The Analysis of Vodka: A Review Paper

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Abstract Vodka is the most popular alcoholic beverage in Poland, Russia and other Eastern European countries, made from ethyl alcohol of agricultural origin that has been produced via fermentation of potatoes, grains or other agricultural products. Despite distillation and multiple filtering, it is not possible to produce 100 % ethanol. The solution with a minimum ethanol content of 96 %, which is used to produce vodkas, also contains trace amounts of other compounds such as, esters, aldehydes, higher alcohols, methanol, acetates, acetic acid and fusel oil. Regarding that fact, it is very important to carry on research on the analysis of the composition and verifying the authenticity of the produced vodkas. This paper summarizes the studies of vodka composition and verifying the authenticity and detection of falsified products. It also includes the methods for analysing vodkas, such as: using gas, ion and liquid chromatography coupled with different types of detectors, electronic nose, electronic tongue, conductivity measurements, isotope analysis, atomic absorption spectroscopy, near infrared spectroscopy, spectrofluorometry and mass spectrometry. In some cases, the use of chemometric methods and preparation techniques were also described.

Keywords Vodka analysis · Chromatography · Electronic senses · Mass spectrometry

Introduction

Vodka is the most popular alcoholic beverage in Poland, Russia and other Eastern European countries. In Russia, vodka is mostly produced from wheat; while in Poland, a rye mash is most frequently used. Vodka is made from ethyl alcohol of agricultural origin that has been produced via fermentation of potatoes, grains or other agricultural products. The obtained ethanol-containing solution is distilled or rectified to selectively reduce the intensity of taste and smell of the raw materials and the by-products of fermentation (Act of 13 September 2002 on the spirit drinks). The distillation process takes place in a distillation column. Vodka owes its neutral character to the separation of the heads fraction (higher alcohols) from the tails fraction (the least volatile esters). The soft taste of vodka is achieved by multiple filtering of alcohol through activated charcoal, followed by dilution with water, the latter being distilled, demineralized or treated with Permutit or water softeners (Regulation, E. C. N. 110/2008; Christoph and Bauer-Christoph 2006; Ng et al. 1996). The minimum strength of vodka is 37.5 % by volume. Besides pure vodkas, there are flavoured vodkas, which are characterized by a dominant flavour different than the taste of raw materials used in their production. Flavoured vodka can be artificially sweetened, blended, flavoured, matured or coloured. It can be sold under the name of any dominant taste, which is added to the name "vodka" (Regulation, E. C. N. 110/2008).

Despite distillation and multiple filtering, it is not possible to produce 100 % ethanol. The obtained solution with a minimum ethanol content of 96 % also contains trace amounts of other compounds such as esters, aldehydes, higher alcohols, methanol, acetates, acetic acid and fusel oil (Regulation, E. C. N. 110/2008; Hu et al. 2010).

The chemical and sensory analyses of flavoured spirit-based beverages concern the three main components of the

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product, i.e. alcohol, water and flavourants. Both analyses are used for assessing the raw materials, production type, quality control, authentication and the detection of possible falsification. The analysis of alcohol used in vodka production encompasses a sensory evaluation, the measurement of alcohol content, and a detailed chemical composition analysis. The sensory evaluation is usually conducted by the group of trained persons on the approved sample. The alcohol content measurement is traditionally performed by using the hydrometric or pycnometric method. The chemical composition analysis is commonly conducted by means of one-dimensional gas chromatography (GC). Due to the requirements imposed on alcohol used in vodka production, mainly the content of methanol, acetaldehyde, ethyl acetate and higher alcohols is measured via direct sample injection into the gas chromatograph equipped with a flame ionization detector (FID). Such content analysis is useful for comparing different alcohols and confirming the compliance with the imposed requirements (Aylott 2003). Presently, besides the aforementioned analyses, studies on alcohol samples are conducted by using ion chromatography (IC), liquid chromatography (LC), mass spectrometry (MS), spectrophotometry, electronic nose, electronic tongue, isotope analysis and others. Due to the low concentration of the analysed compounds, the techniques aimed at increasing the analyte concentration prior to analysis are often used, such as solid-phase microextraction (SPME) and solid-phase extraction (SPE) (Siříšťová et al. 2012).

In this review paper, we describe research conducted by means of various analytical techniques whose aim was to determine more details of vodka composition, to detect falsified vodkas and to identify different vodka types, which are placed in Table 1.

Studies of Vodka Composition

As previously mentioned, vodkas are produced from various raw materials of agricultural origin such as grains and potatoes. Due to diversity of raw materials, the final products are also highly diversified. At present, numerous brands of vodka are offered on the market, including pure and flavoured vodkas produced from one or more raw materials. The types of vodka production also differ, which influences the final composition of the product. Due to the ever increasing number of vodka products and the client's interest in new products, it is necessary to precisely determine their composition.

Low concentrations of the compounds present in vodkas pose a big challenge for chemical analysts. The majority of studies are conducted by means of one-dimensional gas chromatography because this technique has many advantages such as high resolution and high sensitivity. This allows the identification of a large number of analytes. Moreover, the possibility of coupling GC with different detectors makes this

technique applicable to a wide spectrum of alcohol-based products. Flame ionization detector (FID) is most commonly used because of its relatively low price and universal application. A GC-FID system was used, among others, to determine methanol content in commercial and illegally produced vodkas. The obtained results differed depending on the vodka type, and ranged from 17 to 376 mg/l (Chłobowska et al. 2000). The admissible concentration of methanol in pure vodka is 100 mg/l of vodka; while in case of flavoured vodkas, the admissible concentration of methanol is 2 g/l of vodka. All the investigated samples were within these limits. A GC-FID system was also applied to analyse the volatile fraction of vodkas originating from Brazil (Pereira et al. 2013) and Vietnam (Lachenmeier et al. 2009). In the case of Brazilian vodkas, 32 brands were analysed with regard to the content of higher alcohols, acetaldehyde, ethyl acetate and methanol. Both methanol and acetaldehyde were present in these vodkas at the concentrations below the limit of quantification. For most samples, the content of higher alcohols and ethyl acetate did not meet the EU standards although the total content of contaminants was definitely lower than the values prescribed by the Brazilian regulations (Pereira et al. 2013). Lachenmeier et al. (2009) analysed 11 samples of alcoholic beverages available in local stores in Hanoi, which included three vodkas, one whiskey, one brandy, one rum and others. The collected samples were analysed with regard to the content of ethanol, methanol, acetaldehyde, 1-propanol, 1-butanol, 2-butanol, isobutanol, amyl alcohols, 1-hexanol, 2-phenylethanol, ethyl acetate, ethyl lactate and ethyl octanoate. None of the analysed vodkas contained 1-butanol, 2-butanol, 1-hexanol, 2-phenylethanol, ethyl acetate, ethyl lactate and ethyl octanoate (Lachenmeier et al. 2009). The GC-FID technique was also used to determine diethyl phthalate in vodka, ethanol and illegal alcoholic products (Savchuk et al. 2006) as well as for assessing changes in the composition of vodka before and after filtration through activated charcoal (Siříšťová et al. 2012). In both cases, besides GC-FID analysis, the analysis by means of gas chromatography coupled with mass spectrometry (GC-MS) was performed as it gives better results compared to GC-FID analysis. A gas chromatograph coupled with a mass spectrometer is a configuration often used in the analysis of alcoholic beverages. In comparison to FID, the MS detector is more sensitive and allows easier identification of the analysed compound. As previously mentioned, the GC-MS system was used to determine selected compounds in vodkas, ethanol and illegal alcoholic products (Savchuk et al. 2006). A total of 13 samples were analysed, which included three samples purchased at the grocery stores in Stavropol, one reference sample purchased legally in the store in the city, and nine samples bought from individual home owners by the agents from the Kryzyl distillery. All samples were analysed with regard to the content of ethanol, ethyl acetate, methanol, 2-propanol, n-propanol, n-butanol,

Table 1 Examples of analysis of vodkas

Apparatus	Sample	Object of study	Lit.
GC-FID	Polish commercial and illegally produced vodkas	Methanol	Chłobowska et al. 2000
GC-FID	Brazilian vodkas	Higher alcohols, acetaldehyde, ethyl acetate, methanol	Pereira et al. 2013
GC-FID	Vodkas available in local stores in Hanoi	Ethanol, methanol, acetaldehyde, 1-propanol, 1-butanol, 2-butanol, isobutanol, amyl alcohols, 1-hexanol, 2-phenylethanol, ethyl acetate, ethyl lactate, ethyl octanoate	Lachenmeier et al. 2009
GC-FID, GC-MS	Vodkas, ethanol and illegal alcoholic products from Stavropol	Ethanol, ethyl acetate, methanol, 2-propanol, n-propanol, n-butanol, ethylene glycol, diethyl phthalate	Savchuk et al. 2006
GC-FID, GC-MS, LLE	German vodkas	Diethyl phthalate	Leitz et al. 2009
GC-MS	Brazilian vodkas	Dimethyl sulphide	Cardoso et al. 2004
GC-MS, SPME	Canadian vodkas	Ethyl dodecanoate, ethyl tetradecanoate, ethyl hexadecanoate, ethyl hexadecenoate, ethyl oleate, ethyl stearate, ethyl linoleate	Ng 2002
GC-MS, HS-SPME	Russian vodka after and before filtering through activated charcoal	Acetaldehyde, limonene, dodecane, hexyl acetate, 2-methylfuran	Siříšťová et al. 2012
GC-MS	Brazilian vodkas	Ethyl carbamate	Pereira et al. 2013
GC-MS	Vodkas purchased in Ontario	Ethyl carbamate	Clegg et al. 1988
GC-MS/MS	Vietnamese vodkas	Ethyl carbamate	Nordon et al. 2005
GC-ECD HS-SPME	Polish vodkas	Methanal, ethanal, propanal, propenal, butanal, isopenatanal, 2-butenal, pentanal, hexanal, dimethyl ketone	Wardencki et al. 2003
GC-ECD	Polish vodkas	Methanal, ethanal, propanal, propenal, butanal, isopenatanal, 2-butenal, pentanal, hexanal, isobutanal	Sowiński et al. 2005
GC-FPD	Vodkas originating from Finland, Russia and Poland	Dimethyl sulphide, diethyl sulphide, dimethyl disulphide, dimethyl trisulfide	Leppänen et al. 1979
GC×GC-TOFMS	Brazilian vodkas	Alcohols, aldehydes, ketones, esters, terpenes, aromatic compounds	Cardeal and Marriott 2009
HPLC	Żubrówka vodka from Poland	Coumarin	Sproll et al. 2008
NIR, Raman spectroscopy	Vodkas commercially available in UK	Ethanol	Nordon et al. 2005
ATR	Red Riband vodka from India	Ethanol, sugar, tartaric acid	Nagarajan et al.. 2006
AAS	Brazilian vodkas	Lead, copper	Pereira et al. 2013
AES	Vodkas from USA and Russia	Sodium, magnesium, aluminium, iron, calcium	Nascimento et al. 1999
Spectrofluorometry	Russian vodkas	Formaldehyde	De Andrade et al. 1996
Spectrofluorometry	Japanese vodkas	Formaldehyde	Tsuchiya et al. 1994
Spectrofluorometry	Vodkas commercially available in Brazil	formaldehyde	De Oliveira et al. 2007
ICP-MS	Vietnamese vodkas	Alkaline earth metals	Lachenmeier et al. 2009
ICP-MS	Vodkas commercially available in Brazil	Cobalt, nickel, tellurium	De Quadros and Borges 2014
Titration with Na_2H_2EDTA	Vodkas commercially available in Riga	The influence of water hardness on the transparency of vodka	Krosnijs and Kuka 2003
E-nose	Tequila, vodka, whisky, beer and red wine commercially available in France	Differentiation of tequila, vodka, whisky, beer and red wine	Ragazzo-Sanchez et al. 2006
E-nose	Tequila, vodka, whiskey, beer, red wine	Differentiation of tequila, vodka, whisky, beer and wine	Ragazzo-Sanchez et al. 2008
Sensory evaluation, FT-IR	Vodka, gin, whiskey and brandy commercially available in Poland	Differentiation of vodka, gin, whisky and brandy	Sujka et al. 2013
FIA-IRMS	Vodkas	Distinguish between vodkas from different materials	Jochmann et al. 2009
ICP	68 alcoholic beverages included vodka from Russia and Sweden	Distinguish between vodkas and other investigated beverages	Kokkinofta et al. 2003
GC-FID	Vodkas available on the Russian market	Determine the authenticity of a given product by the raw materials used in the production	Reshetnikova et al. 2007
E-tongue	Russian vodkas	Distinguish between vodkas from three quality categories Lux, Extra and High Purity	Legin et al. 2005
Conductivity measurements	Vodkas from Russia, Poland, Sweden, Germany	Distinguish vodkas brands	Lachenmeier et al. 2008

Table 1 (continued)

Apparatus	Sample	Object of study	Lit.
GC-MS, SPME	Vodkas from the USA and Canada	Ethyl esters profiles	Ng et al. 1996
IC	Russian vodkas	Sodium, potassium, magnesium, calcium, chloride, nitrate and sulphate ion	Arbuzov and Savchuk 2002
IC	Russian and German vodkas	Chloride, nitrate, sulphate ions, and the sum of anions	Lachenmeier et al. 2003
FT-IR	Vodka commercially available in Poland	Ethanol	Sujka and Koczoń 2012
NIR spectroscopy	Vodkas from Russia and Western Europe	Distinguish between vodkas from Russia and Western Europe	Kolomiets et al. 2010
GC-MS	Russian and French vodkas	2-butanol, acetone, crotonaldehyde	Savchuk and Kolesov 2005

ethylene glycol and diethyl phthalate. The composition of all analysed samples differed from the composition of reference sample (Savchuk et al. 2006). The content of diethyl phthalate was also the object of investigation in the article on the risk of consuming this compound via intake of various alcoholic beverages, among others, vodkas. Phthalates are highly durable esters of phthalic acid commonly utilized in the chemical industry. They are used as plasticizers in many products such as furniture, car air fresheners, medical devices, toys for children or food packages. Phthalates are not chemically bound to plastic materials, which means they can migrate into the environment. Thus, people are exposed to phthalates via swallowing, inhalation or skin contact. Diethyl phthalate is applied as ethyl alcohol denaturing agent. Acute toxicity of phthalates is LD50 1–30 g/kg. Moreover, chronic toxicity is observed, too. Aforementioned diethyl phthalate is also considered a potential carcinogenic and teratogenic agent. Due to this fact, it is of utmost importance to test spirit-based beverages for diethyl phthalate presence, especially in case of the products sold in Eastern Europe where alcohol is frequently denatured with phthalate in many production processes. Leitz et al. (2009) conducted the study by means of GC-MS, while the sample preparation involved the use of liquid-liquid extraction (LLE). Vodka was used as a blind sample because it did not contain diethyl phthalate (Leitz et al. 2009). Due to the presence of sulphur compounds (including dimethyl sulphide, DMS) in some spirit-based beverages, Cardoso et al. (2004) analysed selected products for the presence of DMS; alcohols popular in Brazil such as cachaça, whiskey, rum, brandy, grappa, tiquira, tequila and vodka were among the investigated samples. The application of GC-MS was described however this technique did not detect DMS in the samples of vodka, tequila and rum (Cardoso et al. 2004). GC-MS was used to determine fatty acids and esters in some alcoholic beverages and tobacco. Vodka was also among the analysed alcohols. Samples were pretreated by solid-phase microextraction (SPME). This allowed for detecting the compounds present at low concentrations such as, ethyl dodecanoate, ethyl tetradecanoate, ethyl hexadecanoate, ethyl hexadecenoate, ethyl oleate, ethyl stearate and ethyl linoleate (Ng 2002).

Siříšťová et al. (2012) described changes in the vodka composition after filtering through activated charcoal; the GC-MS system was used to create a list of volatile organic compounds that had been detected in the analysed vodka samples. As in the previous case, the head space (HS)-SPME technique was applied to preconcentrate the analytes. A total of 29 compounds were detected, including acetaldehyde, limonene, dodecane, hexyl acetate and 2-methylfuran, which were identified based on their retention times and mass spectra (Siříšťová et al. 2012). Studies on the presence of ethyl carbamate (EC) in spirit-based beverages are frequently conducted. Ethyl carbamate occurs naturally in fermented foods and alcoholic beverages such as, bread, yoghurt, soy sauce, wine, beer and particularly in spirits made from stone fruits and the stone fruit pomace obtained from cherries, prunes, mirabelle plums and apricots. The conducted animal studies proved that ethyl carbamate is a carcinogen. The International Agency for Research on Cancer has classified this compound as probably carcinogenic to humans (Balcerek and Szopa 2006; Commission recommendation 133/2010).

The content of EC in Brazilian vodkas (Pereira et al. 2013) and various spirit-based beverages, including vodkas purchased in Ontario (Clegg et al. 1988), was determined by using GC-MS. The gas chromatography coupled with tandem mass spectrometry (GC-MS/MS) was used to detect EC in Vietnamese vodkas (Nordon et al. 2005). In all these studies, ethyl carbamate has not been detected.

Besides the above-mentioned detectors, the electron capture detector (ECD) and flame photometric detector (FPD) have been used for analysing vodkas. The ECD is a nondestructive detector which allows the determination of the concentrations of halogenated compounds at ppb-ppt level. The articles describing the development and application of the method for determining carbonyl compounds in alcoholic beverages can serve as an example here. In both studies, the samples were subjected to derivatization with O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride (PFBHA) in order to separate the investigated compounds (Wardencki et al. 2003; Sowiński et al. 2005). Wardencki et al. (2003) employed the HS-SPME technique for this purpose, while

Sowiński et al. (2005) compared the results obtained by headspace injection with those obtained by SPME. In both studies, the analysis included methanal, ethanal, propanal, propenal, butanal, isopentanol, 2-butenal, pentanal and hexanal. Additionally, dimethyl ketone was determined by Wardencki et al. (2003) and isobutanal by Sowiński et al. (2005). Most carbonyl compounds have a negative impact on the aroma and taste of spirit-based beverages. Some of them, for instance propenal (acrylaldehyde), are highly carcinogenic substances and irritating to the eyes and respiratory tract. That is why it is important to conduct research aimed at their control. Both techniques described in the aforementioned papers proved to be effective in the analysis of carbonyl compounds. HS-GC-ECD analysis revealed higher concentration of some investigated compounds compared to SPME-GC-ECD. This technique allows faster analysis than in the case of using SPME, thanks to the exclusion of preliminary preparation of the samples via solid-phase microextraction technique. With this method, the HS-GC-ECD technique occurred to be better compared to SPME-GC-ECD for most of the investigated carbonyl compounds.

The FPD registers the intensity of light emitted by analyte particles returning to the ground state after excitation in the hydrogen flame. This detector is mainly used to determine the concentrations of compounds that contain sulphur (spectral line at 393 nm) and phosphorus (spectral line at 526 nm). The FPD was used by Leppänen et al. (1979) to determine volatile sulphur compounds present in alcoholic beverages at low concentrations. Even small amounts of sulphur compounds can have a negative effect on the quality of consumed alcoholic beverages. The samples of wine, beer, cognac, brandy, whiskey, rum and vodka were analysed. The vodka brands originating from Finland, Russia and Poland were among the analysed samples. The analysed substances included dimethyl sulphide, diethyl sulphide, dimethyl disulphide and dimethyl trisulfide. The application of FPD allowed the detection of only dimethyl disulphide in vodkas originating from Poland and Russia (Leppänen et al. 1979). Dimethyl sulphide was present in vodkas at very low concentration so its influence on the aroma and taste of the vodkas was insignificant.

Besides one-dimensional gas chromatography, it is also possible to employ two-dimensional chromatography (GC× GC) (Fig. 1) for analysing spirit-based beverages. Despite its many advantages (e.g. improved resolution, better sensitivity
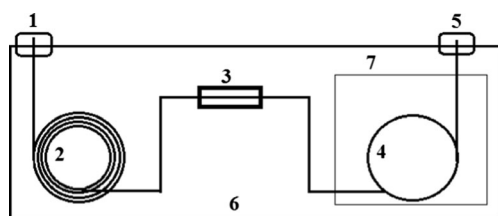

Fig. 1 Schematic diagram of the GC×GC. *1* injector, *2* first column, *3* modulator, *4* second column, *5* detector, *6* first oven *7* second oven

and structured chromatograms), two-dimensional chromatography is not used often. This is due to the fact that these techniques require qualified personnel and expensive equipment, the latter definitely more expensive than a one-dimensional chromatograph. In the case of GC×GC, time-of-flight mass spectrometer (TOFMS) is the most frequently used detector. This technique was employed for analysing the volatile organic compounds in selected spirit-based beverages such as, cachaça, rum, vodka, whiskey, tequila, gin and some liqueurs (melon, banana, strawberry and Tia Maria) (Cardeal and Marriott 2009). The lowest number of compounds was detected in vodkas which demonstrate their poor aroma profile compared to other analysed alcoholic beverages. Among the detected groups of compounds were alcohols, aldehydes, ketones, esters, terpenes and aromatic compounds.

Although the vodka composition is mainly analysed by means of gas chromatography, there are studies in which spectrophotometry, atomic absorption and high-performance liquid chromatography (HPLC) have been applied. The aforementioned techniques are used to determine specific compounds which cannot be determined or are difficult to determine by GC.

In the case of spirit-based beverages, HPLC is used rather rarely. This is due to the composition of such beverages which contain many volatile organic compounds therefore their analysis is easier by using gas chromatography. Coumarin is one of the vodka components which is analysed by means of HPLC. It belongs to lactones and can be found in some plants. Coumarin is present, among others, in Polish vodka Żubrówka which is made from rye and flavoured with the grass species *Hierochloe odorata* growing in Białowieża Forest in Poland. The HPLC analysis of Żubrówka showed that coumarin concentration was at the level admissible by norms, i.e., below 10 mg/kg (Sproll et al. 2008).

In the case of flavoured vodkas, studies aimed at detection of calcium and citrate was also conducted by means of UV–VIS spectrophotometry and artificial neural networks (ANN). The aim of this research was the evaluation of aforementioned techniques in comparison to NMR technique (McCleskey et al. 2003).

Near infrared (NIR) spectroscopy and Raman spectroscopy were used to determine the ethanol content in vodkas (Nordon et al. 2005). NIR spectroscopy is a nondestructive technique characterized by fast and precise measurements, low costs and the possibility of concurrent determination of multiple components. The technique uses radiation in the range of 750–2500 nm (Chodak 2005). In Raman spectroscopy, the mechanism of operation is based on the scattering of radiation by a sample. Both these techniques allowed the ethanol content determination with only a slight deviation from the true value (Nordon et al. 2005). The aforementioned techniques possess some important advantages as compared to the standard techniques utilized for determination of alcohol content. These are

non-invasive techniques that can be applied to the already bottled alcohols without the need to open them. Analysis takes a short time, which makes it suitable for online techniques. NIR and Raman spectroscopies can be employed to determine falsification without destroying the sample. Unfortunately, it is extremely important to verify additional parameters such as bottle glass thickness or the bottle movement on the production belt. These elements limit the applicability of the above techniques on the production lines. Mid infrared (MIR) spectroscopy in attenuated total reflectance (ATR) mode was utilized to analyse ethanol, sugar and tartaric acid content in selected alcohol-based beverages including vodka. This technique was employed as an alternative to chemical analyses. The results were comparable with the ones obtained using the classical chemical analyses. ATR method is fast, precise and easy to operate, which can contribute to its broader implementation for analysis of alcohol-based beverages in future (Nagarajan et al. 2006). Spirit-based beverages, e.g. vodkas were analysed by means of atomic emission spectroscopy and atomic absorption spectroscopy. Atomic absorption spectroscopy (AAS) is characterized by high selectivity, the detection limit at ppb level, and a possibility to analyse ca. 70 elements. Because of that, AAS was used to determine the content of lead and copper in Brazilian vodkas for which the measurements were below the detection limit (Pereira et al. 2013). Atomic emission spectroscopy allows for the concurrent detection or determination of many elements even when they are present in infinitesimal amounts. Both techniques were employed to determine selected metal ions, e.g. sodium, magnesium, aluminium, iron and calcium in spirit-based beverages including vodkas (Nascimento et al. 1999). Unfortunately, the detailed results have been published for cachaça only.

Spectrofluorometry was used to determine formaldehyde in vodka samples (De Andrade et al. 1996; Tsuchiya et al. 1994). This technique is characterized by high sensitivity and good selectivity. Formaldehyde is an irritating and carcinogenic substance so investigation of its content in spirit-based beverages is very important. Spectrofluorometry is the technique suitable for determination of substances, which upon light absorption, emits the radiation of different wavelengths. In the case of aldehydes, it is necessary to conduct derivatization into the radiation-emitting products. Due to this fact, spectrofluorometry is not a common approach to determine other aldehydes. The measured concentrations of formaldehyde in Russian (De Andrade et al. 1996) and Japanese (Tsuchiya et al. 1994) vodkas were 0.33–0.65 mg/l and 18.4 nmol/ml, respectively. Formaldehyde was determined in alcohol-based beverages including two vodka samples using flow injection analysis. A method based on the reaction between Fluoral-P and formaldehyde was used, which yields DDl compound that reveals fluorescence at $\lambda ex=410$ nm and $\lambda em=510$ nm. Formaldehyde was not detected in one sample,

while in the other one, it was at the lowest level with respect to the other investigated alcohols (De Oliveira et al. 2007).

Inductively coupled plasma mass spectrometry (ICP-MS) was used to determine metals in vodkas (Lachenmeier et al. 2009). ICP-MS is a very sensitive technique with high precision, which can be employed to make concurrent determinations of multiple elements and selective determinations of specific isotopes of the same element in complex matrices. It also has low detection limit (at the level of pg/L in solutions) due to highly efficient plasma ionization, and a wide linear range of calibration curves, which allows for determining trace and macro elements by a single measurement (Szpunar and Łobiński 1999; Vanhaecke and Moens 1999). ICP-MS enabled detection of alkaline earth metals, e.g. sodium, potassium, calcium and magnesium at the level of milligrams per liter in vodkas originating from Vietnam (Lachenmeier et al. 2009). This technique supplemented with photochemical vapour generation (PVG) was also utilized for determination of cobalt, nickel and tellurium in three cachaça samples, one vodka sample and one sweet vermouth sample. It occurred to be superior to traditional ICP-MS due to lower limit of detection. The highest content of tellurium was detected in vodka, whereas nickel and cobalt content values are higher than the case of two out of three cachaça samples and lower than the case of vermouth and the third cachaça sample analysis (De Quadros and Borges 2014).

Moreover, studies aimed at assessing the influence of water hardness on the transparency of vodka were also conducted. The samples of tap water, artesian well water and commercial bottled water were analysed. The hardness of water was determined by titration with Na_2H_2EDTA. Based on the study results, it can be concluded that the transparency of vodka depends, to a large degree, on the type of water used in vodka production (Krosnijs and Kuka 2003).

Comparison Vodka to Other Alcoholic Beverages

The important stage of studies on vodkas involves distinguishing vodkas from other spirit-based beverages. These studies allowed the determination of the unique composition of vodka which, in turn, enabled its appropriate identification. Distinguishing among alcohol-based beverages by means of an electronic nose can serve as an example of such investigations (Ragazzo-Sanchez et al. 2006). The electronic nose is an analytical device for the fast detection and identification of odorant mixtures; its mode of operation mimics the human sense of smell. The electronic nose usually employs specific chemical sensors which generate a characteristic aroma profile, a so-called fingerprint, in response to being exposed to the investigated gaseous mixture. The identification of mixture components is based on the comparison with reference profiles. Considering the mode of operation, the

electronic nose is similar to the human nose. Conductometric sensors are the most frequently utilized. Metal oxide semiconductor (MOS) type sensors are the most characteristic ones within this group. They are relatively inexpensive, stable, easy to operate and reveal high sensitivity (ppb v/v). Electronic nose instruments based on sensors are not selective with respect to particular compounds. Each MOS-type sensor utilized in the electronic nose is selective with respect to a particular compound group, which yields a summary aroma profile characteristic for a given mixture. Hence, the electronic nose instruments of this type are suitable for distinguishing the samples, which differ in aroma profile in a significant way. Application of the chemometric methods, which allow identification of the most important data allowing distinguishing the samples, increases the distinguishing abilities of the electronic nose instruments. Ragazzo-Sanchez et al. (2006) analysed the alcoholic beverages such as, tequila, vodka, whiskey, beer and red wine. It was demonstrated that vodkas are characterized by the poorest aroma profile, which translates into the lowest content of volatile substances. Based on the principal component analysis (PCA), it was possible to divide the alcohols into groups. Only tequila and whiskey partially overlapped, while vodka formed a separate, easily distinguishable group (Ragazzo-Sanchez et al. 2006). It can be seen that the electronic nose based on MOS-type sensors enabled distinguishing the alcohol samples, which differ significantly between each other, especially in ethanol concentration. However, there were difficulties in distinguishing the samples exhibiting similar aroma profile. Electronic nose instrument was utilized for distinguishing 21 different alcohol-based beverages (wine, beer, vodka, whisky and tequila). Data analysis was performed with PCA and discriminant factorial analysis (DFA). Both DFA and PCA made it possible to distinguish the spirit-based beverages from wine and beer products. In the case of investigation of only spirit-based beverages, both methods allowed distinguishing particular types of alcohol; however, DFA occurred to be better in this field. In both cases, vodkas were distinguished in the best way, whereas whisky and tequila products were very close to each other on the plots (Ragazzo-Sanchez et al. 2008). Similar research was conducted on vodka, gin, whiskey and brandy by applying sensory evaluation and spectral analysis (Sujka et al. 2013). All samples were purchased in the stores in Warsaw. Sample preparation consisted of lyophilization which resulted in the removal of water and, consequently, in analyte enrichment. The sensory evaluation was performed by profiling with the use of unipolar scale of categories (evaluation of taste and smell), namely, a 7-point scale in which the highest value had been assigned to the highest intensity of the investigated quality. The team conducting the evaluation consisted of five trained persons. The vodkas were analysed with regard to the taste categories (sweet, bitter and grassy) as well as smell categories (sharp, sweet and pear). In comparison to gins, vodkas had a more intense taste and smell; sharp smell and grassy taste were best detected. Samples after lyophilization were analysed by means of Fourier transform infrared spectroscopy (FT-IR). The obtained results were processed by using discriminant analysis which enables the identification or quality evaluation of an unknown sample. The best results were obtained from the model describing vodka because it correctly classified all vodka samples and rejected all samples of brandy, 73 % of whiskey samples, and 97 % of gin samples (Sujka et al. 2013).

The task of distinguishing among the different types of alcohols was performed via ICP spectroscopy (Kokkinofta et al. 2003). A total of 68 alcoholic beverages were analysed, which mainly consisted of different types of zivania and included only four samples of vodka from Russia and Sweden. The obtained data were grouped by using canonical discriminant analysis (CDA) or classification binary trees (CBT) depending on the content of metals in samples. Thanks to the application of the aforementioned statistical methods, it was possible to distinguish between vodkas and other investigated beverages.

Product Authentication and Detection of Falsified Products

Vodkas are produced on a very large scale by various manufacturers, by different production methods and from diverse raw materials. All the aforementioned factors influence the quality of products and, as a consequence, their price. Both the manufacturers and the clients expect that a given product will fulfil specific requirements which are important to them. Due to the costs of alcohol production and prospective revenue from alcohol sales, the cases of falsification of alcohol-based products are frequent. It happens that higher-quality alcohols are substituted with cheaper and lower-quality ones, or raw materials other than the required ones are used in the production of high-quality alcohols. Such types of falsification have become the subject of research for many analytical chemists who employ various analytical techniques, e.g. gas and ion chromatography to authenticate the alcohols and detect falsified products.

In order to determine the authenticity of a given product, it is often necessary to check the raw materials used in the production. Flow injection analysis–isotope ratio mass spectrometry (FIA-IRMS) was employed for the investigation of authenticity of 81 selected alcohol-based beverages including vodkas. Botanic origin of the investigated samples was verified with this method. Eight out of 10 samples were classified as the vodkas produced from potatoes or from crops such as rye and wheat. The remaining two samples were classified as the ones produced from molasses, which is a by-product of sugar cane processing (Jochmann et al. 2009). This method is effective in investigation of botanic origin of the samples,

which can be especially useful in the case of vodka, the producers of which provide its composition on labels. FIA-IRMS makes it possible to detect falsification of vodkas via distillate produced from molasses. Reshetnikova et al. (2007) analysed different vodkas available on the Russian market with regard to the quality of spirit from which they had been made. The study employed gas chromatography (GC-FID), while the data were processed by using fuzzy logic. The investigated vodkas were made from the two types of spirit, i.e. Pure spirit of best quality, Extra and Lux; and Pure spirit of best quality and Extra. Among 12 analysed vodka types, only 1 was incorrectly classified into a better quality group (Reshetnikova et al. 2007). Similar research on the quality of ethanol used in vodka production was conducted by means of an electronic tongue (Legin et al. 2005). The electronic tongue (Fig. 2), also known as artificial tongue or taste sensor, is an analytical device mainly used for classifying tastes of various chemical substances in liquid samples. Its mode of operation is based on the human sense of taste. The electronic tongue can be applied to identify, classify and quantitatively and qualitatively analyse multicomponent mixtures by comparing the reference profiles with the profiles of investigated substances (so-called fingerprint method). Potentiometric sensors, especially ion-selective electrodes, are the most frequently applied sensors in the electronic tongue instruments. The advantages of the potentiometric sensors engulf well-established principle of operation, low cost, ease of production, possibility of obtaining selective sensors and closest similarity to the natural mechanism of molecular recognition (Ciosek and Wróblewski 2007).

Legin et al. (2005) analysed the samples of spirit from three quality categories (Lux, Extra and High Purity) in triplicates. The data analysis was conducted by using partial least squares (PLS) regression, which allowed for distinguishing among the samples. Fourteen samples of vodka were analysed with regard to the prescribed quality standards. Four vodkas fulfilling the standards and nine vodkas departing from the standards were selected. As in the case of analysed spirits, PLS regression enabled the identification of the investigated vodka types. Besides this analysis, a study aimed at distinguishing among vodka brands was also conducted. Ten brands produced from

ethanol of different quality, diluted with various water types and containing defined additives, e.g. sugar, had been compared. The collected data were processed by PCA. Most of the vodkas were very well distinguished in the plotted graph, while some were too close to each other which had made the identification difficult. Nevertheless, this study demonstrated that the electronic tongue can be successfully used for identifying vodka brands (Legin et al. 2005). The application of conductivity measurements to distinguish vodka brands was described by Lachenmeier et al. (2008). According to the authors, each type of vodka displays a specific conductivity due to the raw materials and methods used in the production process. The authors also mentioned that the use of flavourings do not have a significant effect on the conductivity; therefore, the method can be used to distinguish among the vodka brands. In this study, vodkas originating from Russia, Poland, and Sweden and vodkas without the country of origin, but purchased in Germany were investigated. Conductivity measurements allowed the identification of the analysed samples (Lachenmeier et al. 2008). Research on vodka identification also employs chromatography, for example, the study of commercial vodkas from the USA and Canada (Ng et al. 1996). The samples were prepared by SPME technique, while the determinations were performed by GC-MS. The analysed vodkas were produced from various raw materials. The authors distinguished between Canadian and American vodkas by using ethyl esters profiles and checking for the presence of compounds such as, 5-hydroxymethyl-2-furaldehyde (5-HMF) and triethyl citrate (TEC). Besides gas chromatography, ion chromatography was also applied to identify vodkas. In this case, the concentrations of sodium, potassium, magnesium, calcium, chloride, nitrate and sulphate ions were determined in vodkas of Russian origin. In order to supplement the obtained results, GC-FID was used, which allowed for distinguishing among different vodka brands (Arbuzov and Savchuk 2002). Ion chromatography was also employed to detect falsified rum and vodka based on the analysis of chloride, nitrate and sulphate ions, and the sum of anions. This allowed for discriminating between Russian and German vodkas (Lachenmeier et al. 2003). Near infrared (NIR) spectroscopy was used for distinguishing the vodkas made in

Fig. 2 Comparison of the principles of natural and artificial sense of taste
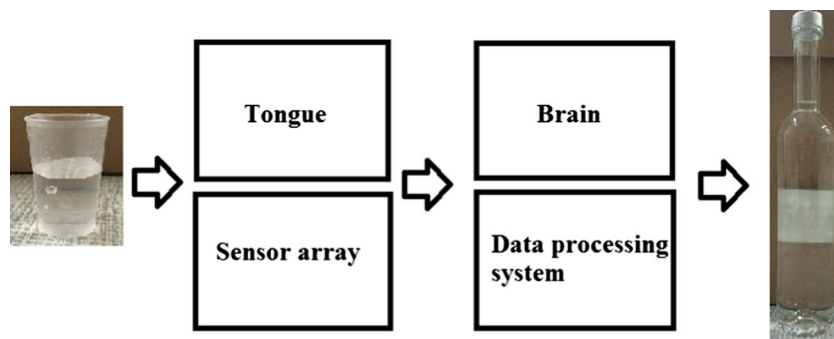
Russia from those produced in other countries. A total of 109 samples were investigated; 67 originated from Russia and 42 from Western European countries. The following chemometric methods were employed to data analysis: soft independent modelling of class analogy (SIMCA) and linear discriminant analysis (LDA). None of the statistical methods allowed ideal distinguishing of the investigated samples (Kolomiets et al. 2010). Despite such results, it can be stated that the technique employed could be useful while coupled with other chemometric methods.

Besides authentication of vodka brands, scientists also check vodkas for possible falsification. Ethanol content different from the one stated on the vodka label can be an example of falsification. The study on this subject was conducted on 17 samples of commercial vodka purchased in Poland by using FT-IR spectrometry and two models, and by applying the alcoholometric method described in the Polish standard PN-A-79529-4:2005. In nine cases, the alcoholometric method gave different results than those stated on the labels of the analysed vodkas. For all samples, the values obtained from experimental models differed from those stated by the vodka manufacturers. This study demonstrated that the true values often depart from the values on the labels, which points to, either conscious or accidental, product falsification. Despite the observed discrepancies, all vodkas fulfilled the EU norm according to which the minimum ethanol content in vodka should be 37.5 % (Sujka and Koczoń 2012). Another possible falsification of vodka concerns the use of synthetic ethanol instead of ethanol from natural fermentation. Studies on this subject were conducted by using GC-MS; three compounds characteristic for synthetic ethanol, i.e. 2-butanol, acetone and crotonaldehyde were determined. All these compounds are present in synthetic ethanol, while 2-butanol does not occur in ethanol from natural fermentation. The samples of whiskey, vodka, cognac and synthetic alcohols were analysed (Savchuk and Kolesov 2005).

Summary

Vodkas are the most frequently consumed spirit-based beverages, particularly in Eastern Europe (Hollensen 2007). Vodkas are not commonly analysed because of their matrix, which mainly consists of ethanol and water, and includes numerous organic and inorganic substances at low concentration levels. In general, gas chromatography is used to analyse the vodka composition; however, there were some reports on the use of other techniques for determining specific analytes. The largest number of compounds comprising the matrix was detected by employing two-dimensional gas chromatography because this technique is characterized by high sensitivity and high peak capacity. Studies conducted my means of HPLC were the rarest due to the fact that the volatile substances present in vodkas are best analysed via GC. Until now, the chemicals belonging to alcohols, aldehydes, ketones, esters, terpenes, aromatic compounds and volatile sulphur compounds have been detected in vodkas. The product authentication and detection of falsified products are of utmost importance in relation to the quality of alcohol consumed. In comparison to other spirit-based beverages, vodka has the poorest aroma profile; therefore, it is easy to distinguish it from other alcohols. Such studies were conducted thanks to the use of electronic nose, infrared spectroscopy and sensory evaluation. The task of identifying different vodka types seems more difficult. Until now, vodkas have been identified based on the quality of ethanol used in their production, which was assessed via electronic tongue or gas chromatography. In addition, vodka brands were also identified because it was necessary for maintaining the high quality of a given brand (by making comparisons with other brands) and for avoiding the attempts of falsifying a given brand. To this end, vodkas were analysed by means of conductivity measurements, gas chromatography, ion chromatography and FT-IR spectroscopy.

This review paper shows that despite many years of research and using numerous techniques, vodka still remains an interesting object of investigations.

References

Act of 13 September 2002 on the spirit drinks, "USTAWA z dnia 13 września 2002 r. o napojach spirytusowych „ No 1362/166 J. Laws, 10582–10589.

Arbuzov VN, Savchuk SA (2002) Identification of vodkas by ion chromatography and gas chromatography. J Anal Chem 57:428–433

Aylott RI (2003) Vodka, gin and other flavored spirits. In Fermented beverage production Springer, US, pp. 289–308.

Balcerek M, Szopa JS (2006) Zawartość karbaminianu etylu w destylatach owocowych. Żywność Nauka Technol Jakość 1:91–101

Cardeal ZL, Marriott PJ (2009) Comprehensive two-dimensional gas chromatography–mass spectrometry analysis and comparison of volatile organic compounds in Brazilian cachaca and selected spirits. Food Chem 112:747–755

Cardoso DR, Andrade Sobrinho LG, Lima-Neto BS, Franco DW (2004) A rapid and sensitive method for dimethyl sulphide analysis in Brazilian sugar cane sugar spirits and other distilled beverages. J Braz Chem Soc 15:277–281

Chłobowska Z, Chudzikiewicz E, Świegoda C (2000) Analysis of alcoholic products at the Institute of Forensic Research. Z Zagadnień Nauk Sądowych 41:52–61

Chodak M (2005) Zastosowanie spektroskopii w bliskiej podczerwieni (NIR) do oznaczania zawartości C, N, S, P i kationów metali w materii organicznej gleb leśnych. Inżynieria Środowiska 10: 213–222

Christoph N, Bauer-Christoph C (2006) Vodka. In: Berger RG (ed) Flavours and fragrances chemistry, bioprocessing and sustainability. Springer, Berlin, p 341

Ciosek P, Wróblewski W (2007) Sensor arrays for liquid sensing–electronic tongue systems. Analyst 132:963–978

Clegg BS, Frank R, Ripley BD, Chapman ND, Braun HE, Sobolov M, Wright SA (1988) Contamination of alcoholic products by trace quantities of ethyl carbamate (urethane). Bull Environ Contam Toxicol 41:832–837

Commission recommendation 133/2010 of 2 March 2010 on the prevention and reduction of ethyl carbamate contamination in stone fruit spirits and stone fruit marc spirits and on the monitoring of ethyl carbamate levels in these beverages. Off J Eur Uni, 53–57

De Andrade JB, Bispo MS, Rebouças MV, Carvalho MLSM, Pinheiro HLC (1996) Spectrofluorimetric determination of formaldehyde in liquid samples. Am Lab 28:56–59

De Oliveira FS, Sousa ET, De Andrade JB (2007) A sensitive flow analysis system for the fluorimetric determination of low levels of formaldehyde in alcoholic beverages. Talanta 73:561–566

De Quadros DPC, Borges DLG (2014) Direct analysis of alcoholic beverages for the determination of cobalt, nickel and tellurium by inductively coupled plasma mass spectrometry following photochemical vapor generation. Microchem J 116:244–248

Hollensen S (2007) Designing the global marketing programme. In Global marketing: a decision-oriented approach. Pearson education, UK, pp. 588–589

Hu N, Wu D, Cross K, Burikov S, Dolenko T, Patsaeva S, Schaefer DW (2010) Structurability: a collective measure of the structural differences in vodkas. Agric Food Chem 58:7394–7401

Jochmann MA, Steinmann D, Stephan M, Schmidt TC (2009) Flow injection analysis–isotope ratio mass spectrometry for bulk carbon stable isotope analysis of alcoholic beverages. J Agric Food Chem 57:10489–10496

Kokkinofta R, Petrakis PV, Mavromoustakos T, Theocharis CR (2003) Authenticity of the traditional cypriot spirit "Zivania" on the basis of metal content using a combination of coupled plasma spectroscopy and statistical analysis. J Agric Food Chem 51:6233–6239

Kolomiets OA, Lachenmeier DW, Hoffmann U, Siesler HW (2010) Quantitative determination of quality parameters and authentication of vodka using near infrared spectroscopy. J Near Infrared Spectrosc 18:59–67

Krosnijs I, Kuka P (2003) Influence of water hardness on the clearness and stability of vodka. Pol J Food Nutr Sci 12:58–60

Lachenmeier DW, Attig R, Frank W, Athanasakis C (2003) The use of ion chromatography to detect adulteration of vodka and rum. Eur Food Res Technol 218:105–110

Lachenmeier DW, Schmidt B, Bretschneider T (2008) Rapid and mobile brand authentication of vodka using conductivity measurement. Microchim Acta 160:283–289

Lachenmeier DW, Anh PTH, Popova S, Rehm J (2009) The quality of alcohol products in Vietnam and its implications for public health. Int. J. Environ. Res. Public Health 6:2090–2101

Legin A, Rudnitskaya A, Seleznev B, Vlasov Y (2005) Electronic tongue for quality assessment of ethanol, vodka and eau-de-vie. Anal Chim Acta 534:129–135

Leitz J, Kuballa T, Rehm J, Lachenmeier DW (2009) Chemical analysis and risk assessment of diethyl phthalate in alcoholic beverages with special regard to unrecorded alcohol. PLoS ONE 4:1–7

Leppänen O, Denslow J, Ronkainen P (1979) A gas chromatographic method for the accurate determination of low concentrations of volatile sulphur compounds in alcoholic beverages. J Inst Brew 85: 350–353

McCleskey SC, Floriano PN, Wiskur SL, Anslyn EV, McDevitt JT (2003) Citrate and calcium determination in flavored vodkas using artificial neural networks. Tetrahedron 59:10089–10092

Nagarajan R, Gupta A, Mehrotra R, Bajaj MM (2006) Quantitative analysis of alcohol, sugar, and tartaric acid in alcoholic beverages using attenuated total reflectance spectroscopy. J Autom Methods Manage Chem 1–5

Nascimento RF, Bezerra CW, Furuya S, Schultz MS, Polastro LR, Lima Neto BS, Franco DW (1999) Mineral profile of Brazilian cachacas and other international spirits. J Food Compos Anal 12:17–25

Ng LK (2002) Analysis by gas chromatography/mass spectrometry of fatty acids and esters in alcoholic beverages and tobaccos. Anal Chim Acta 465:309–318

Ng L-K, Hupe M, Harnois J, Moccia D (1996) Characterisation of commercial vodkas by solid-phase microextraction and gas chromatography/mass spectrometry analysis. Sci Food Agric 70: 380–388

Nordon A, Mills A, Burn RT, Cusick FM, Littlejohn D (2005) Comparison of non-invasive NIR and Raman spectrometries for determination of alcohol content of spirits. Anal Chim Acta 548:148–158

Pereira EV, Oliveira S, Nóbrega IC, Lachenmeier DW, Araújo AC, Telles DL, Silva M (2013) Brazilian vodkas have undetectable levels of ethyl carbamate. Quim Nova 36:822–825

Ragazzo-Sanchez JA, Chalier P, Chevalier D, Ghommidh C (2006) Electronic nose discrimination of aroma compounds in alcoholised solutions. Sensors Actuators B 114:665–673

Ragazzo-Sanchez JA, Chalier P, Chevalier D, Calderon-Santoyo M, Ghommidh C (2008) Identification of different alcoholic beverages by electronic nose coupled to GC. Sensors Actuators B 134:43–48

Regulation, E. C. N. 110/2008 of the European parliament and of the council of 15 January 2008 on the definition, description, presentation, labelling and the protection of geographical indications of spirit drinks and repealing Council Regulation (EEC) No 1576/89 Off. J. Eur. Commun. L, 16–54

Reshetnikova VN, Filatova EA, Kuznetsov VV (2007) Identification of raw materials for the production of vodkas based on the results of gas–liquid chromatographic analysis with the use of fuzzy logic. J Anal Chem 62:1013–1016

Savchuk SA, Kolesov GM (2005) Markers of the nature of ethyl alcohol: chromatographic techniques for their detection. J Anal Chem 60: 1102–1113

Savchuk SA, Nuzhnyi VP, Kolesov GM (2006) Factors affecting the accuracy of the determination of diethyl phthalate in vodka, ethanol, and samples of illegal alcoholic products. J Anal Chem 61:1198–1203

Siříšťová L, Přinosilová Š, Riddellová K, Hajšlová J, Melzoch K (2012) Changes in quality parameters of vodka filtered through activated charcoal. Czech J Food Sci 30:474–482

Sowiński P, Wardencki W, Partyka M (2005) Development and evaluation of headspace gas chromatography method for the analysis of carbonyl compounds in spirits and vodkas. Anal Chim Acta 539:17–22

Sproll C, Ruge W, Andlauer C, Godelmann R, Lachenmeier DW (2008) HPLC analysis and safety assessment of coumarin in foods. Food Chem 109:462–469

Sujka K, Koczoń P (2012) Zastosowanie spektroskopii FT-IR do oceny zawartości alkoholu etylowego w komercyjnych wódkach. Zesz Probl Postep Nauk Rol 571:107–114

Sujka K, Koczoń P, Gorska A, Wirkowska M, Reder M (2013) Sensoryczne i spektralne cechy wybranych wyrobów spirytusowych poddanych procesowi liofilizacji. Żywność Nauka Technol Jakość 4:184–194

Szpunar J, Łobiński R (1999) Spektrometria masowa z jonizacją w plazmie sprzężonej indukcyjnie (ICP MS) In Zastosowanie metod spektrometrii atomowej w przemyśle i ochronie środowiska. IChF PAN, Warszawa, pp 34–36

Tsuchiya H, Ohtani S, Yamada K, Akagiri M, Takagi N, Sato M (1994) Determination of formaldehyde in reagents and beverages using flow injection. Analyst 119:1413–1416

Vanhaecke F, Moens L (1999) Recent trends in trace element determination and speciation using inductively coupled plasma mass spectrometry. Fresenius J Anal Chem 364:440–451

Wardencki W, Sowiński P, Curyło J (2003) Evaluation of headspace solid-phase microextraction for the analysis of volatile carbonyl compounds in spirits and alcoholic beverages. J Chromatogr A 984:89–96