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# THE QUALITATIVE AND QUANTITATIVE MEASUREMENT OF PEAT SMOKE ON DISTILLER'S MALT*

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**In the course of developing a novel peating process it became apparent that the present methods for determining the intensity of peat smoke on distiller's malt are inadequate. While the colorimetric test for peat phenols is fairly accurate at low levels, it can give misleading results with highly peated malts. Furthermore, the 4-aminophenazone reagent used in this test is not sensitive to some of the major phenol constituents of peat smoke. New qualitative gas chromatographic techniques, which monitor a wider spectrum of peat smoke constituents, are now presented together with some suggested improvements to the existing quantitative colorometric analysis.**

Keywords: *analysis, malt, phenol, spirits.*

## Introduction

The traditional process for drying malt used in the production of malt whisky is to use a peat fired kiln with natural air draught. In this way a high ratio of peat smoke to drying air is achieved and hence a highly aromatic malt is produced. In more modern plant using kiln fans, with oil or natural gas as the kiln fuel, the peating process is somewhat different. In most cases the suction from the kiln fans is used to draw air through a secondary peat-furnace which is allowed to smoulder and arbitrarily produce the maximum amount of smoke. In such cases the ratio of smoke to air is somewhat lower than in the traditional process.

In looking at methods of increasing the ratio of peat smoke, it is necessary to have some means of assessing the degree of peating both in a qualitative sense (i.e. in appearance, aroma and flavour of the malt) and in a quantitative sense (i.e. in assessing the amount of peat essences adsorbed on to the malt). In the latter case it is now generally accepted that the intensity of adsorbed peat smoke on malt is directly proportional to the detected levels of simple phenolic substances, such as phenol itself, cresols, xylenols, and guiacol.[7,9] It is certainly true that phenol and some related phenolics are the most distinctive 'marker' compounds in peated malt, since virtually no such compounds can be washed from the husk of unpeated malt. They are not, however, the only constituents of peat smoke. For example, some 80 aroma components have been reported in peated malt,[4] ranging from simple hydrocarbon tars to complex heterocyclic compounds, and, while phenols have been implicated in whisky flavour,[11,12] it is still not certain that the phenolic constituents are the principal contributors to the characteristic flavour of peated malt whiskies. Indeed, the flavour threshold of phenol may be somewhat higher than the normal concentrations of phenols in malt whisky,[1,5,10] although the aroma potential of some other phenols, particularly p-cresol and guiacol, may be greater.[15,16]

Nevertheless, for the purposes of commercial transactions, the concentration of phenol in peated malts has now become the accepted measure of the degree of peating and it is important to have methods for accurately measuring phenol over a wide range of concentrations. It is also important to have methods to assess the quality of peat essences, so that no imbalances of aroma and flavour are created at the expense of other peat constituents. We have, therefore, investigated the analysis of peated malts both by gas liquid chromatography and by colorometric analysis and, in this paper, we discuss the significance of our findings.

* Text of a paper read to a symposium on Whisky Flavour at Inverness Technical College on 28th May 1976.

## Experimental

*Peated Malts.*—Distillers' malts, with varying applications of peat smoke, were random standard production samples from Moray Firth Maltings Ltd. Those samples which were subjected to peat smoke from pyrolysed and partially steam distilled peat were kilned using a prototype peat furnace[14] (see Appendix 1).

Samples of malt which were treated with pure phenol were sprayed evenly with phenol dissolved in the minimum volume of ethanol. The spraying was carried out in a large polythene bag, which was then sealed to prevent evaporation. When the phenol had been totally absorbed by the malt, the samples were transferred to bottles and securely stoppered. Although some evaporation inevitably took place, this was kept to a minimum by carrying out the spraying and the equilibration within the confines of the polythene bag. Malts which were treated with aqueous solutions of peat smoke condensate[4,7] were prepared in a similar manner to those sprayed with solutions of phenol.

*4-Aminophenazone Reagent.*—Malt samples (20 g) were washed with 100-ml aliquots of acidified ether, according to the method of McFarlane.[7] The ether extraction was performed for 30 min with occasional manual shaking. Portions of 25 ml were then subjected to solvent exchange with an aqueous solution consisting of 10 ml of 15% ammonia, 2 ml of 0·3% 4-aminophenazone and 2 ml of 2% potassium ferricyanide. These solutions were shaken for one min and the aqueous layer was allowed to settle for precisely 10 min. The optical density of the aqueous phase was then measured at 460 nm. or in an EEL Colorimeter (Filter No. 623) and the phenol concentration calculated by means of a calibration against a standard phenol solution.

Phenol (AnalaR grade) was standardized by titration,[6] after bromination and exchanging excess free bromine with iodine. Phenol (1 g) was dissolved in 1 litre of water and 50 ml was pipetted into a stoppered 500-ml flask. Distilled water (100 ml) and bromate-bromide reagent (2·784 g potassium bromate and 10 g potassium bromide diluted to 1 litre; 10 ml) were added, and the mixture acidified with 5 ml concentrated hydrochloric acid. Further 10-ml portions of bromate-bromide reagent were added until the brown colour of free bromine persisted. The flask was stoppered and allowed to stand for 10 min and then potassium iodide (1 g) was added. The free iodine was titrated with 0·024-N sodium thiosulphate. A blank solution was similarly titrated and the bromine consumption and hence the phenol concentration was calculated by back titration.

*Preparation of Malt Extract for Chromatographic Analysis.*—One kilogram of the malt sample was steam distilled to obtain 250 ml of distillate. 50 ml of diethyl ether (chromatography grade) and 125 g sodium chloride (AnalaR) were then added to the distillate in a separating funnel and

shaken for 10 min. The aqueous and ether layers were separated after a 15-min stand.

The ether layer was dried with 20 g anhydrous magnesium sulphate and filtered through a sintered glass funnel. The magnesium sulphate was washed twice with 5 ml ether, and the washings were added to the ether solution. The ether was then cooled in liquid nitrogen, and the volume reduced, under vacuum, to just less than 1 ml, with the temperature at all times less than 0°C to prevent evaporation of volatile aroma constituents. The mixture was then allowed to warm to room temperature (at atmospheric pressure). Any solid precipitate was re-dissolved and made up to 1 ml in a volumetric flask. This solution was used for application to the chromatograph.

*Gas Liquid Chromatography.*—The gas chromatograph used was a Perkin Elmer Model F33 programmable unit fitted with stainless-steel columns and flame ionization detectors. The carrier gas was nitrogen. For the separation into groups of hydrocarbons, aldehydes and phenols, two balanced columns packed with 10% Carbowax 20M on Chromosorb W were used and for the specific separation of phenols, columns packed with 5% di-(3, 3, 5 trimethyl cyclo-hexyl)-o-phthalate (di-TCHP) on Chromosorb W were employed. The operating conditions are given in Table I.

TABLE I. G.L.C. Operating Conditions

| | Carbowax column | 5% di-TCHP column |
|---|---|---|
| *Gas Pressures* | | |
| Nitrogen | 25 lb/sq in. | 40 lb/sq in. |
| Hydrogen | 17 ,, | 17 ,, |
| Air | 25 ,, | 25 ,, |
| *Temperatures* | | |
| Injector/Detector | 225°C | 225°C |
| Column Initial | 80°C for 10 minutes | 120°C isothermal |
| Programmed | 5°C/min. | |
| Final | 200°C for 60 mins. | |

## Results and Discussion

A new procedure for applying peat smoke to distiller's malts has recently been developed in these laboratories. This technique is based on partially pyrolysing and steam distilling peat on a moving chain grate[14] (Appendix 1). In the course of analysing these malts for the intensity of application, and also in the routine analyses of conventionally peated malts, it became apparent that the method usually adopted for the determination of peat smoke[7] is not entirely satisfactory. For example, the measurement of phenol as a reference marker assumes that all other constituents are present in consistent proportions. Thus, in developing new peating techniques we may inadvertently optimize the production of phenol while other constituents are diminished. For this reason, the use of GLC was adopted so that a broader spectrum of reference compounds could be used to evaluate the peating process and to ensure that no anomalous products were being applied by changes in the way the peat smoke was produced.

The analytical technique which was eventually adopted involved the steam distillation of the malt followed by extraction of the distilled material into ether. After concentration, at low temperature, the ether solution was injected into a Carbowax column as described above. Typical chromatograms obtained from distillates of peated and unpeated malts are shown in Fig. 1. The unpeated sample (Fig. 1a) contained a large number of volatile constituents which have not been positively identified. However, the fingerprint or profile of these components was consistent over a number

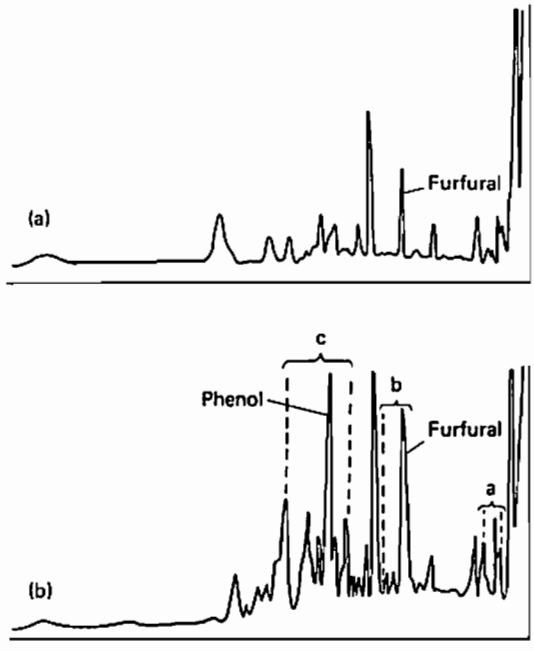


Fig. 1. (*a*) GLC trace (Carbowax column) of steam distillate from unpeated malt.
(*b*) GLC trace (Carbowax column) of distillate from commercial peated malt.
Note: Peaks in brackets are (a) hydrocarbons, (b) furfurals and (c) phenols. These either enhance existing peaks (e.g. furfural) or are new peaks (e.g. phenol).

of chromatograms. When compared with chromatograms from peated malts, (Fig. 1b) it is obvious that the peat smoke superimposes three new families of aroma constituents. These have been partially identified as being: (a) simple hydrocarbons and related tar-like material[9]; (b) a number of compounds related to furfural[10] and (c) the phenols.[4,9,10] Over a number of GLC analyses it was found that the ratio of these smoke constituents is fairly constant for individual kilns, so that a template or fingerprint of a peated malt can be derived. Chromatograms of distillate from malts treated in the new peating processess are shown in Fig. 2 and are, again, almost identical to the control template. Indeed, it was found that malts from a number of maltings, including several with direct peat-fired kilns, were qualitatively similar although the relative intensities of the different constituents varied slightly. In contrast to these results, a chromatograph of a sample treated with a condensate[7] of peat smoke is shown in Fig. 3. While the concentration of phenol constituents in this sample was very high, the relative amount of furfurals was small and there were virtually no tar components present. Also, the amount of phenol, relative to the background basic malt aroma, was completely out of proportion when compared with Fig. 1. This latter example,

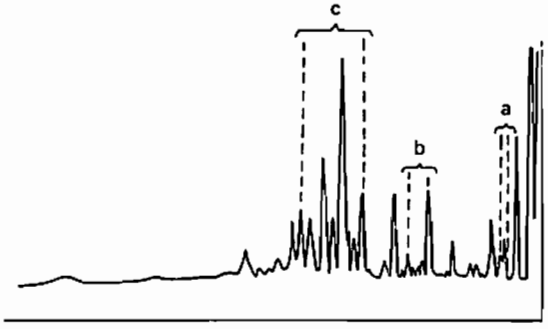


Fig. 2. GLC trace (Carbowax column) of steam distillate of malt peated using prototype peat furnace showing similar pattern to Fig. 1(b).

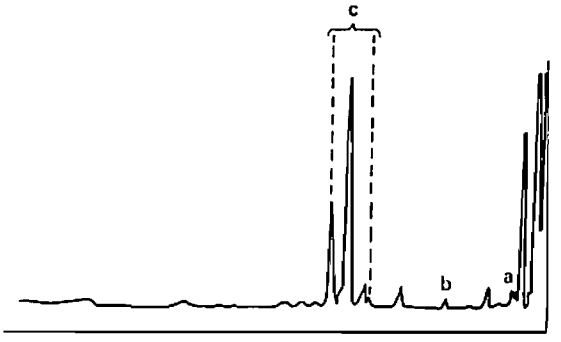


Fig. 3. GLC trace (Carbowax column) of steam distillate of malt which had previously been sprayed with commercial peat smoke condensate.
Note: Disproportion of phenol peaks (c) to each other and to background malt profile. Also virtual absence of furfurals (b) and hydrocarbons (a).

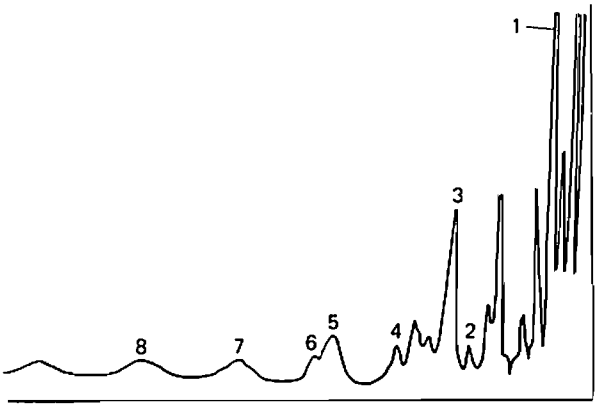


Fig. 4. High resolution G.L.C. trace (Di-TCHP column) of phenols steam distilled from peated malt.
Tentative identity of peaks: (1) Furfural; (2) Guiacol: (3) Phenol; (4) O-Cresol; (5) p-Cresol; (6) m-Cresol; (7) 2,5-Xylenol; (8) p-Ethyl phenol.

therefore, illustrates how misleading a simple phenol determination can be in assessing the adsorption of peat smoke on malt.

Nevertheless, the chromatograms in Figs. 1–3 do show how distinctive the phenols are in the spectrum of aroma compounds in peated malts. While the furfural peak is also distinctive, it must be remembered that unpeated malt also contains this compound which is presumably formed by the breakdown of husk pentosan during kilning.[2] Likewise on burning peat, the cellulose fibre follows a similar breakdown so enhancing this particular family of compounds in the GLC trace. The third group, which we have tentatively identified as hydrocarbons, displayed the greatest variation in concentration from batch to batch, possibly depending on the amounts of tar condensing from the peat smoke. Unpeated malts also produce peaks in this highly volatile area, adjacent to the solvent front. The latter traces can possibly be ascribed to volatile fats and lipids from the malt husks.

Apart from these major constituents of peat smoke, there are undoubtedly many other components[1,4,9,10,11,12,15,16] which have not shown up on these chromatograms. Flavour and aroma are such difficult things to quantify[3] that we should not ignore these minor components since the chemoreceptors of the nose and tongue do not necessarily respond to the obvious. Therefore, while phenols are present in peated malt in several parts per million, their aroma and flavour in malt whisky may be completely outweighed by a minor component of peat smoke perhaps only present in parts per billion. The ideal analysis of peated malts should, therefore, involve the analyses of only those constituents which positively contribute to the flavour of the final product. Unfortunately, such information is not readily available and, until such time, it would appear that phenol analysis will continue. For this reason GLC techniques which give high resolution of phenols have been investigated (Fig. 4). Using a column of 5% Di-(3,3,5-trimethylcyclohexyl)-O-phthalate, the main constituents (phenol, O-, m- and p- cresol, guiacol and possibly a number of isomers of xylenol) have been resolved. After phenol itself, the next most prominent phenolic is p-cresol. Estimates made by measuring relative peak areas indicate that p-cresol constitutes more than 30% of all phenols present. This is very important in relation to the analysis of phenols using 4-aminophenazone. The basis of this analysis is the oxidation of the phenol by alkaline ferricyanide to the corresponding p-quinone which, in turn, condenses with 4-aminophenazone to produce the chromogen[6] shown in Fig. 5. If the phenol is substituted in the para position (e.g. p-cresol or 2,4-xylenol), then the oxidation cannot take place and so such phenols do not react with 4-aminophenazone. This is illustrated in Fig. 6, where the relative reactivities of different phenols to 4-aminophenazone are shown. While p-cresol did not react at all, the xylenol, which was a mixture of isomeric forms including 2, 4-xylenol, did show some reaction but was less than phenol. Guiacol, and o- and m-cresols, on the other hand produced a more intense colour than phenol. It would therefore appear that 4-aminophenazone is insensitive to 30% and sometimes as much as 50% of the phenols present in peat smoke. The phenols which are sensitive also vary in their response to the reagent so that misleading results will occur when the ratio of individual phenols alters.

Apart from these defects, there are other aspects of this analysis which give rise for concern. For example, a number of malt samples which had been intensively peated and which were assessed as being satisfactory both organoleptically and by GLC analysis, gave anomalous results when tested with the 4-aminophenazone reagent. Many of these anomalies are due to the poor recovery of phenols from the ether phase into the aqueous phase. Indeed, this was appreciated by McFarlane[8] who estimated that the recovery was only about 10%. However, this recovery is not constant but varies according to the initial concentration of phenol (Fig. 7) which is only to be expected from the basic laws of partition between solvents. This is also demonstrated in another experiment, in which phenol was sprayed directly onto the malt. The recoveries of phenol from these malts by the standard McFarlane method, are shown in Fig. 8. If we

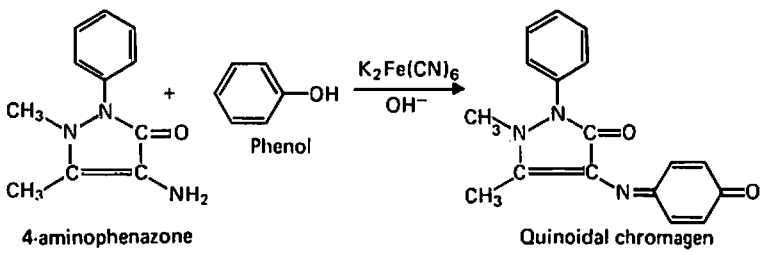


Fig. 5. Reaction of Phenol with 4-Aminophenazone.

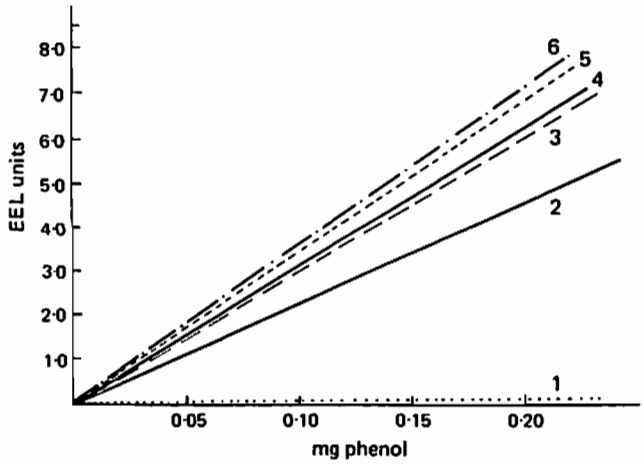


Fig. 6. Relative reactivities of various phenols to 4-aminophenazone.
(1) ····· p-Cresol
(2) ——— Mixed xylenol isomers
(3) — — — — Phenol
(4) ——— m-Cresol
(5) - - - - - - - - Guiacol
(6) —·—·—·— O-Cresol

now assume, as an example, a hypothetical peated malt which has 10 ppm of phenol adsorbed, then 20g of this malt should give rise to an ether solution (100 ml) containing 0·2 mg of phenol. Thus, 25 ml of this solution would contain 0·05 mg of phenol if all the phenol were washed from the malt. When we examine Fig. 7, the estimated recovery from a solution containing 0·05 mg of phenol is about 25%, which is in good agreement with the malt recovery, at 10 ppm, shown in Fig. 8. In other words, the recovery of phenol from malt to ether must be almost 100% while the recovery from the ether to the aqueous phase is only about 25% but will vary considerably according to the initial concentration. This means that fairly accurate and consistent results will only be obtained for malts containing 1–2 ppm phenol (see Fig. 7) but accuracy will then rapidly decrease for all values greater than this. Indeed, it is possible for one malt which, in reality, contains 5 ppm of phenol to yield, on analysis, 2·5 ppm while a second malt, containing 10 ppm will yield 2·8 ppm,

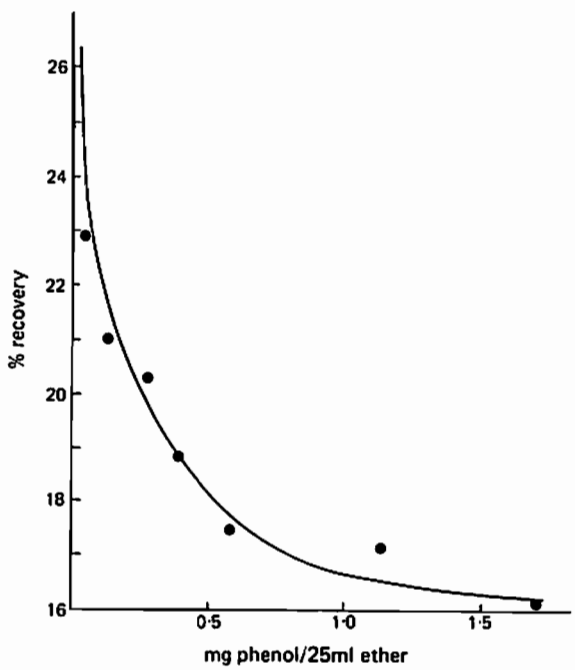


Fig. 7. Recovery of phenol from ether solution by exchange with aqueous ammonia.

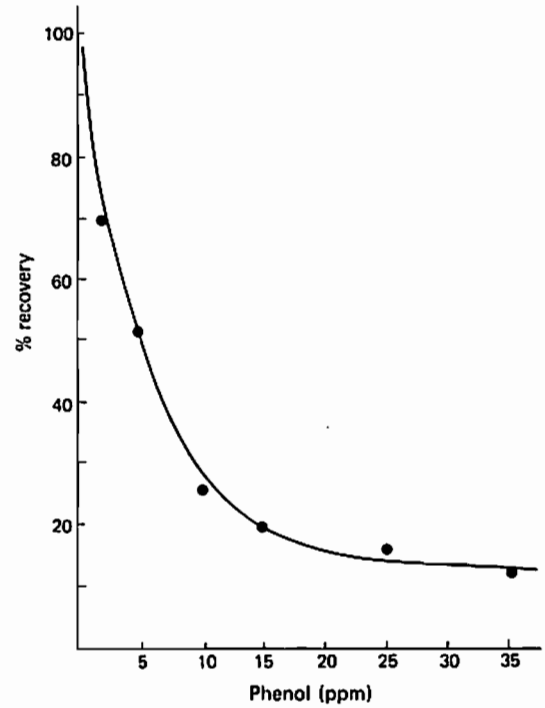


Fig. 8. Total recovery of phenol from malt to aqueous ammonia solution.

so that two malts with phenol contents differing by a factor of two, appear to be within experimental error of each other when analysed by the existing technique.

Needless to say, this situation has serious implications for both process control and customer specification and it is perhaps unfortunate that the McFarlane method has now gained such wide acceptance as a means for specifying peated malts. There is, however, considerable scope for improvement. It is our opinion that specific phenol figures or 'phenol units' quoted by McFarlane should be dropped and 'bands' should be introduced. For example, malts with analyses of 1–3 ppm. should be designated 'lightly peated', 3–6 ppm should indicate 'medium peated' and anything greater than 6 ppm. should be termed 'heavily peated'.

TABLE II. Measured Phenols in 25 ml and 50 ml Portions of Ether Extract

| Wt. of malt sample (g) | Total volume of ether extract (ml) | Volume of ether extract taken for exchange (ml) | Measured phenol (ppm) |
|---|---|---|---|
| 20 | 100 | 50 | 7·7 |
| 20 | 100 | 25 | 10·2 |

As to improving the analytical technique, we have found that it is very important to adhere to one specific portion of ether for solvent exchange. The results shown in Table II, for example, illustrate how the end result may change by 32% simply by altering the volume of ether solution taken for extraction. On the other hand, no great advantage is gained by mechanical shaking compared with occasional shaking by hand in extracting the phenols from malt into the ether phase. (Table III). This confirms our earlier observation that the efficiency of extraction from the malt is fairly satisfactory and the major source of error is transfer from the ether phase to the aqueous phase. Ideally it would be preferable to eliminate the organic phase completely. This can be done by mashing the malt in a standard Institute of Brewing extract and distilling the resulting wort. The phenol

TABLE III. Effect of Mechanical Shaking on Extraction of Phenols from Malt

| Mode of shaking | Extraction time (min) | Measured phenol (ppm) |
|---|---|---|
| Manual | 30 | 9·3 |
| Mechanical* | 30 | 9·8 |

* Using a B.T.L. 'wrist-type' flask shaker at setting 2.

can then be measured directly in the distillate[13] but this method is somewhat laborious and time consuming for routine quality control in a plant with a high output of peated malts. Some improvements can, however, be made to the McFarlane method in light of our observations on recovery. It is now apparent that to recover the maximum amount of phenol from ether solution the concentration of phenol should either be as low as possible or the phenol should be more exhaustively extracted. The phenol concentration can easily be lowered either by using a smaller malt sample as illustrated in Table IV or by decreasing the volume of ether taken for exchange (Tables II and IV). Alternatively, the phenols can be recovered more efficiently by multiple extraction. In

TABLE IV. Effect of Varying Weight of Malt Sample and Volume of Ether on Phenol Extraction

| Wt. of malt sample (g) | Volume of ether extract taken for exchange (ml) | Measured phenol (ppm) |
|---|---|---|
| 40 | 50 | 6·9 |
| 40 | 25 | 8·1 |
| 20 | 50 | 7·7 |
| 20 | 25 | 10·2 |
| 10 | 50 | 8·4 |
| 10 | 25 | 12·3 |

the examples illustrated in Table V, six random production samples of peated malts were analysed by the 'standard' McFarlane method. In a second analysis, carried out simultaneously with the standard method, 25 ml of ethereal malt extract was exchanged with 4 × 2·5 ml portions of 15% ammonia and then treated with 4-aminophenazone and ferricyanide as before. Samples 1 and 2 gave fairly similar analyses by the 'standard' method but, as expected, differed considerably after multiple extraction. The above examples, therefore, amply demonstrate how variable this type of analysis can be and also emphasize the need for an agreed standard analysis which will give phenol indices in direct proportion to the degree of peating. At present there is no agreed standard procedure and it is evident that most laboratories are free to use their own variation of McFarlane's method with the resultant divergence of results illustrated in the above examples. A standard method must give fairly consistent recoveries over a wide range of samples and so must involve (*a*) a fairly small malt sample (say 10 g); (*b*) a small portion of ether for re-extraction (say 25 ml); (*c*) at least two extractions (2 × 5 ml) from the ether with aqueous

TABLE V. Effect of Multiple Extraction of Phenols from Ether Solution to Aqueous Ammonia

| Malt sample No. | Standard extraction (1 × 10 ml) | Multiple extraction (4 × 2·5 ml) |
|---|---|---|
| 1 | 3·9 | 7·3 |
| 2 | 3·4 | 4·5 |
| 3 | 4·8 | 6·9 |
| 4 | 4·5 | 6·8 |
| 5 | 4·5 | 6·6 |
| 6 | 6·7 | 9·7 |

ammonia and (*d*) sub-division of malts into 'bands' rather than stating specific ppm of phenol.

It is our opinion that, in the long run, the GLC methods will give more meaningful results in terms of the overall composition of peat smoke. At present these techniques are still very much qualitative, but work is now in progress aimed at achieving quantitative results.

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## Appendix I

The peat furnace* (Fig. 9) is a chain grate stoker modified by the addition of a light gas oil burner (a) which preheats

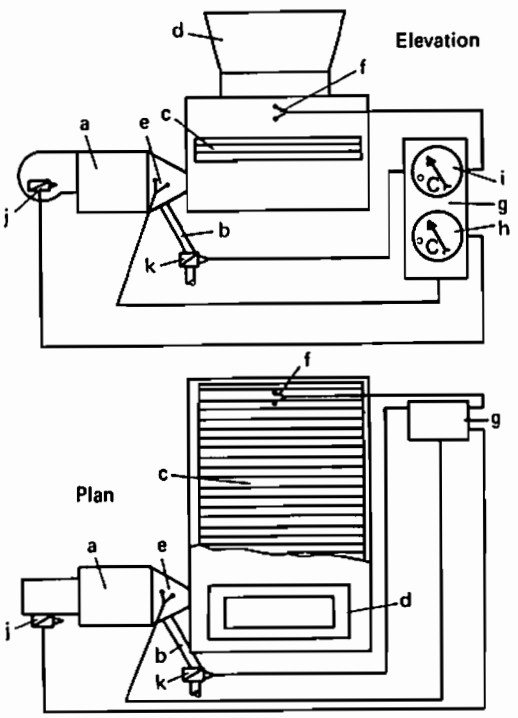


Fig. 9. Prototype peat furnace. For legend refer to Appendix I.

* This process is the subject of a Patent Application.

the incoming air to 400°C. Temperature control is achieved using a thermocouple (e) linked through a temperature indicator (h) to a solenoid valve on the burner (j). Peat is fed from the hopper (d) onto the chain grate (c) where it ignites and is allowed to burn freely until the temperature reaches 350°C. At this temperature a second series of thermocouple, temperature indicator and solenoid valve (f), (i), (k) cause steam to be injected into the air stream (b), thus quenching the combustion and allowing the temperature to fall. Therefore, while the temperature of the peat bed is maintained between 325°C and 375°C, the pyrolysis process can proceed with the minimum amount of flame which previously tended to consume much of the aromatic material in the peat smoke. The complete operation of the furnace is from the control panel (g).

The steam quench also enables a greater proportion of steam-volatile components in the smouldering peat to be removed by steam distillation without causing an imbalance in the overall spectrum of aroma constituents. Thus, the controlled pyrolysis and partial steam distillation of peat at temperatures just below the flash-point produces twice the the amount of aromatic smoke from a given amount of peat.