Investigations into the Use of Copper and Other Metals as Indicators for the Authenticity of Scotch Whiskies

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ABSTRACT

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Trace element analyses were conducted on 35 Scotch Whiskies to investigate if the trace element fingerprint is characteristic for different kinds of Scotch Whiskies. The element concentrations of the eight elements investigated varied considerably; for zinc and iron three orders of magnitude (0.02 to 20 mg Zn L^{-1} and 0.02 to 28 mg Fe L^{-1}), while nickel and magnesium varied within two orders of magnitude (0.002 to 0.6 mg Ni L^{-1} and 0.02 to 4 mg Mg L^{-1}). Small variations were detected for calcium, sodium and copper (0.5 to 4 mg Ca L^{-1}, 2 to 24 mg Na L^{-1}, 0.1 to 1.7 mg Cu L^{-1}), while lead, with one exception was usually below 0.005 mg L^{-1}. Using Cluster analysis no characteristic metal fingerprints were identified for the different geographical regions. However, when a second set of samples (42 malt and 8 blend whiskies) were analysed for copper, the copper concentration could be used as a criterion to distinguish Blended or Grain Scotch from Malt Whisky. The Malt Whiskies had a copper concentration between 385 and 480 ng mL^{-1} (95% confidence limit) while the copper concentration of the blended whiskies was between 143 and 242 ng L^{-1}. Since the difference was highly significant ($p < 0.0001$), it is suggested that a simple copper analysis could be used as one test to distinguish between a Blended and Malt Scotch Whisky.

Key words: Blend, copper, cluster analysis, fingerprint, metals, Malt Whisky, whiskey.

INTRODUCTION

In the past there have been many approaches to identify the authenticity of whiskies and most of them used information from the organic ingredients. Parker and co-workers[10] used the isotope ratio $^{12}C/^{13}C$ of different volatile compounds such as acetaldehyde, ethyl acetate, *n*-propanol, isobutanol and amyl alcohol to differentiate between different types of blended whiskies. This is based on the fact that barley is a C3-plant, which fractionates strongly against the ^{13}C, while in C4-plants such as maize, enzymatic metabolism is less discriminating. Since blended Scotch consists mostly of a mixture of malt and grain whiskies, the isotope ratio reflects the manufacturing process as well as the ingredients. Others have used UV-VIS absorption and/or pH to differentiate between different alcoholic spirits[7], or pyrolysis followed by mass spectrometry to discriminate between the different brands of whisky[1,11]. Recently the volatile organic components in whiskies were analysed directly in the headspace[5] or using a pre-concentration technique: solid-phase micro-extraction with gas chromatography-mass spectrometry (SPME-GC-MS)[4,6]. Only very limited published information is available on the metal concentration in whiskies[8].

In these experiments the copper content of Scotch Whiskies was analysed with a concentration on the differences between the whiskies produced by two different whisky production processes. Malt whiskies are produced in traditional copper stills and grain whiskies, which make up the main contribution in Blended Scotch Whisky, are produced using more industrial style patent stills. The latter runs continuously, while the traditional copper stills for the Malt Scotch Whisky are batch-type reactors. The main analyses involved testing these two different types of whisky for their copper content, to test the hypothesis that the whiskies produced in the copper stills would contain a significantly higher amount of copper than those produced in non-copper environments. Copper compounds have been known to be a problem in the waste products of distilleries and spent lees (distillation residue from the 2nd batch) contain copper up to 20 mg L^{-1} while pot ale is reported[3] to contain copper up to 0.7 mg L^{-1}. In the residue of the distillation process it is well known that soluble organic complexes of copper occur[9]. Care needs to be shown when these wastes are discharged to ensure sufficient dilution of the copper before being released into the environment. These problems prompted investigation into the copper content of the product to ascertain what level of copper can be found in commercial products. Scotch Whisky is an important commercial product and the precise nature of the distilling is believed to have a large impact on the taste and aroma of the finished product. An investigation into the properties of these spirits could perhaps explain some of the idiosyncrasies of this most traditional of Scottish products.

Here we report the analysis of Malt and Blended Scotch Whisky for eight metals: calcium, copper, iron, lead, magnesium, nickel, sodium and zinc, and if it would be possible to use these inorganic analyses for an authenticity test for Scotch Whiskies.

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MATERIALS AND METHODS

Samples

For the analysis of the eight metals – thirty one Single Malts, one Malt Blend, two blended Scotch and one Grain Whisky were analysed, while for the copper analysis an additional six Blended Scotch, eleven Single Malts and one Rye Whisky were sampled. The samples were taken from Whisky bottles bought in the regular market place. The selected Malts were distilled in every region, Lowlands, Speyside, Islay and Highland, and were between 6 and 20 years old.

Analytical method

For the determination of the metals, a graphite-furnace atomic absorption spectrometer (GFAAS) from Jena Analytics (Jena, Germany) was employed. A 10 µL aliquot of the sample was pipetted onto a platform of the solution tube. No matrix modifier was employed. The calibration was carried out using a multi-element solution containing

Table I. Furnace parameters of GFAAS (Jena Analytics, Jena, Germany) for the copper analysis in whisky.

Steps for GFAAS	Temperature (°C)	Ramp rate (°C)	Holding time (s)
Drying	110	7	20
Pyrolysis	1100	501	3
Autozero	1100	0	3
Atomisation	2400	1500	5
Cleanout	2550	1500	7

Integration time was 5.0 s and D_2 background corrections were been made, injection volume was 8 µL.

Table II. Recovery rate using external calibration with standards containing 20% (w/v) ethanol compared to standard addition.

No. of sample	External calibration (ng mL^{-1})	Standard addition (ng mL^{-1})	Recovery (%)
1	186.2	187.6	99.3
2	107.1	109.1	98.2
3	208.4	208.0	100.2

Table III. Metal concentrations of 35 Whiskies in µg/L. (triplicate measurements were conducted)

Name of Distillery	Region	Age	Cu	Zn	Pb	Ni	Fe	Ca	Mg	Na
Bowmore	Islay	12	555	1050	25	61	64	652	347	8291
Bruichladdich	Islay	10	520	54	4.3	1.7	110	1971	456	20191
Bunnahabhain	Islay	12	429	69	3.9	1.1	158	1692	1046	9862
Lagavulin	Islay	16	471	34.5	2.3	<0.1	97	986	337	17861
Laphroaig	Islay	10	139	31	0.5	0.2	20	775	400	11711
Dalmore	Highlands	12	338	32.5	1.2	0.1	62	787	466	10000
Dalwhinnie	Highlands	15	423	165	3.1	6.2	134	946	167	11541
Fettercairn	Highlands	10	396	1565	0.6	35	533	1099	556	10531
Glengoyne	Highlands	10	606	34	1.3	2.2	171	1965	816	10901
Glenmorangie	Highlands	10	321	97	<0.1	24	886	904	217	6831
Glen Ord	Highlands	12	478	24	0.2	1.2	115	1073	571	13901
Highland Park	Highlands	12	605	95	8	0.9	186	1918	1196	16991
Isle of Jura	Highlands	10	581	7966	6.2	555	17005	625	1736	18342
Oban	Highlands	14	345	13203	0.7	1.4	77	856	167	9361
Talisker	Highlands	10	266	73	1.7	0.2	59	749	122	16572
Tobermory	Highlands	8	1681	66	3.0	14	213	530	92	17376
Aberlour	Speyside	10	311	52	1.4	1.2	73	1005	137	18062
Balvenie	Speyside	10	640	19434	1.6	631	27679	429	3916	12000
Cragganmore	Speyside	12	269	46	2.0	1.7	168	820	77	4691
Glenfarcles	Speyside	10	358	20625	2.7	2.1	106	658	67	22631
Glenfiddich	Speyside	8	378	32	2.1	1.0	95	787	27	3151
Glen Grant	Speyside	10	466	21	1.1	1.1	23	714	286	12451
Glenlivet	Speyside	12	480	44	2.2	1.5	77	642	17	6482
King's College (Knockandu)	Speyside	20	720	280	6.8	39	24.5	4257	1256	7162
Knockandu	Speyside	12	538	38	2.08	13	65	987	456	10001
Macallan	Speyside	12	929	389	0.9	22	448	2856	2256	16302
Singleton/Auchroisk	Speyside	10	600	11192	4.2	624	20720	1793	1676	15592
Tamdhu	Speyside	8	778	31	1.2	0.4	129	1550	797	9382
Tamnavulin	Speyside	12	345	19386	2.4	2.1	71	1522	356	13772
Auchentoshan	Lowlands	10	423	39	0.8	19	541	1352	356	13771
Glenkinchie	Lowlands	10	226	44	1.9	0.2	220	714	346	5121
Blairmhor	Blended Malt	8	524	22	0.6	0.2	55	767	97	8951
Chivas Regal	Blend	6	282	29	1.7	0.1	42	434	127	10862
Famous Grouse	Blend	6	147	22	1.2	0.1	57	595	37	10236
Cameron Brig	Grain	6	119	15	1.9	1.0	52	648	20	6911
mean (ng/mL)			477	2751	3	59	2015	1145	600	11937
SD (ng/mL)			276	6138	4	170	6288	767	792	4698
RSD (%)			58	223	150	288	312	67	132	39
Min. (ng/mL)			119	15	<0.1	<0.1	19.7	429	17	3151
Max. (ng/mL)			1681	20625	25	631	27679	4257	3916	22631

SD: standard deviation, RSD: relative standard deviation

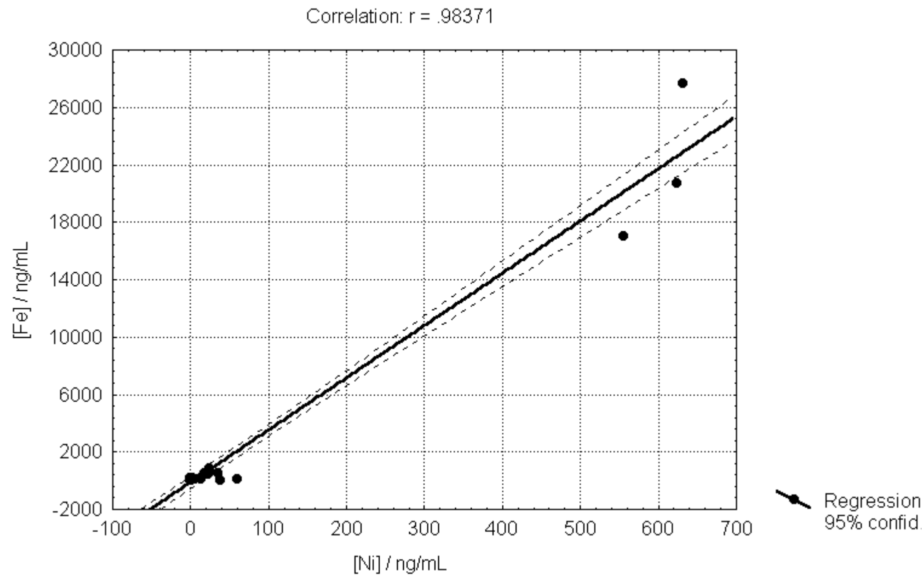

Fig. 1. Correlation of iron versus nickel concentration (ng/mL) in Scotch Whiskies (r = 0.98 and a slope of 36.4) indicates that those elements may have the same origin.

calcium, copper, iron, lead, nickel, magnesium, sodium, and zinc. A stock solution of 100 mg L^{-1} was made from which appropriate standards were generated on a daily basis.

Due to the focus on copper, the furnace parameters are given in Table I. Since no relevant standard reference material was commercially available, the external calibration with standards containing 20% ethanol were applied and validated using standard addition methods for three samples (see Table II). For the data analysis STATISTICA 99 Edition (Release 5.5) for Windows (Tulsa, OK, US) was used.

RESULTS AND DISCUSSION

The analysis of the whisky was satisfactory using matrix-matched standards for the calibration. The recovery of the copper in whisky, using external calibration compared to standard addition, was better than 98% (see Table II).

Metal analyses of the different whiskies are shown in Table III. Some elements showed a normal distribution, while other elements showed the differences of more than three orders of magnitude. For example, some whiskies had zinc and iron concentrations up to 27 mg L^{-1} and nickel up to 0.6 mg L^{-1}, while others had zinc and iron concentrations below 0.02 mg L^{-1} and nickel concentrations below the detection limit of 0.001 mg L^{-1}. The variability for other elements such as copper, calcium and sodium was relatively small with a relative standard deviation (RSD) between 39–67%. Concentration of the toxic element lead was very low, except for one product with a concentration of 0.025 mg L^{-1}. Tests were not conducted to determine if the analysed bottle was representative for this particular brand.

A correlation analysis was performed and only a few significant correlations of metal concentrations were identified. In Fig. 1, the correlation graph of nickel and iron is shown. The correlation was highly significant ($p < 0.05$) with a correlation coefficient of 0.98. Both elements are constituents of special stainless steel tubing, which might have been used in the particular distilleries where higher values were found.

The authors however do not have any explanation for the significant correlation of magnesium and iron ($r = 0.79$). Furthermore, it was noted that calcium correlated with the age of the whisky at $r = 0.52$. With increasing age more calcium was found in the whisky which might point to leachability of calcium from wooden casks. This correlation was not very strong and valued as not significant ($p < 0.05$). Calcium probably has other sources in a manner similar to magnesium and sodium, i.e. the water.

It had been thought that a metal fingerprint could be used to locate the origin of the whisky, although it is known that a few distilleries treat the water using ion exchange cartridges. This would affect the characteristic metal distribution of the water. In order to see if patterns would emerge, cluster analysis was used to classify the different types of whiskies according to their metal fingerprints. A tree clustering approach has been taken. The purpose of this algorithm is to join together samples into successively larger clusters using some measure of similarity or distance. The larger the linkage distance, the larger the dissimilarities are. In Fig. 2, the horizontal cluster tree can be seen. Taking just the different Islay whiskies analysed, no common patterns were recognized. The same was concluded for the whiskies of the other areas. One group of three whiskies however were distinguishable from the others (Singleton, Balvenie and Isle of Jura). This was due to the large concentration of zinc, nickel and iron in these whiskies. This may be ascribed to the process itself, or to the ingredients including the water. The Grain and Blended had low metal concentrations, but they did not appear as a single cluster when all elements were considered for cluster formation.

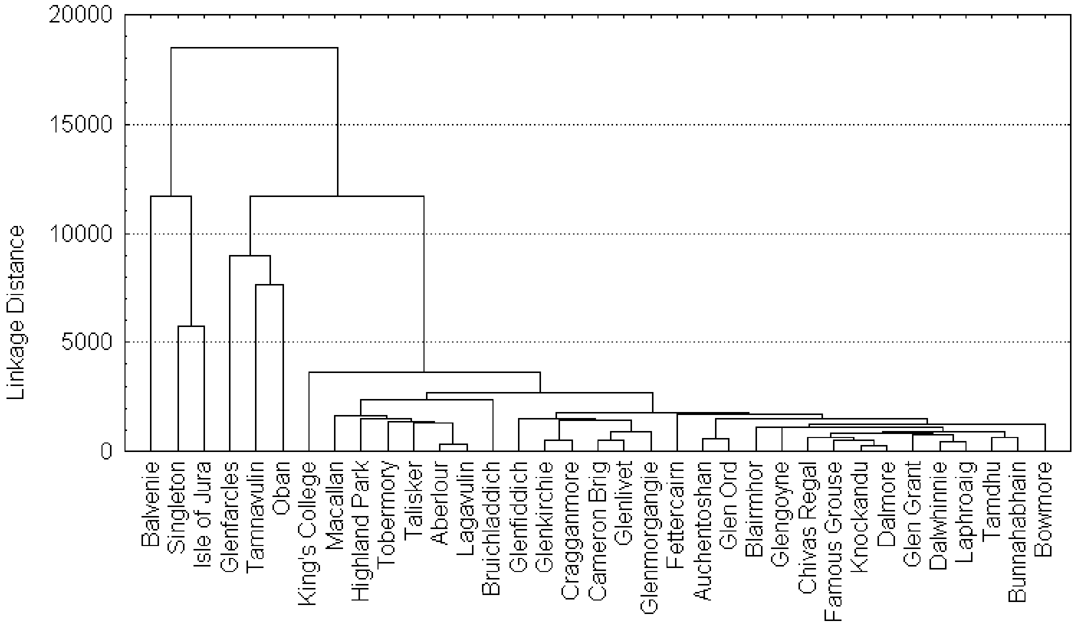

Fig. 2. Cluster analysis using single linkage and Euclidean distances for 35 cases (Whiskies) and 8 variables (metals).

Reactor material may have an influence on the metal concentration in the spirit. Malt Whiskies, distilled in small traditional pot stills, would be expected to have more copper than Blended Scotch Whiskies or Grain Whiskies. Therefore another set of Scotch whiskies were analysed only for copper (additional to the first set, eleven Single Malts, six Blended Scotch and one Rye Whisky). The variability of the copper content in a whisky of one brand was tested by analysing five different bottles of Talisker. The variability of the analysis from five different bottles purchased in three different EU countries was only 15% and the analysis had a standard error of 4–10% (see Table IV). This indicated that the product had a rather uniform copper concentration. If this can be extrapolated to the other whiskies needs further testing. Furthermore the quality of the data was checked by an independent laboratory that used a different analytical technique (ICP-MS). The result was within the error of the mean. Although the reproducibility of the copper concentration in Talisker (Table IV) was satisfactory, this limited information was not enough to assess whether or not the copper concentration was constant in the production process over the years and future studies, possibly involving the speciation of copper in the product, are necessary.

Table IV. Analysis of five different bottles of one type of Malt Whisky (Talisker, 10 years old).

No. of sample	Copper[1] concentration in ng mL^{-1}	RSD[2] (%)
1 (GFAAS)	266 ± 22	8.3
2 (GFAAS)	333 ± 36	10.8
3 (GFAAS)	271 ± 13	4.8
4 (GFAAS)	348 ± 35	10.1
5[3] (ICP-MS)	375 ± 25	6.7
Mean[4]	318 ± 48	15.1

[1] error is the standard deviation of triplicate
[2] RSD: relative standard deviation
[3] measured by an independent laboratory for QC/QA purposes
[4] given are mean concentration and the standard deviation and RSD of the mean values of the other measurements.

In Fig. 3 the mean copper values from the Malt Whiskies and the other type whiskies are compared. The mean copper concentration is significantly higher for all Malt Whiskies (385–480 ng mL^{-1}) than for the Grain and Blended Scotch Whiskies (143–242 ng mL^{-1}) at the confidence limit of 95%. This was tested with the Student's *t*-test ($P < 0.001$). The copper concentration in the Malt Whiskies is shown in Fig. 4. A blended Malt Whisky (Blairmhor) which does not contain any Grain whisky had the expected copper concentration of a Single Malt (524 ng mL^{-1}). In comparison, a Canadian Rye Whisky (Royal Crown) had a relatively high copper concentration of 668 ng mL^{-1} which might be an indication of the production process of those whiskies or an influence of the copper

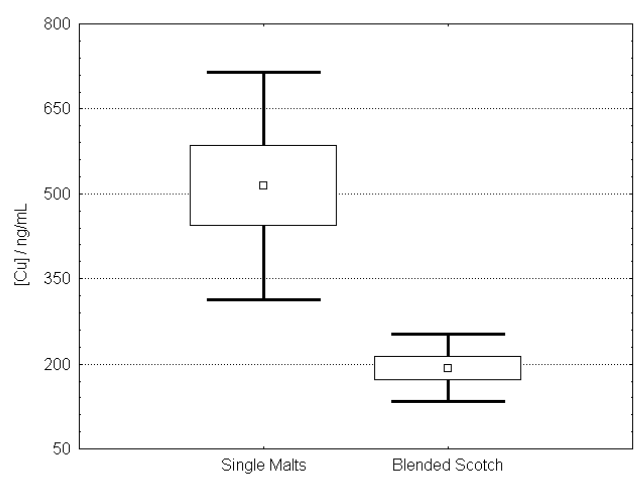

Fig. 3. Box and Whisker Plot of the copper concentration in 42 Single Malts and 8 Blended Scotch; means with standard errors and standard deviations are shown.

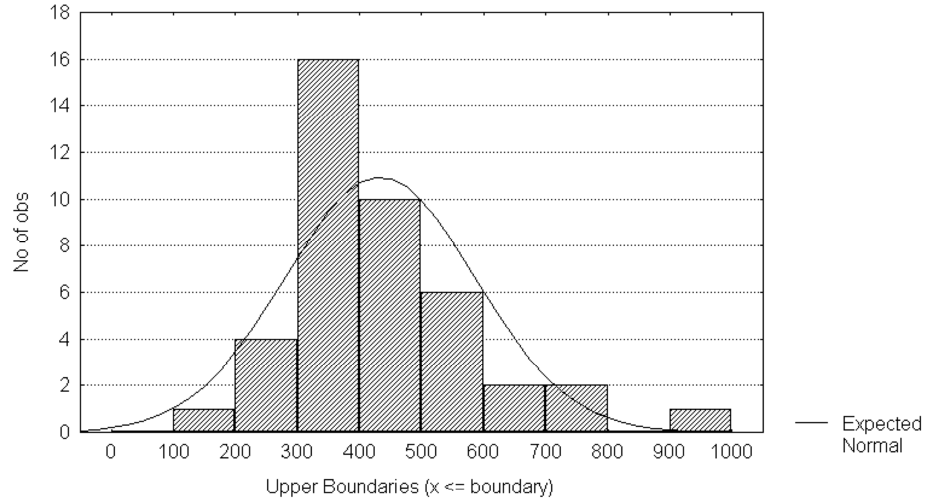

Fig. 4. Distribution of the copper concentration (ng/mL) in 42 Single Malt Scotch Whiskies.

concentration in the rye. A spirit not made from grain, Becherovka, contained hardly any detectable copper < 20 ng mL^{-1}.

Copper in whisky can be traced to two major sources: The copper stills that the whisky is distilled in, and the barley from which the spirit is distilled. An estimation as to which of the two factors is the more important follows. For example the *Talisker* distillery on the Isle of Skye uses approximately 8 t of barley per mash. At 12 mashes a week, they would use 4600 t of barley in a year. Malted barley has a concentration of approximately 8 milligram copper per kilogram[2]. Therefore in one year, 37 kg of copper will go into the distillery from the barley. The stills are split into 6 sections, each section weighing 1.5 t, and are replaced once every ten years as their thickness decreases. Assuming that replacement occurs after an average of one quarter of the copper has dissolved then for the 5 stills, 1.1 t of copper dissolves per year. Therefore, the percentage of the copper that comes from the barley is a mere 3%. Hence, the method of production (use of copper stills) mainly determines the amount of copper and as well as some other elements in the whisky rather than the origin of the water or the barley. Approximately 1 kg copper is released daily by the Talisker distillery with the pot ale and spent lees, indicating that only a minority of the copper is found in the final product.

The sample of Laphroaig appeared to be an anomaly in the results for copper content. It was shown to contain far less copper than the average Malt Whisky (193–263 ng mL^{-1} compared to the 385–480 ng mL^{-1}; 95% confidence limit), a result that was consistent in both samples of this whisky, taken from two different bottles. Laphroaig is known to be an unusual whisky, laden with peat and highly phenolic. Given the high amount of phenolic acids that are present in this whisky, it might be assumed that the copper content would be higher than normal. There may however be some individual characteristic of this Malt Whisky that lowers the amount of copper released into the final product. One explanation could be that the copper is complexed in the still and therefore cannot be volatilised into the final spirit. This complexation would take place in the still between the copper and compounds found in the water used. The water used for Laphroaig is unique in that it is taken straight from the peat bogs that surround the distillery. These compounds might form a stable complex with the copper ions in the still and be washed out in the residue from the still, the 'spent lees'. Another possibility could be that the organic compounds in the spirit are also higher and when the whisky was stored in wooden casks, the organic complex binds the copper and binding to wood also occurred.

In addition a possible correlation between the acidity of the Whisky and its copper content was tested, (since a major part of the copper comes from dissolution of the still itself). A sample of each whisky was titrated against 0.01M NaOH (data not shown here). The Blended Whiskies tested showed the lowest levels of acidity and the Malt Whiskies had higher acid concentrations. This may explain the disparity in copper levels between the two whisky types.

CONCLUSIONS

The fingerprint of the metal concentration of the whiskies cannot be used as criteria to identify different regions of whisky production. However, whisky spirits contain copper in significantly greater quantities than other distilled spirits. The Malt Whiskies have a significantly higher concentration of copper than the blended Scotch Whiskies or pure Grain Whiskies. Since the differences are highly significant, it can be proposed that a simple analysis for the copper concentration could be used to identify a Malt Whisky from a Blended or Grain Whisky. Due to the simplicity of the copper determination, this test could be used to quickly ascertain if a whisky is a Blended Whisky or a pure Malt Whisky. More studies would be needed if whiskies made from Rye or Maize are to be distinguished from the Single Malt product.

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REFERENCES

1. Aylott, R.I., Clyne, A.H., Fox, A.P. and Walker, D.A., Analytical strategies to confirm Scotch Whisky authenticity. *Analyst,* 1994, **119**, 1741–1746.
2. Feldmann, J., Marr, I.L. and Anderson, S., Characterization of copper species discharged into a small sealoch from a whisky distillery in North West Scotland. 4th International Symposium on Speciation of Elements in Biological, Environmental and Toxicological Sciences, June 25-July 1, 2000, Whistler, BC.
3. Duke, J. A., Handbook of phytochemical constituents of grass herbs and other economic plants. CRC Press: Boca Raton, FL, 1992.
4. Fitzgerald, G., James, K.J., MacNamara, K. and Stack, M.A., Characterisation of whiskeys using solid-phase microextraction with gas chromatography-mass spectrometry. *J. Chromatogr. A,* 2000, **896**, 351–359.
5. Gonzalez-Arjona, D., Gonzalez-Gallero, V. Paplos, F. and Gonzalez, A.G., *Anal. Chim. Acta,* 1999, **381**, 257–264.
6. Lee, K.Y.M., Paterson, A., Birkmyre, L. and Piggott, J.R., Headspace congeners of blended Scotch whiskies of different product categories from SPME analysis. *J. Inst. Brew.,* 2001, **107**, 315–332.
7. Lehtonen, P.J., Keller, L.A. and Ali-Mattila, E.T., Multi-method analysis of matured distilled alcoholic beverages for brand identification. *Z. Lebensm. Untersuch. Forsch. A,* 1999, **208**, 413–417.
8. Lendinez, E., Lopez, M.C. Cabrera, C. and Lorenzo, M.L., Determination of chromium in wine and other alcoholic beverages consumed in Spain by electrothermal atomic absorption spectrometry. *J. AOAC Intern.,* 1998, **81**, 1043–1047.
9. Parker, I.G., Kelly, S.D., Sharman, M., Dennis, M.J. and Howie, D., Investigations into the use of carbon isotope ratios ($^{13}C/^{12}C$) of Scotch whisky congeners to establish brand authenticity using gas chromatography – combustion – isotope ratio mass spectrometry. *Food Chem.,* 1998, **63**, 423–428.
10. Quinn, J.P., Barker, T.W. and Marchant, R., Soluble complexes of copper and zinc in whiskey distillery spent wash. *J. Inst. Brew.,* 1982, **88**, 95–97.
11. Sharpe, F.R. and Chappell, C.G., An introduction to mass spectrometry and its application in the analysis of beer, wine, whisky and food. *J. Inst. Brew.,* 1990, **96**, 381–393.

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