Microchim Acta (2008) 160: 283–289
DOI 10.1007/s00604-007-0825-9
Printed in The Netherlands

**Microchimica Acta**

*Original Paper*

# Rapid and mobile brand authentication of vodka using conductivity measurement

**Dirk W. Lachenmeier**[1], **Beke Schmidt**[2], **Thorsten Bretschneider**[2]

[1] Chemisches und Veterinäruntersuchungsamt (CVUA) Karlsruhe, Karlsruhe, Germany
[2] Bacardi GmbH, Hamburg, Germany

Received 27 March 2007; Accepted 14 June 2007; Published online 8 August 2007


**Abstract.** Conductivity measurement is introduced as a rapid, simple and cheap way to identify counterfeit vodka. It was found that the conductivity of vodka derives exclusively from its content of inorganic anions which were previously suggested as markers for vodka authenticity using ion chromatographic determination. The conductivity of vodka is very stable between different batches of bottle filling of the same brand, but there are large differences between different brands. Especially discount brands have significantly higher conductivities than premium products. The applicability of conductivity measurement was demonstrated in authentic forensic cases of brand fraud. A large advantage above other methods of authentication is the possibility to conduct conductivity measurements with mobile meters directly in gastronomy.

**Keywords:** Identity of spirits; vodka; conductivity measurement; ion chromatography; brand fraud

Research on the detection of illicit spirits was so far focused on adulterations such as blending high-quality distillates with ethanol made from a cheaper raw material, adding synthetic volatile components to neutral alcohol or by misleading labelling of the variety and origin of the raw material [1–3]. The classic approach of spirit authentication is the gas chromatographic analysis of volatile compounds (congeners of alcoholic fermentation). However, the wide range of composition for each type of spirit and the considerable overlap between them made the unambiguous identification of many spirit types difficult and it was found that the modern 'bootlegger' can manufacture spirits of such quality that the profile is not egregious so that the extended spirit may still appear authentic [4]. In addition, if a high degree of rectification takes place during distillation, volatile components will be reduced so that application of gas chromatography for the identification of the raw material appears to be inappropriate. In these cases, the natural isotope ratios may be used as descriptive analytical parameters [3]. For example, rums and corn alcohols from $C_4$ plants (cane and corn) can be easily distinguished from alcohols from $C_3$ plants such as grape, potato, beet, or $C_3$ cereal alcohols (pure malt whisky). The botanical origin of the alcohols used in gins or vodkas can be checked, where this has a bearing on the quality or price of the end-product [5]. The use of isotope ratios to establish spirit authenticity was demonstrated for whisky [6, 7], tequila [8, 9] and cherry spirits [10, 11]. Isotopic criteria may also be used for short-term dating of brandies and spirits (i.e. the time of storage in casks) [12]. Recently, infrared spectroscopy with mul-

Correspondence: Dirk W. Lachenmeier, Chemisches und Veterinäruntersuchungsamt (CVUA) Karlsruhe, Weißenburger Str. 3, D-76187 Karlsruhe, Germany, e-mail: Lachenmeier@web.de

tivariate data analysis was successfully applied to the authentication of fruit spirits [13], brandies [14], cognacs [15] and tequila [16]. Direct infusion electrospray ionization mass spectrometry was applied for chemical fingerprinting of whisky samples for type, origin and quality control [17].

Less research was focused on the classic fraud scenario. Especially in the case of premium or brand spirits, there exists a large economic incentive to mix or completely substitute one brand with another less expensive brand. This usually occurs in bars or restaurants and therefore affects the consumer and places honest traders at a financial disadvantage [6]. If the fraud is conducted on a larger scale, the substituted products may contain illegal additives, which may be very toxic and which are normally not permitted for use in commercial production. In the worst case, denatured industrial alcohol may be used as substitute. For example, counterfeit Johnnie Walker whisky containing 4.3% of methanol was found on sale in London; one person died in Finland after drinking counterfeit Captain Morgan Jamaica rum, which contained ethylene glycol [18]. Besides those grave health consequences for the consumer, the industry faces erosion of brand equity if such lower quality or even dangerous counterfeit products reach the market. Of course, the counterfeiting of spirits is an offence against national and European trademark laws as well as food laws.

For all these reasons, industrial as well as governmental spirit control laboratories require efficient methods to authenticate spirit brands. As mentioned above, highly rectified spirits like vodka are the most problematic product group due to the near absence of volatiles besides ethanol. We have previously shown that the brand fraud of vodka can be determined by analysing the composition of inorganic anions using ion chromatography (IC) [19]. However, IC needs relatively expensive equipment, trained personnel and cannot be conducted in a mobile way "on site" in the gastronomy, production or storage facilities. In this study, we have evaluated if a simple conductivity measurement can be used to authenticate vodka using laboratory as well as portable instruments. Authentic examples demonstrate the method's suitability for detecting brand fraud.

## Experimental

### *Samples*

Two different types of vodka samples were evaluated. On the one hand, vodkas of different plants and batches of Bacardi were analyzed (for details see Table 1). On the other hand, vodka samples submitted by local authorities to the CVUA Karlsruhe in the context of governmental food control were analysed. In the latter case, the samples were selected randomly in wholesale and retail trade and should be representative for the German market.

### *Instrumentation*

The measurements at Bacardi were conducted with the microprocessor conductivity meter LF 537 by WTW (Weilheim, Germany, www.wtw.com). The CVUA Karlsruhe used the inoLab Cond Level 2 P by WTW (Weilheim, Germany, www.wtw.com) and the pocket conductivity meter DIST 3 by Hanna Instruments (Kehl am Rhein, Germany, www.hannainst.com). All three instruments automatically compensated for temperature.

### *Statistics*

All data were evaluated using standard statistical packages for Windows. Statistical significance was assumed at below the 0.05 probability level. One-way analysis of variance (ANOVA) was used to test whether three or more cases have the same mean including the Bonferroni post hoc means comparison. Pearson's test was used to evaluate the significance of linear relations.

## Results and discussion

### *Origin of vodka's conductivity*

To evaluate the suitability of conductivity measurement to authenticate vodka, we first looked at the production of vodka and tried to identify conductive constituents in vodka. By European law, vodka is a spirit drink produced by rectifying ethyl alcohol of agricultural origin or filtering it through activated charcoal, possibly followed by straightforward dis-

**Table 1.** Batch stability of the conductivity of different vodka brands from Bacardi

| Vodka brand | Place of bottle filling | No. of batches analyzed | Time frame | Conductivity [$\mu S\,cm^{-1}$] (mean $\pm$ standard deviation) |
|---|---|---|---|---|
| Grey Goose vodka, 40% vol | Gensac, France | 5 | June 2006–Feb. 2007 | $3.0 \pm 0.2$ |
| Eristoff vodka, 37.5% vol | Beaucaire, France | 5 | Jan. 2006–Feb. 2007 | $4.9 \pm 1.3$ |
| Finlandia vodka, 40% vol | Rajamäki, Finland | 33 | Sept. 2006–Feb. 2007 | $17.2 \pm 1.0$* |

* Includes 2 flavoured batches with Mango aroma ($16.1\,\mu S\,cm^{-1}$) and Cranberry aroma ($16.4\,\mu S\,cm^{-1}$).

tillation or an equivalent treatment. This selectively reduces the organoleptic characteristics of the raw materials. Flavouring may be added to give the product special organoleptic characteristics, such as a mellow taste [20]. The raw spirit put through rectification is usually produced from grain (rye and wheat) and potatoes. In vodka production, the quality of water has the utmost importance. For premium vodka brands, demineralised water is filtered through activated carbon to absorb unwanted organic and inorganic materials. Then it is passed through deionization columns, which remove other impurities present. The rectified spirit and demineralised water are blended in the correct proportions. The blended spirit is charcoaled for up to 8 h. The charcoal adsorbs impurities that cannot be removed by distillation alone. The vodka is now reduced to its bottling strength by adding further demineralised water [19]. After a final filtration and bottling, the vodka will remain stable for many years if very well demineralised water is used. Otherwise, an increased content of calcium, magnesium or other compounds can lead to instability or precipitation over time.

As water and ethanol have neglectable electrical conductivities, we can conclude that the only conductive constituents of vodka appear to be inorganic ions contained in the water used for production. If demineralised water is used, a rather low conductivity is expected. The conductivity of vodka can be affected during the production process by a specific water treatment or by different additives for the adjustment of alkalinity (e.g. alkalinisation with sodium bicarbonate, neutralization with 0.1 M hydrochloric acid), which enhance the softness of taste [21].

To confirm our considerations that the conductivity of vodka purely derives from inorganic ions, we have analyzed 107 different vodkas samples for anions (chloride, nitrate, phosphate and sulphate), cations (sodium and potassium) and conductivity. The total ion content (i.e. the sum of all analyzed anions and cations) has an excellent linear relation with the conductivity ($R = 0.99226$, $p < 0.0001$). Two things can be concluded from this result: (i) the conductivity of vodka derives exclusively from inorganic ions, (ii) due to the co-linearity between the anionic content of vodka and its conductivity, conductivity measurement alone may be an adequate means for vodka authentication.

*Batch stability of vodka conductivity*

To use conductivity to check the authenticity of specific vodka and perhaps even assign or exclude a brand of an unknown product, a stability of the conductivity between different batches (i.e. different days of bottle filling at the plants) would be required. The analysis results of three vodka brands of Bacardi from different filling plants and production dates are presented in Table 1. It can be seen that the conductivity of the three products is quite stable. The differences are in the range to be expected from the error of analysis alone. The very low differences can be explained by the control of water quality inside the manufacturers framework of quality control and HACCP (hazard analysis and critical control points). In case of Grey Goose and Eristoff vodka, drinking water is demineralised and purified by filtration through ion-exchange resins. The removal of ions is checked by conductivity. In case of Finlandia vodka, water of glacial origin is taken from their own wells near Rajamäki (Finland). Only filtration to remove possible impurities is applied. Therefore, higher ion concentrations compared to demineralised water are present.

In addition, a flavouring of vodka with fruit aromas did not change the conductivity. Two flavoured products had no significantly different conductivities than the unflavoured types of the same vodka. Furthermore, we have analyzed different batches of vodkas available on the German market (Table 2). The results confirm for other manufacturers that the conductivity is very stable between different batches.

**Table 2.** Batch stability of the conductivity of different vodka brands from commercial trade in Germany

| Vodka brand | Origin according to label | No. of batches analyzed | Conductivity [$\mu S\,cm^{-1}$] (mean ± standard deviation) |
|---|---|---|---|
| Moskovskaya vodka, 40% vol | Produced in Russia, filled in Riga, Latvia | 3 | 21.0 ± 1.6 |
| Wyborowa vodka, 40% vol | Poland | 3 | 4.4 ± 0.3 |
| Absolut vodka, 40% vol | Ahus, Sweden | 3 | 3.1 ± 0.4 |
| German discount vodka 1, 37.5% vol | Unknown | 2 | 61.8 ± 1.9 |
| German discount vodka 2, 37.5% vol | Unknown | 2 | 81.5 ± 4.2 |

As the conductivity depends exclusively on the ionic composition of vodka, our results are also confirmed by a number of previous ion chromatographic studies. Arbuzov and Savchuk found very stable anion-cation compositions in vodkas manufactured at the same distillery [22]. Savchuk et al. concluded that vodka is characterised by the ionic composition of the water used in its production [2]. In our previous study, we likewise found no significant differences in anion concentration between samples of the same brand but with different dates of bottling [19].

It is concluded that the relatively stable conductivity of each specific vodka allows an allocation or a differentiation of vodka brands. Even on this stage, large differences of conductivity between different vodka brands were noted. It appears that Finlandia can be differentiated from the other vodka brands of Bacardi shown in Table 1. Most notably, the German discount brands had significantly higher conductivities than the mark products in Table 2.

### *Differences in conductivity between premium and discount vodka brands*

To demonstrate the applicability of the method developed, vodka samples of different origins were analyzed. The results are shown in Fig. 1. The conductivities between the four sub-groups of vodkas (Russian, Polish, Premium Brand and Discount Brand) vary in a highly significant way (ANOVA $p < 0.0001$). The discount brands have a significantly higher conductivity than all other groups. However, no significant differences between Russian, Polish and Premium Brand vodkas could be proven.

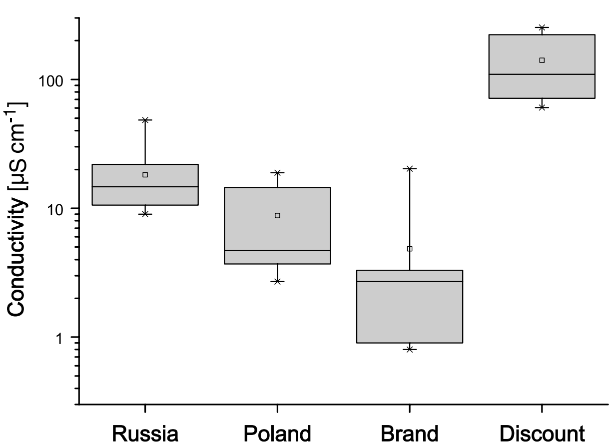


**Fig. 1.** Box charts of the analysis results of vodkas ($n = 60$) from different origins in a logarithmic scale. The vodkas from so-called discount shops have significantly higher conductivities than Russian, Polish or other premium brand products

The difference between the discount brands and all others can be easily explained by the manufacturers' effort about water quality and treatment. We previously determined that Russian vodkas had a significantly lower total anion concentration (mean 3.8 mg $L^{-1}$) than the ones bottled in Germany (mean 78.4 mg $L^{-1}$). Particularly low anion concentrations were determined in premium products, which are manufactured using ion exchange or reverse osmosis for deionisation [19]. In contrast, manufacturers of discount brands tend to bottle their vodkas with standard tap water without any further water treatment; therefore, those brands have higher ionic contents and conductivities.

In fact, the most common form of brand fraud is the ''re-filling'' of premium brand bottles with discount brand vodkas in the gastronomy. Therefore, the simple measurement of conductivity is an easy way to differentiate counterfeit from authentic vodkas.

### *Mobile brand authentication of vodka*

In the literature, only a single possibility for mobile brand authentications of spirits was described so far by MacKenzie and Aylott [23]. It consisted of a portable UV/visible diode-array spectrophotometer, which was used to confirm Scotch whisky authenticity by measuring the absorbencies of whisky mainly derived from substances extracted from oak casks or caramel sugars used for colour consistency. However, the operation appeared to be relatively complicated because a calibration using reference data and a complex statistical treatment of the measured spectra were required. For vodka, it appears unsuitable as such specific absorptions in the UV/visible range do not exist.

As we have shown using laboratory-type conductivity meters that the brand differentiation of vodka is possible, the question remained if we could conduct those measurements directly in the gastronomy using mobile conductivity meters. A range of such mobile, battery-powered meters is available from different manufacturers. Our experiments were conducted with a so-called pocket conductivity meter. Nevertheless, the instrument contains a LCD display and automatic temperature compensation. The meter must only be dipped into the vodka sample and the conductivity can be read on the display. The measurement is feasible for food inspectors during their controls of gastronomy.

**Table 3.** Validation results for the determination of vodka with laboratory and pocket conductivity meters

| | Mean conductivity [$\mu S\,cm^{-1}$] | Intraday CV [%] ($n=10$) | | Interday CV [%] ($n=18$) | |
|---|---|---|---|---|---|
| | | Laboratory | Pocket | Laboratory | Pocket |
| Vodka 1 | 10 | 0.5 | 6.8 | 2.9 | 13 |
| Vodka 2 | 70 | 0.5 | 0.0 | 1.4 | 1.4 |
| Vodka 3 | 280 | 0.4 | 0.5 | 1.2 | 1.4 |

*CV* coefficient of variation.

To check the stability and reproducibility of measurements with the pocket conductivity meter, we have analyzed 229 samples during a three-month period with both the laboratory and the pocket conductivity meter. The results showed an impressive consistency ($R=0.99992$, $p<0.0001$) with no detectable differences between both meters. Furthermore, we have made a method validation for both meters (Table 3). With the exception of very low conductivities (around $10\,\mu S\,cm^{-1}$), the pocket device showed comparable validation data to the laboratory meter. The higher coefficients of variation (CV) at low conductivities derive purely from the fact that the pocket meter does not show decimals. But even a CV of around 10% is sufficient to differentiate premium brand vodka with conductivity below $20\,\mu S\,cm^{-1}$ from discount brand vodka with a conductivity above $60\,\mu S\,cm^{-1}$. All in all, the pocket conductivity meter fulfilled our requirements for mobile brand authentication.

In contrast to the portable UV/visible spectrophotometer [23], mobile conductivity measurement needs no product specific calibration or statistically treatment of a spectrum. The conductivity measurement can be used for all kinds of spirits and not only for spirits with absorptions in the UV/visible range like oak-matured products.

### *Forensic case examples*

To validate the conductivity measurement as method for brand authentication, we have re-analyzed samples of an authentic forensic brand-fraud case, which was previously solved using ion chromatography [19]. Three suspicious vodka samples and four suspicious rum samples were taken by the local authorities in a discotheque and submitted to the CVUA Karlsruhe for examination. The samples were taken from opened bottles at the bar labelled as "Smirnoff vodka" and "Bacardi rum". According to the menu, "Smirnoff" and "Bacardi" were the only brands on offer. Customers' complaints had led to suspicion that the Bacardi and Smirnoff bottles were regularly being filled with discount-type rum and vodka. Besides original "Smirnoff" and "Bacardi" bottles in the storeroom of the discotheque, which were taken as authentic samples for comparison, vodka and rum of two discount brands of German origin were found and also taken for examination.

The case of the vodka samples is presented in Table 4. We previously detected that there were significant deviations in the concentrations of the anions chloride, nitrate and sulphate. Therefore, the results of the chemical examination of the suspicious "Smirnoff" vodkas did not correspond to those of the comparison sample. The suspicious vodka samples were judged to be counterfeit. The anionic profile of the suspicious samples corresponded significantly to the profile of the German vodka. It could therefore be assumed that this vodka had been poured into the Smirnoff bottles. The same judgements can be done using the conductivity of the samples alone. There is such a large difference between

**Table 4.** Authentic forensic case #1. Three suspicious vodkas were sold as Smirnoff. For comparison, the results of reference vodka samples are given. These findings indicate that the suspicious samples were not Smirnoff

| | Suspicious vodka samples | | | Reference vodka samples | |
|---|---|---|---|---|---|
| | "Smirnoff" 1 | "Smirnoff" 2 | "Smirnoff" 3 | Authentic Smirnoff | Authentic German discount vodka |
| Chloride [$mg\,L^{-1}$] | 8.0 | 8.7 | 9.3 | ND | 9.3 |
| Nitrate [$mg\,L^{-1}$] | 14.5 | 14.4 | 12.8 | ND | 15.5 |
| Sulphate [$mg\,L^{-1}$] | 15.5 | 17.4 | 21.1 | ND | 17.1 |
| Sum of anions [$mg\,L^{-1}$] | 38.0 | 40.4 | 43.1 | ND | 41.8 |
| Conductivity [$\mu S\,cm^{-1}$] | 74.4 | 74.6 | 75.6 | 5.5 | 75.0 |

**Table 5.** Authentic forensic case #2. Four suspicious rums were sold as Bacardi. For comparison, the results of reference rum samples are given. These findings indicate that the suspicious samples were not Bacardi

| | Suspicious white rum samples | | | | Reference white rum samples | |
|---|---|---|---|---|---|---|
| | "Bacardi" 1 | "Bacardi" 2 | "Bacardi" 3 | "Bacardi" 4 | Authentic Bacardi | Authentic German discount rum |
| Chloride [mg $L^{-1}$] | 21.5 | 21.4 | 21.4 | 23.3 | 1.3 | 18.5 |
| Nitrate [mg $L^{-1}$] | 0.6 | 0.6 | 0.6 | 0.7 | ND | 0.9 |
| Sulphate [mg $L^{-1}$] | 76.8 | 76.5 | 76.5 | 82.0 | 1.4 | 21.5 |
| Sum of anions [mg $L^{-1}$] | 98.8 | 98.5 | 98.5 | 106.0 | 2.7 | 40.9 |
| Conductivity [μS $cm^{-1}$] | 185.8 | 184.2 | 179.3 | 186.4 | 14.2 | 118.8 |

the conductivity of the authentic Smirnoff samples and the suspicious samples, that the counterfeiting can be determined from conductivity measurement without any doubt.

Likewise, the results of the chemical examination of the suspicious "Bacardi" rum samples did not correspond to those for the comparison sample (Table 5). There were significant deviations in the content of the anions chloride, nitrate, and sulphate. The suspicious rum samples were also judged adulterated and misleadingly designated. Here, it was not possible to correlate the anionic profile of the suspicious samples with that of the German discount rum. The brand of rum filled into the "Bacardi" bottles could not be determined. Possibly, it was a mixture of both rum brands. Like in the vodka case, the rums can be differentiated by conductivity measurement alone without any doubt.

## Conclusion

Valuable information about the identity of spirits can be obtained by the simple and rapid measurement of conductivity. Besides its low cost, a large advantage of conductivity measurement against other possible methodologies for brand authentication (e.g. ion chromatography, gas chromatography or isotope ratio mass spectrometry) is the fact that it can be performed on-site in the gastronomy using portable conductivity meters. Samples for further and more in-depth laboratory measurement can be selected. It was shown that conductivity measurement allows detecting counterfeit spirits in the context of forensic examinations. Besides the authentication of vodka, the methodology was suitable in the authentication of rum. In the future, it appears possible to expand the spectrum of application to other spirit types.

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