Sensitive determination of impurities in samples of vodka by gas chromatography with flame-ionization detection

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Vodka is one of the most popular alcoholic drinks around the world. Adulteration of vodkas lead to many negative consequences. A number of analytical methods covers a wide range of analytes and allows detection of adulterated alcoholic beverages, however, most of these methods are very labor and time consuming or require expensive analytical instrumentation. The simplest and thus most popular method is based on direct analysis by gas chromatography (GC) with flame-ionization detection (FID). The main drawback of this method for discovery of adulterated vodka samples is insufficient sensitivity. The aim of this study was to increase sensitivity of the method for determination of key vodka impurities. Optimized parameters included split ratio 10:1, inlet temperature >120°C, initial oven temperature 60°C, flow rates of make-up gas, air and hydrogen 50, 400 and 40 mL/min, respectively. Obtained calibration plots are linear in the concentration range between 1 and 1000 mg/L with approximation coefficients $R^2>0.99$. Compared to a standard method, slope factors are about 4 times higher when optimized method is used proving its higher sensitivity.

Keywords: gas chromatography; flame ionization detector; analysis; vodka; impurities; adulteration.

Арақ үлгілерің құрамындағы негізгі микроқоспаларды жалынды-ионизациялайтын детекторымен газды хроматография әдісімен сезімталды анықтау

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Арақ дүние жүзінде ең кең тараған алкоголь ішімдігі болып табылады. Арақты бұрмалау көптеген кері әсерін тигізеді. Аналитикалық әдістердің көбі анықталатын заттардың кең ауқымын анықтауға және бұрмаланған алкогольді ішімдіктерді анықтауға мүмкіндік береді. Алайда, осы әдістердің көбі еңбексыйымдылығы жоғары, көп уақытты және қымбат аналитикалық құрал-жабдықтарды қажет ететін болып табылады. Ең қарапайым және кең тараған әдіс үлгіні жалынды-ионизациялайтын детекторымен жабдықталған газды хроматографтың үлгі енгізетін құрылғысына тура енгізуге негізделген. Арақтың бұрмаланған үлгілерін анықтау әдісінің негізгі кемшілігі – төмен сезімталдығы. Осы зерттеу жұмысының мақсаты – арақ үлгілерінде негізгі микроқоспаларды анықтау әдісінің сезімталдығын жоғарлату. Келесі параметрлер оңтайландырылған: ағын қатынасы – 10:1, үлгіні енгізу температурасы – >120°C, пештің бастапқы температурасы – 60°C, ағынды газ, ауа және сутегі ағындарының жылдамдықтары – сәйкесінше, 50, 400 және 40 мл/мин. Алынған калибрлеу тәуелділіктері концентрациялардың 1-1000 мг/л аймағында аппроксимация коэффициенті $R^2>0{,}99$ болып, сызықты болып келеді. Стандартты әдіске қарағанда, анықтау шектері төрт есе жоғарлады.

Түйін сөздер: газды хроматография; жалынды-ионизациялайтын детектор; арақ; қоспалар.

Чувствительное определение микропримесей в образцах водок методом газовой хроматографии с пламенно-ионизационным детектором

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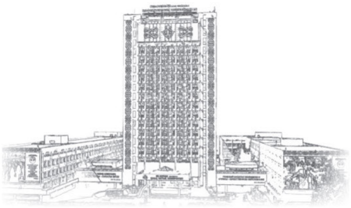
Водка является одним из самых популярных алкогольных напитков во всем мире. Фальсификация водок приводит к многочисленным негативным последствиям. Ряд аналитических методов охватывают широкий спектр аналитов и позволяют обнаружение фальсифицированных алкогольных напитков, однако, большинство из этих методов трудоемки и занимают много времени и требуют дорогих аналитических приборов. Самый простой и наиболее распространенный метод основан на прямом вводе образца в устройство для ввода пробы газового хроматографа (ГХ) с пламенно-ионизационным детектором (ПИД). Основным недостатком этого метода обнаружения фальсифицированных образцов водки является недостаточная чувствительность. Целью данного исследования было увеличить чувствительность метода для определения основных микропримесей в образцах водок. Оптимизированы следующие параметры: деление потока – 10:1, температура ввода пробы >120°C, начальная температура печи 60°C, скорости подачи поддувочного газа, воздуха и водорода 50, 400 и 40 мл/мин, соответственно. Полученные калибровочные зависимости линейной в всем диапазоне концентраций от 1 до 1000 мг/л с коэффициентами аппроксимации $R^2>0{,}99$. По сравнению со стандартным методом, угол наклона в 4 раза выше оптимизированной методикой.

Ключевые слова: газовая хроматография; пламенно-ионизационный детектор; водка; примеси.



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1. Introduction

According to International Wines and Spirits Record (IWSR) [1], vodka is one of the most popular alcoholic drinks around the world. In 2012, 4.5 billion liters of vodka were drunk in world. Half of that amount was drunk in Russia (13.9 liters per capita). In Belarus, average citizen drunk 11.3 liters of vodka a year. Every citizen of Kazakhstan accounted for 5.9 liters of vodka a year [2].

Vodka is a colorless alcoholic beverage having characteristic spirituous odor and consisting from ethanol and water. Concentration of ethanol is normally 40%, but it may also reach 56% in different countries depending on state regulatory requirements for vodka quality. Most vodkas are produced by a fermentation and a distillation of grains with subsequent filtration through charcoal or carbon filters. From the chemical point of view, vodkas are the purest alcoholic beverages.

According to independent experts, 46% of vodkas in markets are adulterated (counterfeit). Counterfeit vodka is mostly produced from poor-quality raw materials. Such vodkas are often illegally sold under known brands of vodka.

Consequences of the using of this “counterfeits” are unpredictable: from strong hangover to disability and death. Vodka refers to the most commonly adulterated group of alcoholic beverages. Therefore it is very important to discover and prevent it’s adulteration. Laboratory analyses of vodka is the most efficient and reliable method for disclosing adulterated samples.

The presence of a number of impurities, e.g., acetone, is often associated with the use of synthetic ethanol. Normally such alcohol have different “burning” smell and taste. In accordance with the Law of the Republic of Kazakhstan [3], the quality of alcoholic beverages as an industrial product should comply with the request of the public or industry standard according to certain parameters, that are responsible for its quality. Non-compliance with GOST-standard [4], [5] indicates artisanal beverage production. However, there are cases where counterfeit drinks correspond to standard parameters. This is because parameters of GOSTs have a wide range of values, some parameters limit total concentrations of a class of substances (such as fusel oils). Concentrations of many compounds are not limited by standards. Thus, the definition of the correspond parameters to the values of GOSTs is necessary but not sufficient condition for the study of adulterated alcohol products, which makes it necessary to develop, implement and continuously updated method to reflect advances in science and technology.

A number of analytical methods (Table 1) covers wide range of analytes and allows detection of adulterated alcoholic beverages. However, most of these methods are very labor and time consuming or require expensive analytical instrumentation.

The most popular methods for determining impurities in vodka based on GC-FID [4], [5] This method is standardized in former USSR countries including Kazakhstan. GOST R 51786-2001 and GOST R 51698-2000 methods are based on direct sample injection into GC inlet. These methods work well on samples having high concentrations of impurities (>10 mg/L). However, development of technology made it easier and cheaper

Table 1 – Methods of analysis of alcohol used in the detection of falsified objects

#	Method	Objects	Determined compounds	Ref
1	GC-FID, capillary column	Alcohols, vodkas, cognacs, rums, wines	Ethanol, trace impurities: ethyl acetate, methanol, n-propanol, iso-butanol, n-butanol, isoamylol alcohol	[6]
2	GC-FID, capillary column	Factory and home-made alcoholic drinks (home-brewed beer, chacha, arrack)	a. Ethanol, trace impurities: ethyl acetate, methanol, n-propanol, iso-butanol, n-butanol, isoamylol alcohol. b. Sugar: (trimethylsilyl derivatives)	[7]
3	GC-thermionic detector	Factory and home-made alcoholic drinks (home-brewed beer, chacha, arrack)	Allyl oil in wine (by identification and determination of allyl isocyanate - a main component, whose purity is 95%)	[7]
4	GC-FID	Cognacs, vodkas	Acetaldehyde, ethyl formate, ethyl acetate, methanol, 2-butanol, n-propanol, iso-butanol, n-butanol, isoamyl alcohol. Caffeine from tea used for coloring falsification.	[8]
5	GC-FID, GC-MS/MS, GC-MS, ICP-MS	Samohon, cheapest vodka, medical liquids	Methanol, acetaldehyde, higher alcohols, ethyl carbamate, anions, and inorganic elements. Data was compared to acceptable daily intake	[9]
6	IR, ICP/MS, GC/FID	Artisanal alcohol, cuxa	methanol, acetaldehyde, 1-propanol, 1-butanol, 2-butanol, iso-butanol, 2-/3-methyl-1-butanol and ethyl acetate, metals	[10]
7	NIR Spectroscopy	Whiskey, brandy, rum and vodka	Whole spectra of compounds; PCA, SIMCA	[11]
8	Flow injection analysis with photometric detector	Brandies, cachacas, rums, whiskies and vodkas	Schlieren effect, SIMCA	[12]

to produce adulterated alcoholic samples having low concentration of impurities being determined. In addition, these samples may be produced chemically, not from natural raw material (e.g. wheat, grape, etc.), that is illegal according to legislation.

Standard methods often do not provide sufficient sensitivity for the determination of trace impurities in highly pure vodka samples thus making differentiation and solution of forensic task impossible. In connection with this, the goal of present work was to increase sensitivity of standard methods for determination of trace impurities in vodka by GC-FID.

The aim of this study was to optimize GC-FID method for sensitive determination of vodka impurities.

2. Experimental

2.1 Chemicals

For analysis, the following pure substances (purity>98%) were taken: acetone, ethyl acetate, methanol, 2-butanol, 1-propanol, iso-butanol, isoamyl alcohol and 1-pentanol. Purity of these substances was established by their direct injection to 6890N/5973N GC-MS (Agilent, USA). Helium (99.995%) was purchased from “Tehgas” (Orenburg, Russia).

2.2 Vodka standard solution for method optimization

For analysis, 1 mL of a standard solution of acetone, ethyl acetate, methanol, 2-butanol, 1-propanol, iso-butanol, isoamyl alcohol, 1-pentanol with concentration 10 mg/L of each compound were prepared. Pure substances were dissolved in 40% ethanol solution “that was proven by GC-FID to be free of impurities. Vials were placed into the 7683 (Agilent, USA) autosampler tray for further analysis by gas chromatography with flame ionization detector 6890N (Agilent, USA).

2.3 Analysis by gas chromatography with flame ionization detection

All samples were analyzed on 6890N/5973N (Agilent, Santa Clara, USA) gas chromatograph with mass spectrometric and flame ionization detectors equipped with split/splitless inlets. For separation of impurities, 0.5-1 µL of the sample was injected into GC inlet. Separation was performed using a 50 m x 0.32 mm HP-FFAP capillary column having film thickness of 0.5 micron under constant flow of helium 1 mL/min. Duration of the analysis depended on the number of determined impurities (20 to

45 minutes). Other method parameters were optimized for an increased sensitivity. All experimental samples were analyzed in triplicates.

2.4 Optimization of split ratio

The experiment was carried out by varying the split ratio: 10:1, 15:1, 20:1, 30:1, 40:1 and 50:1. One µL of sample was injected directly into GC inlet heated to temperature 200°C. Gas saver was activated 1 min after injection. Oven temperature was programmed from 60°C (10 min) to 100°C (10 min) at a heating rate of 20°C/min.

2.5 Optimization of inlet temperature

One µL of prepared sample was injected into GC inlet in 20:1 split mode at the following inlet temperatures: 120, 140, 160, 180, 200, 220, 240 and 250°C. Oven temperature was programmed from 60°C (10 min) to 100°C (10 min) at a heating rate of 20°C/min.

2.6 Optimization of initial oven temperature

According to manufacturer's specifications, working range of a column lies between 60 and 240°C. The following initial oven temperatures were studied: 40, 50, 60, 70 and 80°C (10 min) to 100°C (10 min) at a heating rate of 20°C/min. One µL of samples were injected directly into GC inlet at 120°C and 20:1 split ratio.

2.7 Optimization of FID make-up flow rate

The following make-up flow rates were studied: 10, 20, 30, 40, 50 and 60 mL/min. One µL of sample was injected directly into GC inlet at 120°C in 20:1 split mode. Oven temperature was programmed from 60°C (10 min) to 100°C (10 min) at a heating rate of 20°C/min.

2.8 Optimization of air flow rate

The following air flow rates were studied: 300, 400, 500 and 600 mL/min. One µL of sample was injected directly into GC inlet at 12 °C in 20:1 split mode. Oven temperature was programmed from 60°C (10 min) to 100°C (10 min) at a heating rate of 20°C/min. Run time was 22 minutes.

2.9 Optimization of hydrogen flow rate

The following hydrogen flow rates were studied: 40, 60 and 80 mL/min. One µL of sample was injected directly into GC inlet at 120°C in 20:1 split mode. Oven temperature was programmed from 60°C (10 min) to 100°C (10 min) at a heating rate of 20°C/min. Run time was 22 minutes.

2.10 Calibration of GC-FID by using optimized parameters

For calibration, the following pure substances (purity>98%) were taken: acetone, ethyl acetate, methanol, 2-butanol, 1-propanol, iso-butanol, isoamyl alcohol and 1-pentanol. Purity of these substances was established by their direct injection to 6890N/5973N GC-MS (Agilent, USA).

On the first stage, 10 mL of 40% ethanol solution in water not containing target analytes was introduced into a 10 mL vial. Then, 10.0 mg of each analytes were injected into the vial using 25 µL syringe (Agilent, Australia). Concentrations of analytes in the prepared solution made up 1000 mg/L. The prepared solution was subsequently diluted to concentrations of analytes 1.0, 3.0, 5.0, 10.0, 30.0, 50.0, 100.0, 300.0, 500.0 and 1000.0 mg/L. Every solution was prepared in triplicates. All prepared samples were analyzed on Agilent 6890N GC-FID at the optimized parameters and parameters given in GOST R 51786-2001 method.

Table 2 – The list of studied vodkas

#	Sample name	Sample origin
1	Russkiy standart	Russia
2	Khlebnaya dusha	Russia
3	Yeni Raki	Turkey
4	Rodnaya Derevenskaya	Russia
5	Tri reki	Russia
6	Khaoma gold	Kazakhstan
7	Khaoma origin	Kazakhstan
8	Ladoga Khlebnaya	Russia
9	Moy gorod Semey	Kazakhstan
10	Jelzin	France
11	Russkaya marka	Russia
12	Dikiy gus	Russia
13	Belenkaya zolotaya	Russia
14	Classic Rzhanaya	Russia
15	Finka	Russia
16	Khaoма Yubileynnaya	Kazakhstan
17	Gramulka	Russia
18	Kara Zhorga	Russia
19	Casino	Russia
20	Medovukha	Russia
21	Syktyvkarskaya	Russia
22	Rusitsa	Russia
23	Vivat	Russia
24	Arassa Aragy	Kazakhstan
25	Zero$_3$	USA

Obtained chromatograms were integrated. Peaks were identified using previously established retention times of single analytes. Calibration dependences were plotted using MSD ChemStation software (version E.02.02 Service pack 1) and double-checked using MS Excel software.

2.11 Application of the optimized method

The optimized method was applied on 26 vodka samples (Table 2) purchased in shops in Kazakhstan (Almaty, Shymkent, Semipalatinsk), Turkey (Istanbul) and USA (Ames, Iowa).

3. Results and Discussions

3.1 Optimization of split ratio

Split ratio is most important parameter affecting method sensitivity. Its increase leads to the decrease of amount of analytes introduced into the column. For highest sensitivity, splitless injection should be used. However, in this case, we deal with samples containing 60% of water being undesirable in the column. Injection in splitless mode or at low split ratios may potentially lead to problems with column lifetime, analytes peaks shape and efficiency of resolution.

The goal of this experiment was to establish the effect of split ratio on analytes response and peak shape. Column lifetime is difficult and expensive to estimate and it was excluded from list of dependent variables.

The increase of split ratio (the injected volume of sample) leads to the proportional decrease of peak area (Figure 1). Maximum total peak area was observed at split ratio 10:1, which was selected as optimal.

3.2 Optimization of inlet temperature

Increase of inlet temperature is required to achieve fast and efficient introduction of analytes into the column. However, it can also facilitate chemical reactions between analytes and lead to problems with quantification. The goal of this experiment was to determine optimal injection port temperature.

The increase of inlet temperature leads to the decrease of responses of all analytes except acetone and methanol (Figure 2). Highest impact is observed for ethyl acetate response of which decreased by 25% at the increase of temperature from 120 to 240°C. Decrease of response may be caused by degradation of analytes due to excessive temperature. Thus, the inlet temperature 120°C was selected as optimal.

3.3 Optimization of initial oven temperature

Initial oven temperature significantly affects peak shapes of volatile analytes and efficiency of their separation. Decrease of initial oven temperature may help to reconcentrate analytes in the front of a column thus improving peak shapes. It is especially helpful when splitless injection is used.

The goal of this experiment was to establish the optimal initial oven temperature for separation of vodka impurities on a 50 m x 0.32 mm HP-FFAP (film thickness 0.50 µm) at the constant flow rate of carrier gas (helium grade "A") of 1 mL/min.

According to manufacturer's specifications, working range of a column lies between 60 and 240°C. The following initial oven temperatures were studied: 40, 50, 60, 70 and 80°C (10 min) to 100°C (10 min) at a heating rate of 20°C/min. One µL of samples were injected directly into GC inlet at 120°C and 20:1 split ratio. Sample was analyzed in 3 replicates for each initial oven temperature. Chromatograms were integrated, peaks were identified, areas of each peak and RSDs of each compound were calculated.

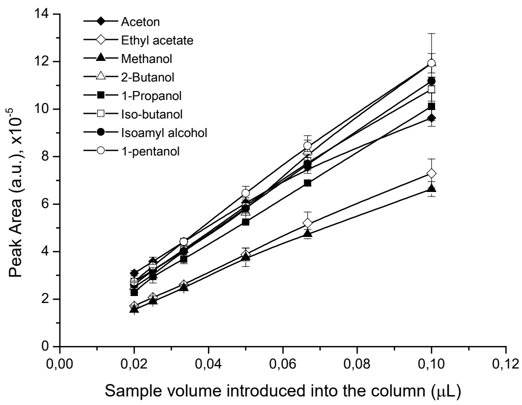


Figure 1 – Effect of the injected volume of sample on the peak area of vodka impurities

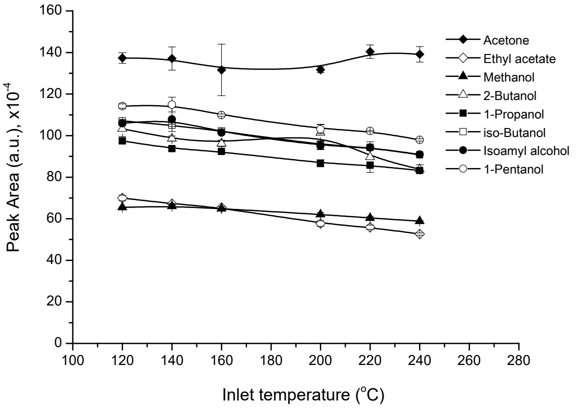


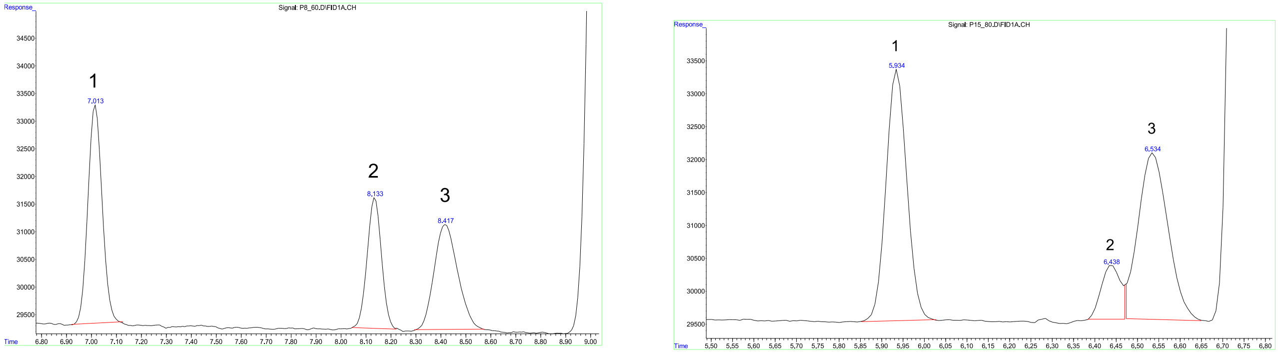
Figure 2 – Effect of the inlet temperature on peak area of impurities

Change of oven temperature virtually does not lead to any change of responses of most analytes. Only responses of ethyl acetate and methanol decrease at 70-80 °C probably due to their poor retention at these temperatures (Figure 3). Initial oven temperature 60 °C was selected as optimal. In a case of problems with separation of methanol and ethyl acetate, this temperature may be decreased to 50°C.

3.4 Optimization of FID make-up flow rate

Make-up gas is necessary in FID to increase flow rate through detector and decrease peak width. However, excessive increase of make-up flow may lead to decrease of response due to dilution of the flow eluting from the column. In addition, it may lead to excessive consumption of expensive high-grade helium. According to manufacturer, recommended make-up flow rate is 50 mL/min (Table 3), but standard methods require 40 mL/min. The goal of this experiment was to establish the optimal flow rate providing highest sensitivity for detection of vodka impurities by GC-FID.

Increase of a make-up gas flow rate leads to the increase of peak areas of all analytes (Figure 4). Maximum



a

b

Figure 3 – GC-FID chromatograms of impurities in vodka standard obtained at initial oven temperatures 60 °C (a) and 80°C (b): 1 – acetone, 2 – ethyl acetate, 3 –methanol

increase of response at the increase of make-up flow from 10 to 50 mL/min was observed for acetone – 40%; for other compounds, the difference was 15-20%. Because the difference of analytes responses between 50 and 60 mL is insignificant, 50 mL/min was selected as optimal.

The goal of next two experiments was to optimize flow rates of air and hydrogen in FID. According to manufacturer's specifications, 450 and 40 mL/min are optimal flow rates of air and hydrogen, respectively (Table 3). Increase of flow rates of these gases may potentially lead to a better efficiency of ionization of analytes, especially at higher concentrations. However, excessive flow of these gases may lead to dilution of gas eluted from the column and decrease of analytes response. In addition, it may lead to increase of consumption of gases and decreased lifespan of hydrogen and zero air generators.

3.5 Optimization of air flow rate

Air flow rate does not affect peak areas of vodka impurities. Therefore, flow rate recommended by the manufacturer (400 mL/min) was selected as optimal.

3.6 Optimization of hydrogen flow rate

Increase of hydrogen flow rate decreases peak areas of analytes (Figure 5). It may be caused by the decrease of ionization efficiency due non-stoichiometric ratio with air and dilution of gas eluted from the column. Thus, hydrogen flow rate 40 mL/min was selected as optimal.

Table 3 – Recommended flow rates for Agilent 6890 FID

Detector gases	Flow range, mL/min	Recommended flow, mL/min
Hydrogen	0 to 100	40
Air	0 to 800	450
Column capillary make up Recommended: nitrogen Alternate: helium	0 to 100	50

3.7 Calibration using optimized parameters

Obtained calibration plots are linear in the whole studied concentration range with approximation coefficients $R^2>0.99$ (Table 4). Compared to standard method, slope factors are about 4 times higher when optimized method is used proving its higher sensitivity.

Similar calibration plots were obtained using 6850 GC-FID (Agilent, USA) in Almaty Institute of Forensic Expertise (Table 5). Slope factors were also 4 times higher when using optimized method.

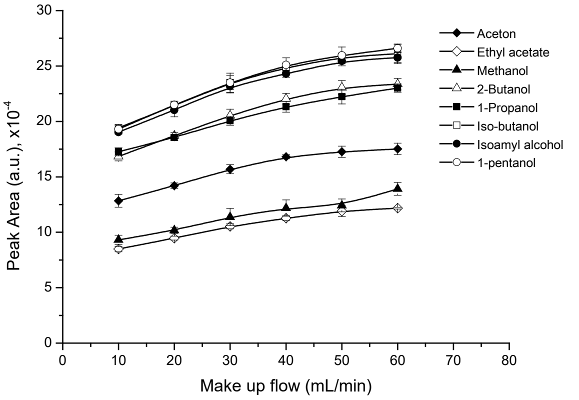


Figure 4 – Effect of a make-up gas flow rate on peak area of vodka impurities

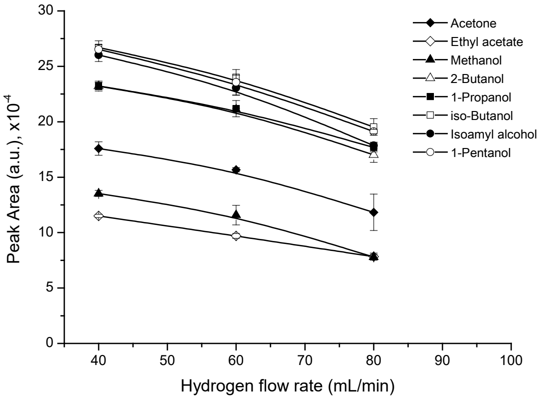
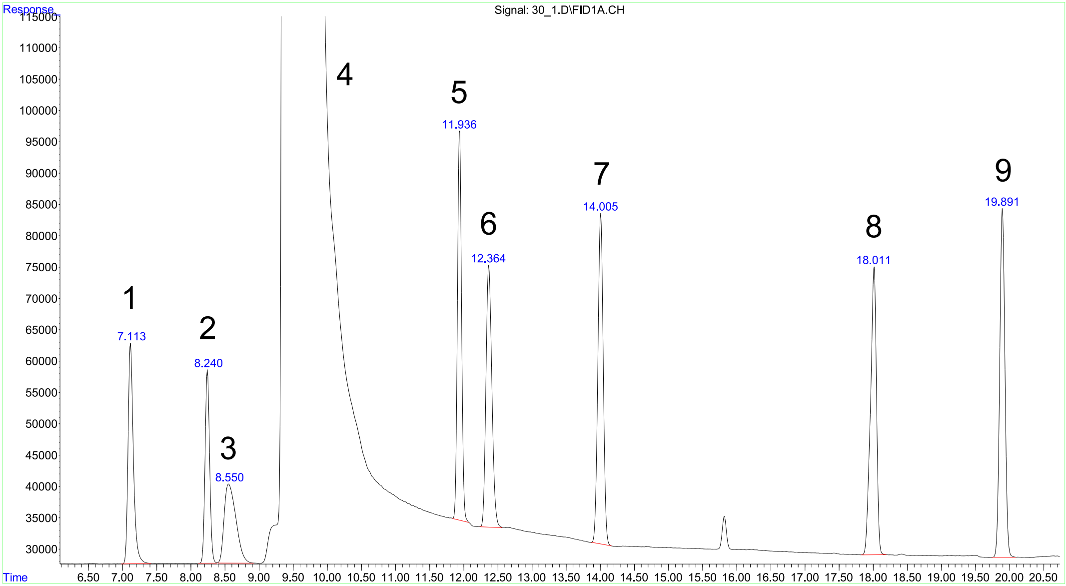


Figure 5 – Effect of the hydrogen flow rate on peak area of impurities



Peaks: 1 – acetone; 2 – ethyl acetate; 3 – methanol; 4 – ehanol; 5 – 2-butanol; 6 – 1-propanol; 7 – iso-butanol; 8 – isoamyl alcohol; 9 – 1-pentanol; C = 30 mg/L

Figure 6 – GC-FID chromatograms of vodka standard obtained by the optimized method

Table 4 – Results of calibration using optimized method in comparison with standard method

Compound	Concentration range, mg/L	Method with optimized parameters		GOST R 51786-2001	
		Slope	R^2	Slope	R^2
Acetone	1-1000	58571	1.000	14179	0.999
Ethyl acetate	1-1000	47195	0.998	11055	0.996
Methanol (ppmV)	1.26-1260	46474	1.000	12224	0.999
2-Butanol	1-1000	80698	1.000	20229	0.999
1-Propanol	1-1000	77926	1.000	18928	0.999
iso-Butanol	1-1000	93912	1.000	21844	0.999
Isoamyl alcohol	1-1000	88064	1.000	21110	0.999

Table 5 – Results of GC calibration according to optimized parameters and standard method GOST R 51786-2001 obtained on Agilent 6850 GC-FID located in Almaty Institute of Forensic Expertise

Compound	Optimized method		GOST R 51786-2001	
	Slope	R^2	Slope	R^2
Acetone	0.5461	0.998	0.1665	0.999
Ethyl acetate	0.0995	0.972	0.1161	0.995
Methanol	0.5001	0.996	0.1218	0.999
2-Butanol	0.8574	0.997	0.2199	0.996
1-Propanol	0.8466	0.996	0.2186	0.999
iso-Butanol	1.0409	0.997	0.2765	0.999
Isoamyl alcohol	0.8785	0.998	0.2452	0.999

3.8 Application of the optimized method

Application of the optimized method on real samples showed about 4-fold higher sensitivity compared to the standard method (Table 6). Highest concentrations were detected in sample 3 originated from Turkey. Such high concentrations are unusual for “pure” vodkas and may indicate presence of aroma additive. Therefore, this sample was not considered within the discussion of the results. Other samples have concentrations of impurities close to detection limits as was already mentioned in the Introduction.

Methanol was detected in all studied samples where it’s concentrations varied from 5 (sample 8) to 723 (sample 9) ppmV. In samples 8 and 15, only methanol was detected in concentrations 5 and 374 ppmV. For detection of methanol in all samples, sensitivity of the standard method was enough. However, detection of other impurities in almost all samples was possible only using the optimized method.

1-Propanol often used as adulteration marker was detected in 10 samples. However, it’s concentrations were very low reaching 3 mg/L in sample 25 (originated from the US). This sample also contained 3 mg/L of iso-butanol, which was not detected in all other samples. 1-Pentanol was only detected in samples 2 and 22.

As is clear from the obtained results, the optimized method having higher sensitivity compared to a standard one provides much more information about analyzed samples. This information may be used for disclosing adulterated samples and their origin.

Table 6 – Concentrations of impurities in studied vodka samples

#	Methanol	Acetone	Ethyl acetate	2-Butanol	1-Propanol	iso-Butanol	Isoamyl alcohol
	Concentration						
	ppmV	mg/L					
1	46±1	n/d	n/d	n/d	n/d	n/d	n/d
2	118±1	3±1	n/d	n/d	n/d	n/d	n/d
3	155±2	n/d	44.0±0.5	8.0±0.4	90±1	112±2	266±2
4	22±1	1.0±0.7	n/d	n/d	n/d	n/d	n/d
5	7±1	1.0±0.2	n/d	n/d	n/d	n/d	n/d
6	14.0±0.5	2.0±0.3	n/d	n/d	n/d	n/d	n/d
7	11.0±0.4	1.0±0.1	n/d	n/d	n/d	n/d	n/d
8	5.0±0.1	n/d	n/d	n/d	n/d	n/d	n/d
9	723±4	4.0±0.1	n/d	n/d	1.0±0.1	n/d	30.0±0.1
10	432±3	n/d	n/d	n/d	0.6±0.1	n/d	n/d
11	115±1	n/d	n/d	1.0±0.1	n/d	n/d	4.0±0.1
12	100±1	2.0±0.1	n/d	1.0±0.1	n/d	n/d	0.5±0.1
13	495±5	n/d	n/d	1.0±0.1	n/d	n/d	2.0±0.1
14	422±7	n/d	n/d	n/d	n/d	n/d	n/d
15	374±2	n/d	n/d	n/d	n/d	n/d	n/d
16	205±0.5	4.0±0.1	n/d	n/d	n/d	n/d	7.0±0.4
17	80±1	1.0±0.1	n/d	2.0±0.1	0.4±0.1	n/d	2.0±0.2
18	36±1	1.0±0.4	n/d	n/d	n/d	n/d	n/d
19	42.0±0.1	n/d	n/d	n/d	0.5±0.1	n/d	n/d
20	375±4	1.0±0.3	n/d	n/d	0.4±0.1	n/d	n/d
21	6±1	n/d	n/d	n/d	0.4±0.1	n/d	n/d
22	14±1	4.0±0.8	n/d	n/d	n/d	n/d	n/d
23	9.0±0.5	1.0±0.3	n/d	n/d	0.8±0.1	n/d	n/d
24	5.0±0.6	n/d	1±0.3	n/d	0.5±0.1	n/d	n/d
25	415±4	n/d	5±0.1	n/d	3±0.1	3.0±0.1	3.0±0.2
26	9.0±0.3	n/d	n/d	n/d	n/d	n/d	n/d

Note: n/d – not detected (below detection limit)

4. Conclusion

Thus, GC-FID method was optimized for sensitive determination of vodka impurities. The main parameters of GC and FID, which can influence on sensitivity of method determination of impurities were optimized: split ratio, inlet temperature, oven temperature, flow rates of make-up gas, air and hydrogen. The split ratio 10:1, the inlet temperature 120°C, initial oven temperature 60°C, make-up flow rate 50 mL/min, air flow 400 mL/min and hydrogen flow rate 40 mL/min were selected as optimal.

Obtained calibration plots are linear in concentration ranges 1-1000 mg/L with approximation coefficients $R^2>0.99$. Compared to standard GOST R 51786-2001 and GOST R 51698-2000 methods, slope factors are about 4 times higher when optimized method is used proving its higher sensitivity.

Application of the optimized method for analysis of real samples confirmed it's higher sensitivity. For detection of methanol in all samples, sensitivity of the standard method was enough. However, detection of other impurities in almost all samples was possible only using the optimized method. Due to the higher sensitivity of the optimized method, it can be recommended for disclosing adulterated samples in forensic laboratories.

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