



BSU INP

Direct Determination of Volatile Compounds in Spirits Products

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Introduction

Over the world day-and-night according to the Official Methods the thousands accredited testing laboratories should determine the following 9 volatile compounds in spirit drinks: *acetaldehyde, methyl acetate, ethyl acetate, methanol, 2-propanol, 1-propanol, isobutyl alcohol, n-butanol, isoamyl alcohol.*

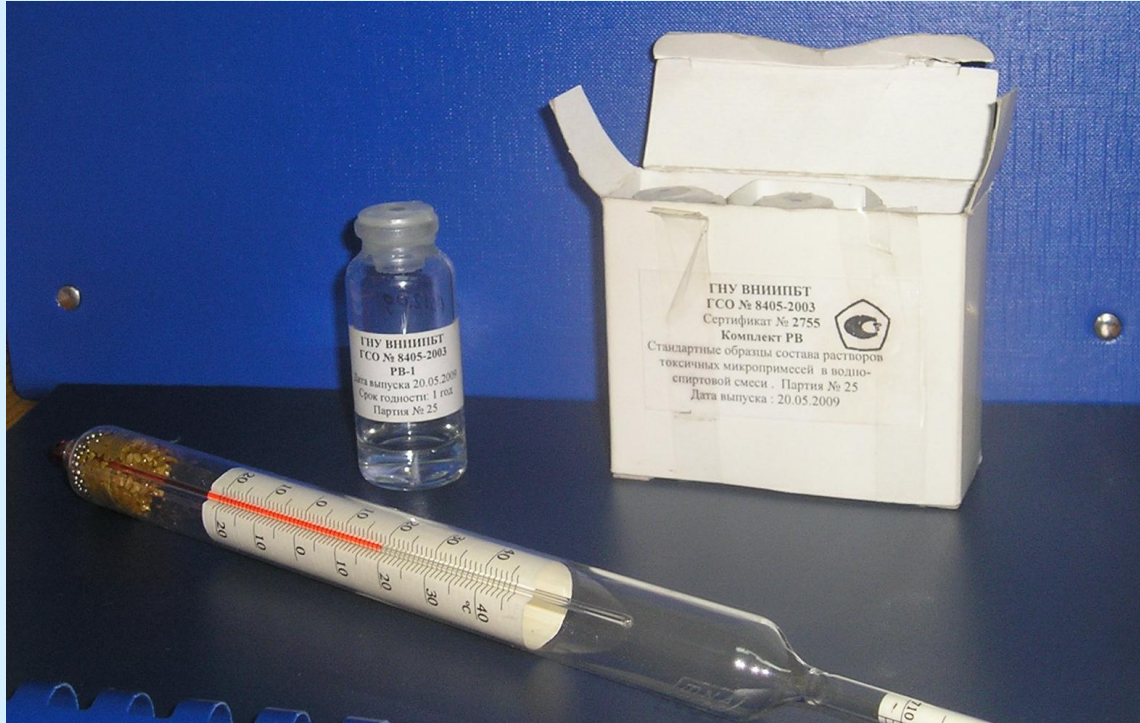
Concentrations of these compounds are expressed in milligrams per liter of absolute alcohol '**mg/L (AA)**'.

In accordance with “Compendium of international methods of wine and must analysis” Commission Regulation EC 2870-2000 and International Organisation of Vine and Wine (OIV, 2009, v. 1-2) for quantitation the Internal Standard (**IS**) method is used. These documents propose to use pentan-3-ol as IS.

Researchers from former Soviet States (NIS) make calculation by means of the External Standard (**ES**) method (GOST R 51698).

Finally, to get quantitative values of impurity concentrations in **mg/L (AA)** it is also required to measure **alcohol strength** (v/v ethanol concentration) of the analyzed sample.

Unsolved 2 problems. 1st



How to measure the volumetric content of ethanol (strength) in a brandy/cognac/whisky sample of less than 15 mL ?

Distillation of the sample must be at least 250 ml .

Unsolved 2 problems. 2nd



How to measure the volumetric content of ethanol (strength) in alcohol products with accuracy less 0,1% when concentration of impurities, for example iso-amylol, are more than 0,3% ?

Note: Concentration of iso-amylol in raw alcohol products often is more than 10 %.

Innovation

We propose the new methodical approach of using ‘**ethanol-as-IS**’ in GC analysis of volatile compounds in spirit products in daily practice of analytical and testing laboratories.

This method is absolutely new, original, and innovative. **It improves the reliability of the measured data** as well as substantially **simplifies the total measurement procedure**.

Its substance thoroughly described in the recently published paper - Direct Determination of Volatile Compounds in Spirit Drinks by Gas Chromatography // Journal of Agricultural and Food Chemistry, 2013, 61 (12), 2950–2956
[DOI:10.1021/jf3044956](https://doi.org/10.1021/jf3044956).

Method was repeatedly proven in our measuring practices and many times presented to the professional audience last time at:

- Association of Analytical Centers of Russia Annual Meeting, April, 15-17, 2013, Moscow, Russia;
- “In Vino Analytica Scientia”, July, 2-5, 2013, Reims, France;
- The 1st International scientific conference “Reference materials in measurement and technology”, September, 10-14, 2013, Ekaterinburg, Russia.

Innovation

This method provides direct determination of volatile compound concentrations in spirit drinks expressed directly in **mg/L (AA)** without measuring the alcohol content in the analyzed sample.

The analysis of the experimental results show possibility of developing;

- **New international standard of measurement procedure (to OIV),**
- **New approach to prepare certified references materials (CRF)**

of component composition of alcohol products.

These new methodical approaches will allow significantly increasing the data accuracy and considerably simplify the measurement procedure.

Theoretical background

In our case the GC calibration includes traditional measuring of relative detector response factors RRF_i for every analyzed compound relative to IS (**ethanol**).

RRF_i are calculated from the chromatographic data for standard solutions prepared by gravimetric method with known concentrations of analyzed compounds in **mg/L (AA)**. They may be expressed by the following equation:

$$RRF_i = RF_i / RF_{IS} = \frac{C_i^{st} (sol)}{A_i^{st}} / \frac{C_{IS}^{st} (sol)}{A_{IS}^{st}} = \frac{A_{IS}^{st} \cdot C_i^{st} (sol)}{A_i^{st} \cdot C_{IS}^{st} (sol)} = \frac{A_{IS}^{st} \cdot C_i^{st}}{A_i^{st} \cdot \rho_{Et}} \quad (1)$$

where $\rho_{Et} = 789300$ mg/L is the known density of ethanol.

Finally the concentration C_i of the i -th sample compound relative to **absolute alcohol** has the following form

$$C_i = RRF_i \cdot \frac{A_i}{A_{Et}} \cdot \rho_{Et} = C_i^{st} \cdot \frac{A_{Et}^{st}}{A_i^{st}} \cdot \frac{A_i}{A_{Et}} \quad (2)$$

**The method does not require additional measurements
volumetric content of ethanol in the sample**

Validation. Standard solutions

Concentration:
$$C_*^i(A) = \rho_{Et} \cdot \frac{C^i \cdot m_A^i + C^i(Et) \cdot m_A^{Et}}{C^{Et}(Et) \cdot m_A^{Et} + \sum_{j=1}^9 C_j^{Et} \cdot m_A^j}, \quad i = 1, \dots, 9 \quad (1)$$

Uncertainty:

$$u(C_*^i(A)) = \left[\left(\frac{\rho_{Et} \cdot C^i - C_*^i(A) \cdot C_i^{Et}}{Z(A)} \cdot u(m_A^i) \right)^2 + \left(\frac{\rho_{Et} \cdot m_A^i}{Z(A)} \cdot u(C^i) \right)^2 + \left(\frac{\rho_{Et} \cdot C^i(Et) - C_*^i(A) \cdot C^{Et}}{Z(A)} \cdot u(m_A^{Et}) \right)^2 + \left(\frac{\rho_{Et} \cdot m_A^{Et}}{Z(A)} \cdot u(C^i(Et)) \right)^2 + \left(\frac{C_*^i(A) \cdot m_A^{Et}}{Z(A)} \cdot u(C^{Et}) \right)^2 + \sum_{\substack{j=1 \\ j \neq i}}^9 \left(\frac{C_*^i(A) \cdot C_j^{Et}}{Z(A)} \cdot u(m_A^j) \right)^2 + \sum_{j=1}^9 \left(\frac{C_*^i(A) \cdot m_A^j}{Z(A)} \cdot u(C_j^{Et}) \right)^2 \right]^{1/2} \quad (2)$$

$$Z(A) = C^{Et}(Et) \cdot m_A^{Et} + \sum_{j=1}^9 C_j^{Et} \cdot m_A^j \quad u(C^i) = \left(\sum_{j=1(j \neq i)}^9 u^2(C^j(i)) \right)^{1/2}$$

Method of measurement № 253.0169/01.00258/2013

Validation. Characteristics of standard solutions

Table 1. Concentrations of analyzed volatile compounds are expressed in **mg/L (AA)**. 1-pentanol was introduced as traditional **IS**.

Compound	Concentration, mg/L (AA)							Relative error, % (P=0,95)
	VC-1	VC-2	VC-3	VC-4	VC-5	VC-6	VC-7	
acetaldehyde	4275	1096	111	56,2	11,2	2,22	1,13	± 3 %
methyl acetate	4397	1128	114	57,8	11,5	2,29	1,17	± 3 %
ethyl acetate	4173	1070	108	54,9	10,9	2,17	1,11	± 3 %
methanol	41995	10774	1092	555,5	113,3	24,96	14,3	± 3 %
2-propanol	3991	1025	105	54,1	12,1	3,69	2,70	± 3 %
1-propanol	4012	1029	104	52,8	10,5	2,08	1,06	± 3 %
isobutyl alcohol	3975	1020	103	52,3	10,4	2,06	1,05	± 3 %
n-butanol	4071	1044	106	53,5	10,7	2,11	1,08	± 3 %
isoamyl alcohol	4071	1044	106	53,5	10,7	2,11	1,08	± 3 %
1-pentanol (IS)	27,1	27,1	27,1	27,1	27,1	27,13	27,13	± 3 %

Validation. Standard solutions



Prototype of a novel CRM of component composition of alcohol products. Traditional 2 ml amber glass vials using sealed septa with crimped caps for liquid autosampler. One-off.

Validation. Traditional GC conditions

There were a traditional GC conditions:

GC equipped with FID, a split/splitless injector;

- liquid autosampler;
- Unichrom software;
- capillary column Rt-Wax, 60 m x 0.53 mm, phase thickness 1 μm ;
- initial isotherm at 75 $^{\circ}\text{C}$ (9 min), raised to 155 $^{\circ}\text{C}$ at rate 7 $^{\circ}\text{C}/\text{min}$;
- with final isotherm of 155 $^{\circ}\text{C}$ (2.6 min);
- carrier gas was nitrogen;
- gas flow was 2.44 mL/min;
- injector volume 0.5 μL and split ratio 1:20.

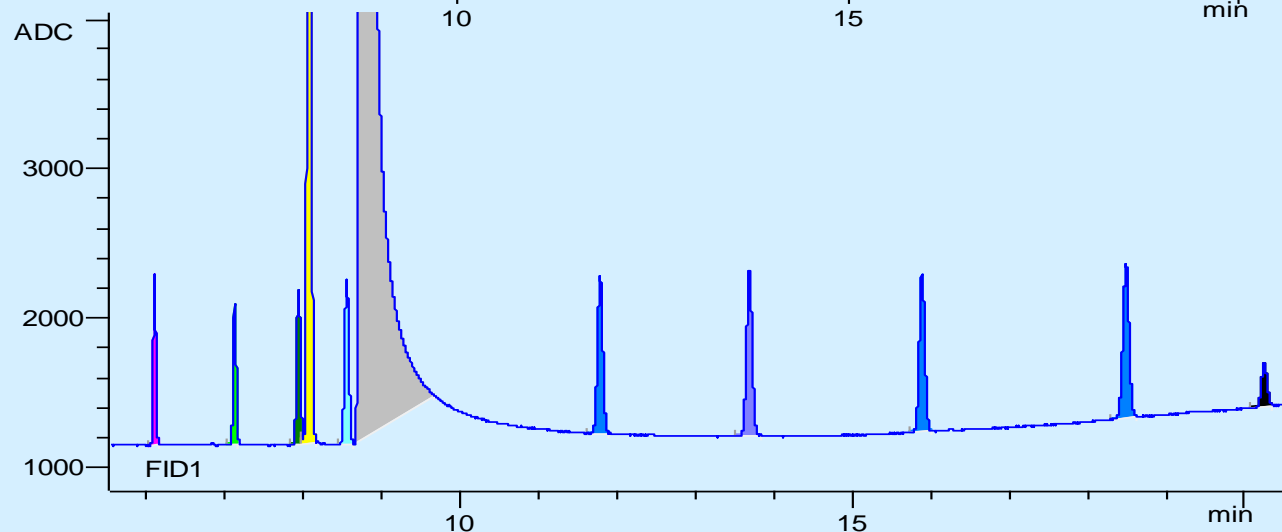
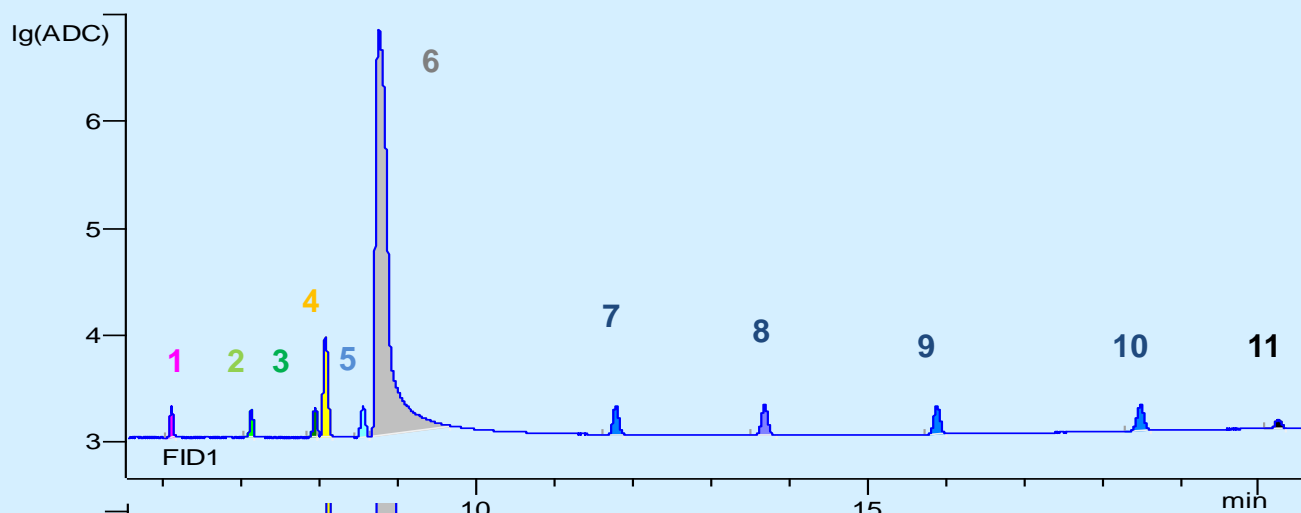
Validation. Standard solutions

In order to study accuracy of the proposed methodical approach in the case of large ranges of volatile compounds concentrations 6 – 20000 mg/L for methanol and 1 – 2000 mg/L for another 8 volatile compounds reference ethanol-water solutions were gravimetrically prepared with known concentrations of volatile compounds.

Validation of this method was been planed in accordance with ISO 5725.

Every reference solution was injected 30 (15 x 2) times.

Validation. Chromatograms



- 1 - acetaldehyde
- 2 - methyl acetate
- 3 - ethyl acetate
- 4 - methanol
- 5 - 2-propanol
- 6 - ethanol
- 7 - 1-propanol
- 8 - isobutyl alcohol
- 9 - n-butanol
- 10 - isoamyl alcohol
- 11 - 1-pentanol (IS)

Fig.1. Typical chromatogram of standard ethanol-water (40% vs 60 %) solutions. To show the dominant component ethanol and another compounds synchronously the logarithm scale of response signal is chosen.

Validation. Response factors

Table 2. Analytical characteristics of the obtained calibration graphs

Compound	1-pentanol as IS		ES		Ethanol as IS		LOD* (mg/L)
	RRF	Correlation coefficient, R ²	RF (mg/L)/(pA*min)	Correlation coefficient, R ²	RRF	Correlation coefficient R ²	
acetaldehyde	2,396	0,9997	266,1	0,9997	1,710	0,9997	0,344
methyl acetate	2,491	0,9997	276,7	0,9996	1,779	0,9999	0,683
ethyl acetate	1,757	0,9997	195,1	0,9997	1,254	0,9999	0,322
methanol	2,133	0,9998	236,9	0,9997	1,523	0,9999	0,231
2-propanol	1,400	0,9998	155,5	0,9997	0,999	0,9999	0,119
ethanol	1,413	N/A	155,5	N/A	1	N/A	N/A
1-propanol	1,179	0,9997	130,9	0,9996	0,841	0,9999	0,222
isobutyl alcohol	1,018	0,9998	113,0	0,9997	0,727	0,9999	0,178
n-butanol	1,117	0,9999	124,1	0,9998	0,798	0,9999	0,189
isoamyl alcohol	1,030	0,9999	114,4	0,9998	0,735	0,9999	0,179
1-pentanol	1	N/A	110,1	N/A	0,708	N/A	0,271

* limit of detection (LOD)

Validation. Linearity for methanol

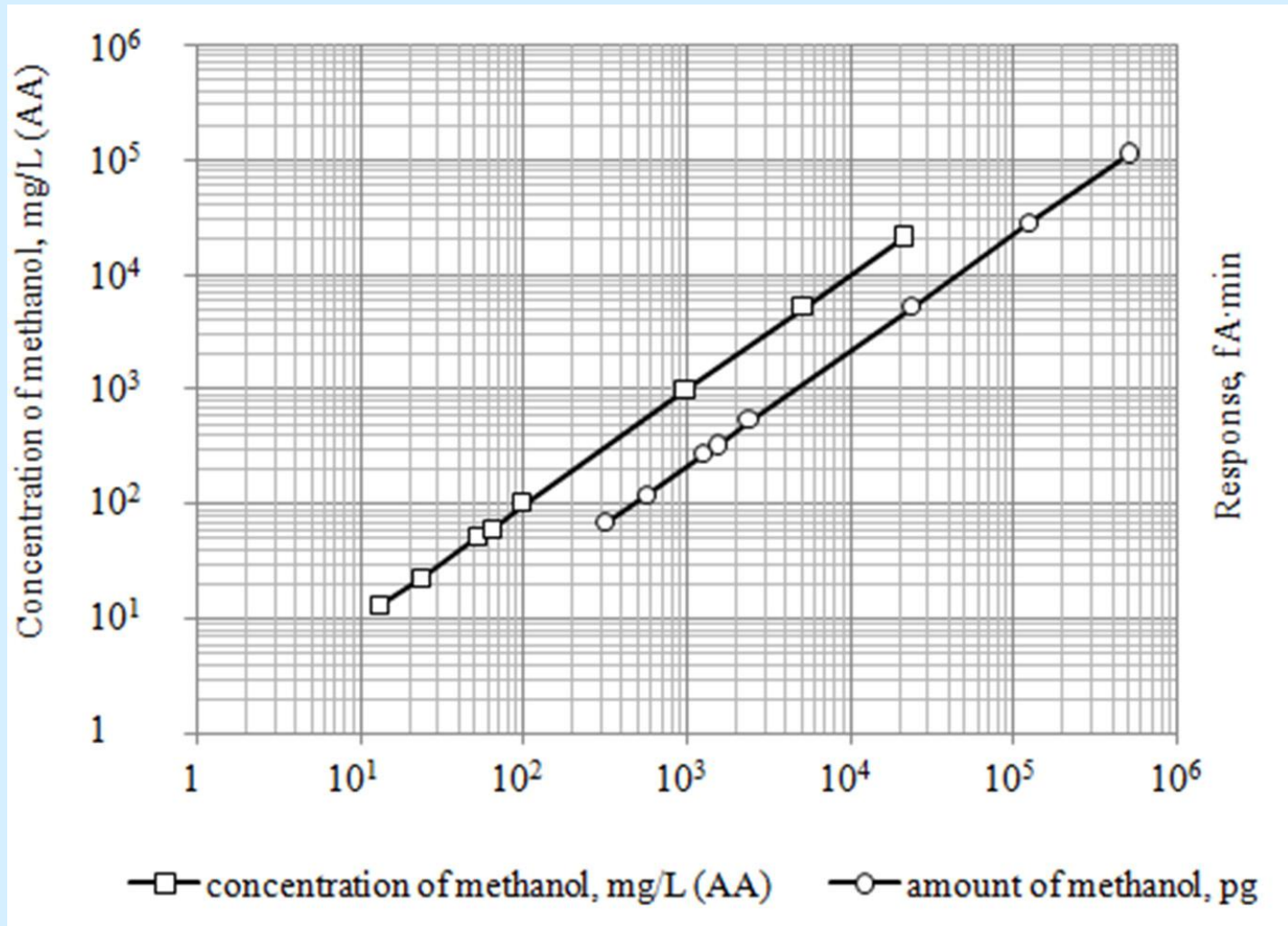


Fig. 2. Analytical characteristics of the obtained calibration graphs for **methanol**.

Validation. Linearity for all other 8 compounds

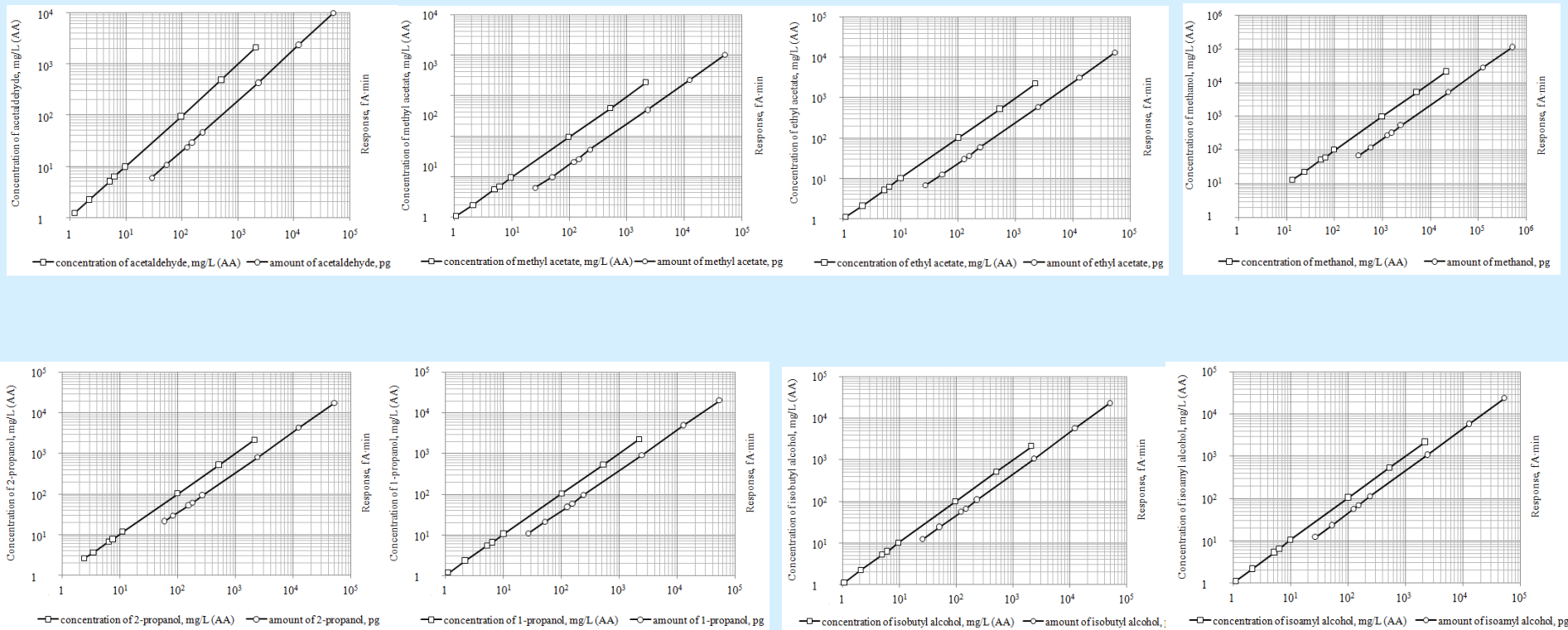


Fig. 3. Analytical characteristics of the obtained calibration graphs for all other 8 compounds.

Validation. Stability versus dilution

The standard ethanol-water (96:4) solution of volatile compounds: acetaldehyde, methyl acetate, ethyl acetate, methanol, 2-propanol, 1-propanol, isobutyl alcohol, n-butanol, isoamyl alcohol was analyzed after dilution with water in the ratios 1:1, 1:9, 1:99, 1:999, and 1:9999.

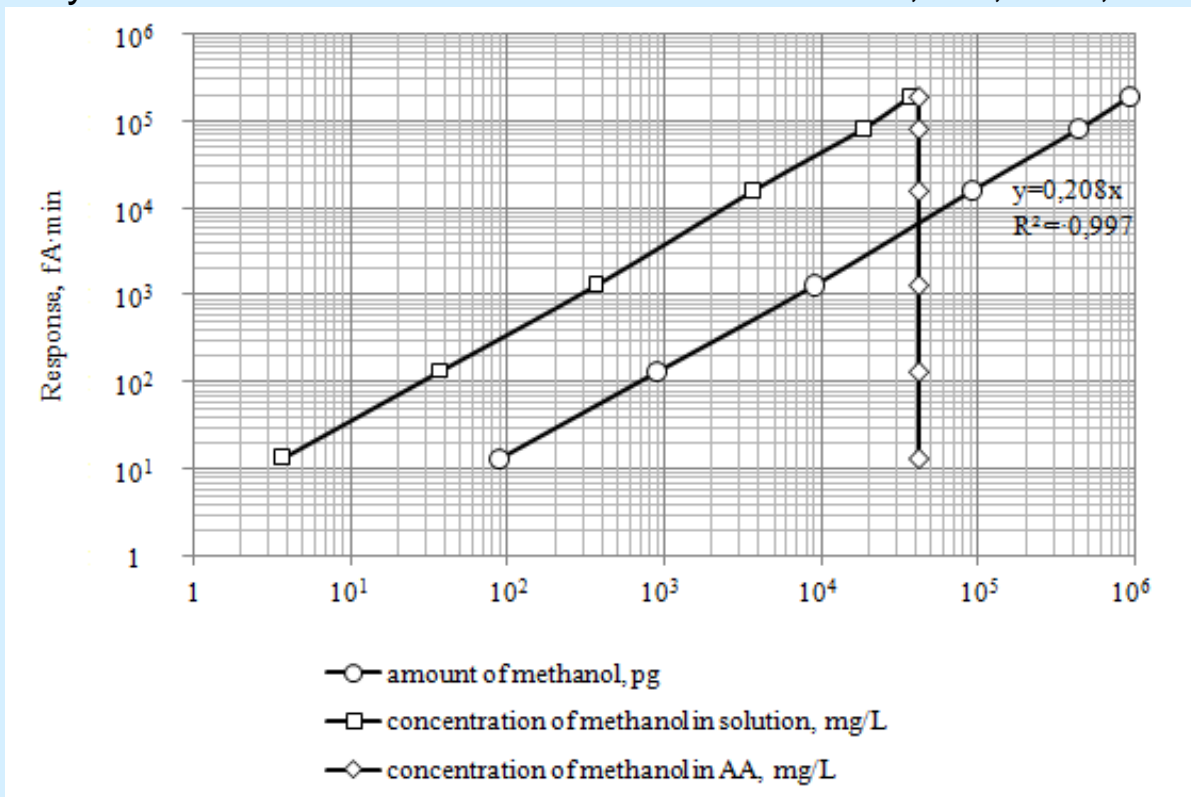


Fig. 4. The first line is the detector response versus the amount of the compound. The second and the third ones are the detector response versus the concentration of the compound, expressed in mg per litre of solution and in mg per litre of absolute alcohol. A corresponding linear dependence is added. Even after dilution with water in the ratio 1:999, the difference between the measured concentrations of all compounds and their values calculated using the gravimetric method does not exceed 7.7 % . .

Validation. Metrological characteristics of 'ethanol-IS' method

№ St Sol	acetaldehyde			methyl acetate			ethyl acetate			methanol			2-propanol			1-propanol			isobutyl alcohol			n-butanol			isoamyl alcohol		
	C st, u(C), mg/l	C exp, S(TO), mg/l	Δ, u, %	C st, u(C), mg/l	C exp, S(TO), mg/l	Δ, u, %	C st, u(C), mg/l	C exp, S(TO), mg/l	Δ, u, %	C st, u(C), mg/l	C exp, S(TO), mg/l	Δ, u, %	C st, u(C), mg/l	C exp, S(TO), mg/l	Δ, u, %	C st, u(C), mg/l	C exp, S(TO), mg/l	Δ, u, %	C st, u(C), mg/l	C exp, S(TO), mg/l	Δ, u, %	C st, u(C), mg/l	C exp, S(TO), mg/l	Δ, u, %	C st, u(C), mg/l	C exp, S(TO), mg/l	Δ, u, %
1	1,23	1,23	-0,1	1,08	1,08	-0,5	1,13	1,10	-2,3	13,39	12,82	-4,2	2,45	2,55	4,0	1,13	1,15	1,8	1,08	1,08	-0,3	1,08	1,07	-0,7	1,12	1,08	-3,8
	0,024	0,07	6,1	0,001	0,04	3,5	0,002	0,05	5,2	0,376	0,22	5,4	0,20	0,07	9,6	0,001	0,07	6,3	0,001	0,05	4,4	0,001	0,07	6,3	0,001	0,06	7,0
2	2,25	2,26	0,2	2,11	1,99	-5,4	2,20	2,08	-5,8	23,72	22,29	-6,0	3,50	3,58	2,2	2,21	2,30	3,8	2,11	2,17	2,6	2,11	2,19	4,0	2,19	2,11	-3,5
	0,025	0,09	4,3	0,005	0,08	6,7	0,005	0,07	6,7	0,382	0,14	6,3	0,20	0,10	6,8	0,005	0,10	5,8	0,005	0,09	5,3	0,005	0,13	7,5	0,005	0,13	7,1
3	5,16	5,10	-1,0	5,04	4,90	-2,9	5,27	5,08	-3,5	53,15	51,28	-3,5	6,49	6,55	1,0	5,29	5,36	1,4	5,05	5,11	1,2	5,03	5,15	2,3	5,22	5,24	0,4
	0,03	0,10	2,2	0,01	0,08	3,3	0,01	0,11	4,1	0,38	0,19	3,6	0,20	0,08	3,5	0,01	0,13	2,9	0,01	0,10	2,3	0,01	0,11	3,3	0,01	0,17	3,4
4	6,44	6,25	-2,9	6,34	5,75	-9,2	6,62	6,16	-7,0	66,17	59,71	-9,8	7,81	7,53	-3,5	6,65	6,41	-3,6	6,34	6,12	-3,6	6,32	6,14	-2,9	6,57	6,30	-4,0
	0,03	0,11	3,4	0,01	0,11	9,4	0,01	0,07	7,0	0,38	1,01	9,9	0,20	0,08	4,5	0,01	0,16	4,3	0,01	0,09	3,9	0,01	0,12	3,5	0,01	0,19	5,0
5	9,75	9,81	0,7	9,68	9,56	-1,2	10,11	10,01	-1,0	99,70	99,78	0,1	11,21	11,50	2,7	10,15	10,51	3,5	9,69	9,98	3,1	9,66	10,07	4,3	10,03	10,38	3,5
	0,03	0,31	3,4	0,01	0,26	3,0	0,01	0,22	2,4	0,39	0,55	0,7	0,20	0,10	3,4	0,01	0,16	3,8	0,01	0,13	3,4	0,01	0,12	4,5	0,01	0,13	3,7
6	96,65	94,06	-2,7	97,38	95,68	-1,7	101,8	101,1	-0,7	980,5	990,3	1,0	100,5	101,2	0,7	102,2	103,3	1,1	97,47	98,97	1,5	97,18	99,28	2,2	100,9	103,6	2,7
	0,15	1,44	3,1	0,12	1,77	2,6	0,13	1,57	1,7	0,85	1,86	1,0	0,23	0,31	0,8	0,12	0,17	1,1	0,12	0,25	1,6	0,13	0,20	2,2	0,12	0,38	2,7
7	506,0	486,8	-3,8	510,5	491,6	-3,7	533,5	520,7	-2,4	5129	5124	-0,1	521,3	515,6	-1,1	535,6	530,8	-0,9	511,0	507,0	-0,8	509,5	506,0	-0,7	529,1	526,2	-0,5
	0,98	5,79	4,0	0,90	12,5	4,5	0,96	9,93	3,1	7,46	11,8	0,3	0,90	0,57	1,1	0,90	0,55	0,9	0,88	0,95	0,8	0,93	1,82	0,8	0,90	2,50	0,7
8	2085	2080	-0,2	2104	2113	0,4	2198	2202	0,2	21128	21130	0,0	2144	2139	-0,2	2207	2206	-0,1	2106	2107	0,1	2099	2104	0,2	2180	2187	0,3
	2,77	20,9	1,1	2,25	10,1	0,7	2,46	5,29	0,3	11,05	20,0	0,1	2,08	5,04	0,3	2,10	2,28	0,2	2,14	3,61	0,2	2,43	6,81	0,4	2,12	11,0	0,6

Table 3. The analysis of experimental data shows that the value of **relative uncertainty u** in the determination of the impurities concentration in experiments in the whole range of concentrations for all examined impurities **does not exceed 10%**.

Validation. Method was certificated in Rosstandart

 001340

ФЕДЕРАЛЬНОЕ АГЕНТСТВО
ПО ТЕХНИЧЕСКОМУ РЕГУЛИРОВАНИЮ И МЕТРОЛОГИИ
(Росстандарт)
Федеральное государственное унитарное предприятие
«Уральский научно-исследовательский институт метрологии»
(ФГУП «УНИИМ»)
Государственный научный метрологический институт

СВИДЕТЕЛЬСТВО
об аттестации методики (метода) измерений
№ 253.0169/01.00258/2013

Методика измерений массовой концентрации летучих компонентов в водке и спирте
наименование методики, включая наименование измеряемой величины, и, при необходимости,
этиловым методом газовой хроматографии
объекта измерений, дополнительных параметров и реализуемый способ измерений

предназначенная для измерений массовой концентрации летучих компонентов в водке и
область использования
спирте этиловым методом газовой хроматографии в лаборатории аналитических
исследований НИИ ЯП БГУ.

разработанная Научно-исследовательским учреждением "Институт ядерных проблем"
наименование и адрес организации (предприятия), разработавшей методику
Белорусского Государственного Университета (НИИ ЯП БГУ).
220030 Беларусь, г. Минск, ул. Бобруйская, д. 11.

и содержащаяся в документе "Определение летучих компонентов в водке и спирте
обозначение и наименование документа, содержащего методику, год утверждения, число страниц
этиловым методом газовой хроматографии. Методика измерений"

Методика аттестована в соответствии с ФЗ № 102 "Об обеспечении единства измерений"
и ГОСТ Р 8.563-2009.

Аттестация осуществлена по результатам метрологической экспертизы материалов по
теоретических и (или) экспериментальных исследований
разработке методики измерений и экспериментальных исследований

В результате аттестации методики измерений установлено, что методика измерений
нормативно-правовой документ в области обеспечения единства измерений (при наличии) и ГОСТ Р 8.563
соответствует требованиям, предъявляемым ГОСТ Р 8.563-2009

Показатели точности измерений приведены в приложении на 2 л.

Зам. директора по качеству		Ю.С. Бессонов
Зав. лабораторией		Е.В. Осинцева
Дата выдачи		12.07.2013
Рекомендуемый срок пересмотра методики измерений:		12.07.2018

М.П.

Россия, 620000, г. Екатеринбург, ул. Красноармейская, 4
Тел.: (343) 350-26-18, факс: (343) 350-20-39. E-mail: unim@unim.ru



 013400

Federal Agency
for Technical Regulation and Metrology
(Rosstandart)
The Federal State Unitary Enterprise
"Ural Scientific-Research Institute of Metrology"
(Federal State Unitary Enterprise "UNIIM")
State Scientific Institute of Metrology

CERTIFICATE
of certification procedure (method)
№ 253,0169/01.00258/2013

Method of measurement of the mass concentration of volatile compounds in alcohol drinks
name of method, including the name of the measured values and, if appropriate, measurement object,
by Gas Chromatography
additional parameters and implemented method for measuring
designed for measuring of the mass concentration of volatile components in alcohol drinks by
area of use
gas chromatography in the Laboratory of Analytical Research of INP BSU.

developed by the Research Institute "Institute of Nuclear Problems" of Belarusian State University (INP BSU)
name and address of the organization (enterprise) developed the method
220030 Belarus, city of Minsk, Bobrujskaya Str., 11

and contained in the document "Determination of volatile compounds in alcohol drinks by gas chromatography"
designation and name of the document containing the method, year of approval, number of pages

Method is certified in accordance with the Federal Law № 102 "On ensuring the uniformity of measurements" and
GOST R 8.563-2009.

Certification carried out on the results of metrological examination of theoretical and experimental materials
development of measurement techniques and (or) experimental studies
As a result of evaluation of the measurement procedure is established that the method meets the
legal document in the area of traceability (if available) and GOST R 8.563
requirements of GOST R 8.563-2009.

Performance measurement accuracy is given in Appendix on 2 pages.

Deputy Director		Yu.S. Bessonov
Head of Laboratory		E.V. Osintseva
Date of issue		12.07.2013
Recommended for revision of the measurement procedure		12.07.2018

Россия, 620000, City of Ekaterinburg, Красноармейская Str., 4
Tel.: (343) 350-26-18, fax: (343) 350-20-39. E-mail: unim@unim.ru

Prospection

How to introduce this new method '**ethanol-as-IS**' in the daily practice ?

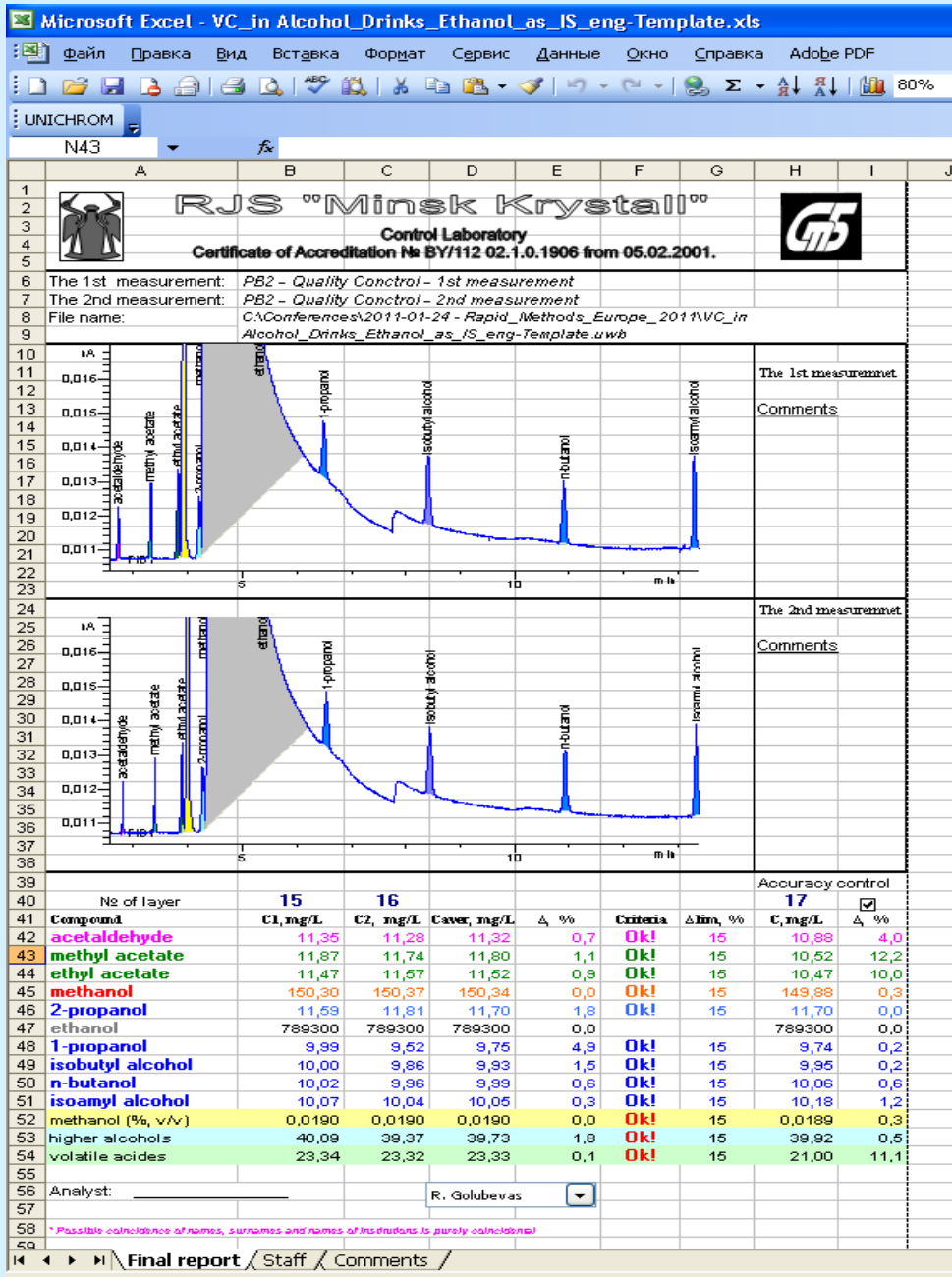
There is only one working way: to propose for customers more easy, attractive and effective way for laboratory business..

Thousands of testing laboratories over the world day-and-night carry out gas chromatographic analysis of volatile compounds in spirit drinks.

They may test and validate this new method in their real practice. It is important to note that there is no need to perform any additional measurements.

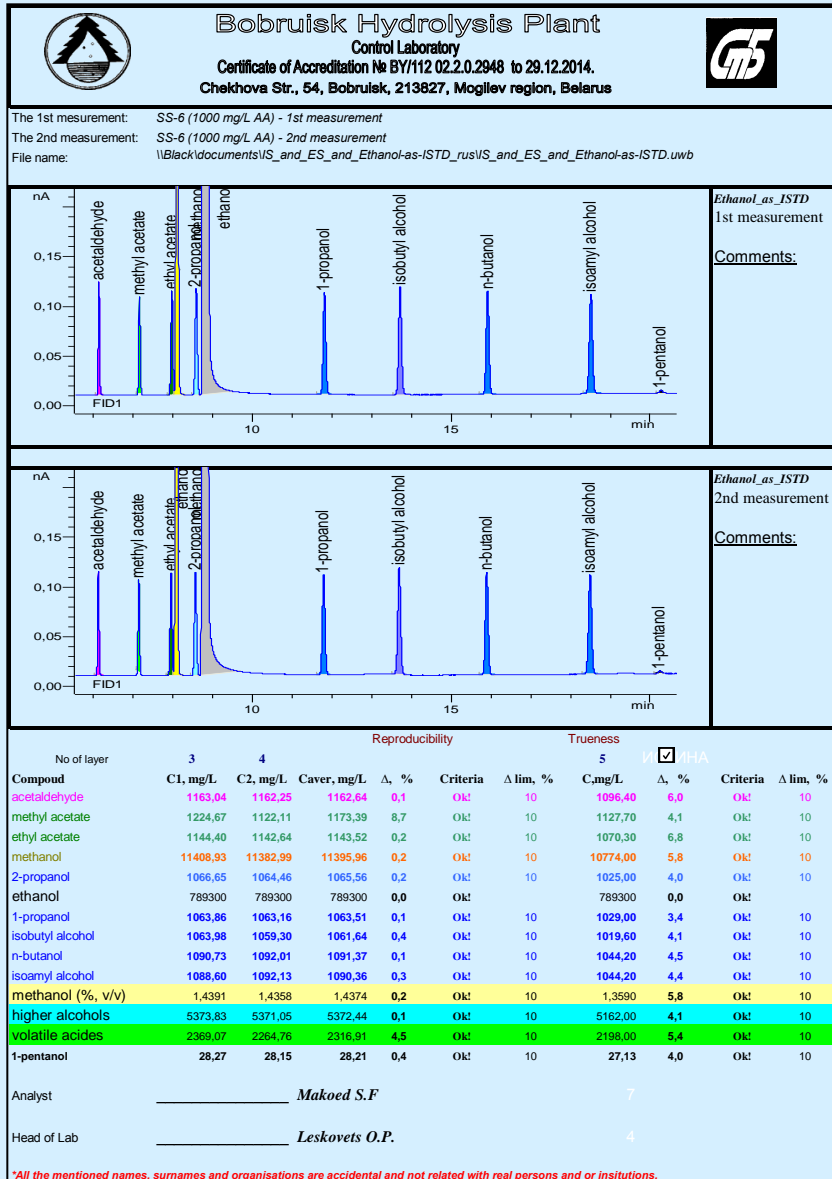
Everybody could test and validate '**ethanol-as-IS**' method while performing current measurements with existing instrumentation and calculations could be done in parallel according to the traditional way with addition of '**pental-3-ol**' as IS and using '**ethanol-as-IS**'.

Road map. Unification of final report generation

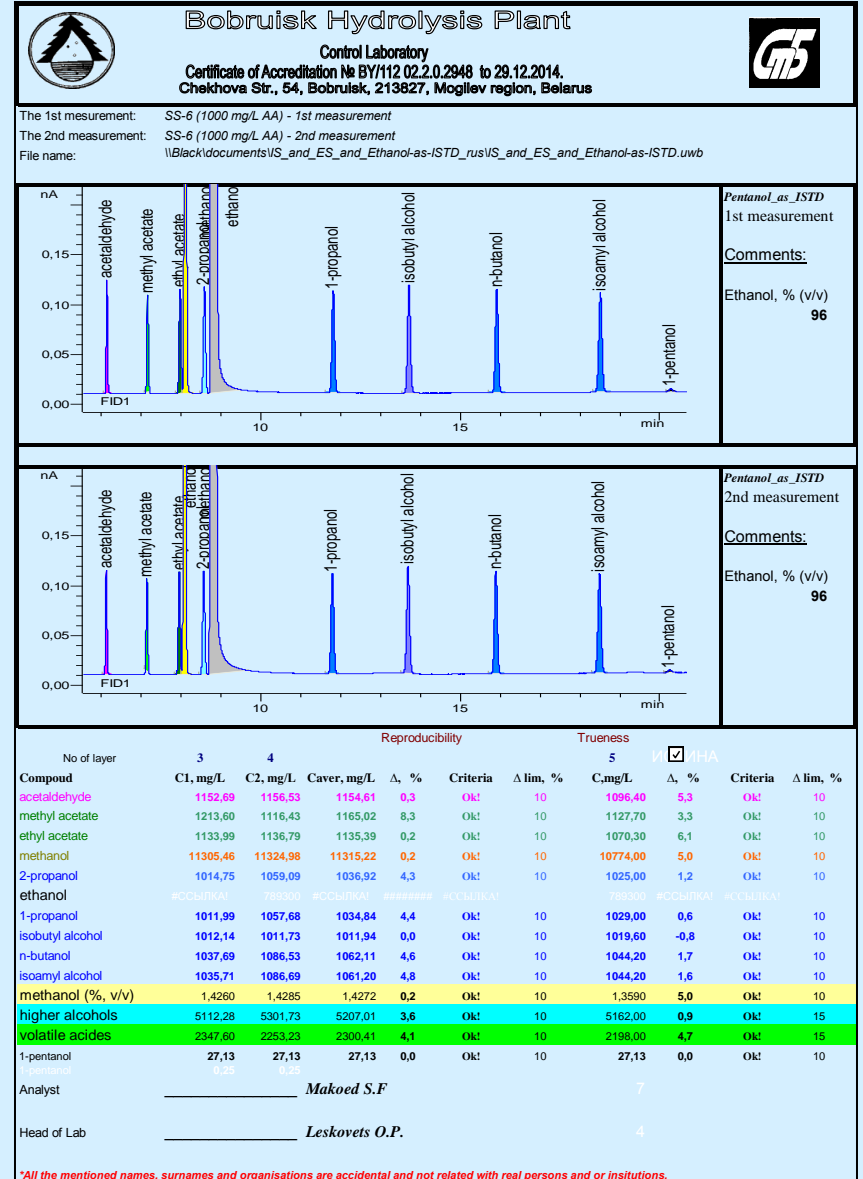


Generation of final report of any official documents with help of OLE Automation technology.

Road map. Traditional '1-pentanol-as-IS' and 'ethanol-as-IS'

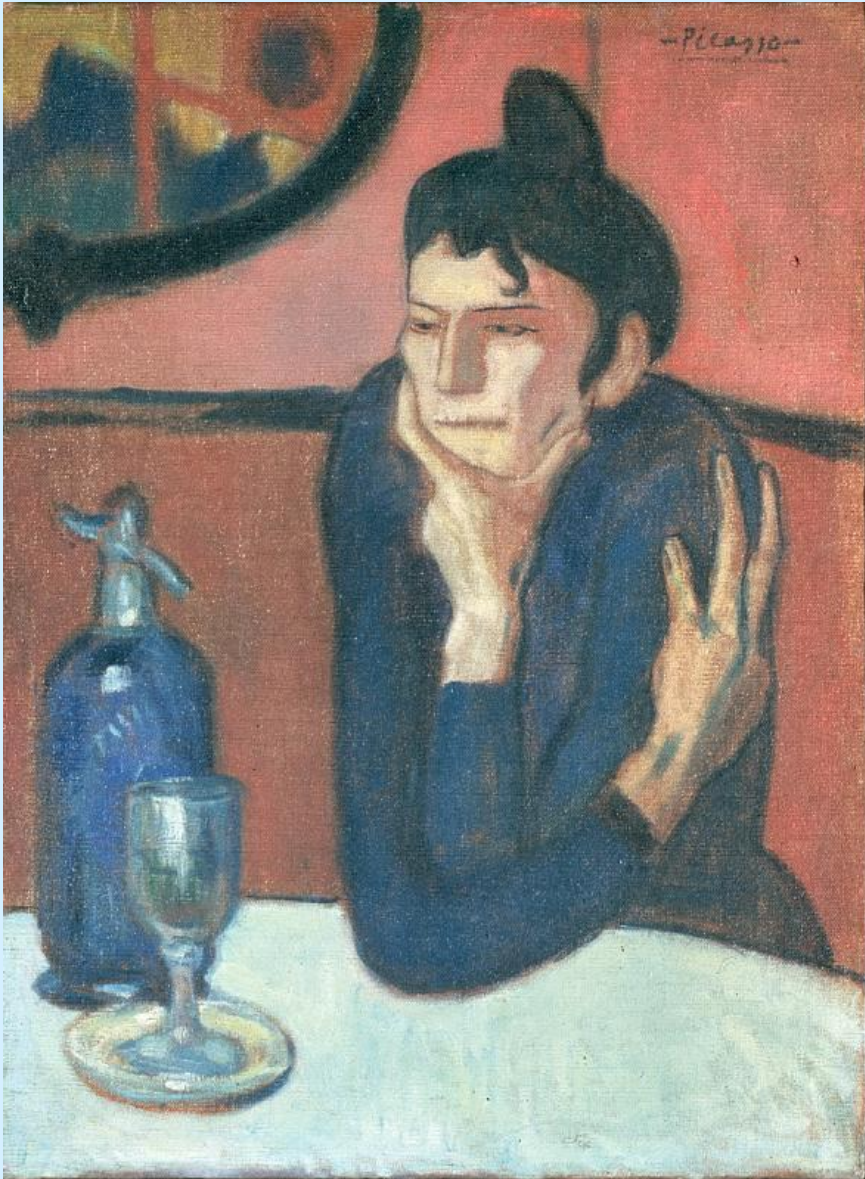


*All the mentioned names, surnames and organisations are accidental and not related with real persons and or insitutions.



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Thanks You for attention !



I have a dream...

...ethanol should be the ISTD !