ETHANOL AS INTERNAL STANDARD FOR DETERMINATION OF VOLATILE COMPOUNDS IN SPIRIT DRINKS BY GAS CHROMATOGRAPHY

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Quality and Safety Control of Alcohol Drinks.

Over the world day-and-night according to the Official Methods the thouthands accredited laboratories should determine the following 9 (nine) 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 - mg/L of absolute alcohol (AA).

For calculation of concentrations the internal standard (IS) method is used (AOAC Official Methods 972.10, Commission Regulation EC 2870-2000). These documents propose to use pental-3-ol as IS.

Some researchers (GOST R 51698, Russia) make calculation by means of the external standard (ES) method to avoid the introduction of another source of error, such as the addition of an internal standard.

Finally, to get quantitative values of impurity concentrations per liter of absolute alcohol it is also required

- to measure alcohol strength (v/v concentration) of the analyzed sample.

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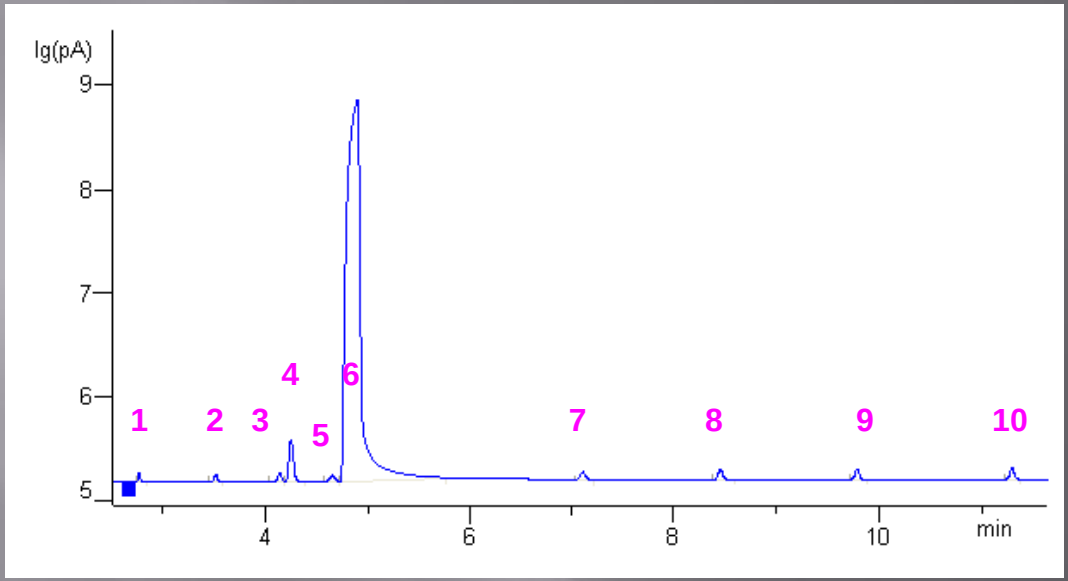
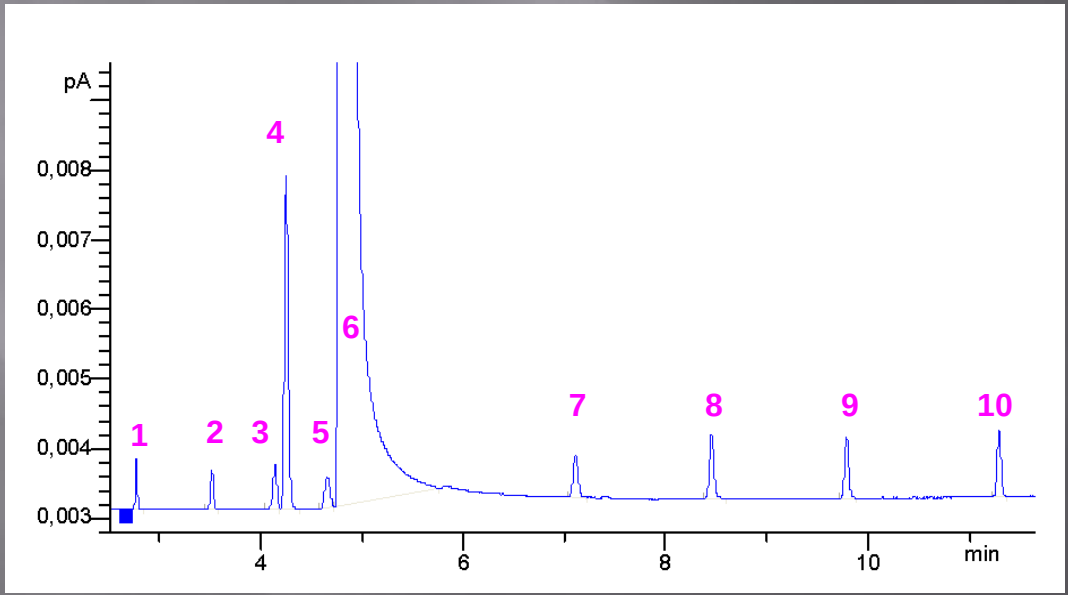
Introduction

Early in the paper (Journal of Analytical Chemistry, 2003, v. 58, 368 – 371) the idea to use main component (solvent) for determination of impurities concentration was proposed.

This method provides determination of volatile compounds concentrations in spirit drinks directly expressed in milligrams per liter (mg/L) of absolute alcohol (AA) according to the Official Methods without measuring of alcohol strength of analyzed sample.

It is possible at the present time to introduce this new approach for routine practice of analytical laboratories due to modern GC with wide range of signal registration from flame ionization detector (FID). The linear range of modern FID is generally more than 10^7. Signal registration from impurities compounds and from main component ethanol takes place without any distortions.





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

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

Calculations

Calibration of chromatograph includes the measuring of response factors (RF) for every analyzed compound relative to ethanol. Numeric values of RF are calculated from chromatographic data for certified reference material (CRM) with known concentrations of analyzed compounds and may be expressed by the following equations:

$$RF_i = \frac{A_{Et}^{CRM}}{A_i^{CRM}} / \frac{C_{Et}^{CRM}}{C_i^{CRM}} = \frac{A_{Et}^{CRM} \cdot C_i^{CRM}}{A_i^{CRM} \cdot C_{Et}^{CRM}} \qquad \textbf{(1)}$$

$$C_i = RF_i \times \frac{A_i}{A_{Et}} \times \rho_{Et} \qquad \textbf{(2)}$$

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ρ_{Et} = 789300 mg/L - density of ethanol

Gas Chromatographic 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 °C (9 min), raised to 155 °C at rate 7 °C/min with final isotherm of 155 °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.

6 standard ethanol-water (96:4) solutions were prepared to measure RF relative to ethanol.

Compound	Linear range (mg/L)	Slope (RF)	Correlation coefficient	LOD* (mg/L)
acetaldehyde	2.24 - 1990	1.559	0.9996	0.289
methyl acetate	2.09 - 2000	1.517	0.9997	0.333
ethyl acetate	2.20 - 2094	1.247	0.9998	0.322
methanol	*1.9 - 20 045*	1.377	0.9999	0.394
2-propanol	3.74 - 2033	0.914	0.9998	0.319
1-propanol	1.99 - 2094	0.809	0.9998	0.262
isobutyl alcohol	2.23 - 2000	0.674	0.9998	0.235
n-butanol	1.98 - 2000	0.737	0.9998	0.267
isoamyl alcohol	2.18 - 2073	0.681	0.9999	0.276
* limit of detection (LOD)				

Table 1. Analytical characteristics of the obtained calibration graphs of volatile compounds in standard ethanol-water (96:4) solutions.

Experimental results

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 prepared with known concentrations of volatile compounds.

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

There were 8 weight-method prepared reference solutions.

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

Compound	Concentration according to certificate, (mg/L) CRM, mg/L	Concentration measured by IS method, (mg/L) experiment, mg/L	Relative discrepancy, %
acetaldehyde	1.158	1.129	-2.50
	5.137	5.182	0.88
	10.11	9.921	1.87
	99.64	93.86	-5.80
	497.6	481.1	-3.32
	1989	2037	2.42
methyl acetate	1.000	1.005	0.50
	5.000	5.121	2.42
	10.00	9.905	-0.95
	100.0	96.35	-3.65
	500.0	484.9	-3.02
	2000	2042	2.10
ethyl acetate	1.047	1.072	2.39
	5.234	5.374	2.67
	10.47	10.45	-0.19
	104.7	102.0	-2.58
	523.4	512.2	-2.14
	2093	2115	1.02
methanol	5.975	6.044	1.15
	53.07	53.51	0.83
	103.2	102.97	-0.22
	1005	988.1	-1.68
	5013	4987	-0.52
	20045	20118	0.36
2-propanol	2.636	2.645	0.34
	6.698	6.754	0.84
	11.78	11.77	-0.08
	103.0	101.0	-2.13
	509.0	503.2	-1.22
	2033	2047	0.69
1-propanol	1.047	0.997	-4.78
	5.234	5.223	-0.21
	10.21	10.23	0.20
	103.2	100.2	-3.10
	523.4	513.6	-1.87
	2094	2125	1.51
isobutyl alcohol	1.000	0.971	-2.90
	5.000	5.033	0.66
	10.00	9.82	-1.80
	100.0	97.7	-2.30
	500.0	491	-1.80
	2000	2032	1.60
n-butanol	1.000	0.991	-0.90
	5.000	5.061	1.22
	10.00	9.89	-1.10
	100.0	97.10	-2.90
	500.0	491.0	-1.80
	2000	2036	1.80
isoamyl alcohol	1.036	1.003	-3.19
	5.182	5.169	-0.25
	10.37	10.21	-1.54
	104.0	101.0	-2.60
	518.0	510.0	-1.58
	2073	2110	1.78

Experimental results

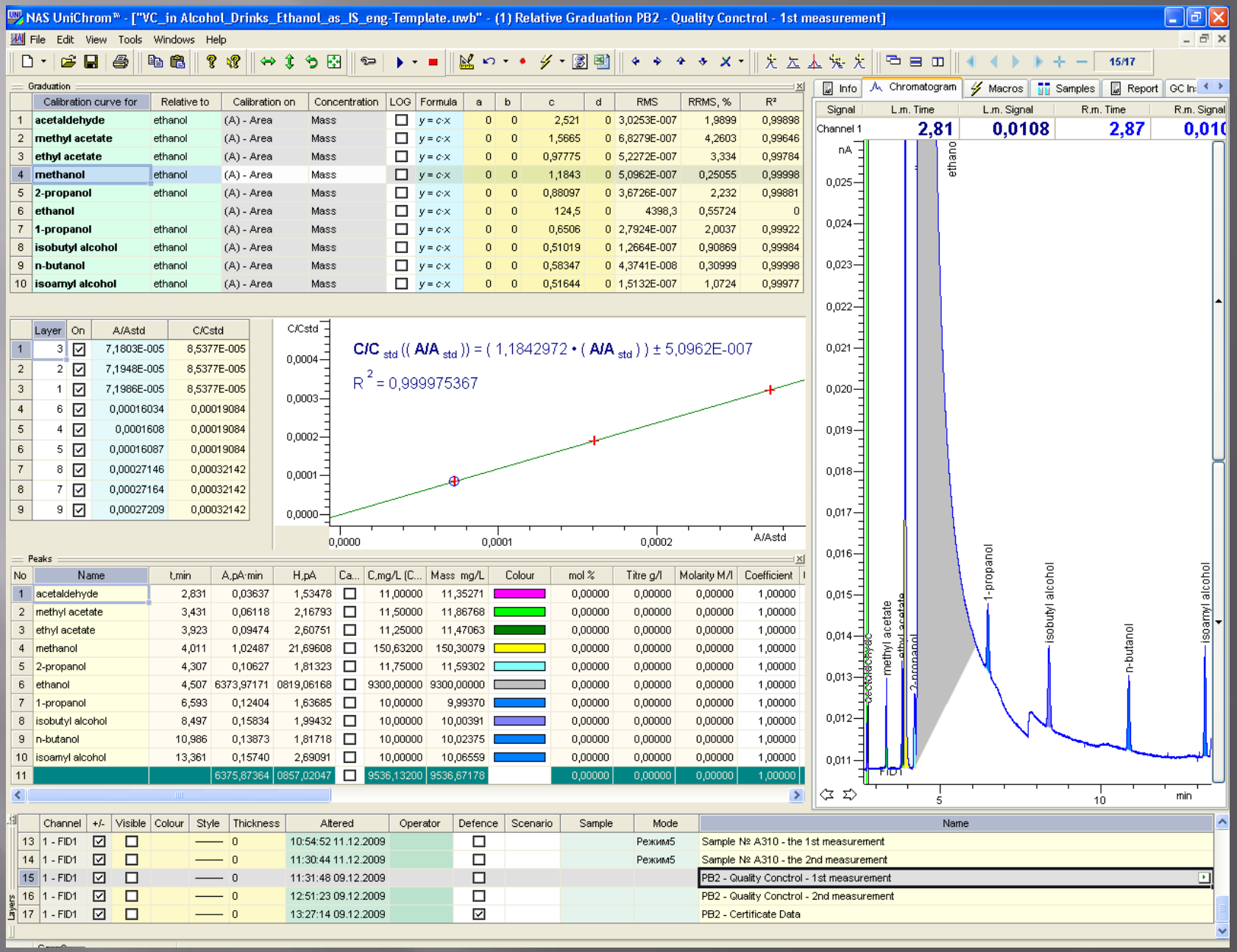
Resume:

The repeatability in the worst case for lower concentrations 1 mg/L did not exceed 3.6 %.

Relative accuracy did not exceed 11 %.

Compound	Concentration according to certificate, (mg/L)	Measured concentration after dilution 1:1, (mg/L)	Relative discrepancy, %	Measured concentration after dilution 1:3, (mg/L)	Relative discrepancy, %
acetaldehyde	10.11	10.34	2.2	10.50	3.8
	99.64	97.28	-2.4	97.40	-7.3
	497.6	483.3	-2.9	473.1	-4.9
methyl acetate	10.00	10.25	2.5	9.78	-2.2
	100.0	92.76	-7.2	89.17	-10.8
	500.0	463.7	-7.3	452.4	-9.5
ethyl acetate	10.47	10.18	-2.8	10.63	1.6
	104.7	100.0	-4.5	95.46	-8.8
	523.4	489.6	-6.5	477.3	-8.8
methanol	103.2	97.99	-5.0	95.18	-7.8
	1005	921.9	-8.3	904.1	-10.0
	5013	4654	-7.2	4514	-9.9
2-propanol	11.80	11.63	-1.2	10.56	-10.4
	103.2	97.86	-5.2	93.13	-9.7
	509.4	479.5	-5.9	463.7	-9.0
1-propanol	10.21	10.36	1.5	10.01	-1.9
	102.1	98.00	-4.0	96.23	-5.7
	523.4	482.9	-5.8	483.2	-7.7
isobutyl alcohol	10.00	10.42	4.2	10.35	3.5
	100.0	96.87	-3.1	94.32	-5.7
	500.0	480.1	-4.0	471.5	-5.7
n-butanol	10.00	10.17	1.7	9.98	-0.2
	100.0	97.02	-3.0	95.21	-4.8
	500.0	482.9	-3.4	475.2	-5.0
isoamyl alcohol	10.37	11.28	8.8	10.35	-0.2
	103.7	103.0	-0.6	99.52	-4.0
	518.2	509.0	-1.8	500.6	-3.4

Table 3. Verification of method stability against dilution. Three reference ethanol-water solutions were analyzed after dilution with water in ratio 1:1 and 1:3.



Metrologic parameters presentation of graduation curves.

Ethanol as Internal Standard for Determination of Volatile Compounds in Alcohol Drinks by Gas Chromatography with UniChrom Datasystem - Mozilla Firefox

Файл Правка Вид Журнал Закладки Инструменты Справка

http://www.unichrom.com/vodka/ethanol-solutione.shtml

Ethanol as Internal Standard for Det...

Ethanol as Internal Standard for Determination of Volatile Compounds in Alcohol Drinks by Gas Chromatography

There are the following prepared templates TemplateWork_for_VC_in Alcohol_Drinks_Ethanol_as_IS_eng.uwb and TemplateReport_for_VC_in Alcohol_Drinks_Ethanol_as_IS_eng.xls for illustration how this method is working.

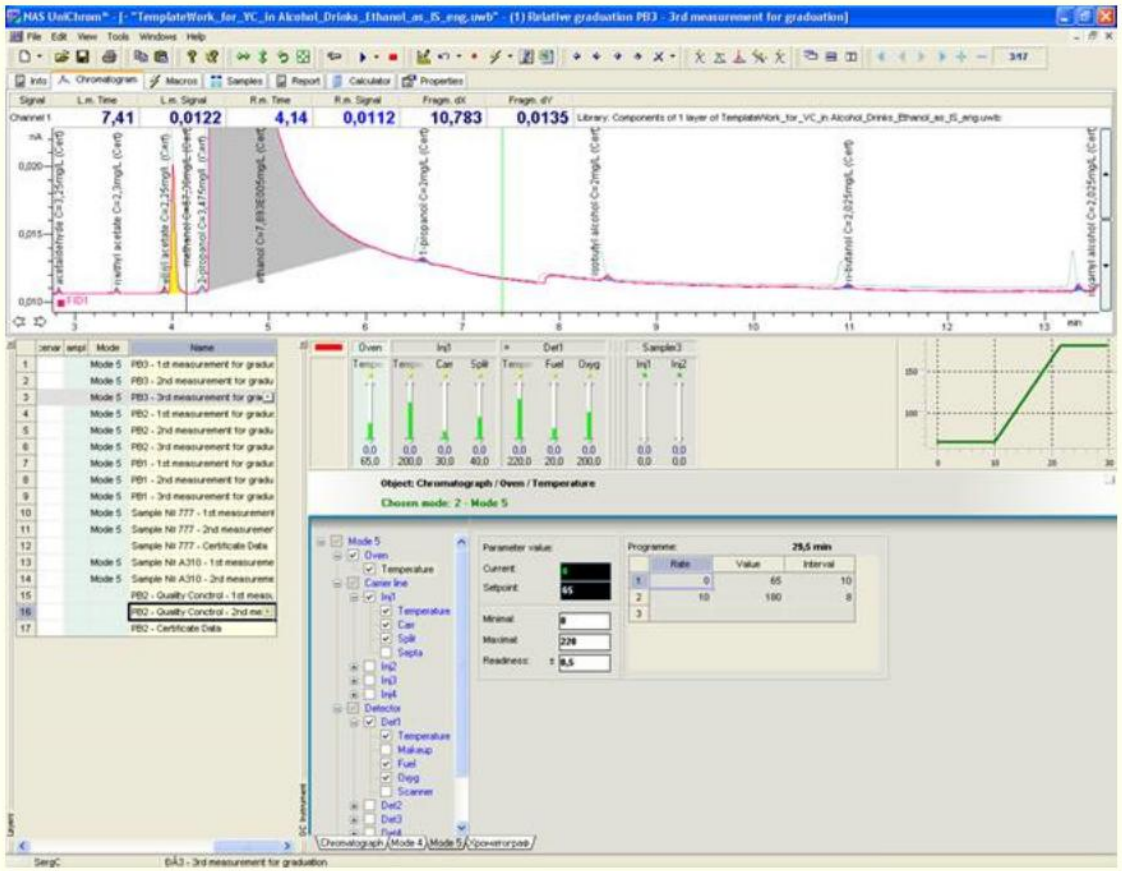


Fig. 1. GC control panel. The carrier gas was hydrogen.

http://www.unichrom.com/vodka/TemplateReport_for_VC_in Alcohol_Drinks_Ethanol_as_IS_eng.xls

Detailed method description is presented in the internet here:

Microsoft Excel - VC_in Alcohol_Drinks_Ethanol_as_IS_eng-Template.xls

Файл Правка Вид Вставка Формат Сервис Данные Окно Справка Adobe PDF

UNICHROM

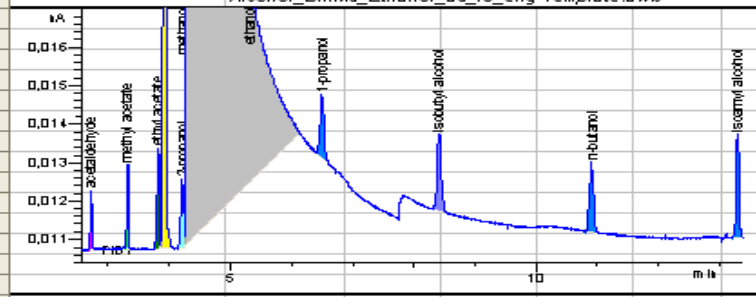
N43

RJS "Minsk Krystall"

Control Laboratory

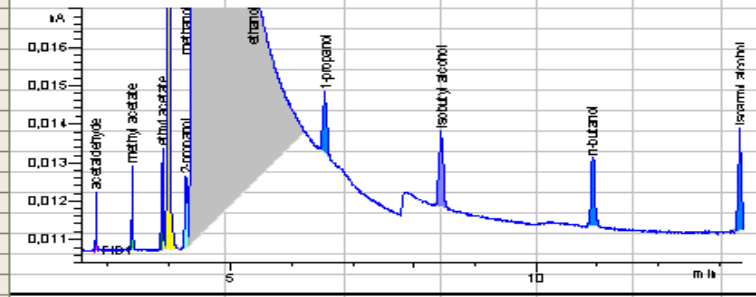
Certificate of Accreditation № BY/112 02.1.0.1906 from 05.02.2001.

The 1st measurement:	*PB2 - Quality Conctrol - 1st measurement*
The 2nd measurement:	*PB2 - Quality Conctrol - 2nd measurement*
File name:	*C:\Conferences\2011-01-24 - Rapid_Methods_Europe_2011\VC_in Alcohol_Drinks_Ethanol_as_IS_eng-Template.uwb*



The 1st measuremnet

Comments



The 2nd measuremnet

Comments

№ of layer	15	16					Accuracy control 17	☑
Compound	C1, mg/L	C2, mg/L	Caver, mg/L	Δ %	Criteria	Δlim, %	C, mg/L	Δ %
acetaldehyde	11,35	11,28	11,32	0,7	Ok!	15	10,88	4,0
methyl acetate	11,87	11,74	11,80	1,1	Ok!	15	10,52	12,2
ethyl acetate	11,47	11,57	11,52	0,9	Ok!	15	10,47	10,0
methanol	150,30	150,37	150,34	0,0	Ok!	15	149,88	0,3
2-propanol	11,59	11,81	11,70	1,8	Ok!	15	11,70	0,0
ethanol	789300	789300	789300	0,0			789300	0,0
1-propanol	9,99	9,52	9,75	4,9	Ok!	15	9,74	0,2
isobutyl alcohol	10,00	9,86	9,93	1,5	Ok!	15	9,95	0,2
n-butanol	10,02	9,96	9,99	0,6	Ok!	15	10,06	0,6
isoamyl alcohol	10,07	10,04	10,05	0,3	Ok!	15	10,18	1,2
methanol (%, v/v)	0,0190	0,0190	0,0190	0,0	Ok!	15	0,0189	0,3
higher alcohols	40,09	39,37	39,73	1,8	Ok!	15	39,92	0,5
volatile acides	23,34	23,32	23,33	0,1	Ok!	15	21,00	11,1

Analyst: _____ R. Golubevas

* Possible coincidence of names, surnames and names of institutions is purely coincidental

Final report / Staff / Comments

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

How introduce this new methodological approach

in the world market ?

There is only one working way.

To propose for customers more easy, attractive and effective way for laboratory business.

There is the following situation in the researches and control laboratories over the world:

- very heterogeneous park of analytical equipments.

Gas chromatographs

Liquid chromatographs

Spectrometers UV, IR, Vis, AES, AAS, MS

The analogue situation was approximately 30 years ago.

The were many text processor software packages in your laboratories.

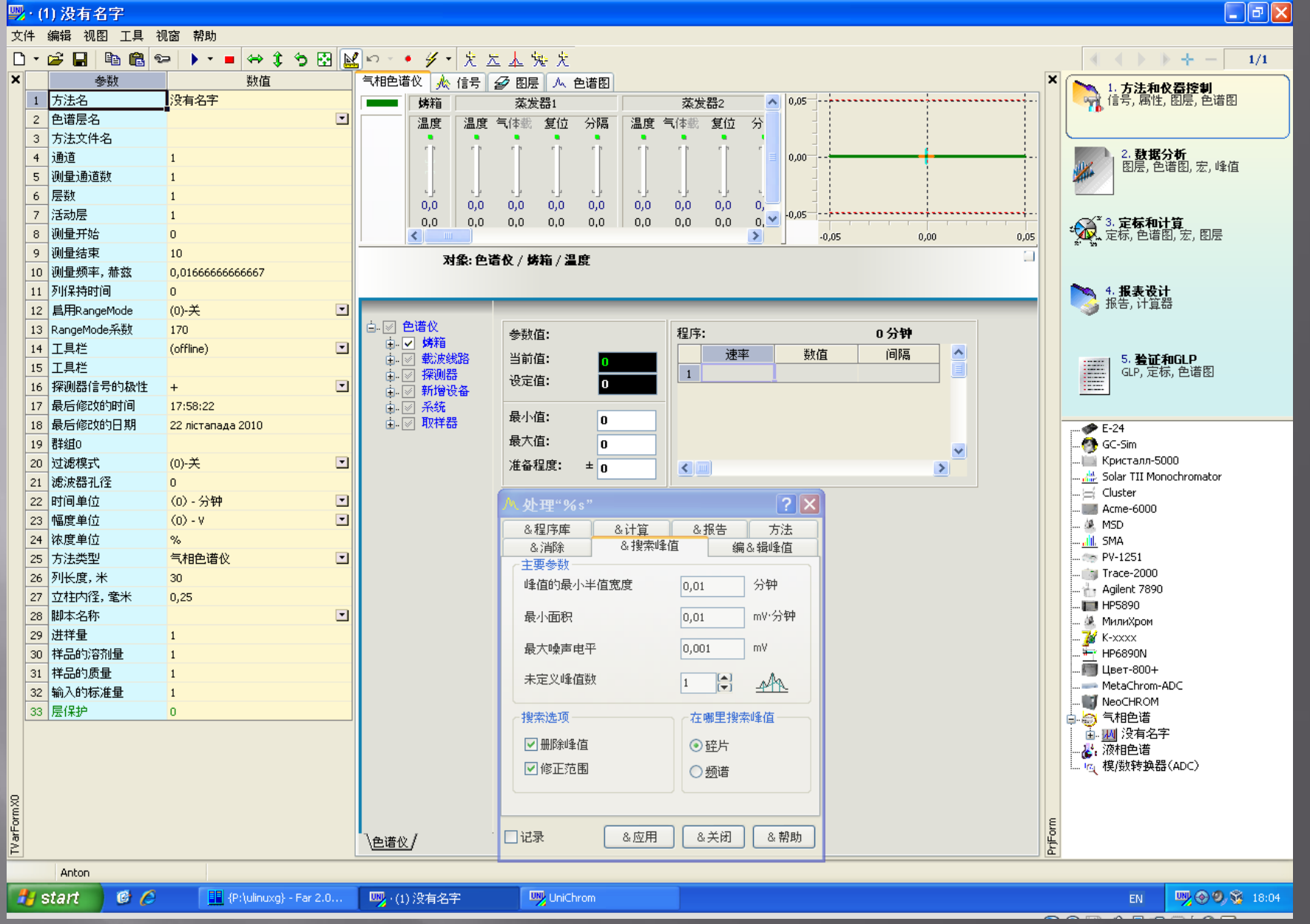
Demand of free migration of text documents between different computers has generated the following situation:

- the PC may be different but the text processor software Microsoft Word is the same in the most offices computers over the world.

To unifiy work with different analytical equipments Unichrom software package was proposed.

Control laboratory in the biggest petrochemical JS “Nevynnommuski Azot” .

Unichrom from one PC controls simultaneously: Crystal-5000 (3), Crystall-2000M (3), HP6890 (1), Schimadzu-2010 (1), Tsvett-800 (2).



Installation with local market language: English, France, German or ….Chinese.

(Real screenshot - no Photoshop !)

Resume 1st

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

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

This methodical approach could be tested while performing current measurements with existing instrumentation and calculations could be done in parallel according to the following different methods:

- External Standard (ES);
- traditional Internal Standard with addition of pental-3-ol as IS;
- using ethanol as IS.

Resume 2nd

1.) Analyzing of obtained data from many testing laboratories showed that RF for different GC very close to each other and they may be …..**tabulated !**

2.) Significant decrease requirements for graduation of GC - until the once in a year !

3.) Detailed information with ready working templates are placed in the Internet here: http://inp.bsu.by/labs/LAR_For_site/Ethanol_as_Internal_Standart.html

Acknowledgments

The authors wish to thank Grisha Deitch from State of Israel and Ilya Kuselman from the National Physical Laboratory of Israel for their capacitated opportunity to present results on this Conference.

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We thanks Prof. Nataliya I. Zayats from Belarus State Technology University for assistance in metrological treatment of experimental data.

Thanks You for Your attention !