The Impact of Copper in Different Parts of Malt Whisky Pot Stills on New Make Spirit Composition and Aroma

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ABSTRACT

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In Scotch malt whisky production, the use of copper for the construction of the pot stills for distillation is regarded as having an important effect on whisky aroma. During distillation in copper pot stills, the copper acts to reduce sulphury aromas in the resultant spirit by reducing the levels of sulphur compounds such as dimethyl trisulphide (DMTS). This work has shown that the copper is more effective in this role in some parts of the pot stills than others. This information can be used to help distillers maintain or, indeed, to alter new make spirit aroma. It was also noted that in addition to DMTS, other, as yet unidentified, compounds make a significant contribution to sulphury aromas, so future research efforts should focus on identifying such compounds.

Key words: copper, dimethyl trisulphide, pot stills, whisky.

INTRODUCTION

The importance of copper in Scotch whisky production has long been established[6]. In malt whisky production, the pot stills used for distillation are generally constructed entirely from copper and the presence of this copper during distillation is regarded as having a positive effect on whisky aroma. This positive effect is attributed predominantly to a reduction in the level of sulphur compounds[1]. At high levels these compounds are generally considered to possess unpleasant, and therefore undesirable, vegetable, rotten egg, gassy or rubbery aromas. However, at lower levels sulphur compounds may make a positive contribution to the complexity of whisky aroma.

One sulphur compound of particular interest in malt whisky production is dimethyl trisulphide (DMTS)[2]. The aroma of DMTS has been described as rotten vegetables. Threshold test analysis carried out at the Scotch Whisky Research Institute showed that DMTS has a very low detection threshold (33 ppt in 20% ethanol), so though only found at very low levels in whisky, can have an influence on aroma. In whisky production, DMTS is thought to be formed from methanethiol and hydrogen sulphide, which are in turn derived from the amino acids methionine and cysteine, respectively[4].

Copper has been shown previously to be involved in both reducing and increasing the levels of sulphur compounds[3,4,8–10]. Using laboratory scale glass stills to simulate malt whisky pot distillation, where copper salts were added to model solutions, copper has been found to promote the formation of DMTS from methionine during distillation[4]. Other laboratory scale work has shown that the addition of copper wool to glass stills has the effect of reducing the DMTS level in the distillate produced from malt whisky wash[8]. Therefore, the role of copper on influencing DMTS levels during distillation is not straightforward. Depending on the circumstances, copper can either cause an increase or a reduction in the level of this compound.

In different parts of the stills, copper is exposed to liquids and vapours of various compositions and temperatures. If copper was found to be better at removing sulphur compounds in some parts of the stills than others, this information would assist distillers in troubleshooting new make spirit defects and could allow the manipulation of new make spirit aroma by altering the level of copper contact in the stills. This information would also be essential should the need arise to reduce copper in the distillation system in order to minimise the environmental burden of copper in the pot ale and spent lees[5]. In addition, if copper is found to be particularly effective in some parts, it may be possible to use knowledge of the characteristics of the liquid or vapour with which it is interacting at such points to help explain the mechanisms of the copper-sulphur compound reactions. An increased understanding of the exact mechanisms of the copper-sulphur compound reactions would allow greater control of new make spirit quality and help maintain individual distillery character. In this work, copper laboratory scale pot stills, designed to give more representative copper contact during distillation than previously obtained, and identical stainless steel stills have been used to examine the importance of copper in different parts of the stills in influencing both new make spirit aroma and composition.

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MATERIALS AND METHODS

Chemicals and solvents

Authentic samples of the following sulphur compounds were purchased: dimethyl sulphide (DMS), dimethyl di-

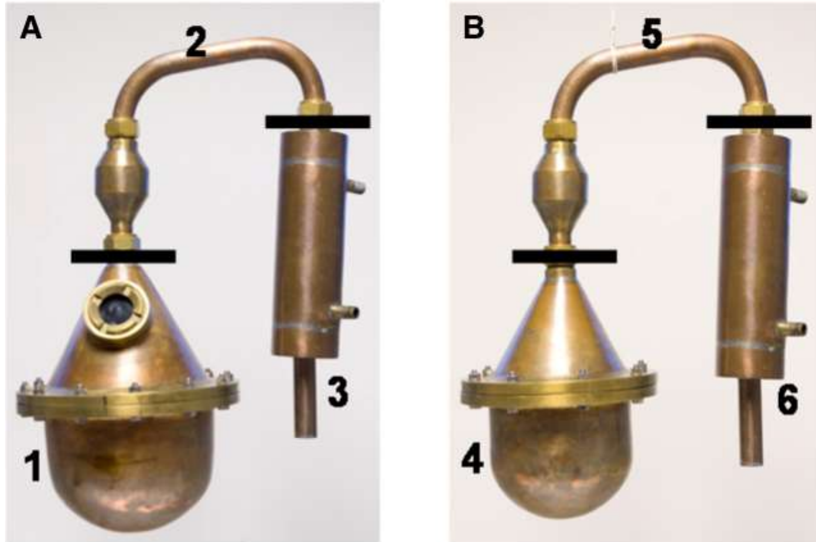

Fig. 1. (A) Copper wash still. (B) Copper spirit still. Numbers 1–6 indicate the individual sections for copper placement.

Table I. Sample codes for new make spirits produced with copper placed in various sections of the stills.

Sample ID	Still construction material[a]	Position of stainless steel placement[b]	Position of copper placement[b]
C	C		
S	S		
S1	S	1	
S2	S	2	
S3	S	3	
S4	S	4	
S5	S	5	
S6	S	6	
C1	C		1
C2	C		2
C3	C		3
C4	C		4
C5	C		5
C6	C		6

[a] C = copper, S = stainless steel.
[b] See Fig. 1 for explanation of number codes.

sulphide (DMDS), dimethyl trisulphide (DMTS), methyl-2-methyl-3-furyl disulphide (MMFDS), thianaphthene (all from Sigma-Aldrich Company Ltd.), thiophene, S-methyl thioacetate and diethyl disulphide (DEDS) (all from Alfa Aesar).

Ethanol was purchased from McQuilkin & Co. Ultra High Quality (UHQ) water produced using an ELGA LabWater Purelab UHQ 11 purification system (ELGA LabWater Global Operations).

Laboratory scale stills

Laboratory scale wash and spirit stills were manufactured in both copper and stainless steel by Forsyths Ltd, one of the main producers of distillation equipment for the Scotch whisky industry. Figure 1 shows the lab scale copper wash and spirit stills (the stainless steel stills were produced to the same specification). The capacities of the wash still pots were 2 L and the spirit still pots 1 L.

Initial studies were carried out comparing new make spirits produced from double distillations (wash distillation followed by spirit distillation) using full copper and full stainless steel stills. Subsequently, to determine the most important sections for copper contact within the stills in terms of impact on new make spirit aroma and composition, copper was placed in different sections of the stainless steel stills (labelled 1–6 in Fig. 1, sample codes are listed in Table I). New make spirits produced using these various configurations were compared with those produced using full copper and full stainless steel stills.

Distillations

A conditioning distillation using 100% ethanol was carried out to clean the stills prior to each experimental distillation. All distillations were carried out using wash from the same batch collected from a typical malt distillery. Wash was stored in a freezer at –20°C and left on the laboratory bench overnight to thaw prior to use. All distillations were carried out at least in triplicate.

Wash stills were charged with 1.65 L of wash and 0.5 mL antifoam (Y-30 emulsion molecular biology reagent (Sigma-Aldrich Company Ltd.). A few Teflon boiling stones were added to each still. Isomantles were used to provide the same heating level to each distillation. Condenser temperature was maintained at 5°C for each distillation. Low wines (550 mL) were collected from each 1.65 L wash charge. A 500 mL aliquot of the low wines was used for the spirit distillation.

Spirit stills were charged with 500 mL of low wines. A few Teflon boiling stones were added to each still. Isomantles were used to provide the same heating level to each distillation. Condenser temperature was maintained at 5°C for each distillation. Foreshots (25 mL), new make spirit (100 mL) and feints (160 mL) were collected from each 500 mL of low wines.

Sensory analysis

Quantitative Descriptive Analysis was used to assess the aroma of the new make spirits. Evaluations were carried out by the Scotch Whisky Research Institute's Sensory Panel, a trained and experienced group of assessors with wide experience in the evaluation of whisky, new make spirits and related samples. Tests were carried out under controlled conditions, in individual booths with data collected using Compusense C4 v4.0 (Compusense Inc.) sensory software.

Composites of the replicate samples were prepared, after an initial sensory screen to ensure that there were no unusual samples in any of the sets. These were then diluted to 20% abv using water and presented to panellists in clear 120 mL nosing glasses. These glasses were covered using watch glasses and identified using three figure random codes. Assessments were based on the aroma of the new make spirits, with panellists scoring intensities of individual attributes using a line scale of 0–3. Sensory comparison of the full copper and full stainless steel systems used the following vocabulary: pungent, feinty, cereal, green/grassy, floral, fresh fruit, solventy, soapy, sweet, oily, sour, sulphury, meaty, stale and clean. This vocabulary was selected from attributes found on the Scotch Whisky Flavour Wheel[7], based on previous knowledge of the key characteristics of most importance in new make spirit. Later sensory work, comparing copper placement in specific sections of the stills, focussed on the levels of sulphury and meaty aromas in the new make spirits. Average scores were calculated across the panel.

Analysis of sulphur compounds

Standard preparation. To calibrate the instrument response, a dilution series of mixed calibration standards was prepared for DMS, DMDS, DMTS, MMFDS, thiophene, thianaphthene and S-methyl thioacetate. Mixed calibration standard solutions were prepared in ethanol. A standard solution of internal standard (DEDS) was also prepared in ethanol.

In a 22 mL headspace vial, a 0.4 mL mixed calibration standard was adjusted to 20% ethanol using 1.6 mL UHQ water. A 50 µL internal standard solution was added to this and the vials were capped immediately to minimise loss of volatiles.

Sample preparation. In a 22 mL headspace vial, a 0.55 mL sample was adjusted to 20% ethanol using 1.45 mL of UHQ water. A 50 µL internal standard solution was added to this and the vials were capped immediately to minimise loss of volatiles.

Analytical instrumentation. A Perkin Elmer Turbomatrix 40 trap headspace autosampler was used in conjunction with a Perkin Elmer Clarus 500 gas chromatograph (GC) and a Sievers 355 Sulphur Chemiluminescence Detector.

The headspace autosampler oven was set to equilibrate each vial at 70°C for 12 min. The vial was then pressurised to 30 psi using carrier gas (helium) introduced via the autosampler needle which was held at 110°C. The vial was pressurised for 1 min, then for 1.5 min, the pressurised contents of the vial headspace were passed onto the trap (Tenax TA), which had an initial temperature of 35°C. This pressurisation and decay cycle was repeated twice and subsequently the analytes on the trap were desorbed by heating the trap to 280°C. The desorbed analytes passed, via the transfer line (Hydroguard FS, 0.32 mm id (Restek), which was held at 200°C, onto the GC column.

The GC column used was a 30 m RTX-1, 0.32 mm id, 5 µm film thickness (Restek). The GC oven temperature was held at 40°C for 1 min then increased at 10°C/ min up to 200°C and the final hold time was 5 min. The column head pressure was controlled by the autosampler and was maintained at 11 psi.

The plasma burner temperature was 800°C. The air flow to the burner was 40 mL/ min and the hydrogen flow was 100 mL/ min.

Quantification. DMS, DMDS, DMTS, MMFDS, thiophene, thianaphthene and S-methyl thioacetate were quantified using internal standard calibration by relating sample response ratios with calibration lines prepared for each compound. Calibrated compounds were reported as ppb in 20% ethanol. Peaks detected in chromatograms for which the identity of the compound was unknown were reported as response ratios (peak area/internal standard peak area). Unknowns are identified by their retention time in min.

Data analysis. Analysis of Variance (ANOVA) was carried out to determine which, if any, sensory or compositional attributes showed significant differences between samples (Unistat version 5.0 (Unistat Ltd.)). A p value of less than 0.05 was considered significant. To relate analytical to sensory data, correlation coefficients were calculated to establish the degree of linear relationship between the two variables.

RESULTS AND DISCUSSION

Replacement of copper with stainless steel

Sensory analysis. Sensory profiles of the new make spirits produced using the full copper and full stainless steel stills are shown in Fig. 2.

This analysis showed the impact of using stainless steel stills in place of copper ones. The sensory attributes which most characterised the copper stills new make spirit were cereal, feinty, pungent and clean. Using stainless steel resulted in the new make spirit being described as significantly less clean. This was attributed to, as might be expected, a significant increase in the levels of sulphury and meaty aromas when using stainless steel.

Sulphur compounds. The new make spirits produced using the full copper and stainless steel stills were compared in terms of sulphur compound levels (Fig. 3). Figure 3A shows the levels of known sulphur compounds. Of these, only DMTS showed a statistically significant difference between the copper and stainless steel stills. This compound was present at significantly higher levels in new make spirit produced using stainless steel stills. When the aroma detection threshold is considered (33 ppt in 20% ethanol), DMTS was detected at levels likely to have a direct impact on new make spirit aroma. This suggested that DMTS was a contributor to the elevated levels of sulphury and meaty aromas in the stainless steel stills new make spirit.

Several unknown sulphur compounds were also detected in the new make spirits produced. The levels of the four most quantitatively important of these are shown in

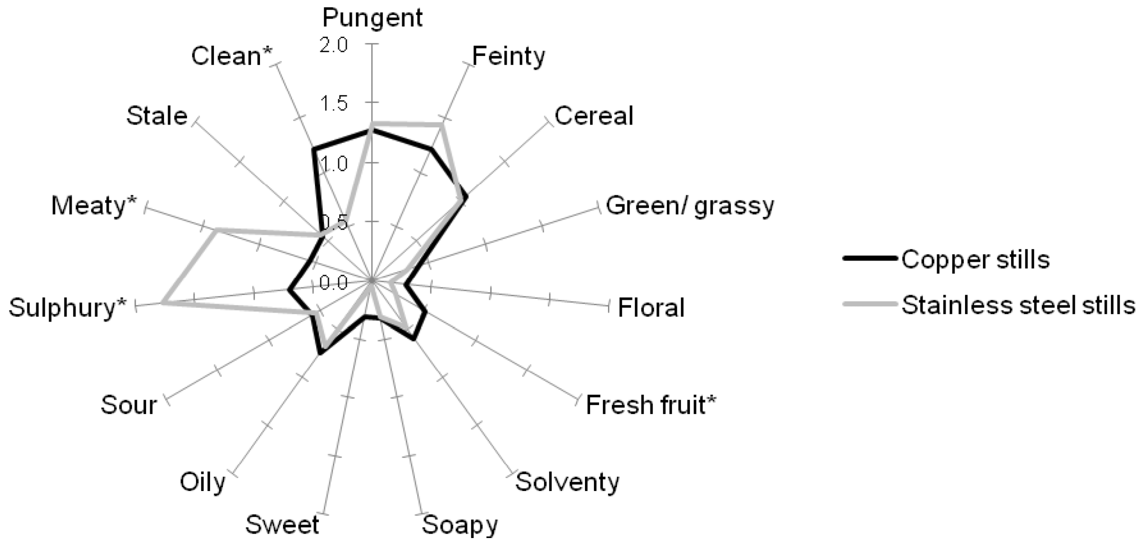

Fig. 2. Sensory profiles of new make spirits produced using copper and stainless steel stills. * Shows attributes present at significantly different levels in the two samples (p values less than 0.05).

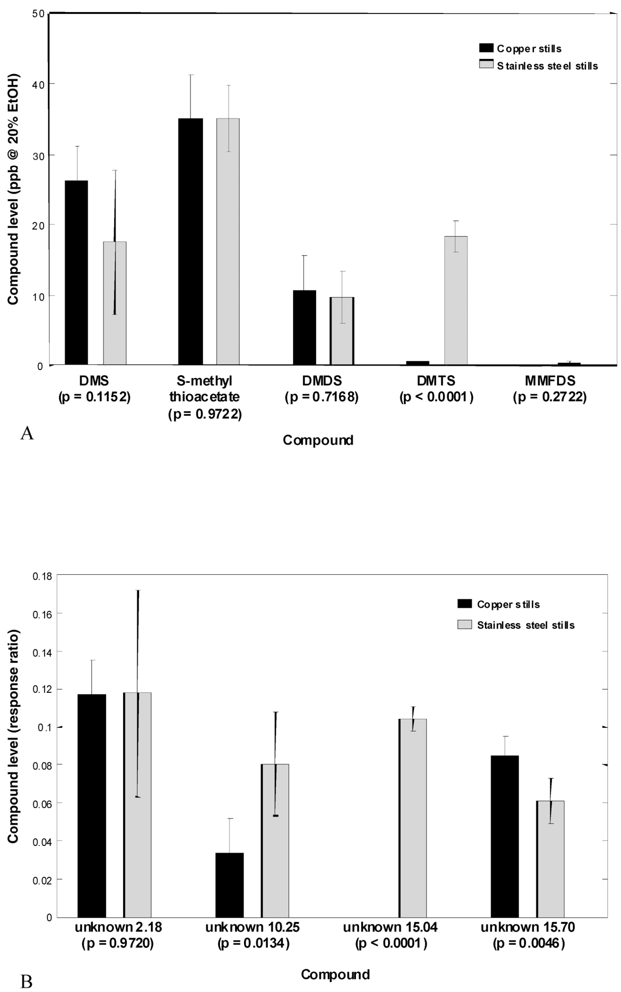

Fig. 3. (A) Levels of known sulphur compounds in new make spirit produced from copper and stainless steel stills. (B) Levels of unknown sulphur compounds in new make spirit produced from copper and stainless steel stills (only unknowns with a response ratio of 0.10 or over in at least one replicate are presented).

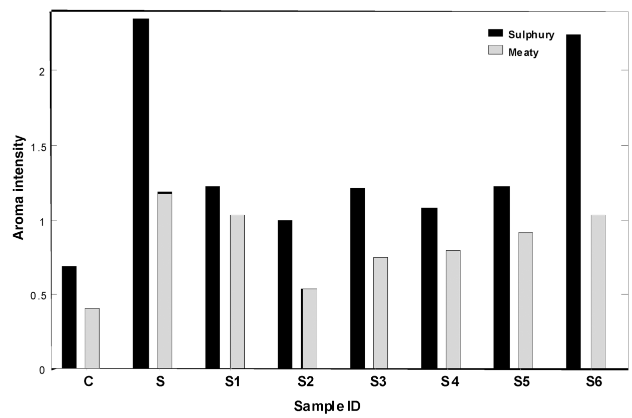

Fig. 4. Average sensory scores for sulphury ($p < 0.0001$) and meaty ($p < 0.0001$) aromas in new make spirits.

Fig. 3B. It was found that three of these unknown compounds were present at statistically significantly different levels in the new make spirits produced from the copper and stainless steel stills. Unknown 15.70 was found at a higher level in the copper stills new make spirit whilst unknown 10.25 and unknown 15.04 were found at higher levels in the stainless steel stills new make spirit. Unknown 10.25 and unknown 15.04 were therefore more likely to have made a contribution to the sulphury and meaty aromas which characterised the stainless steel stills new make spirit.

Copper placement

Sensory analysis. Copper was separately placed in individual sections 1–6 of the stainless steel stills. The levels of sulphury and meaty aromas in each of the new make spirits produced are shown in Fig. 4. The level of sulphury aroma was particularly high when copper was placed only in the spirit still condenser (S6). Indeed, in this case the sulphury aroma level was similar to the full stainless steel still new make spirit. When copper was

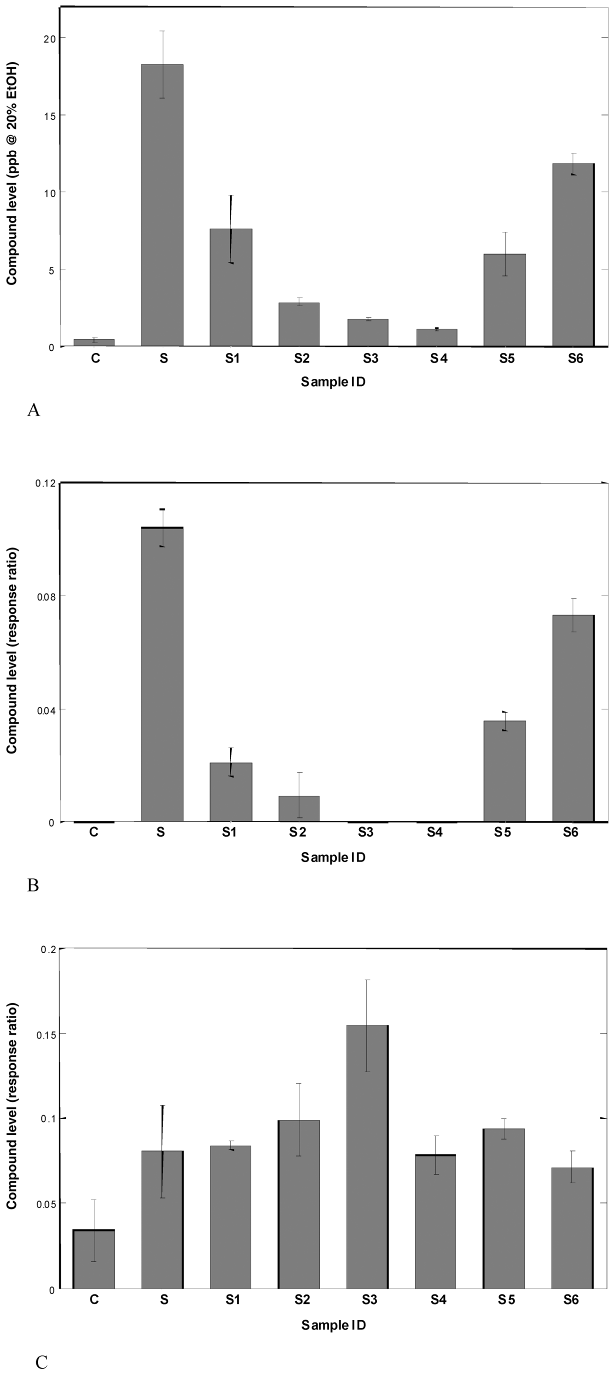

Fig. 5. Sulphur compound levels in new make spirit samples. (A) DMTS ($p < 0.0001$), (B) unknown 15.04 ($p < 0.0001$), (C) unknown 10.25 ($p < 0.0001$).

placed in sections 1–5 of the stainless steel stills it was found that the presence of copper in any one of these sections resulted in a new make spirit with higher levels of sulphury aroma than the full copper stills, though not as high as that of S or S6 new make spirit.

For meaty aroma, the level of variance was found to be somewhat lower than for sulphury aroma when comparing copper in sections 1–6 (Fig. 4). As with sulphury, S6 new make spirit had a level of meaty aroma similar to that of the full stainless steel stills. Also, as with sulphury, whilst placing copper in any single section could not replicate the effect of full copper stills, the presence of copper in any of sections 1–5 generally reduced the meaty aroma level relative to the full stainless steel stills. However, this reduction was only marginal for copper in section 1.

Sulphur compounds. The new make spirit samples produced using stainless steel stills with copper placed singly in the sections 1–6 were then analysed for sulphur compounds. This would show in which, if any, sections of the stills copper had most impact on the sulphur compound levels in new make spirit. Here, only those compounds that were present in full stainless steel stills new make spirit at significantly higher levels than in full copper stills new make spirit were considered, as these were most likely to have contributed to sulphury and meaty aromas (Fig. 5).

The impact of the presence of any copper during distillation was to reduce the DMTS levels in new make spirit (Fig. 5A). However, it was found that the positioning of the copper in the stills had a large effect on the ability of the copper to reduce the level of DMTS in the new make spirit and placing copper in any single section was unable to replicate the effect of the full copper stills. There was found to be opposing trends in the wash and spirit stills. In the wash still, the pot (S1) was the least effective at reducing DMTS whilst the condenser (S3) was most effective. In the spirit still, the pot (S4) was most effective and the condenser (S6) was least effective. The most effective sections for reducing the DMTS level were therefore the wash still condenser and the spirit still pot (S3 and S4).

The same pattern was found for unknown 15.04 as for DMTS (Fig. 5B). Again the wash still condenser and spirit still pot (S3 and S4) were most effective at removing this compound. The reason why DMTS and unknown 15.04 were more efficiently removed at these sections may relate to the fact that the wash still condenser and spirit still pot are areas where copper corrosion is known to be relatively high in industrial stills. It would appear therefore, that either sulphur compound-copper reactions are particularly prevalent in these sections causing an increase in corrosion, or that copper corroded by other mechanisms is more active in terms of sulphur compound removal. It has been shown previously that acidification of sulphur compound model solutions was an important contributing factor for the removal of these compounds by copper during distillation[8]. So it may be that the environment at these particular sections makes them relatively susceptible to acid corrosion, which in turn improves their ability to remove sulphur compounds. In this regard, the usage of the stills may influence the ability of the copper to remove sulphur compounds. When used for the first time, the laboratory scale copper stills produced a spirit with a relatively sulphury and meaty aroma. Several repeat distillations were required prior to the start of this experiment to reduce this aroma suggesting that some corrosion of the copper may have been required in order to activate it. The actual mechanism of sulphur compound removal, however, remains to be elucidated.

Unknown 10.25 did not follow the same pattern as the other two compounds (Fig. 5C). Here, the difference in levels in new make spirits produced using the full copper

Table II. Correlation between sensory and sulphur compound data (correlation coefficients calculated using data for C, S and S1-6 new make spirits).

Compound	Sulphury	Meaty
DMTS	0.93	0.84
Unknown 10.25	0.02	0.13
Unknown 15.04	0.94	0.78

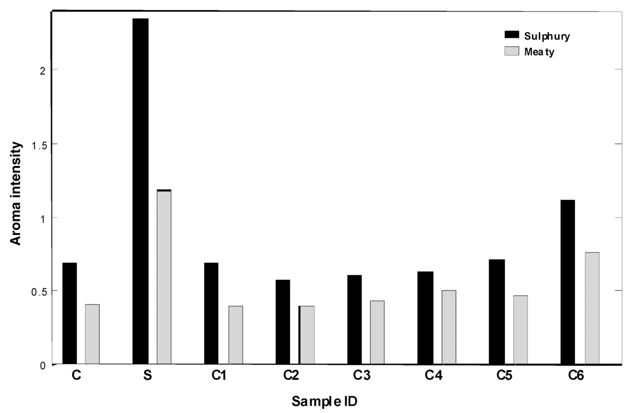

Fig. 6. Average sensory scores for sulphury ($p < 0.0001$) and meaty ($p < 0.0001$) aromas in new make spirits.

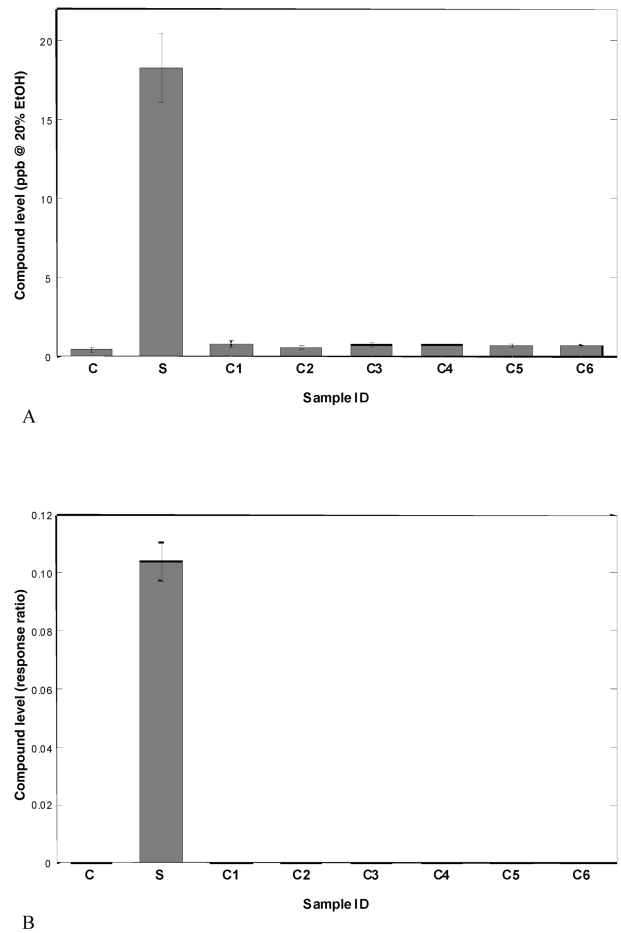

Fig. 7. Sulphur compound levels in new make spirit samples. (A) DMTS ($p < 0.0001$), (B) unknown 15.04 ($p < 0.0001$).

and stainless steel stills was relatively small. Only having copper in one section did not decrease the level of this compound relative to the stainless steel stills and, other than a slightly elevated level in S3 new make spirit, this compound was found at a similar level irrespective of the section where copper was placed. This suggests that it was the overall surface area of copper, not any specific positioning, which was important for the removal of this compound.

Correlation between sensory and sulphur compound data

To determine how well sulphur compound data could explain the sensory data, correlation coefficients between sulphury and meaty aromas and analytical data for DMTS, unknown 10.25 and unknown 15.04 were calculated (Table II).

Both DMTS and unknown 15.04 showed strong positive correlations with sulphury aroma, and to a slightly lesser extent, with meaty aroma. This suggests that these compounds may have contributed to these aromas. Unknown 10.25 did not correlate well with the sulphury and meaty aromas so this compound was less likely to have been a contributor to these aromas. The fact that DMTS and unknown 15.04 were found at a high level in new make spirit from stainless steel stills and stainless steel stills with a copper spirit condenser (S6) might help explain why these new make spirits had a high level of sulphury and meaty aromas. The new make spirits from S1-S5 had levels of DMTS higher than the full copper stills, but lower than S6 and the full stainless steel stills. This correlates somewhat with the levels of sulphury and meaty aromas in these new make spirits, which were also found to be between the two extremes.

Spirit still condenser

It was found that the level of DMTS and unknown 15.04 generally showed a good correlation with sulphury and meaty aromas. The high level of these compounds, DMTS and unknown 15.04, and high levels of sulphury and meaty aromas in the new make spirit from the stainless still stills with copper only in the spirit still condenser (S6) suggested that copper in this section was relatively unimportant for the control of sulphur compounds and therefore sulphury and meaty aromas. However, replacing the copper in the spirit still condenser with stainless steel in copper stills (C6) caused an increase in sulphury and meaty aromas relative to full copper stills (C) or stills with copper replaced in any of the other sections (C1-C5) (Fig. 6).

This was despite the level of DMTS or unknown 15.04 not being significantly higher in the C6 new make spirit (Fig. 7). It seems that copper in the spirit still condenser controls sulphury and meaty aromas by an additional mechanism other than purely by removing sulphur compounds and this additional mechanism is only effective when copper present in the stills prior to the spirit condenser has acted to significantly reduce sulphur compound levels.

The fact that replacement of copper with stainless steel in each of sections 1–6 had very little impact on sulphur

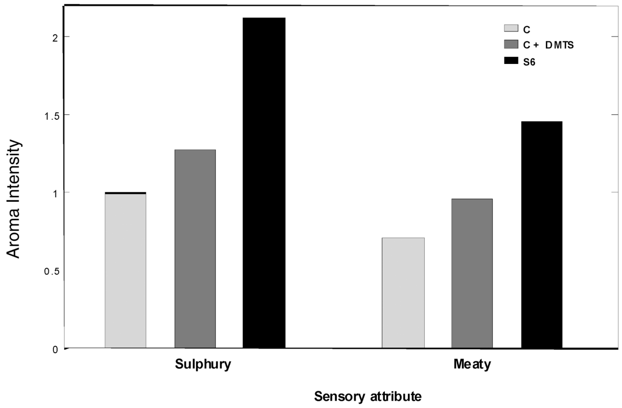

Fig. 8. Sulphury and meaty aroma levels in spiked and unspiked new make spirits.

compound levels and, other than in the case of C6, sulphury and meaty aromas suggests that replacement of any one of these sections in industrial scale stills could be achieved with little effect on new make spirit aroma. However, the lower surface area to volume ratio in industrial scale stills means that there will be a relatively low level of copper contact overall in these stills, so replacement of a single section of copper with stainless steel is likely to have a greater impact than in the laboratory scale stills.

Aroma impact of DMTS

Generally, DMTS and unknown 15.04 levels correlated well with sulphury and meaty aromas. It was therefore of interest to establish what extent such compounds contributed to these aromas. This was done by spiking a new make spirit with a low level of sulphury and meaty aroma (C) with DMTS so that the compound concentration was increased to that of a new make spirit with a high level of sulphury and meaty aromas (S6). Obviously this could not be carried out for unknown 15.04, as its identity is as yet unknown. S6 was used rather than S so that any potential influence of copper contact in the spirit still condenser was accounted for. The spiked and unspiked new make spirits were then assessed for the levels of sulphury and meaty aromas and the results are shown in Fig. 8.

From Fig. 8 it can be seen that the addition of DMTS to the C new make spirit did cause an increase in sulphury and meaty aromas. However, given that the S6 new make spirit was still more sulphury and meaty than the spiked C new make spirit, there was clearly an additional contribution to the sulphury and meaty aromas from another source. The identity of this source is as yet unclear but it would appear that there are aroma active compounds other than DMTS that are influenced by copper contact during distillation. Though DMTS has been demonstrated to be a good marker for sulphury aroma here, the identification of additional contributing aroma compounds will further improve the ability to control and manipulate sulphury and meaty aroma in new make spirit. Unknown 15.04 would appear to be a good candidate for such a compound, correlating strongly both with DMTS levels and the sulphury and meaty aromas.

CONCLUSIONS

The presence of copper in pot stills was confirmed as being important for the control of sulphury and meaty aromas in new make spirit, and DMTS levels showed a good correlation with these aromas. In these laboratory scale distillations, copper was found to reduce the level of this compound best when placed in the wash still condenser or spirit still pot. In order to improve control of this compound, the reasons why these areas of the stills are more efficient than others at reducing DMTS need to be elucidated. Copper in the spirit still condenser also appeared to play a role in controlling sulphury and meaty aromas, but the mechanism for this effect is, as yet, unclear. These results suggest that removing copper from any of these sections in industrial scale stills is likely to have the most significant impact on new make spirit aroma. Additionally, it was noted that whilst DMTS made a significant contribution to sulphury and meaty aromas, other, as yet unknown, compounds make an important contribution and future research efforts should focus on identifying such compounds.

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