Eur Food Res Technol (2003) 218:105–110
DOI 10.1007/s00217-003-0799-8

ORIGINAL PAPER

Dirk W. Lachenmeier · Rainer Attig · Willi Frank · Constanze Athanasakis

The use of ion chromatography to detect adulteration of vodka and rum

Received: 14 July 2003 / Revised: 15 August 2003 / Published online: 1 October 2003

Abstract The use of ion chromatography to determine anions (chloride, nitrate, and sulphate) for the characterisation of colourless spirits, such as vodka or white rum, is presented. After evaporation to remove the volatiles, the sample was injected directly into the ion chromatograph. The assay showed good precision, never exceeding 1.6% RSD. The analytical results of 51 samples under study reveal that, in particular, the adulteration of brand spirits can be proven by the method described.

Keywords Identity of spirits · Vodka · Rum · Ion chromatography · Brand fraud

Introduction

In the context of food and restaurant controls or charges against restaurant operators and barkeepers, the question frequently arises as to whether there are chemical-analytical methods apart from organoleptic evidence to determine the brands of spirits. Sometimes, instead of a high-quality brand (e.g. Smirnoff vodka or Bacardi rum) shown on the menu, cheap or possibly inferior quality products may be sold.

Traditionally colourless, extract-free spirits (e.g. vodka and white rum) are identified by the detection of volatile substances using gas chromatography (GC) [1, 2, 3]. This requires a preconcentration of analytes, for example by distillation. Recently, special methods have been introduced for the isolation of volatiles, such as solid-phase extraction (SPE) or solid-phase microextraction [3, 4, 5, 6]. All these methods are complex and expensive, and they do not always produce unambiguous evidence of brand fraud. Often, there are no significant differences in the composition of volatiles between different brands of the same type of spirit. Only differentiation among several kinds of spirits is possible. Therefore, Lehtonen et al. [7] developed a complex, multi-method analysis for brand identification using statistical processing on the basis of chemical composition, ultraviolet absorption, and pH. An alternative possibility for checking the authenticity of alcoholic beverages is the determination of natural isotope ratios using ^{2}H-NMR or ^{13}C isotope mass spectrometry [8, 9, 10]. However, the high cost of instruments limit the possibilities for applying these methods in official food control.

This paper describes a simple, fast method of proving identity or brand on the basis of anion composition. This will enable the testing of suspicions that arise during food control. Spirits are reduced to bottling strength with water from rectified distillates. The ionic content of the water and brand-specific water additives used give rise to differences in the ionic composition of the product. The simple, cost-saving, and reliable method of ion chromatography, which is already approved in water analysis, can therefore be used for the determination of anions in spirits.

Vodka is a spirit drink produced by rectifying ethyl alcohol of agricultural origin or filtering it through activated charcoal, possibly followed by straightforward distillation 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 [11]. The raw spirit put through rectification is usually produced from grain (rye and wheat) and potatoes. In vodka production, the quality of water is of 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 deionisation 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 then reduced to its bottling strength by adding further demineralised water [12]. After a final filtration and bottling, the vodka will remain stable for

D. W. Lachenmeier · R. Attig · W. Frank · C. Athanasakis (✉)
Chemisches und Veterinäruntersuchungsamt (CVUA) Karlsruhe,
Weißenburger Str. 3, 76187 Karlsruhe, Germany
e-mail: Constanze.Athanasakis@cvuaka.bwl.de

Table 1 Precision, limit of detection and calibration range for determining anions in spirit samples

	Precision intraday[a] (%)	LOQ[b] (mg/l)	Calibration range[c] (mg/l)	
			10 µS	100 µS
Chloride	0.78	0.13	0.5–8	6–100
Nitrate	1.50	0.13	0.5–12	10–150
Sulphate	1.55	0.50	2–40	40–180

[a] Precision is expressed as RSD (%), n=5
[b] Limit of quantification (in reference to the spirit samples)
[c] Calibration ranges (in reference to the 4:1 concentrated measurement solutions)

many years, if very well-demineralised water is used. Otherwise, increased contents of calcium, magnesium, or other compounds can lead to instability or precipitation over time. The anionic composition 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 $NaHCO_3$, neutralisation with 0,1 M HCl), which enhance the softness of taste [13].

Rum is a spirit drink produced exclusively by alcoholic fermentation and distillation from molasses or syrup produced in the manufacture of cane sugar, or from sugarcane juice itself, and distilled at less than 96% vol. so that the distillate has discernible specific organoleptic characteristics [11]. After distillation, the fresh spirits are diluted by pure demineralised water to an alcoholic strength of about 60–70% vol. and aged in used oak barrels. During the aging process, the rum acquires a golden colour. White rum is charcoaled to remove this colour and give it a light, clean taste. After blending, the rum is reduced to bottling strength (often in the importing country). No other spirit possesses such divergent types and qualities as rum [13].

Today, ion chromatography is a routine technique in environmental analysis [14], as well as food analysis [15]. Several applications of ion chromatography for the analysis of vodka have been reported, in particular by Russian groups. Obrezkov et al. have described methods for determining inorganic anions [16] and transition-metal cations [17] for use in the vodka and liqueur industry. The latter method allowed a contamination of the product with metals during dispensing or during storage in metal containers to be determined. However, these cations occur only in traces, so a preconcentration using SPE is necessary for determining lead and cadmium. A further method for analysing the impurities of alkali metal and alkaline earth metal cations was developed by Bruce [18]. Vodka samples from various distilleries were identified by Arbuzov and Savchuk [19] using ion chromatography in combination with GC.

In this work, ion chromatography for the determination of anions (chloride, nitrate and sulphate) following ISO 10304–2 [20] is applied for the first time to a large range of vodka samples. The method's applicability to other extract-free spirits, such as white rum, is evaluated. Actual examples demonstrate the method's suitability for preventing brand fraud.

Materials and methods

Spirit samples. Since 2002, all 51 vodka and white rum samples submitted by local authorities to the Chemisches und Veterinäruntersuchungsamt (CVUA) Karlsruhe have been analysed for chloride, nitrate, and sulphate using ion chromatography. In all cases, there was a full organoleptical and chemical examination, which included the determination of relative density and ethanol using pycnometry [21], as well as the determination of higher alcohols and other volatile substances using gas-chromatography [2].

Instrumentation. The chromatographic analyses were performed on a metal-free Dionex DX-100 system (Dionex, Idstein, Germany) equipped with an autosampler ASM and a conductometric detector including a temperature-compensated conductivity cell and a self-regenerating suppressor ASRS-ULTRA (4 mm). Substances were separated on an anion-exchange column (IonPac AS4A, 4×250 mm i.d.) fitted with a guard column (AG4A, 4×50 mm i.d.). Separations were carried out with a flow rate of 2 ml/min and an injection volume of 25 µl. The current applied to the conductivity suppressor was 100 mA. The volume of the conductivity flow cell was 1.0 µl. The Dionex PeakNet chromatography workstation was used for instrument control, data acquisition, and processing.

Eluent solutions and chemicals. Ten millilitres of an eluent concentrate [14.3 g/l sodium bicarbonate (0.17 M) and 19.1 g/l sodium carbonate (0.18 M)] was diluted with deionised water to 1 l. The mobile phase was transferred to a 2-l eluent container and pressurised with nitrogen. All chemicals and stock solutions were purchased from Merck (Darmstadt, Germany).

Sample preparation. The spirit sample (100 ml) was evaporated by heating under mild conditions to approximately 20 ml. It was then transferred to a 25 ml measuring flask, and filled up after thermostatting to 20 °C. The clear and colourless sample solutions were injected directly into the ion chromatograph.

Quantification. The validated procedure ISO 10304–2 [20] was used without modification. The calculation was carried out automatically using the standard software supplied by the manufacturer against a previously prepared calibration using two regression lines for the different calibration ranges (Table 1). The limit of quantification (LOQ) was set at the lowest calibration point (Table 1); analytical results of samples below LOQ were given as "not detected". Repeated analysis of an authentic rum sample was used to examine the precision of the method.

Statistics. All data were evaluated using standard statistical packages for Windows. Statistical significance was assumed at below the 0.05 probability level. Groups of cases were compared using *t*- and Wilcoxon-tests.

Results and discussion

A major advantage of ion chromatography as an analytical technique is that it often requires little or no sample

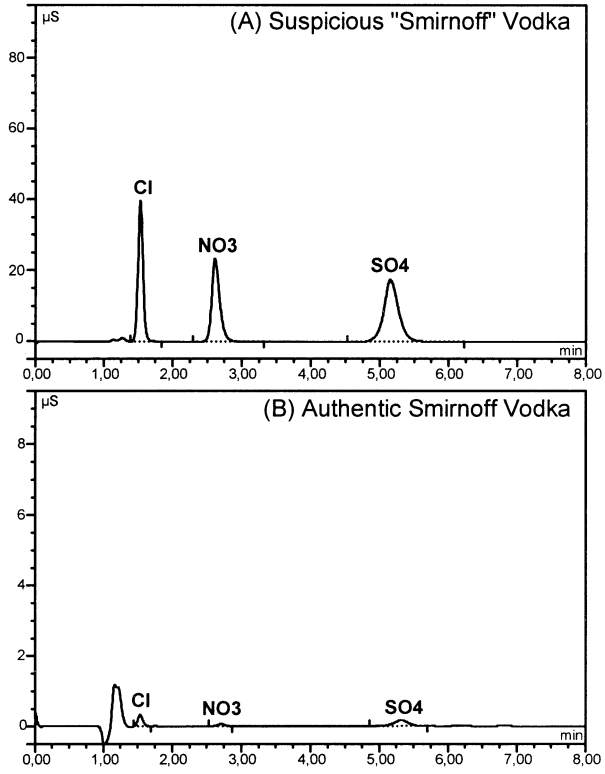

Fig. 1A, B Ion chromatograms of vodka samples from an actual case. **A** Suspicious vodka sold in a discotheque as Smirnoff. **B** Authentic Smirnoff vodka for comparison. For the results of the analysis, see Table 4

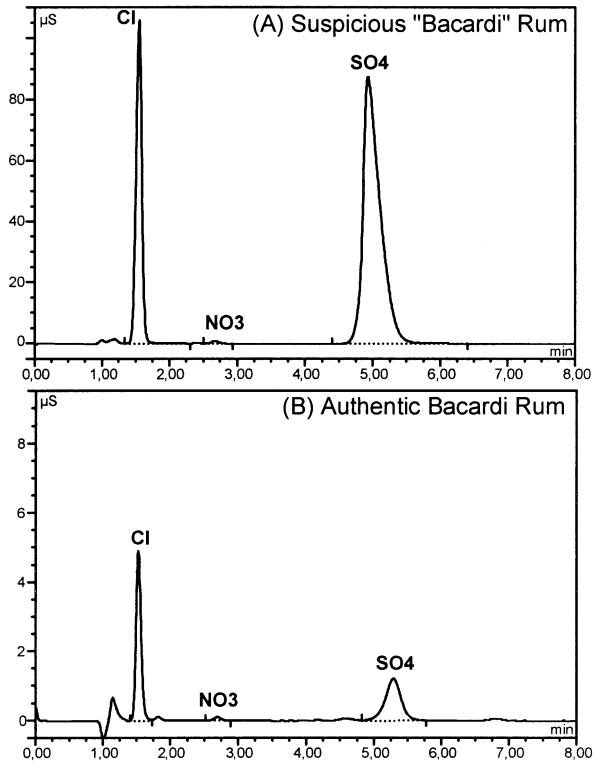

Fig. 2A, B Ion chromatograms of vodka samples from an actual case. **A** Suspicious white rum sold in a discotheque as Bacardi. **B** Authentic Bacardi white rum for comparison. For the results of the analysis, see Table 5

preparation and it uses only a small amount of sample. Even in the analysis of a complex matrix, as is typical of food samples, it shows high selectivity, sensitivity and reproducibility [15]. Thus, the method already validated for determining anions in waste water [20] could be applied without modification to the analysis of spirits. Results were obtained within 8 min. To optimise the sample preparation before ion chromatography, the sample was concentrated to a quarter of its initial volume. In addition to the enrichment of anions, the distillate portion of the alcoholic beverage was removed, leading to a reduction of the matrix load of the ion chromatograph, and thus resulting in interference-free chromatograms (Fig. 1 and Fig. 2). During routine analyses of 51 authentic samples, no interfering peaks from the matrix were observed. As a result, the precision never exceeded 1.6% RSD, indicating good assay precision (Table 1).

To demonstrate the applicability of the method developed, spirit samples were analysed (Table 2 and Table 3). Significant differences between the individual spirits were recognisable. In particular, large differences exist between spirits bottled in Russia and in Germany. The Russian vodkas analysed had a significantly (P=0.028) lower anion concentration (range 0.2–7.2 mg/l; mean 3.8 mg/l) than the German ones (range 11.5–147.6 mg/l; mean 78.4 mg/l) (Fig. 3). In Russia, the content of anions is regulated in distillery production. Usually the contents

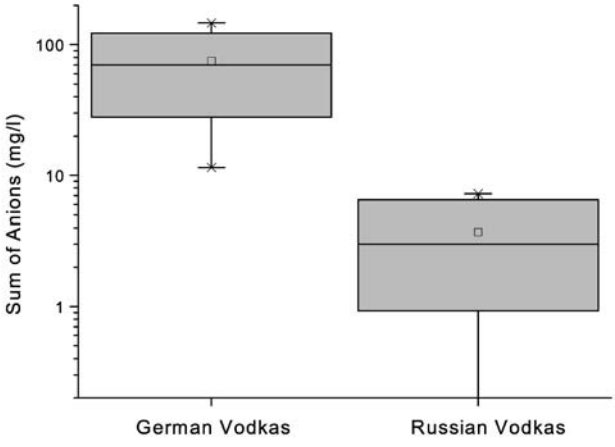

Fig. 3 Box charts of the analysis results of German and Russian vodkas in a logarithmic scale. The Russian vodkas have significantly lower anion concentrations than the German ones

of anions in Russian vodkas lie in the ranges 0.5–10 mg/l (chloride), 0.5–3.5 mg/l (nitrate), and 3.5–30 mg/l (sulphate) [16]. This was confirmed by our study. Particularly low anion concentrations were determined in premium products, which are manufactured using ion exchange or reverse osmosis for deionisation (e.g. Smirnoff Vodka, Fig. 1B, and Table 2).

Table 2 Results of analysis for different brands of vodkas. *ND* Not detected

Brand	Origin	Relative density	Ethanol (% vol)	Chloride (mg/l)	Nitrate (mg/l)	Sulphate (mg/l)	Sum of anions (mg/l)
Boris Jelzin	France	0.9539	37.5	ND	0.3	ND	0.3
Boris Jelzin	France	0.9539	37.3	0.2	0.4	ND	0.5
Borisov	Germany	0.9539	37.3	23.3	0.3	41.5	65.1
Czerwi Premium	Germany	0.9536	37.6	2.8	3.4	6.8	13.0
Czerwi Premium	Germany	0.9537	37.5	3.3	3.5	7.0	13.8
Czerwi Premium	Germany	0.9536	37.5	2.8	2.2	6.6	11.5
Fürst Uranov	Germany	0.9537	37.4	14.9	1.8	55.0	71.8
Fürst Uranov	Germany	0.9537	37.4	14.5	1.6	53.7	69.8
Gorbatschow	Germany	0.9542	37.5	22.0	1.9	51.5	75.5
Kaiserkrone	Germany	0.9537	37.4	13.5	1.4	51.5	66.3
Rachmaninoff	Germany	0.9539	37.5	37.5	13.8	34.5	85.8
Rachmaninoff	Germany	0.9539	37.3	44.3	15.0	85.8	145.0
Rodina	Germany	0.9505	39.9	23.2	10.4	35.5	69.1
Zarewitsch	Germany	0.9534	37.6	47.0	16.2	84.0	147.2
Zarewitsch	Germany	0.9539	37.3	43.3	17.0	84.0	144.3
Smirnoff	Italy	0.9537	37.3	ND	ND	ND	ND
Cristall Premium	Russia	0.9497	40.0	2.4	0.3	2.3	4.9
Jewish Kosher	Russia	0.9499	39.9	4.2	ND	3.1	7.2
Jewish Kosher	Russia	0.9499	39.9	4.2	ND	3.0	7.2
Kremlyovskaya	Russia	0.9501	39.8	0.2	ND	ND	0.2
Moskovskaya	Russia	0.9501	39.7	1.1	0.2	0.6	1.8
Moskovskaya	Russia	0.9499	40.0	1.1	0.1	0.5	1.7
Moskovskaya	Russia	0.9500	39.8	1.3	0.2	1.5	3.0
Absolut	Sweden	0.9497	40.0	0.3	ND	ND	0.3
Russkaja	Ukraine	0.9498	39.9	5.7	0.3	0.6	6.6
Kaliskaya	unknown	0.9538	37.6	22.1	0.3	41.0	63.4
Kaliskaya	unknown	0.9538	37.3	22.3	0.3	41.1	63.7
Original	unknown	0.9499	39.9	23.7	9.7	33.8	67.1
Penkovskaya	unknown	0.9502	39.7	15.4	0.1	132.0	147.6

Table 3 Results of analysis for different brands of white rums. ND Not detected

Brand	Origin of distillate	Origin of water	Relative density	Ethanol (% vol)	Chloride (mg/l)	Nitrate (mg/l)	Sulphate (mg/l)	Sum of anions (mg/l)
Havana Club Silver Dry	Cuba	Cuba	0.9540	37.7	0.3	ND	ND	0.3
Bacardi light-dry	Bahamas	Spain/Germany	0.9538	36.9	1.9	ND	1.6	3.4
Bacardi light-dry	Bahamas	Spain/Germany	0.9541	37.2	1.6	ND	0.6	2.2
Bacardi light-dry	Bahamas	Spain/Germany	0.9541	37.2	1.5	ND	1.5	2.9
Bacardi light-dry	Bahamas	Spain/Germany	0.9539	36.9	0.6	ND	1.6	2.2
Bacardi light-dry	Bahamas	Spain/Germany	0.9534	37.5	0.5	ND	0.7	1.2
Liberte White	West-Indies	unknown	0.9539	37.5	43.3	15.6	82.3	141.1
Maringa White	West-Indies	unknown	0.9536	37.4	10.7	17.8	19.5	48.0
Old Pascas White	West-Indies	unknown	0.9542	37.1	30.8	0.5	94.3	125.5
White Blossom light	West-Indies	unknown	0.9540	37.7	28.3	0.1	94.0	122.4
White Blossom light	West-Indies	unknown	0.9539	37.7	27.2	0.3	103.6	131.0

Analysis found no significant differences in anion concentrations between samples of the same brand but with different dates of bottling (Table 2 and Table 3). This verified the findings of Arbuzov and Savchuk [19], who also found very stable anion-cation compositions in vodkas manufactured at the same distillery, as well as the conclusion of Savchuk et al. [3] that vodka is characterised by the ionic composition of the water used in its production. Therefore, these findings allow an allocation or a differentiation of spirits. The following authentic cases of the CVUA Karlsruhe demonstrate the application of the method.

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 “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 cheap 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 other brands of German origin were found and taken for examination.

Using the standard GC method for determining higher alcohols in spirit samples [2], only acetaldehyde and isoamyl alcohol were detected in the vodka samples

Table 4 Results of analysis from an actual case. 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. ND Not detected

	Suspicious vodka samples			Reference vodka samples	
	"Smirnoff" 1	"Smirnoff" 2	"Smirnoff" 3	Authentic Smirnoff	Authentic German Vodka
Relative density	0.9537	0.9538	0.9538	0.9538	0.9536
Ethanol (% vol)	37.4	37.3	37.3	37.3	37.5
Acetaldehyde (mg/100 ml Ethanol)	2.1	2.2	2.2	2.6	2.2
Isoamyl Alcohol (mg/100 ml Ethanol)	1.6	1.9	1.6	1.5	1.4
Chloride (mg/l)	8.0	8.7	9.3	ND	9.3
Nitrate (mg/l)	14.5	14.4	12.8	ND	15.5
Sulphate (mg/l)	15.5	17.4	21.1	ND	17.1
Sum of anions (mg/l)	38.0	40.4	43.1	ND	41.8

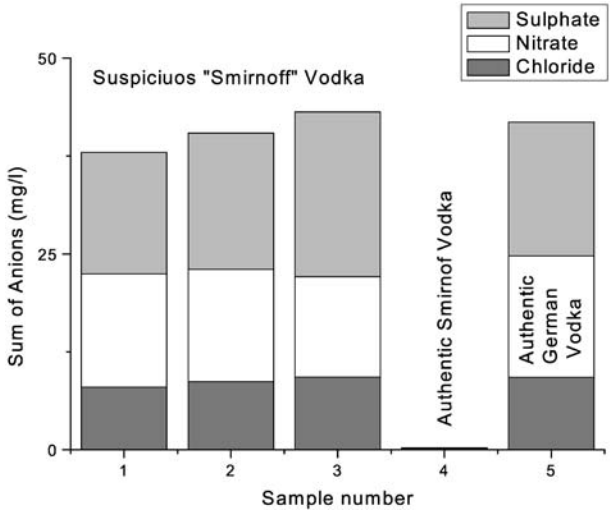

Fig. 4 Results of analysis from an actual case of adulterated vodkas (see Table 4)

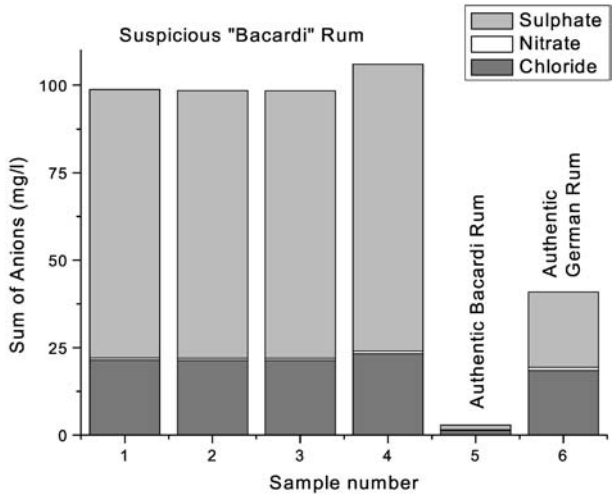

Fig. 5 Results of analysis from an authentic case of adulterated rum (see Table 5)

(Table 4). All other volatile substances were below the detection limit of 0.5 mg/100 ml ethanol. No significant difference could be found between the acetaldehyde and isoamyl alcohol contents of the suspicious samples and the authentic comparison samples. However, there were significant deviations in the concentrations of the anions chloride, nitrate and sulphate (Table 4). Therefore, the results of the chemical examination of the suspicious "Smirnoff" vodkas did not correspond to those of the comparison sample. In Fig. 1, the chromatogram of a suspicious sample is compared with that of an authentic sample. For illustration, Fig. 4 gives a stacked column graph of the analysis results of all vodka samples. The suspicious vodka samples were judged to be adulterated and misleadingly designated. The anionic profile of the suspicious samples corresponded significantly to the profile of the German vodka (Table 4, Fig. 4). It could therefore be assumed that this vodka had been poured into the Smirnoff bottles.

The results of the chemical examination of the suspicious "Bacardi" rum samples did not correspond to those for the comparison sample. In this case, the result of ion chromatography could be confirmed by the results of GC (Table 5). Only slight deviations were determined in the parameters density and alcohol, but there were significant deviations in the content of higher alcohols, as well as in the contents of the anions chloride, nitrate, and sulphate. In this case, according to Arbuzov and Savchuk [19], the identification is a very reliable way of characterising the two major constituents of vodka: water is characterised using ion chromatography and alcohol using GC. In Fig. 2 and Fig. 5 are shown ion chromatograms and stacked column graphs of the rum samples. 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 rum (Table 5, Fig. 5). The brand of rum filled into the Bacardi bottles could not be determined. Possibly, it was a mixture of both rum brands.

The owner of the discotheque was fined for offences against the food law.

To conclude, valuable information about the identity of spirits can be obtained by analysing their anionic compositions using ion chromatography. In the case described, an adulteration of premium-brand spirits could be determined beyond doubt. Appropriate sample clean-

Table 5 Results of analysis from an actual case. 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 rum
Relative density	0.9541	0.9541	0.9541	0.9541	0.9538	0.9541
Ethanol (% vol)	37.2	37.2	37.2	37.2	37.3	37.2
Methanol (mg/100 ml ethanol)	4.2	4.4	4.6	4.2	3.3	3.1
Acetaldehyde (mg/100 ml ethanol)	1.4	2.2	2.5	2.8	5.8	3.2
n-Propanol (mg/100 ml ethanol)	3.7	3.9	3.9	3.7	13.3	ND
Iso-Butanol (mg/100 ml ethanol)	0.9	0.7	1.0	0.8	9.1	ND
Isoamyl Alcohol (mg/100 ml ethanol)	2.0	2.2	2.0	1.9	35.8	1.5
Ethyl acetate (mg/100 ml ethanol)	0.3	ND	0.7	0.9	7.2	2.6
Chloride (mg/l)	21.5	21.4	21.4	23.3	1.3	18.5
Nitrate (mg/l)	0.6	0.6	0.6	0.7	ND	0.9
Sulphate (mg/l)	76.8	76.5	76.5	82.0	1.4	21.5
Sum of anions (mg/l)	98.8	98.5	98.5	106.0	2.7	40.9

up procedures before ion chromatography will make it possible to extend the application to extract-containing spirits, such as brandy or whisky. It may also be possible to distinguish between directly imported original rum and domestically made rum.

Acknowledgments The authors thank S. Gonzalez and H. Heger for excellent technical assistance.

References

1. Simpkins WA (1985) J Sci Food Agric 36:367–376
2. Frank W (2002) Qualitätssicherung, Organisation und Analysenmethoden. In: Kolb E (ed) Spirituosen-Technologie. Behr's Verlag, Hamburg, Germany, pp 425–472
3. Savchuk SA, Vlasov VN, Appolonova SA, Arbuzov VN, Vedenin AN, Mezinov AB, Grigor'yan BR (2001) J Anal Chem 56:214–231
4. Ng L-K, Hupé M, Harnois J, Moccia D (1996) J Sci Food Agric 70:380–388
5. Ng L-K (1999) Analysis of vodkas and white rums by SPME-GC-MS. In: Pawliszyn J (ed) Applications of solid phase microextraction. Royal Society of Chemistry, Cambridge, UK, pp 393–406
6. Pino J, Marti MP, Mestres M, Perez J, Busto O, Guasch J (2002) J Chromatogr A 954:51–57
7. Lehtonen PJ, Keller LA, Ali-Mattila ET (1999) Z Lebensm Unters Forsch A 208:413–417
8. Bauer-Christoph C, Wachter H, Christoph N, Roßmann A, Adam L (1997) Z Lebensm Unters Forsch A 204:445–452
9. Cross JL, Gallaher TN, Leary JJ, Schreiner S (1998) Chem Educator 3:1–9
10. Cordella C, Moussa I, Martel AC, Sbirrazzuoli N, Lizzani-Cuvelier L (2002) J Agric Food Chem 50:1751–1764
11. European Council (1989) Off J Eur Comm L160:1–17
12. Smirnoff group (2002) The distillation process. Available http://www.smirnoff.com
13. Ströhmer G (2002) Extraktfreie und extraktarme Spirituosen. In: Kolb E (ed) Spirituosen-Technologie. Behr's Verlag, Hamburg, Germany, pp 56–153
14. Lopez-Ruiz B (2000) J Chromatogr A 881:607–627
15. Buldini PL, Cavalli S, Trifiro A (1997) J Chromatogr A 789:529–548
16. Obrezkov ON, Tolkacheva VA, Zaikanova GI, Yamnikov VA, Krokhin OV, Shpigun OA (1997) Ind Lab Diagn Mat 63:71–73
17. Obrezkov ON, Tolkacheva VA, Zaikanova GI, Yamnikov VA, Krokhin OV, Zhukov SP, Shpigun OA (2000) Ind Lab Diagn Mat 66:18–21
18. Bruce J (2002) Analysis of vodka by ion chromatography. Available http://www.laboratorytalk.com
19. Arbuzov VN, Savchuk SA (2002) J Anal Chem 57:428–433
20. International Organisation for Standardisation (1995) ISO 10304–2 Water quality—Determination of dissolved anions by liquid chromatography of ions—part 2: Determination of bromide, chloride, nitrate, nitrite, orthophosphate and sulphate in waste water
21. European Commission (2000) Off J Eur Comm L333:20–46