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AN ACTUAL CASE OF EXAMINATION OF COUNTERFEITED WHISKY

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In this paper it is presented a case of falsification of whisky in which empty bottles of genuine spirit were re-used as containment for low price whisky. Activation analysis was made of bottle-caps (a lead and tin alloy) of counterfeited bottles and of genuine imported ones as well as of a stock of bottle-caps found at the place where the material was apprehended. Results for trace and main elements indicated common origin for the bottle-caps in the counterfeited bottles and the ones found at the place where the material was apprehended and different origin for the bottle-caps in the imported bottles, indicating re-use of the imported bottles.

Introduction

Most of the applications of activation analysis to indicate fabrication or distribution of illicit spirits have been made in cases of the so-called "moonshine whiskies".[1,2] In illicit distilleries very crude equipment is commonly used, the utilization of old automobile radiators as condensers and of tubing made up with soldered copper being not unusual. Further, little care is exercised in selecting raw materials and storage containers.[1]

Illicit distilleries are frequently located in places where soil and debris can fall into the fermenting bath. The result of the improper fabrication conditions mentioned is that a variety of chemical elements may be found in moonshines, some of them being toxic and harmful to human health. Hoffmann et al.[1] report that concentrations as high as 143 ppm for zinc, 28 ppm for lead, 37.6 ppm for cadmium and 15.8 ppm for mercury have been found in moonshines. Many other elements are present in moonshines and also in rather large concentrations, lead and mercury being of special importance due to their high toxicity.

The common origin of samples of moonshine whiskies is usually ascribed by comparison of the result of activation analysis for chemical elements present in the samples being compared.

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Another type of counterfeiting of spirits is when there are two sources from which the merchandise can be obtained the imported merchandise and the locally-made one. Both types of spirits are of licit fabrication but the locally-made whisky is frequently much cheaper than the imported one. In such cases the counterfeiting consists in using empty bottles of imported spirit and filling them with cheaper locally-made spirit. Packing boxes, labels, stamps, etc. are usually reproduced to look as original and the counterfeited merchandise is then sold at compensating prices for the counterfeiter.

In this paper a case such as this is presented in which locally-made whisky was sold as imported Scotch. Neutron activation was used to analyse various fraudulent materials and also their counterparts in genuine imported Scotch.

Case history

A large stock of bottled whisky, ready to be sold, and claimed by the proprietor as genuine Scotch, was found and apprehended. The bottles were packed in cardboxes made to look as original and labelled as such, as were the bottles, which were provided with non-refillable fitments. Various trade-marks were represented, the majority in this particular case being "Johnnie Walker, Black and Red Label".

At the same place was found a stock of bottle caps, cork rings, capsules and non-refillable fitments, the owner did not deny that these had been fabricated in the country, legally, and had been acquired, also legally, from a local manufacturer who supplied local distilleries.

This material, and especially bottle-caps, is furnished by the manufacturer with no trade-marks on it, and is then printed with the mark and colour of the particular distillery. What is important to note is that any colour and mark could be stamped on the bottle-caps with fairly simple machinery.

The proprietor of the whisky, however, claimed that the bottle-caps, for instance, were used only in some cases when the original caps, on the original bottles, had been accidentally damaged, that none of the bottle caps of the apprehended whisky bottles had been substituted, and that the material was original.

In order to check all the information, so that it could be decided what legal procedures should be adopted, against falsification and/or smuggling, a stock of legitimate bottle caps was secured from the local manufacturer. These caps were not printed with the colour of any particular trade-mark.

The same type of caps were obtained from bottles of genuine imported "Johnnie Walker" Scotch. Some genuine material, such as cork-rings, capsules, bottle caps, were also kindly provided by "James Buchanan & Company Limited", Devonshire House, London.

In this way the following material was available for analysis:

(a) caps from the found stock; caps secured form the local manufacturer; caps from the apprehended whisky bottles; caps from genuine Scotch bottles;

(b) labels from the found stock; labels from genuine Scotch bottles;

(c) cork rings from the found stock; cork rings supplied by "James Buchanan & Company Limited";

(d) whisky from the bottles of the found stock; genuine Scotch whisky.

Item (b) (labels) did not prove a suitable material for comparison. No genuine labels with the same trade mark as those found in the stock were available. Only labels removed from original bottles could be obtained. However, the paste with which the labels had been placed on the bottles interfered on activation, and the result was that the test always showed materials of different origins. Even if a good cleaning procedure was applied to the labels that had been pasted on the bottles, the "history" of the paste was always present.

Item (c) (cork rings) could not be successfully used to indicate different origins either. Curiously enough, activation analysis for trace elements showed very similar compositions for the rings of the apprehended stock and those sent by James Buchanan. It was later learnt that practically all cork distributed throughout the world comes from the same origin (Portugal). The slight differences between rings from James Buchanan and the ones found in the stock did not allow a definite conclusion concerning different origins.

Items (a) (bottle caps) and (d) (spirit) were taken for analysis and the results compared, as will be shown.

Experimental

Bottle caps taken from the apprehended stock, those furnished by the local manufacturer and those taken from legitimate imported bottles were submitted for spectrographic analysis. Such analysis showed that the caps had lead as main component and tin and antimony as minor elements. Trace elements found by spectrographic analysis were copper, silver and cadmium.

The samples were then analysed by activation analysis. Samples of about 30 mg were washed with acetone to remove paint, and irradiated in a thermal neutron flux of $5 \cdot 10^{12}$ n $\cdot$ cm^{-2} $\cdot$ sec^{-1} for 5 to 15 min. After irradiation the samples were etched in dilute nitric acid, washed with water, weighed and counted after a cooling period of two hours. Standards of tin (0.5 mg Sn) and antimony (10 μg Sb) were irradiated together with the samples. Samples and standards were counted using a 4096-channel Hewlett Packard Model 5401 analyzer coupled to a 27.8 coaxial Ge(Li) detector (Ortec; 2.1 keV resolution for ^{60}Co 1.33 MeV; peak-to-Compton ratio, 26/1), through a Spectroscopy Amplifier (Ortec, Mod. 451) using a bias supply of 2500 volts.

Areas under the peaks corresponding to ^{123}Sn (160 keV, T = 40 m) and ^{122}Sb (564 keV and 686 keV, T = 67.2 h) were determined for samples and standards, and

the amounts of each of these elements in the alloys were calculated from the known masses of the standards. Decay curves were drawn to check for interferences, especially in the cases where peaks due to ^{76}As (559 and 657 keV)

Table 1

Antimony and tin in bottle caps. Results in ppm. Number of samples analysed: 10 for each type. Errors as standard deviation

Element	Samples			
	A	B	C	D
Sn	4350±155	4186±256	3522±78	12694±1901
Sb	2374± 72	2381±120	2297±26	564± 74

A - caps from apprehended stock;
B - caps from apprehended bottles;
C - locally-made;
D - taken from imported bottles.

might be present. The apparent antimony content formed by second-order interference $^{120}Sn(n,\gamma)\,^{121}Sn \rightarrow {}^{121}Sb(n,\gamma)\,^{122}Sb$ was calculated by means of the data of De Beeck[3] and since it was very small for 8 hr irradiation, it was not subtracted from the ^{122}Sb value for the reaction $^{121}Sb(n,\gamma)^{122}Sb$.

Results for tin and antimony analysis are presented in Table 1.

The same samples were analysed for trace elements. Samples weighing about 500 mg were irradiated for 8 hrs in a thermal neutron flux of 10^{12} n · cm^{-2} · sec^{-1} left to decay for 16 hrs, etched in dilute nitric acid, washed and weighed. Standards for Cu, Ag, As, Zn, Cd, and Co were also irradiated together with the samples. Carrier solutions (nitrates) were put into a 50 ml beaker (about 40 mg for each carrier) and the solution was carefully evaporated on a water bath. The irradiated alloy and 50 mg of metallic tin were put into the beaker containing the carriers, 5 ml of 1:1 nitric acid was added, and the mixture was carefully heated until dissolution of the alloy and the tin carrier.

The resulting solution was heated on a water bath until the volume was reduced to about 2 ml, and 30 ml of boiling water was added, followed by 2 ml of a 0.25 mg/ml sodium sulfate solution. The lead sulfate precipitate was centrifuged, washed three times with 2 ml of hot 5% nitric acid solution and next with hot water. The precipitate was used to count the activity of ^{76}As by means of the peaks corresponding to 0.657 and 1.215 MeV. In order to reduce pile-up and distorsion effects caused by the gamma-rays from ^{123m}Sn (T = 40.3 m) and ^{125m}Sn (T = 9.6 m),

the precipitate was counted after a cooling period of 18 hrs inside a lead cylinder 4 mm thick. A 1 mm cadmium slab was placed between the detector and the lead absorber to reduce the effect of the lead X-ray fluorescence, as recommended by

Table 2

Trace elements in bottle caps. Results in ppm. Number of samples analysed: 5 for each type

Element	Samples			
	A	B	C	D
Co	0.49	0.55	0.59	0.05
As	n.d.	n.d.	n.d.	6.8
Ag	71	84	68	34
Zn	16.0	15.3	15.8	12
Cd	5.4	6.5	5.1	7
Cu	56.1	81.0	72.1	380

Maenhaut et al.[4] The 0.657 MeV and 1.215 MeV ^{76}As peaks are thus reduced to 48% and 58%, respectively. A counting time of from 100 to 200 min, however, was sufficient to accumulate enough counts for a standard deviation of less than 10%.

After separation of the lead sulfate precipitate by centrifugation the solution was carefully evaporated to dryness and heated to eliminate nitric acid. The residue was taken up with water, made up to 10 ml in a volumetric flask, and 1 ml of the solution was taken to count ^{64}Cu. From the rest of the solution copper and silver were eliminated by deposition on iron wire and the solution was used for the determination of the other traces. ^{64}Cu and ^{110}Ag were counted on the iron wire. Correction for ^{115}Cd formed from $^{118}Sn(n,\alpha)^{115}Cd$ was made by irradiation of the alloy with and without cadmium shield. The contribution of ^{65}Zn to the 0.51 MeV annihilation peak for ^{64}Cu was discounted.

Experiments carried out with traces of the elements to be analysed showed a recovery of above 95%. Results are shown in Table 2.

Analysis of cork rings

Cork rings provided by "James Buchanan and Co. Ltd " were irradiated for various periods of time, simultaneously with cork rings apprehended in the counterfeiter's premises. Peak energy identification and half-life determinations showed that the trace element compositions for the two types of samples were practically the same. Differences in the proportions of some elements were of the same order as counting standard deviations and did not allow the inference of different compositions. Trace

elements positively identified in the samples were Cu, As, Br, Ag, W and Mn. No quantitative determination of these elements was made, but only a peak-ratio comparison, which did not show any flagrant differences.

Table 3
Elements present in apprehended and in legitimate whiskies (ppm)

Element	Apprehended	Legitimate
Au*	0.027	0.017
Sb*	0.34	0.33
Sc*	0.005	0.008
Cr	0.027	0.016
Zn	0.22	0.17
Co*	0.30	0.32
Cu	0.13	0.20
Br	0.007	0.009
Cd	0.04	0.06
Mn	0.012	0.009
Hg	n.d.	n.d.
Pb	1.0	1.0

*ppb

Analysis of the spirit

The apprehended whisky was analysed for lead by atomic absorption spectrometry, giving less than one part per million. Mercury was not detected by activation analysis of 5 ml samples irradiated for 8 hours in a thermal neutron flux of $5 \cdot 10^{12}$ n · cm^{-2} · · sec^{-1}.

In order to check differences in trace element compositions between licit imported whisky and the apprehended spirit, 100 ml samples of both types were concentrated under reduced pressure to volumes of 1 ml. The 1 ml residues were placed in quartz ampoules and irradiated for 8 hrs in the same fluxes as before.

After a decay of 18 hrs the ampoules were cooled in liquid nitrogen, broken and the irradiated residue transferred, with 2 ml of concentrated hydrochloric acid, to the top of hydrated antimony pentoxide (HAP) columns, previously washed with 5 ml of concentrated hydrochloric acid, in order to remove sodium. 30 ml of concentrated hydrochloric acid was passed through the HAP column and the solution collected in a 50-100 ml beaker containing carrier solutions for Cu, Hg, Sb, As, Cr, Se, Zn, Br, Cd and Au. The final solution was concentrated on a water bath to 1 - 2 ml, and transferred to small counting bottles. The beaker was washed with about 1 ml of 1 : 1 hydrochloric acid and the washings added to the counting bottles, the final volume being made up to 3 ml. The bottles were counted in the same counting equipment as described before, and the counting results compared with the values for standards irradiated simultaneously with the samples. Results are presented in Table 3.

Discussion

From the results in Table 1 it is seen that the proportions of tin are of the same order for the apprehended stocks caps (samples A), the caps on the apprehended bottles (B), and the locally made caps (C). On the other hand, the proportion of tin in the samples taken from imported bottles (samples D) was much larger than the other three. The antimony concentration is smaller for samples D than for samples A, B and C, which were all of the same order.

The manufacturer of the locally-made caps informed us that due to the somewhat lower price of the low proportion tin alloy, this alloy was preferred to the high proportion tin alloy. In fact, all high tin alloys were in general of imported origin and not used for manufacture of bottle caps.

Based only on the tin and antimony analyses, the results of which are presented in Table 1, it might be inferred that the caps from the apprehended stock, those from the apprehended bottles and the ones of local fabrication, were of the same origin.

Trace element analyses for the same samples (Table 2) showed a similarity of composition for samples A, B, and C, and a difference for sample D. The cobalt concentration is much smaller for sample D than for A, B, and C; arsenic was not detected in samples A, B and C; the silver concentration for sample D is about half that for samples A, B and C.

Differences for zinc and cadmium are not very large in the four samples. Copper is higher in sample D than in samples A, B and C. Gold was not detected in samples A, B and C.

The results form Table 2 confirmed the conclusions based solely on the tin and antimony analyses. This meant that all of the examined bottles (ten specimens) were covered with caps fabricated from the same lead-tin alloy as those sold by the local manufacturer. This did not agree with the information of the proprietor of the apprehended material that they had not been substituted.

Data on the analysis of the spirit contained in the apprehended bottles and of imported whisky of the same trade mark as labelled on the apprehended bottles, are presented in Table 3. It seen that, at least for the analysed elements, the differences are not very pronounced (five samples analysed). It is important to note that mercury was not detected in either type of sample and that the proportion of lead was less than one part per million in both the apprehended and the legitimate whiskies. This was to be expected since both types of spirits were of legitimate fabrication and the process of counterfeiting was simply the transfer of liquid from one container to another, with no contact with materials that might contain lead or mercury.

In fact the whisky used to fill the empty bottles, being of legitimate fabrication, should not contain any large excess of trace elements that might be introduced during the fabrication procedures, since distilleries are in general built of the same standard materials, such as stainless steel.

A larger survey analysis of locally-produced whisky is necessary for trace elements that might be systematically introduced during local fabrication.

The analysis of the few elements listed in Table 3 does not allow a conclusion concerning the difference of the samples. However, a peak-height ratio comparison of the two types of samples showed differences indicating non-common elements or different proportions of certain common elements.

Since organic constituents, ethyl alcohol percentage and density are within the limits permitted by sanitary laws, the spirit being licitly produced, the only way to differentiate imported whisky from the licit locally-produced one would be by identification of the chemical elements responsible for the peak-height ratio differences.

A large survey analysis of trace elements present in locally-produced whisky is planned.

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References

1. C.M. Hoffmann, R.L. Brunelle, M.J. Pro, C.E. Martin, J. Assoc. Off. Agri. Chem., 51 (1968) 380.
2. M.J. Pro, H.L. Schlesinger, C.M. Hoffmann, Proc. of the First International Conference on Forensic Activation Analysis, General Atomic Laboratories, San Diego, Calif., September 19-21, 1966, p. 103.
3. J.P. Op De Beeck, J. Radioanal. Chem., 4 (1970) 137.
4. W. Maeenhaut, F. Adams, J. Hoste, J. Radioanal. Chem., 9 (1971) 27.