80–100 mesh.

(*c*) 0·1% SP1000 coated on 80–100 mesh Carbopack C.

The operating conditions are given in Table 1.

TABLE I. GLC Operating Conditions.

Column	5% PEG	5% di-TCHP	0·1% SP 1000
Temperatures			
Injector/Detector	225°C	225°C	250°C
Column Initial	80°C for zero initial time	120°C isothermal	200°C isothermal
Programmed	5°C/min		
Final	250°C		
Gases			
Nitrogen	60ml/min	60ml/min	20ml/min
Hydrogen	17 psi	17 psi	17 psi
Air	25 psi	25 psi	25 psi
Column Length	3 metres	2 metres	2 metres

Results and Discussion

The phenolic extracts of the malts were all prepared by steam distillation followed by extraction with ether, washing with sodium bicarbonate and hydrochloric acid, removal of the phenolic fraction with sodium hydroxide and subsequent neutralization and re-extraction with ether. The ether extract was finally concentrated by distillation at 35°C and atmospheric pressure to 1 ml.

The extracts were initially analysed using columns (as used by the Japanese workers) packed with 5% polyethylene glycol (PEG) 20M coated on 80–100 mesh chromasorb GAW. It was at this point that the results differed from those of Deki and Yashimura (2) on whose work the method had been based.

Although the chromatograms (Figs 1, 2) looked very similar to that produced by Deki and Yashimura (ref 2, p. 1750) they differed in the resolution of the peaks used to determine the ratio of phenol to 4-ethylphenol. The latter ratio was used by the above authors to determine whether the malt was peated or unpeated, since they assumed that 4-ethylphenol was present in approximately the same concentration in both peated and unpeated malt. The above authors also claimed that phenol and o-cresol were well resolved, but the peak in their chromatogram which was claimed to be o-cresol, was (in the present work (Figs 1,2)) a mixture of m-cresol and p-cresol.

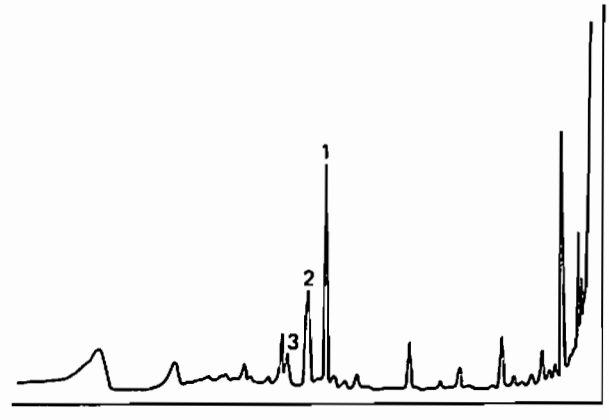

Fig. 1. GLC trace of extract of lightly peated malt on PEG column. (1) phenol + o-cresol, (2) m-cresol + p-cresol, (3) 4-ethylphenol + unknown.

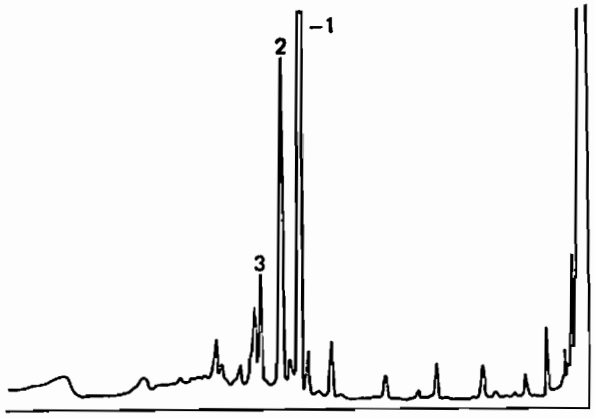

Fig. 2. GLC trace of extract of heavily peated malt on PEG column. (1) phenol + o-cresol, (2) m-cresol + p-cresol, (3) 4-ethylphenol + unknown.

The o-cresol peak was, in fact, coincident with the phenol peak.

Chromatograms obtained by other workers (4) (who have used a similar column), also show one peak for phenol and o-cresol, one peak for m-cresol and p-cresol and one standard peak for 4-ethylphenol. Due to the occurrence of these double peaks and the difficulties in interpreting the results, the same malt extracts were analysed on a column which had previously given good resolution of phenol, o-cresol and 4-ethylphenol (1) (Figs. 3,4). The packing in this column was 5% di-(3,3,5-trimethylcyclohexyl)-o-phthalate (di-TCHP) on chromasorb-GAW DMCS 80–100 mesh. The operating conditions are given in Table I. The ratio of phenol to 4-ethylphenol had now increased considerably, despite the fact that the o-cresol was no longer included in the ratio as in the previous chromatograms. To confirm that no thermal decomposition had occurred, a standard mixture of phenol, o-cresol and 4-ethylphenol was run on both columns. The ratios from each were similar (Table II). From this, it can be inferred that the

TABLE II. Ratio of Standard Mixture of phenol, o-cresol and 4-ethylphenol.

	Carbowax	Phthalate
Ratio of phenol + o-cresol 4-ethylphenol	0·77:1	0·78:1

4-ethylphenol peak was also unresolved when using PEG columns. Some 40–60% of this fraction was not therefore 4-ethylphenol but some other component from the peat smoke

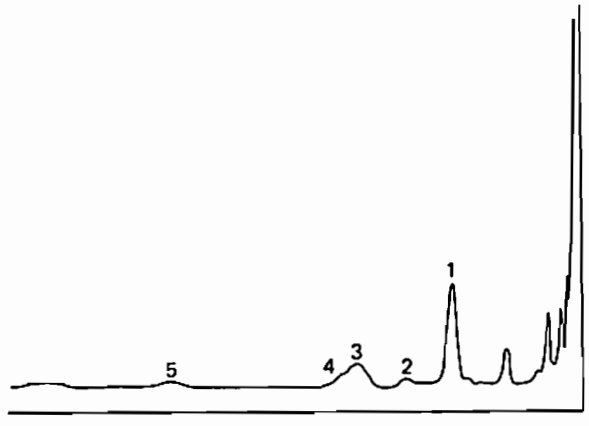

Fig. 3. GLC trace of extract of lightly peated malt on di-TCHP column. (1) phenol, (2) o-cresol, (3) p-cresol, (4) m-cresol, (5) 4-ethylphenol.

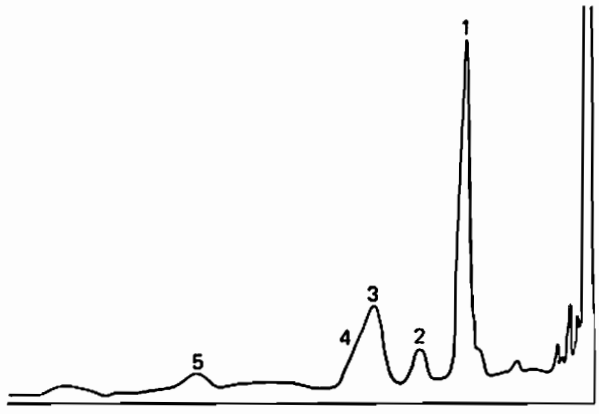

Fig. 4. GLC trace of extract of heavily peated malt on di-TCHP column. (1) phenol, (2) o-cresol, (3) p-cresol, (4) m-cresol, (5) 4-ethylphenol.

and hence this peak is not suitable as a calibration standard when using PEG columns.

It was therefore decided to use a chromatographic column which gives a better resolution of m-cresol and p-cresol. A suitable material is graphitized carbon black modified with carbowax 20M and terephthalic acid, (0·1% SP1000 coated on Carbopack C 80–100 mesh). A typical separation of phenol, o-cresol, m-cresol, p-cresol and 4-ethylphenol using this column is shown in Fig 5. The operating conditions were as shown in

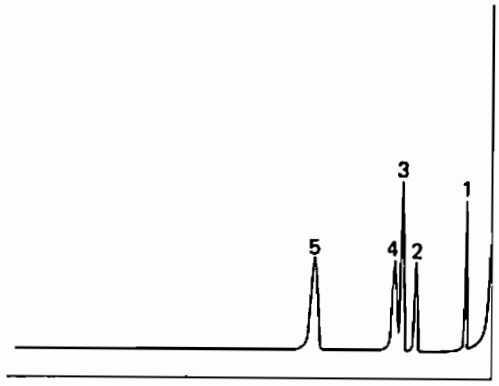

Fig. 5. GLC trace showing separation of mixture of phenols using a column of 0·1% SP1000 on Carbopack C. (1) phenol, (2) o-cresol, (3) m-cresol, (4) p-cresol, (5) 4-ethylphenol.

Table I. This column also has the added advantage of having no overlap in the order of elution of the methylphenols, the ethylphenols and the dimethylphenols. It was felt that the selection of a peak already present in the chromatogram as a standard was ill advised and that an internal standard should be introduced before steam distillation. Tentatively p-chlorophenol has been selected as an internal standard. Although not perfectly resolved from the 4-ethylphenol, it is the most suitable marker presently available. Other possible compounds are still being investigated.

Results obtained to date using the graphitized carbon with 0·1% SP 1000 column and p-chlorophenol as internal standard are encouraging and so far little difficulty has been found in distinguishing between peated and unpeated samples of malt. The amount of p-chlorophenol being used at present is 200 μl of 1·000% w/v solution in ethanol for a 500 g malt sample.

Typical chromatograms are illustrated in Fig 6, 7 & 8 and relative ratios of phenolic constituents are shown in Table IV.

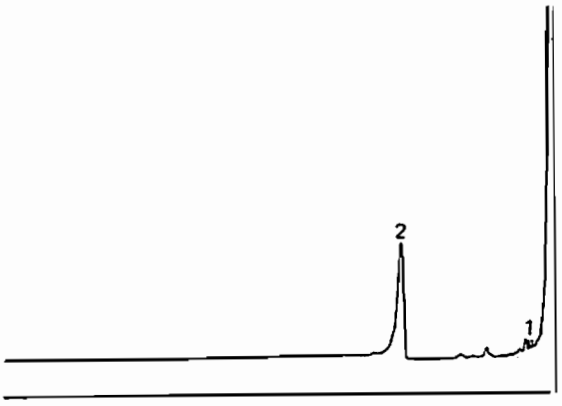

Fig. 6. GLC trace of extract of unpeated malt with internal standard using a column of 0·1% SP 1000 on Carbopack C. (1) phenol, (2) p-chlorophenol.

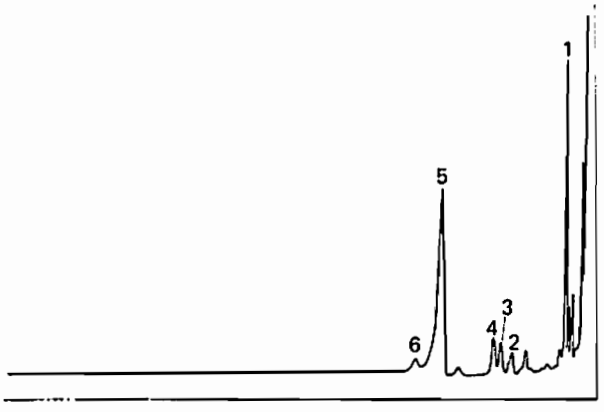

Fig. 7. GLC trace of lightly peated malt with internal standard using a column of 0·1% SP 1000 on Carbopack C. (1) phenol, (2) o-cresol (3) m-cresol (4) p-cresol, (5) p-chlorophenol, (6) 4-ethylphenol.

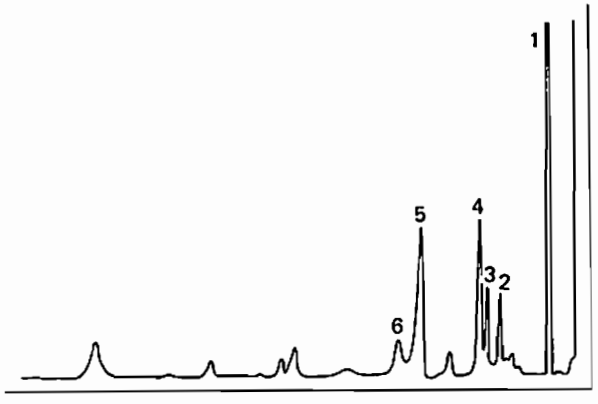

Fig. 8. GLC trace of heavily peated malt with internal standard using a column of 0·1% SP 1000 on Carbopack C. (1) phenol, (2) o-cresol, (3) m-cresol, (4) p-cresol, (5) p-chlorophenol, (6) 4-ethylphenol.

These chromatograms now clearly differentiate between lightly and heavily peated samples (*cf* Tables III and IV).

TABLE III. Ratios of phenol, o-cresol to 4-ethylphenol.

	Lightly peated	Heavily peated
Using carbowax columns Phenol + o-cresol: 4-ethylphenol	7·7:1	7·8:1
Using Phthalate column Phenol: 4-ethylphenol	12·9:1	17·2:1
Phenol + o-cresol: 4-ethylphenol	14·2:1	19·2:1

TABLE IV. Ratios of Phenolic Compounds to the p-chlorophenol Internal Standard using the 0·1% SP 1000 Column (ref figs. 6,7,8).

Malt sample	Phenol	o-Cresol	m-Cresol	p-Cresol	4-Ethylphenol
Unpeated	0·04	—	—	—	—
Lightly peated	0·39	0·08	0·19	0·21	0·06
Heavily peated	1·86	0·19	0·24	0·53	0·17

Preliminary work shows a good degree of reproducibility for this method of analysis. Figures are given in Table V showing triplicate analysis of samples of a batch of heavily peated malt. The values given are the ratio of each component measured relative to the internal standard, p-chlorophenol.

TABLE V. Ratios showing Reproducibility of Analysis.

Analysis	Phenol	o-Cresol	m-Cresol	p-Cresol	4-Ethylphenol
1	1·87	0·23	0·24	0·56	0·18
2	1·86	0·19	0·24	0·53	0·19
3	1·66	0·25	0·25	0·56	0·16

Work is continuing to assess this method as a standard, quantitative analysis, of peat smoke on malt.

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