Laboratory of Analytical Research: yesterday, today, tomorrow

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*Motivation

History, main trends and prospects of scientific work of the Laboratory of Analytical Research of the Institute for Nuclear Problems of Belarusian State University

Outline

- What is the Institute for Nuclear Problems (INP) of Belarusian State University
- What is the Laboratory of Analytical Research of INP
- What is Volume Free Electron Lasers (VFEL)
- Experimental discover of parametric radiation
- Mathematical modeling of nonlinear dynamics of VFEL
- Information technology based on free software
- Establishment of nuclear knowledge management system in the Republic of Belarus and development of Belarusian portal of nuclear knowledge BelNET https://belnet.by/
- New methods of quality control of alcohol and alcohol-containing products

* What is the Institute for Nuclear Problems (INP) of Belarusian State University (BSU)

In April 1986, by resolution of the Council of Ministers of the USSR, it was decided to create in Minsk a new research institute to solve the problems of developing ultra-powerful generators of electromagnetic radiation for the purposes of strategic missile defense.

It was ***Institute for Nuclear Problems***.

The corresponding resolution of the Council of Ministers of Belarus and the Order of the Belarusian Ministry of Education appeared on September 1, 1986.

The basis for creation of such types of generators was the theoretical and experimental discovery of Parametric X-ray Radiation (PXR) made in 1985 by BSU scientists.

Subsequently, these generators were called Volume Free Electron Lasers (VFEL).

Now VFEL has become a common acronym https://www.acronymfinder.com/Volume-Free-Electron-Laser-(VFEL).html.

What is the Institute for Nuclear Problems (INP) of Belarusian State University

Major areas of R&D

- Basic research in fields of nuclear physics, high energy and particle physics, astrophysics and cosmology
- Research of extreme states of matter under ultra-high temperatures and pressures using magnetic cumulation of energy
- New composite materials, nano- and micro-structured materials
- Radiation and nuclear technologies using radioactive sources, particle accelerators and nuclear reactors; new methods of ionizing radiation measurements

Staff total – *120*
Researchers – *95*
D.Sc. – *10*
Ph.D. – *28*

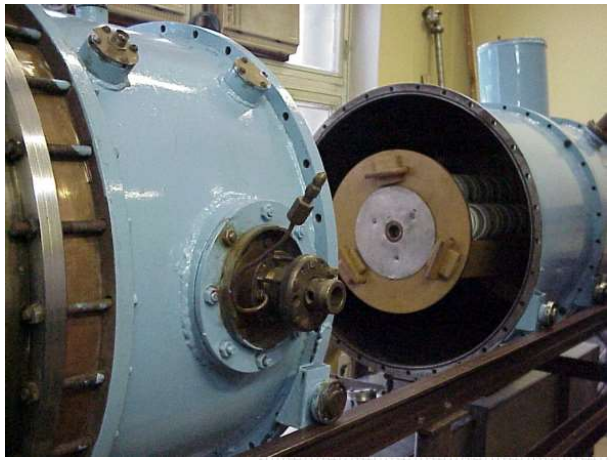
* What is the Laboratory of Analytical Research of INP

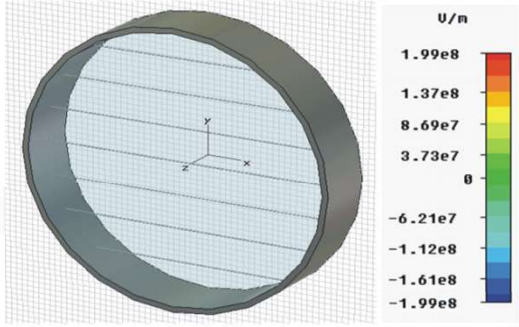
Main research areas:

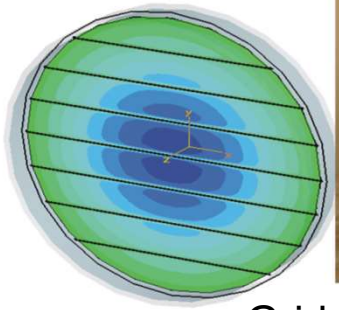
- advanced methods of quality control of alcohol and alcohol-containing products;
- development of electronic document management system of the testing laboratory (framework) eLab based on free software;
- establishment of nuclear knowledge management system in the Republic of Belarus and development of Belarusian portal of nuclear knowledge BelNET (Belarusian Nuclear Education and Training) https://belnet.by/;
- explore ways to develop unification of working with various analytical instruments.

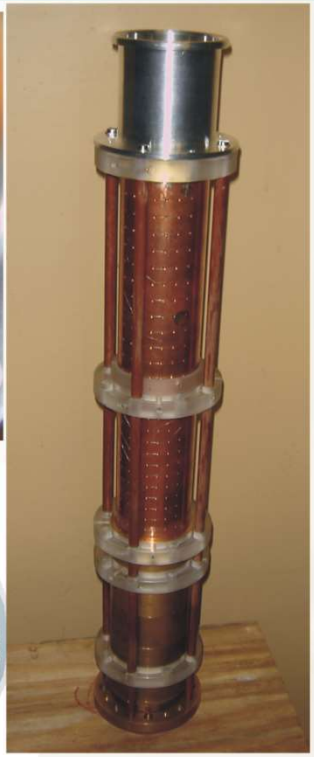
Dr. Siarhei Charapitsa

* What is Volume Free Electron Lasers (VFEL)







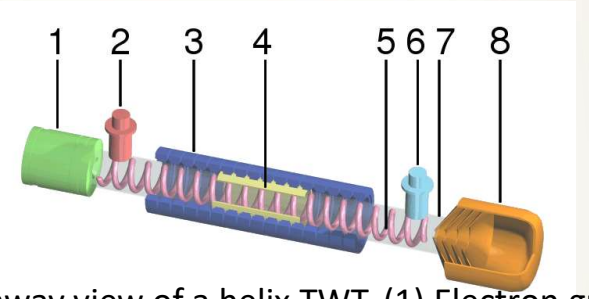


Grid resonator with photonic crystal

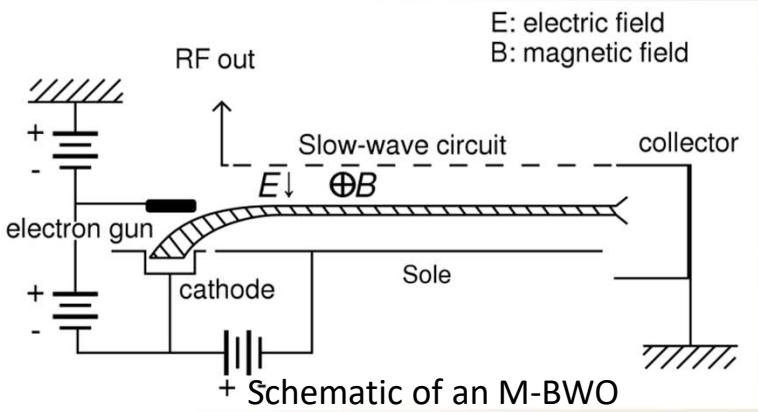
Professor Vladimir Baryshevsky

*Vacuum electronic devices

- There is a variety of such devices with their obvious generality in used physical principles, as well as the complex nonlinear dynamics of their functioning.
- Their performance and reliability are based on complex electromagnetic structures, new materials and advanced technologies.
- The widespread use of such devices in military and commercial applications requires them to operate reliably with high power, high efficiency, and low cost.
- The basis of the operation is the emission of electrons, grouped in bunches and interacting in a cavity (slow-wave spatially periodic medium) with slow electromagnetic waves. The generated electromagnetic wave power has its group velocity directed along or oppositely to the direction of motion of the electrons.



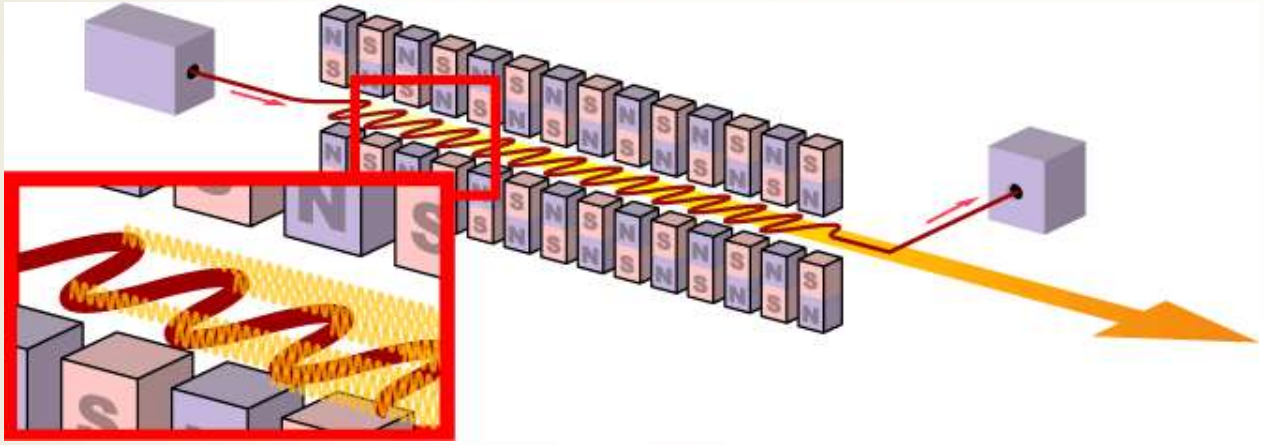
Cutaway view of a helix TWT. (1) Electron gun; (2) RF input; (3) Magnets; (4) Attenuator; (5) Helix coil; (6) RF output; (7) Vacuum tube; (8) Collector



Schematic of an M-BWO

R. Kompfner. Wireless World LII (1946), 369
R. Kompfner, N. T. Williams. Proc. IRE 41 (1953), 1602

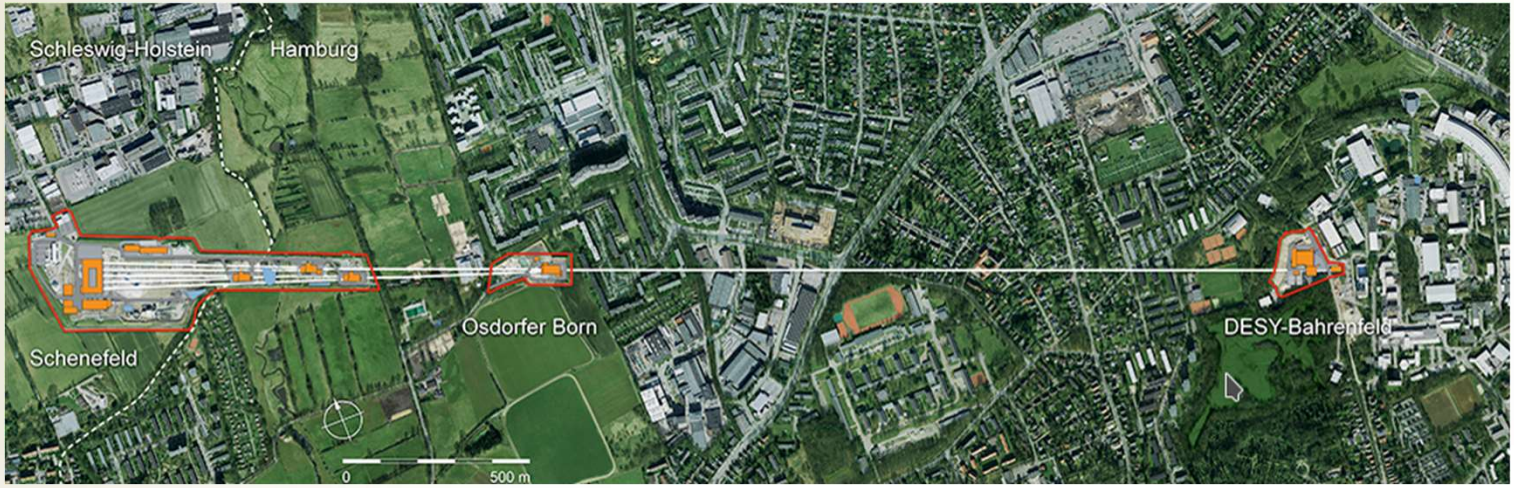
*Free electron lasers (FEL)



A Free Electron Laser* differs from conventional lasers in using a relativistic electron beam as its lasing medium, as opposed to bound atomic or molecular states, hence the term free-electron. FELs generate tunable, coherent, high power radiation in wavelengths from millimeter till ultraviolet and X-ray.

J. M. J. Madey. J. Appl. Physics, 42(1971), 1906
W. B. Colson. Phys. Let., 59A (1976), 187
D. A. Deacon et al. Phys. Rev. Let. 38 (1977), 892
M. Billardon et al. Phys. Rev. Let. 51 (1983),1652
J. Madey, M. O. Scully, P. Sprangle. Physica Scripta, 91 (2016), 063003

*Free electron lasers



European XFEL (DESY)

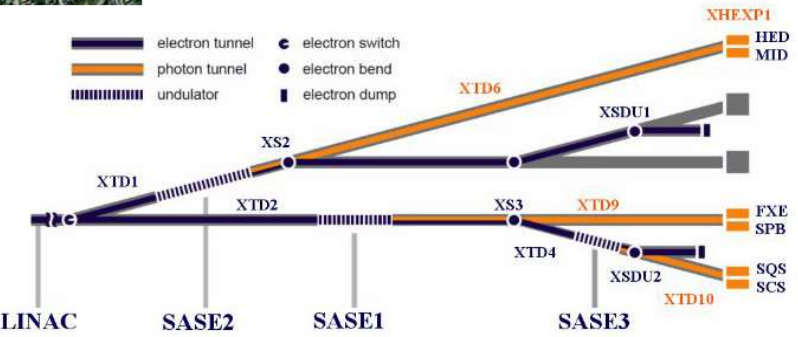
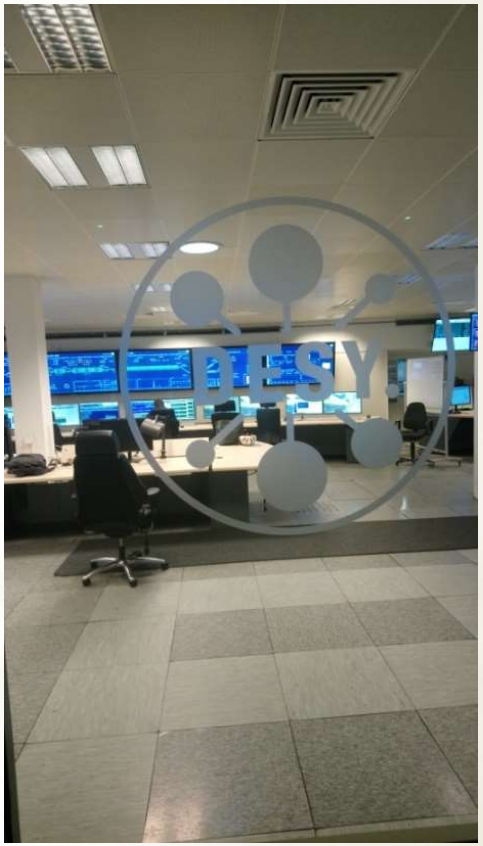


Figure 1: Schematic layout of the European XFEL facility showing the SASE undulators and corresponding experimental end stations.

*Free electron lasers

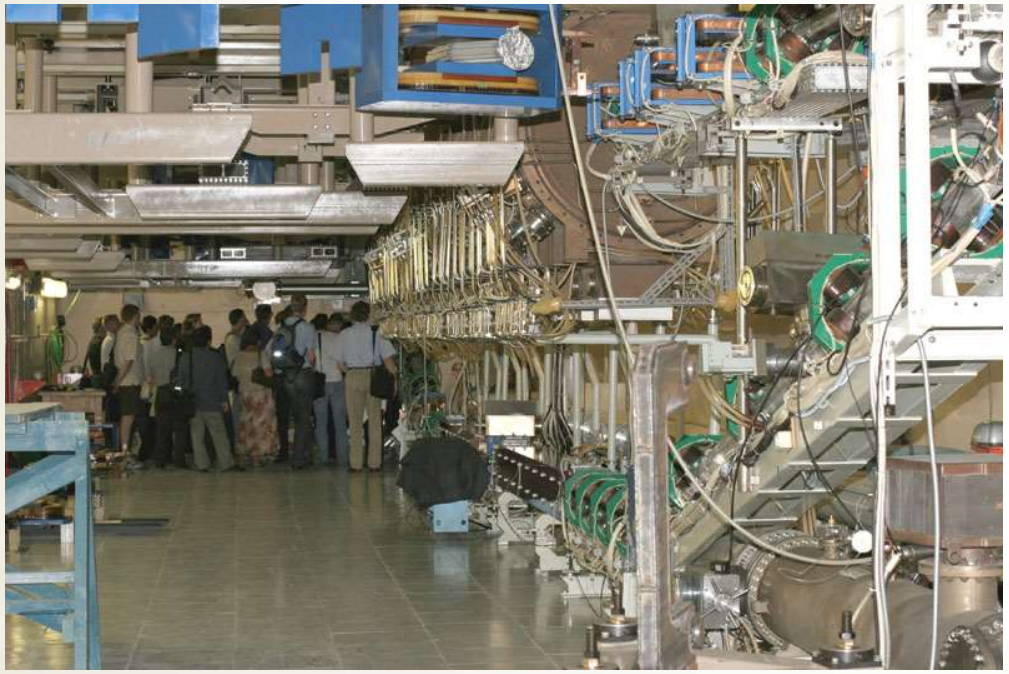
Linear accelerator+XFEL



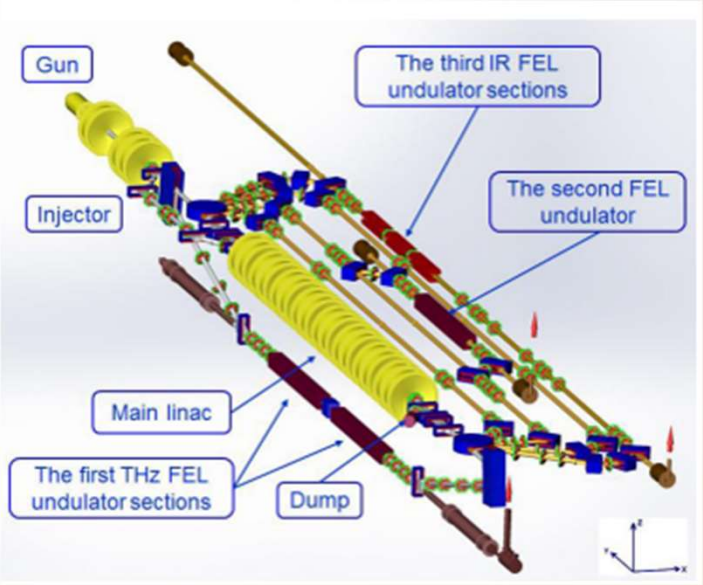
Booster

Control room

*Free electron lasers



Novosibirsk FEL*



The first FEL has been in operation since 2003. It provides a narrow-band (less than 1%) terahertz radiation in the wavelength range of 80 240 μm at an average power of up to 0.5 kW and a peak power of up to 1 MW (100-ps pulses at a repetition rate of 5.6 MHz). About 30 user research projects in different fields of science were carried out at the facility in recent years.

**Kulipanov et al. IEEE Trans. on Therahertz Sience and Technology. 2015. Vol. 5, No. 5. P. 798–809*

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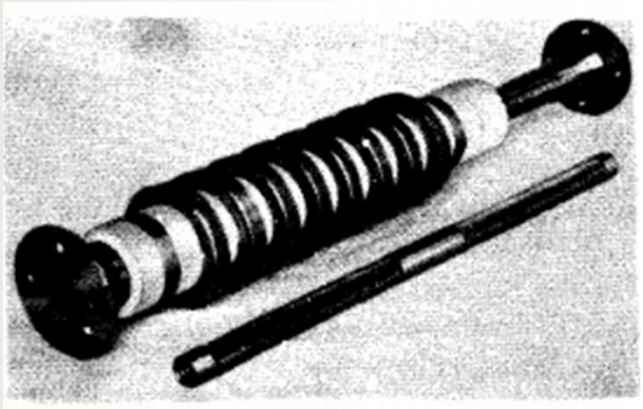
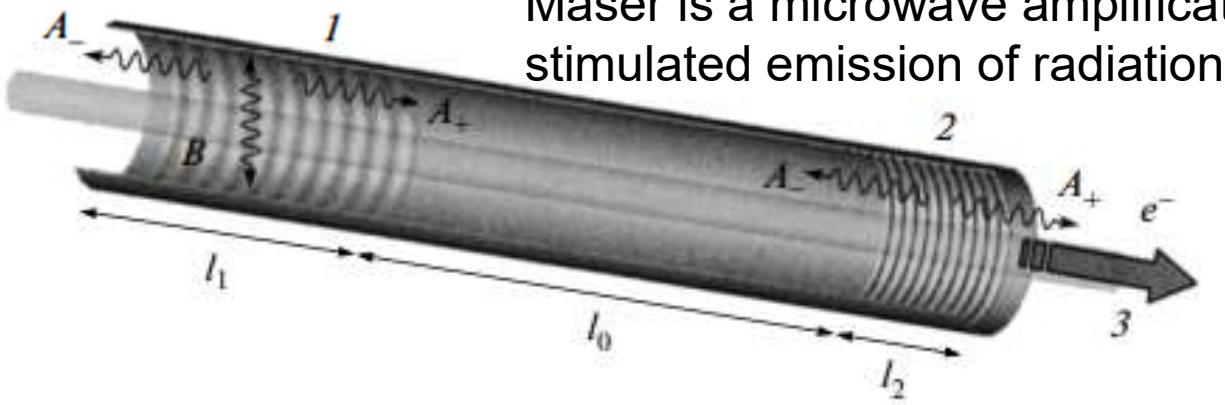
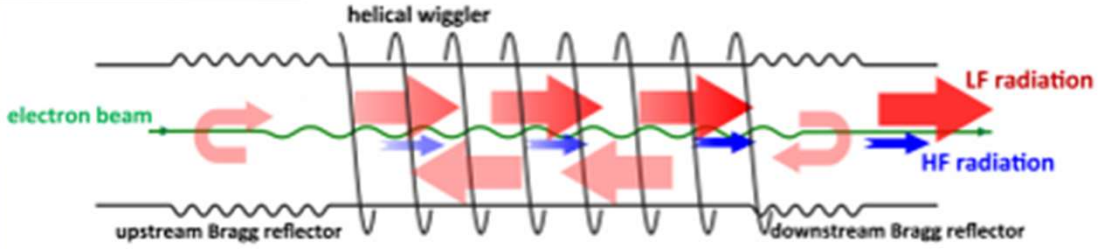
Free electron masers





Maser is a microwave amplification by stimulated emission of radiation.

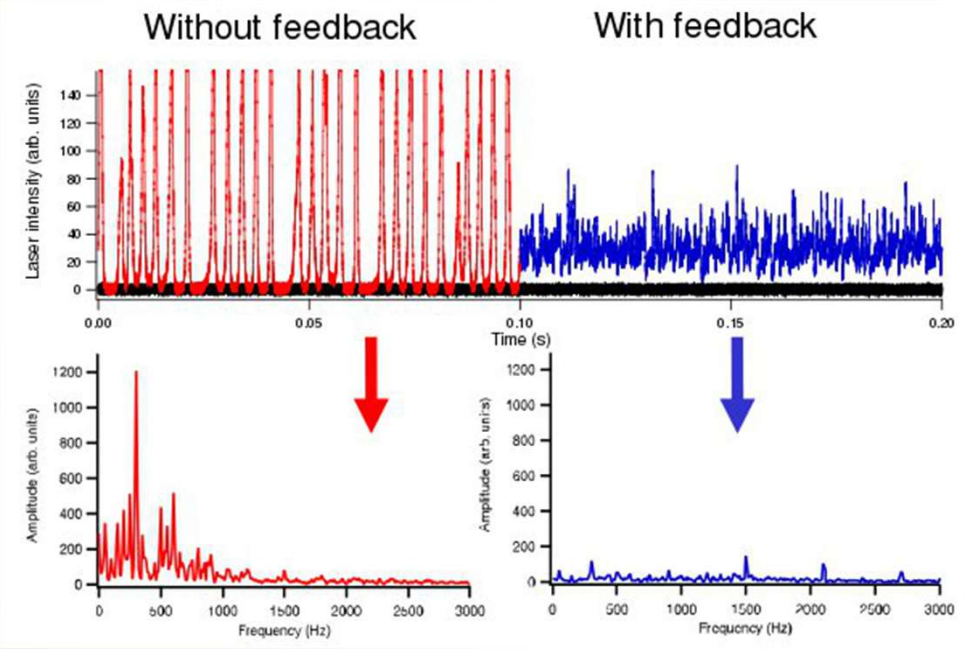
Fig. 1. Schematic diagram of a FEM with a combined double-mirror resonator: (*1*) modified Bragg reflector (*2*) traditional 1D Bragg reflector; (*3*) electron beam. Wavy lines show the directions of propagation of the electromagnetic flows $A_{\pm}$ and B. The corrugation period of the modified Bragg structure (*1*) is about twice that of the traditional structure (*2*).

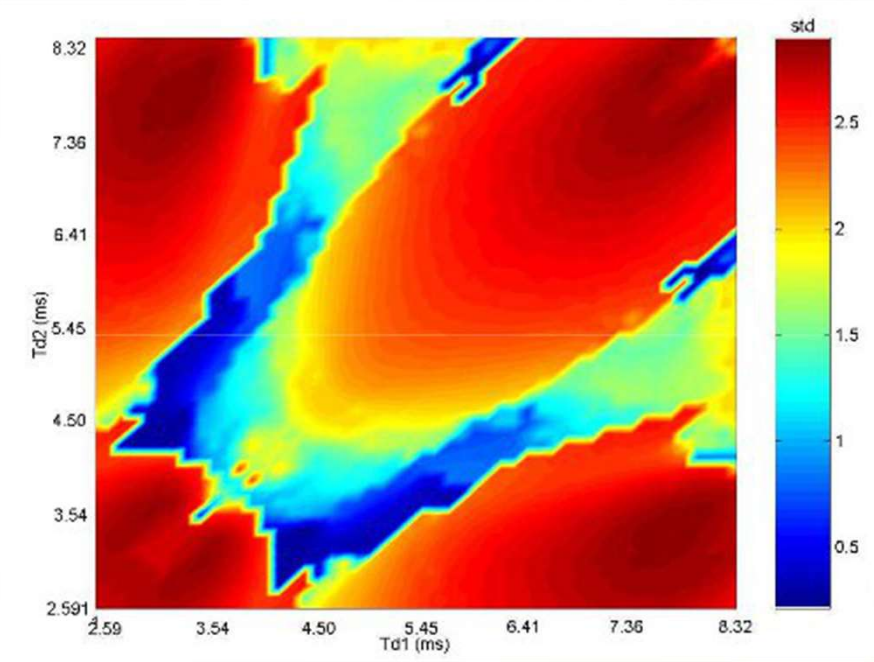


Scheme of the FEM multiplier with a helical wiggler and a two-mirror Bragg resonator.

I. Botvinik et al. Letter JETP 35, 418 (1982)
N. S. Ginzburg et al. Tech. Phys. Let. 36 (2010), 952
N. Yu. Peskov et al. Phys. Rev. Accel. Beams. 19 (2016), 060704

*Chaos in FEL





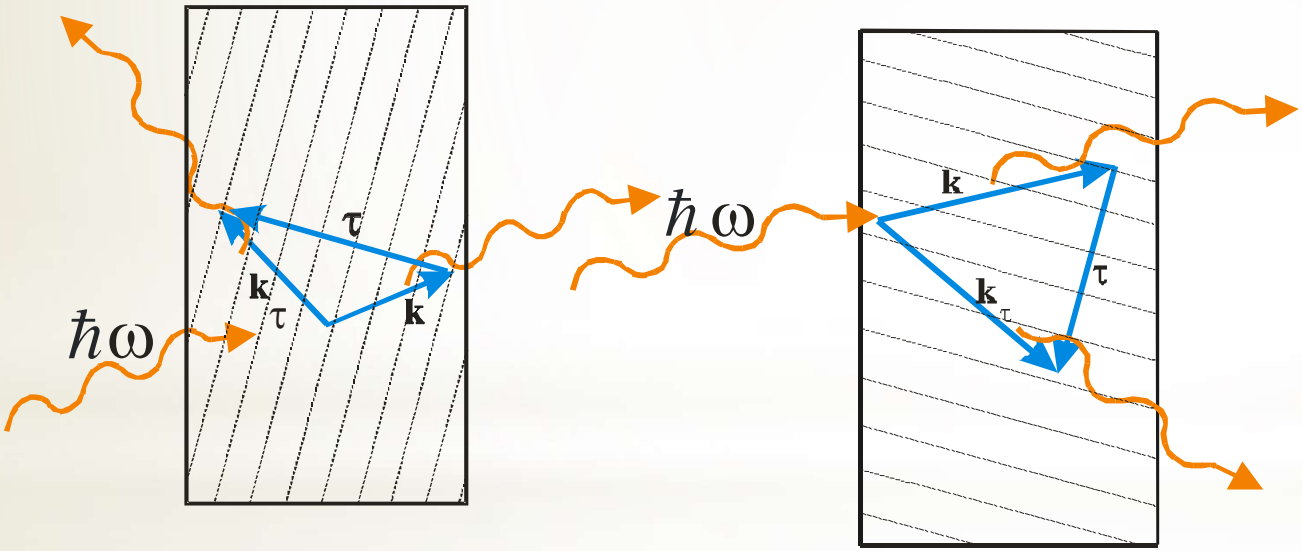
M. Billardon. Phys. Rev. Lett. 65 (1990), 713
S.J. Hahn, J.K. Lee. Phys. Let. A 175 (1993), 339
De Ninno, G., Fanelli, D., Bruni, C. et al. Eur. Phys. J. D 22 (2003), 269.
C. Bruni et al. Eur. Phys. J. D 55, 669-677 (2009)

Dynamical diffraction

**Bragg, W.H.; Bragg, W.L. Proc. R. Soc. Lond. A. 88 (1913), 428*

Bragg geometry

Laue geometry

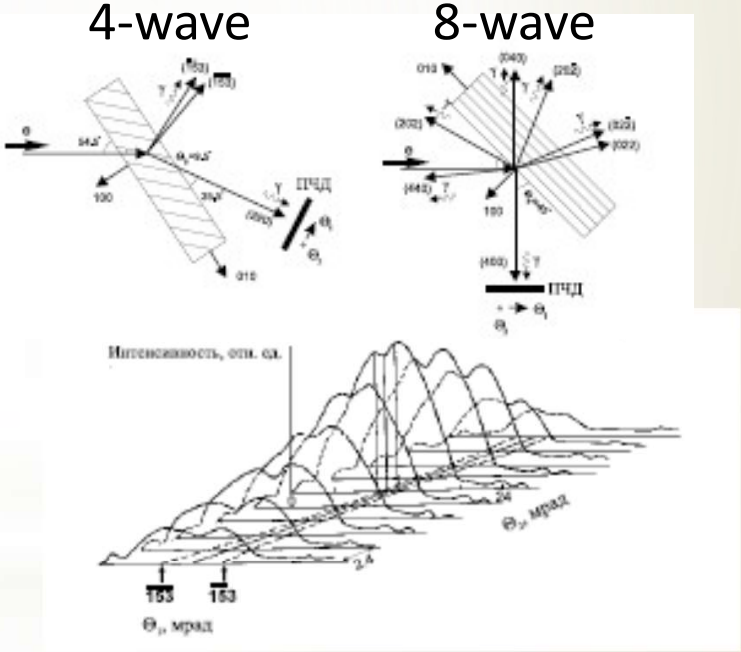


τ is a reciprocal lattice vector.
Principles of diffraction are valid from X-ray to THz range.

Scheme of multi-wave experiments**

4-wave

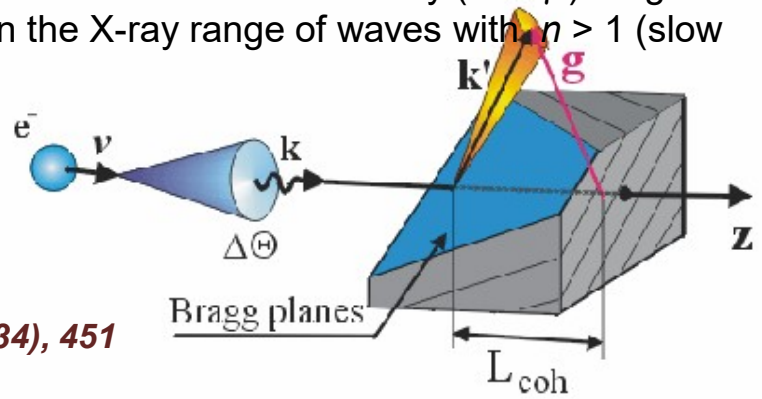
8-wave



***V.Afanasenko, V.Baryshevsky et al. Tech.Phys. Let. 15 (1989) 33*
V.Afanasenko, V.Baryshevsky et al. Phys. Lett. A141 (1989) 311
V.Afanasenko, V.Baryshevsky et al. JETP Let. 51 (1990) 213

* Parametric(quasi-Cherenkov) X-ray radiation

Cherenkov radiation* is electromagnetic radiation emitted when a charged particle passes through a dielectric medium at a speed greater than the phase velocity of light in that medium.
According to Landau (vol.VIII), the dielectric permittivity $\varepsilon < 1$ (the refractive index $n = \sqrt{\varepsilon} < 1$) and Cherenkov radiation in the X-ray region should be absent.
However, in 1971** it was showed that, nevertheless, when a large-energy particle moves through a crystal due to the diffraction of emitted photons in a crystal, it is possible that X-ray induced radiation (and, as a consequence, spontaneous) Cherenkov radiation.
A new type of radiation was called **Parametric X-ray radiation** (**PXR**).
Its origin is due to the fact that in a periodic medium, which is a crystal, photons have several refractive indices, among which there are refractive indices of $n > 1$ in the X-ray (and γ-) range. PXR generation in a crystal is accompanied by excitation in the X-ray range of waves with $n > 1$ (slow waves) and waves with $n < 1$ (fast waves).
PXR was experimentally discovered in 1985***.



*Cherenkov P. A. Doklady Akademii Nauk SSSR, 2(1934), 451

**Baryshevsky V.G., Feranchuk I.D.Sov. J. Exp. Tech. Phys, 61, N 3(9) (1971), 944; Sov. J. Exp. Tech. Phys, 64 (1973),760; Baryshevsky V. G., Feranchuk I.D. Doklady Akad. Sci. BSSR, 18, N 6 (1974), 499

***Adischev Yu.N., Baryshevsky V.G. et al. // Sov. JETP. Lett. 41 (1985) 295

*VFEL new law of instability

New law of instability* for an electron beam passing through a spatially-periodic medium, valid for all wavelength range and any type of spontaneous radiation (PXR, Smith-Purcell, diffraction or Cherenkov radiation, radiation in laser wave etc.)

The increment of instability in degeneration points:

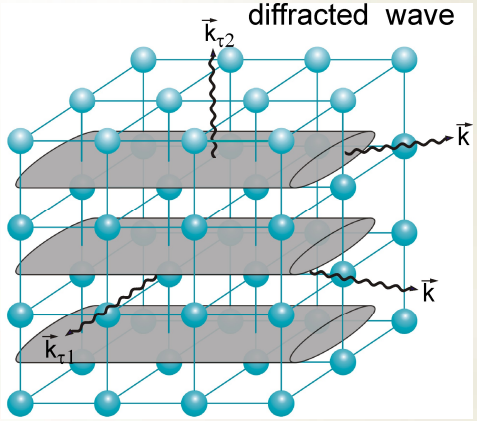
$$G \sim \sqrt[3+s]{\rho}$$

instead of $\sim \sqrt[3]{\rho}$ for other systems (TWT, BWT, FEL etc.)

Threshold current in degeneration points:

$$j_{start} \sim 1/(kL)^{3+2s}$$

instead of $\sim (kL)^{-3}$ for other systems.



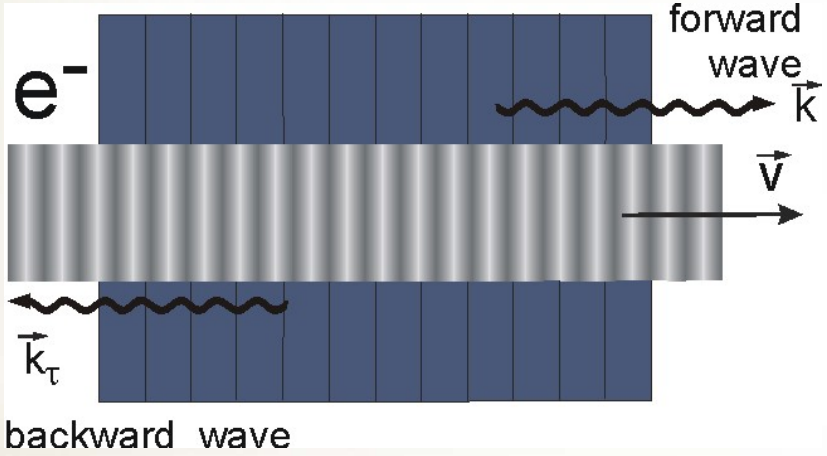
s is the number of surplus waves appearing due to diffraction.

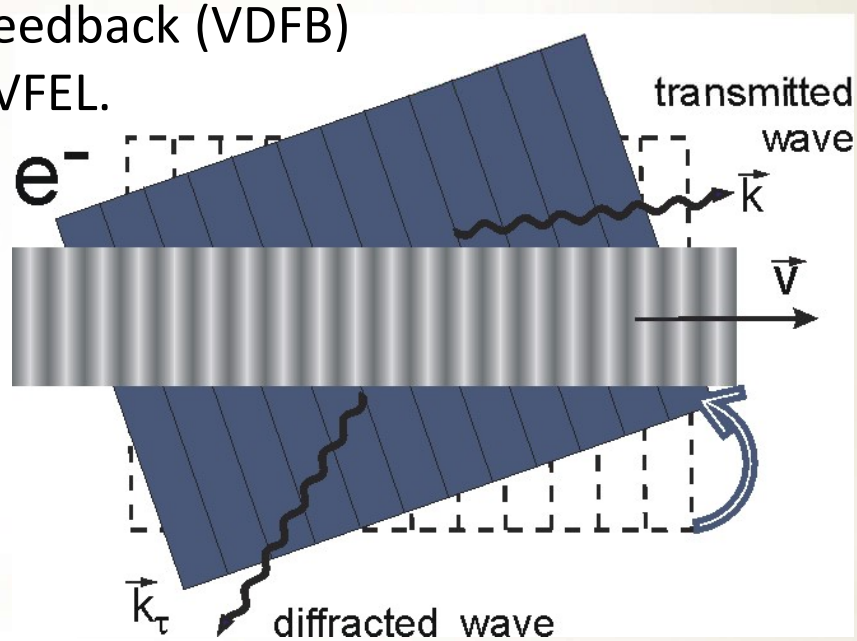
V.G.Baryshevsky, I.D.Feranchuk, Phys.Lett. 102A (1984) 141,

V.G.Baryshevsky, Proc. of the USSR Nat. Ac. Sci., 299(1988), 1363

*Volume free electron lasers (VFEL)

Volume (non-one-dimensional) multi-wave distributed feedback (VDFB) under diffraction conditions is the distinctive feature of VFEL.





Diffraction condition

$$2\mathbf{k\tau} + \boldsymbol{\tau}^2 \approx 0$$

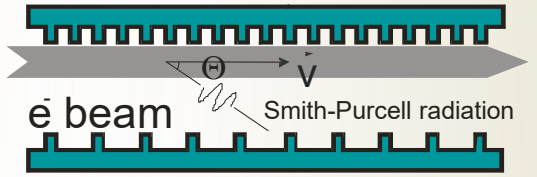
Synchronism condition

$$\left|\omega - \mathbf{ku}\right| = \delta\omega \approx 0$$

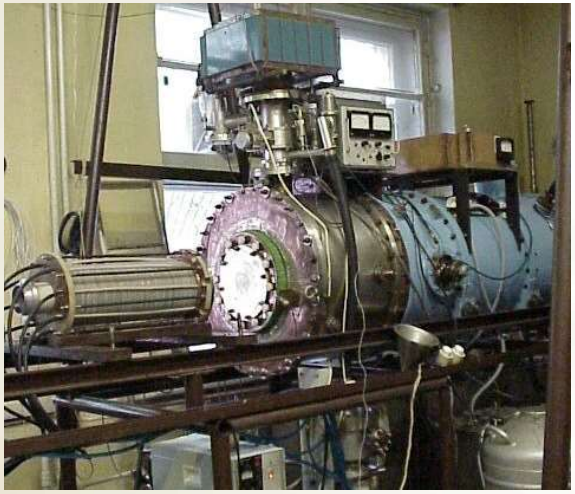
Interacting of the electron beam with electromagnetic field in VFEL is much more efficient than in one-dimensional situation because the group velocity of electromagnetic waves decreases sharply due to continuous reflections of them at periodic planes of resonator. VFEL is an oversized system where electron beams of broad cross-section can be used. Due to this and VDFB electron beam radiates more effectively.

*VFEL experiments at INP

1996 Experimental modeling of electrodynamic processes in volume diffraction grating made from dielectric threads *V.G.Baryshevsky et al., NIM 393A (1997) 71*

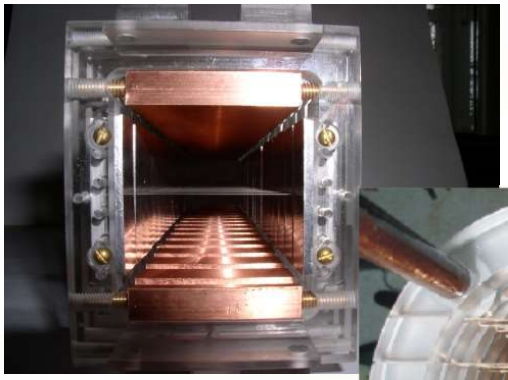


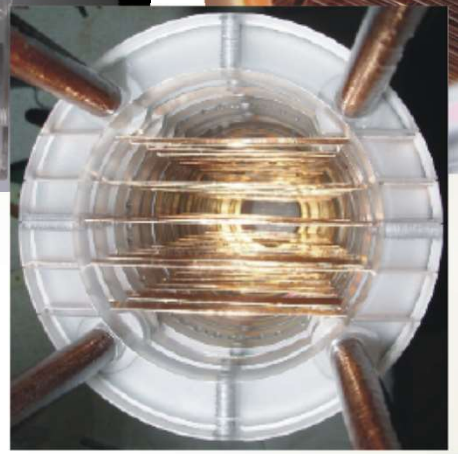
2001 The first VFEL generation in the millimeter range. Experimental verification of VFEL principles. Demonstration of frequency tuning for a fixed electron energy *V.G.Baryshevsky et al., NIM 483 A (2002) 21*

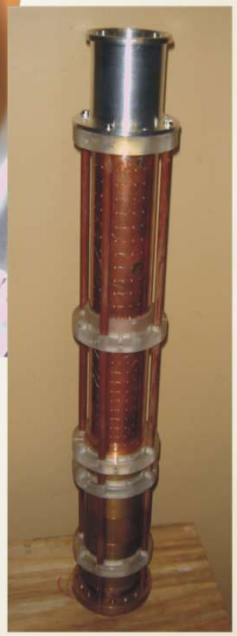


2004 VFEL with grid rectanglular resonator

V.G. Baryshevsky et al., NIM. B 252 (2006) 86





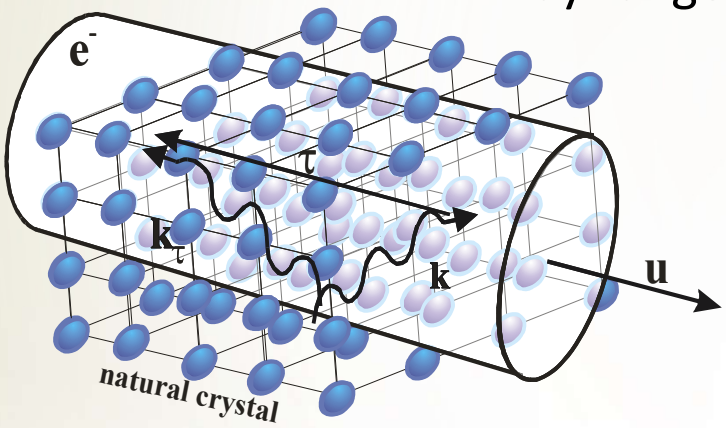


2007 VFEL with grid and foil resonators (photonic crystals)

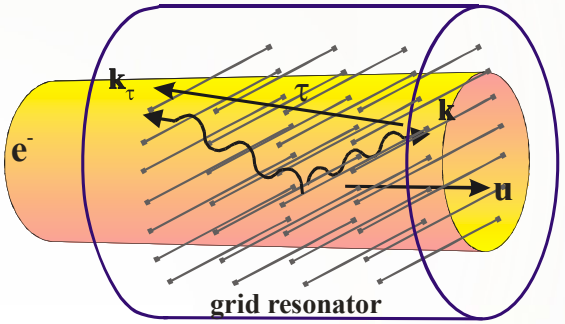
V. G. Baryshevsky et al. Proc FEL2007, 496;
Proc. IRMMW-THz 2010; Proc. FEL2010. Nuovo Cimento 34 (2011), 199

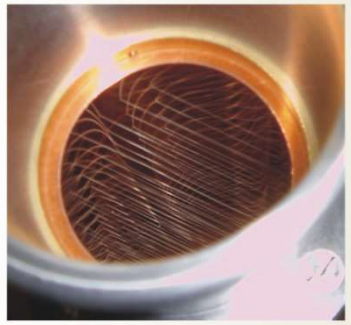
* VFEL in different wavelenght range

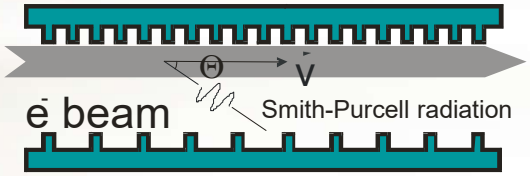
X-ray range



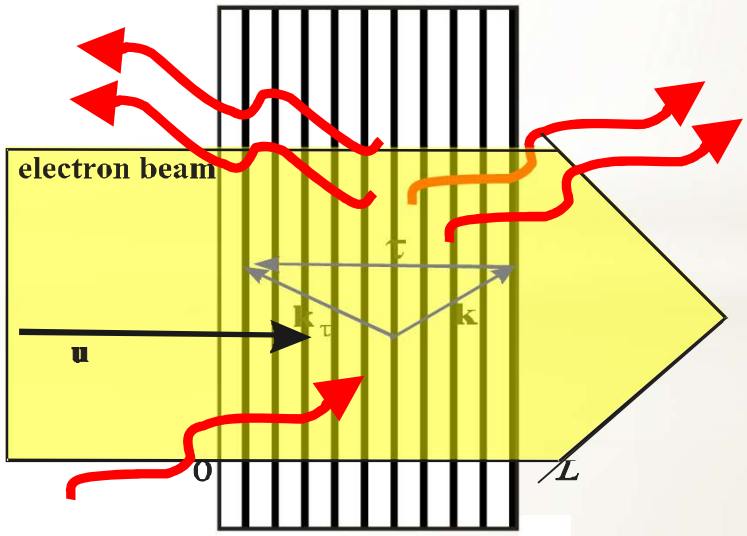
Microwave range (2007)







VFEL with ribbon electron beam (2001)



Photonic crystal (resonator)

VFEL main equations

$$\frac{\partial E}{\partial t}+\gamma_0 c\frac{\partial E}{\partial z}+0.5il E-0.5i\omega\chi_\tau E_\tau = I,$$

$$\frac{\partial E_\tau}{\partial t}+\gamma_1 c\frac{\partial E_\tau}{\partial z}-0.5i\omega\chi_{-\tau} E+0.5i\omega l_1 E_\tau = 0,$$

$$I = 2\pi j\Phi\int_0^{2\pi}\frac{2\pi-p}{8\pi^2}\left(e^{-i\theta(t,z,p)}+e^{-i\theta(t,z,-p)}\right)dp,$$

$$E(t,0)=E_0,\quad E_\tau(t,L)=E_{\tau 0}$$

Two-wave VFEL in Bragg geometry

$\gamma_{0,1}$ are direction cosines, δ is departure from synchronism conditions.

$\chi_{0,\pm\tau}$ are Fourier components of the dielectric susceptibility of the target.

$\theta(t, z, p)$ is an electron phase in a wave.

We use the method of averaging over initial phases of electron entrance in the resonator that takes into account as initial phase of an electron not only the moment of time t_0 but also transverse spatial coordinate of an electron entrance in the resonator at $z = 0$.

$$\frac{d^2\theta(t,z,p)}{dz^2}=\frac{e\Phi}{m\gamma^3\omega^2}\left(k-\frac{d\theta(t,z,p)}{dz}\right)^3\mathrm{Re}\left(E(t-z/u,z)\exp(i\theta(t,z,p))\right),$$

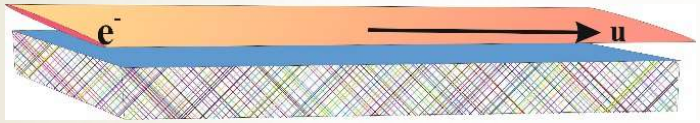
$$\frac{d\theta(t,0,p)}{dz}=k-\omega/u,\quad \theta(t,0,p)=p,$$

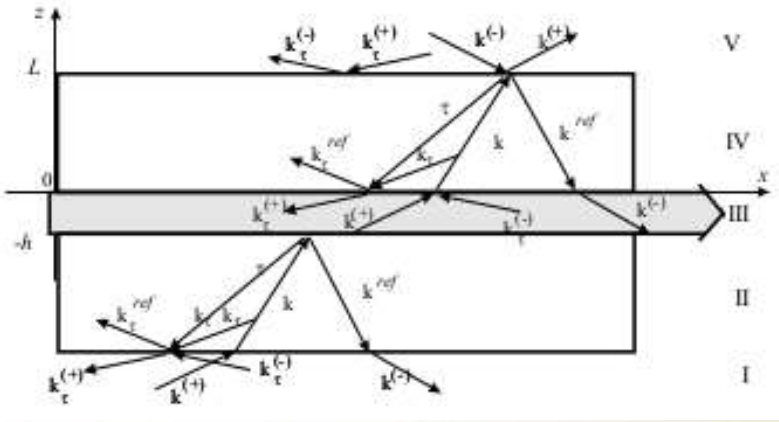
$$t>0,\quad z\in[0,L],\quad p\in[-2\pi,2\pi]$$

*Batrakov K., Sytova S. Comp. Math. Math. Phys. 45 (2005), 666

* Surface VFEL with diffraction gratings

Baryshevsky et al. NIM (1994),A341,274; NIM (1995), A358, 508





$$\frac{\partial E^{(\pm)}}{\partial t} \pm \frac{k_z^0 c^2}{\omega}\frac{\partial E^{(\pm)}}{\partial z} + \frac{k_x c^2}{\omega}\frac{\partial E^{(\pm)}}{\partial x} = \frac{2\pi i}{\omega}\frac{\partial j^{(\pm)}}{\partial z} - 2\pi\frac{\partial j^{(\pm)}}{\partial z} \qquad \text{(III)}$$

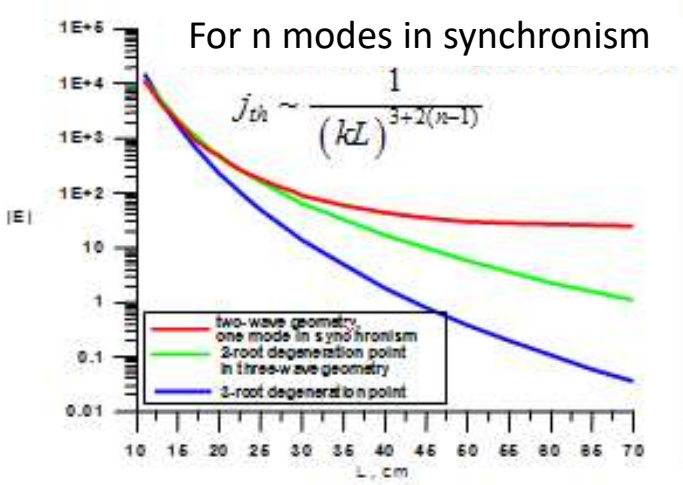
$$\frac{\partial E}{\partial t} + \frac{k_z c^2}{\omega\varepsilon_0}\frac{\partial E}{\partial z} + \frac{k_x c^2}{\omega\varepsilon_0}\frac{\partial E}{\partial x} + \frac{i(\mathbf{k}^2 - \omega^2/c^2\varepsilon_0)}{2\omega\varepsilon_0}E + \frac{i\omega\chi_\tau}{2\varepsilon_0}E_\tau = 0,$$

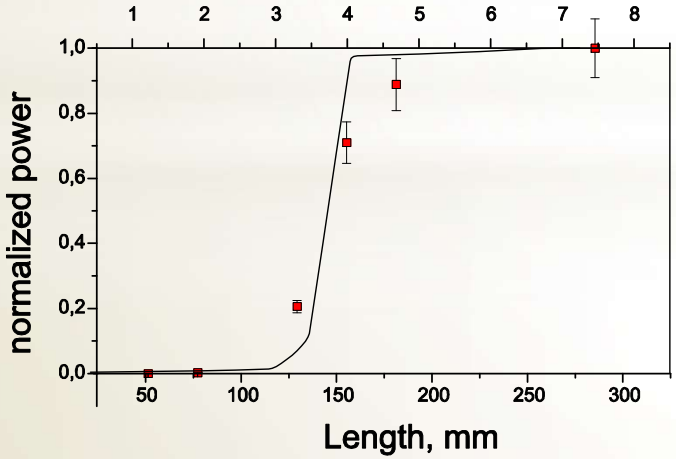
$$\frac{\partial E_\tau}{\partial t} + \frac{k_{\tau z} c^2}{\omega\varepsilon_0}\frac{\partial E_\tau}{\partial z} + \frac{k_{\tau x} c^2}{\omega\varepsilon_0}\frac{\partial E_\tau}{\partial x} + \frac{i\omega\chi_{-\tau}}{2\varepsilon_0}E + \frac{i(\mathbf{k}_\tau^2 - \omega^2/c^2\varepsilon_0)}{2\omega\varepsilon_0}E_\tau = 0. \qquad \text{(II), (IV)}$$

$$\frac{\partial E^{ref}_{\cdot,\tau}}{\partial t} \mp \frac{k_{z,\tau z} c^2}{\omega}\frac{\partial E^{ref}_{\cdot,\tau}}{\partial z} + \frac{k_x c^2}{\omega}\frac{\partial E^{ref}_{\cdot,\tau}}{\partial x} = 0$$

$$\mathbf{A}\frac{\partial \mathbf{E}}{\partial t} + \mathbf{B}\frac{\partial \mathbf{E}}{\partial z} + \mathbf{C}\frac{\partial \mathbf{E}}{\partial x}\mathbf{E} + \mathbf{D}\mathbf{E} = \mathbf{F}(\mathbf{E}^{(0)}, j^{(\pm)})$$

*VFEL main numerical results





It was obtained numerically all main VFEL physical laws.
It was demonstrated that there exists an optimal set of VFEL parameters for effective generation.
It was obtained generation thresholds for INP VFEL experimental setups
It was denoted the necessity of taking into account the dispersion of electromagnetic waves on photonic crystal for microwave VFEL
It was demonstrated numerically one of VFEL physical features of suppression of spurious modes inside the resonator.

VFEL was investigated as dynamical chaotic system.
A gallery of different chaotic regimes for VFEL laser intensity with corresponding phase space portraits, bifurcation diagrams, attractors and Poincare maps was proposed.
It was obtained analytically solution for the stationary problem with electron beam and for non-stationary small-scale periodic regimes. It was demonstrated the origin of oscillations.

V.G.Baryshevsky et al., Proc. FEL06, 331

*Photonic and Nano FEL

Photonic Free-Electron Lasers

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(Invited Paper)

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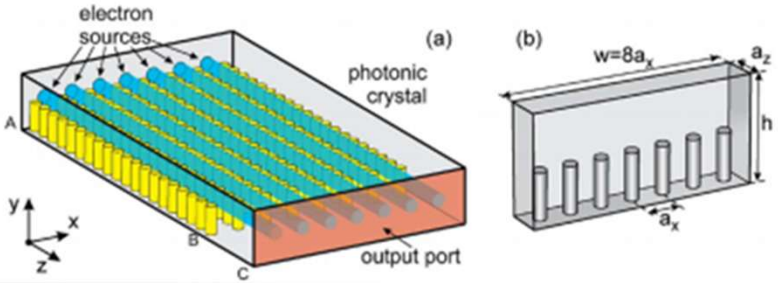
1943-0655/$31.00 ©2012 IEEE

Manuscript received February 16, 2012; revised March 7, 2012; accepted March 7, 2012. Date of current version April 20, 2012. This work was supported by the Dutch Technology Foundation STW, applied science division of NWO, and the technology program of the Dutch Ministry of Economic Affairs. Corresponding author: P. J. M. van der Slot (e-mail: p.j.m.vanderslot@utwente.nl).

Abstract: A photonic free-electron laser (pFEL) produces coherent Cerenkov radiation from a set of parallel electron beams streaming through a photonic crystal. The function of the crystal is to slow down the phase velocity of a copropagating electromagnetic wave, such that also mildly relativistic electrons (of about 10-keV energy) can emit coherent Cerenkov radiation. Starting from spontaneous emission, the feedback of the radiation on the electrons results in bunching of the electrons on the scale of the radiation wavelength, and consequently, coherent radiation can build up. The frequency of the coherent mode is set by the electron velocity and wave dispersion of the photonic crystal and can, *a priori*, be continuously varied by varying the electron energy. The scale invariance of Maxwell's equation allows operation from Gigahertz to Terahertz and possible infrared (IR) frequencies without the need to increase the electron beam energy. Therefore, the pFEL is a very



news & views

X-RAY OPTICS

Highly efficient nanoscale X-ray sources

Irradiating arrays of metal nanowires with intense femtosecond laser pulses produces high-brightness picosecond X-ray pulses. By specifically tailoring the plasma properties, up to 20% conversion efficiency of optical light into X-rays can be achieved.

Daniel Rolles

When it comes to intense and short-pulse X-ray sources, much of the attention in recent years has focused on X-ray free-electron lasers[1,2] and high-harmonic-generation sources[3,4]. Rightfully so, since their extreme intensities of up to 10^{20} W cm^{-2} and their ultrashort pulses down to a few tens of attoseconds have enabled studies of light–matter interactions in regimes that had previously been far beyond reach[3,4], and have spurred the development of ground-breaking techniques such as serial femtosecond nanocrystallography[2].

However, there are many time-resolved X-ray imaging and spectroscopy applications that do not require such mind-boggling intensities nor few-femtosecond or even attosecond pulses, but would benefit from a compact and high-brightness picosecond X-ray source. This is where the recent work of Reed Hollinger and co-workers, reported in *Optica*, can play out its full potential[5]. By irradiating an array of metal nanowires with high-power femtosecond laser pulses, the team is able to generate extraordinarily bright picosecond X-ray pulses, overcoming previous limitations in the conversion efficiency of optical laser light into X-rays by specifically tailoring the plasma properties to favour X-ray emission over competing cooling processes.

Although various methods for generating X-ray pulses from dense plasmas produced by irradiating solids with intense femtosecond laser pulses have been studied for several decades, most schemes suffer from a very low conversion efficiency of optical laser light into X-rays. Typically, less than 0.1% of the laser energy impinging on the target is converted into X-ray photons with a photon energy of 1 keV or above. Even the use of nanostructured surfaces, such as arrays of metal clusters or nanowires, which increase the fraction of the laser energy that is absorbed by the plasma, could not increase the conversion efficiency beyond 1% due to the rapid expansion of the plasma and the associated hydrodynamic cooling[6].

Guided by detailed numeric modelling of the plasma formation and evolution, Hollinger et al. have now managed to

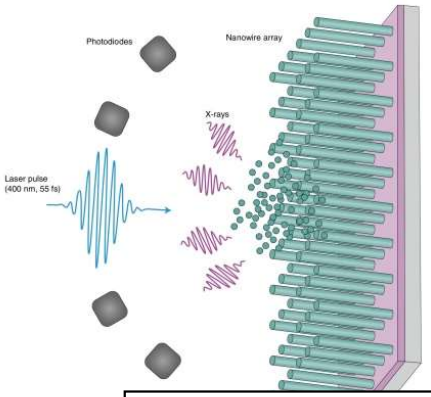


Fig. 1 | Generation of picosecon
irradiated by a 400-nm femtos
a short burst of X-rays that are
(not shown). Through an appro
of the laser pulse parameters, t
hydrodynamic cooling, thus inc
than one order of magnitude as

optimize the nanowire array
pulses to tailor the plasma p
such a way that they achieve
the conversion efficiency by
order of magnitude to about
experiment, an ultrahigh con
laser pulse with a pulse durat
a pulse energy up to 1 J was
array of free-standing, ver

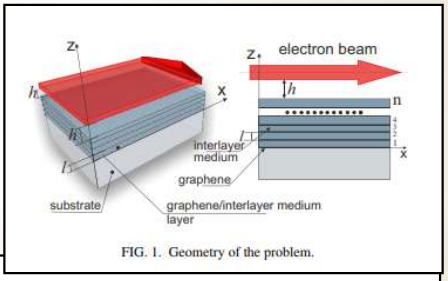


FIG. 1. Geometry of the problem.

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ELSEVIER

Toward the nano-FEL: Undulator and Cherenkov mechanisms of light emission in carbon nanotubes

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Available online 24 August 2007

*Prospects for VFEL

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Radical increase of the parametric X-ray intensity under condition of extremely asymmetric diffraction

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Extremely asymmetric diffraction

ABSTRACT

Parametric X-ray radiation (PXR) from relativistic electrons movi
interface is considered. In this geometry the emission of photons
asymmetric diffraction (EAD). In the EAD case the whole crystal
X-ray radiation opposed to Laue and Bragg geometries, where
X-ray absorption length. We demonstrate that this phenom
dynamical theory of diffraction and predict a radical increase o
realistic electron-beam parameters, an increase of two orders
be obtained in comparison with conventional experimental geo
in details the experimental feasibility of the detection of PXR-E

1. Introduction

Parametric X-ray radiation (PXR) occurs when a charged particle moves uniformly in a periodic medium [1,2] and possesses unique features such as high brightness, narrow spectral width and the possibility of tuning the X-ray frequency simply by rotating a crystal target. Moreover, PXR is emitted under a large angle with respect to the particle velocity and its brilliance is competitive with other X-ray sources, as already demonstrated experimentally [3]. Consequently, all these properties make it a suitable candidate for the development of novel-laboratory-compact X-ray sources with high brightness and tunable, quasi-monochromatic frequency.

angle to its surface, i.e., trar
according to kinematic model
is proportional to the smallest
tion L_{abs} lengths. In the X-ray
therefore in most cases $L_{abs} \ll$
of the electron trajectory cont

As was mentioned above,
with respect to the electron v
change the geometry of an e
entire crystal length will co
Accordingly, this will lead to
quanta in the PXR peak.

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Parametric X-ray radiation in the Smith-Purcell geometry for non-destructive beam diagnostics

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ARTICLE INFO

Keywords:
Parametric X-ray radiation
Smith-Purcell effect
Dynamical diffraction
Extremely asymmetric diffraction

ABSTRACT

We investigate parametric X-ray radiation (PXR) under condition of the extremely asymmetric diffraction, when the ultra-relativistic electron bunch is moving in *vacuum* parallel to the crystal-vacuum interface, close to the crystal surface. This type of geometry coincides with the well known mechanism of generation of radiation, when the self-field of the particle beam interacts with the reflecting metal grating, namely the Smith-Purcell effect. We demonstrate that in this geometry the main contribution is given via a tail region of the beam distribution, which penetrates the crystal and X-rays are radiated along the normal to the crystal surface. We determine the electron beam characteristics, when this phenomenon can be observed. It is essential that in this geometry the majority of electrons does not undergo multiple scattering and consequently the characteristics of the particle beam are not changed, thus allowing the usage of the emitted X-rays for the purpose of non-destructive beam diagnostics, which can complement the traditional knife-edge method.

1. Introduction

Parametric X-ray radiation (PXR) is generated when a charged particle moves uniformly in a periodic medium [1,2]. The typical property of this type of radiation is that it is emitted under the large angle to the velocity of the charged particle. In addition, it is characterized by high brightness, narrow spectral interval and possibility to uniformly tune the frequency of the radiated photons. Moreover, the intensity of radiation is relatively weakly dependent on the particle energy. Furthermore, the large angle of the emitted photons allows one to employ non-conventional geometries, which can lead to the improvements of the various characteristics of the emitted radiation [3].

Recently, it was demonstrated [4] that the intensity of the radiation can be significantly increased if the grazing geometry under condition of the extremely asymmetric diffraction of the emitted photons (PXR-EAD) is employed. However, in that case the electrons were moving *inside* a crystal, parallel to the crystal vacuum interface. Consequently, in that situation the effective length of the electron trajectory, which electrons exhibits moving inside the crystal.

For this reason, it is essential to investigate the geometry, in which the whole crystal length contributes to the intensity, but the limiting factor of multiple electron scattering is removed. The most natural way is to consider that the electron beam is moving *outside* of a crystal in vacuum, at a small distance to it, but still parallel to the crystal-vacuum interface. This geometry corresponds to the Smith-Purcell effect [5,6], but in the X-ray frequency range due to the parametric radiation mechanism (PXR-SPG). In this case the electronic density of a crystal corresponds to the metal surface grating, interaction with which generates the radiation in optical or microwave ranges [7,8] and for X-rays [9,10]. For this reason, the radiation field is formed due to the diffraction of the electron beam self-field on the periodic atomic density of the crystal. Consequently, the determination of the characteristics of PXR-SPG, the discussion of its possible observation and applications for the beam diagnostics [11] are the main goals of the present work.

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PHYSICS OF SOLID STATE AND CONDENSED MATTER

FLAP Collaboration: Tasks and Perspectives. Study of Fundamentals and New Applications of Controllable Generation of Electromagnetic Radiation by Relativistic Electrons Using Functional Materials

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Abstract—We present the scope of research of a new collaboration FLAP (Fundamental & applied Linear Accelerator Physics collaboration) devoted to the study of the basics of electromagnetic interactions and new applications of controllable generation of electromagnetic radiation by relativistic electrons using functional materials.

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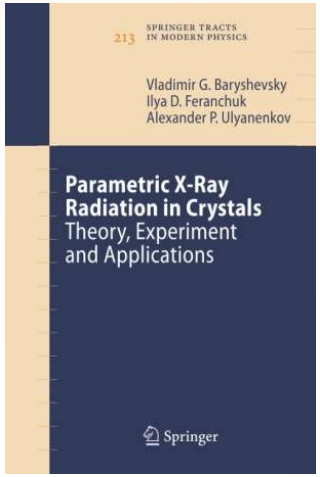

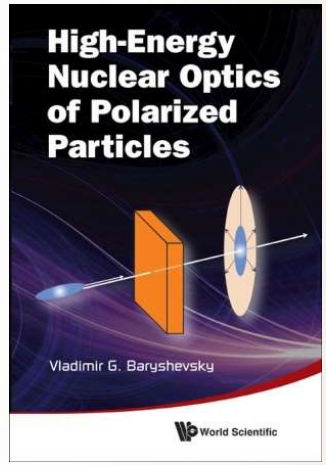

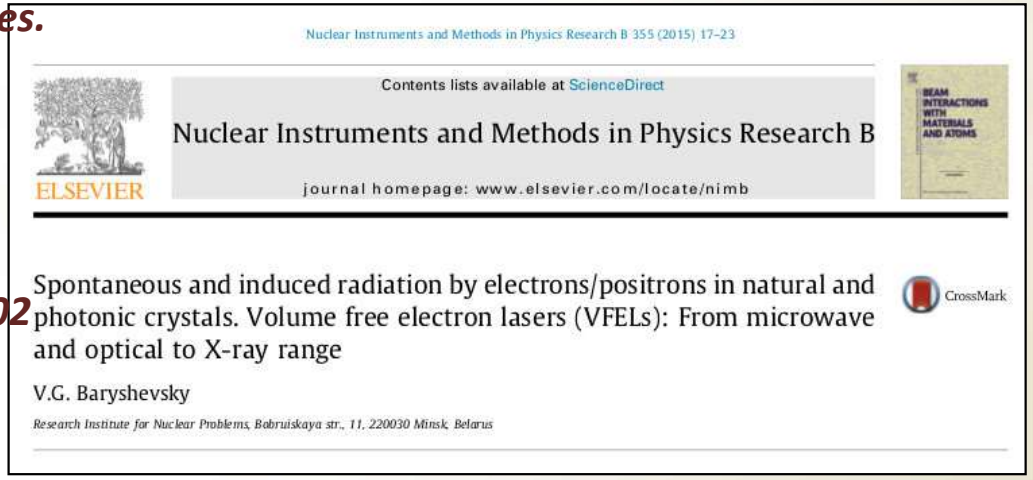
Nuclear Instruments and Methods in Physics Research B 355 (2015) 17–23

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ELSEVIER

Spontaneous and induced radiation by electrons/positrons in natural and photonic crystals. Volume free electron lasers (VFELs): From microwave and optical to X-ray range

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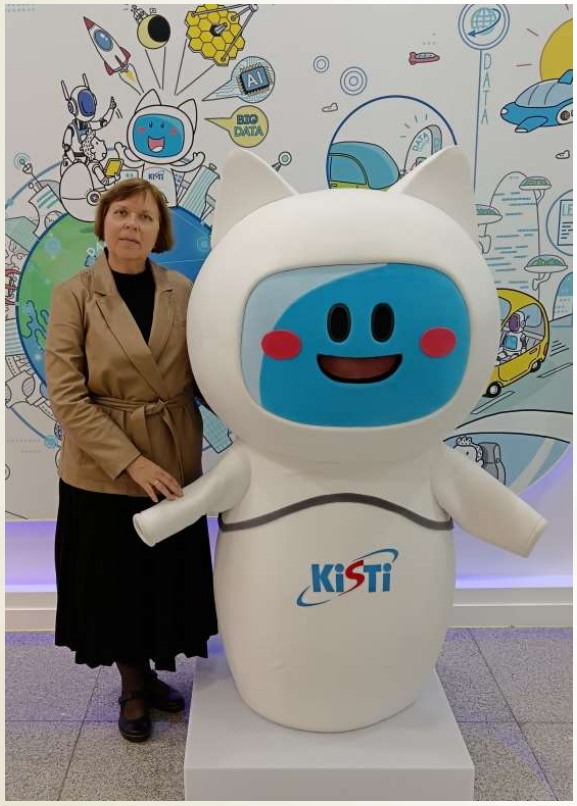
*VFEL last info

Supercomputing Center, Korean Institute of Science and Technology Information (KISTI), Daejeon, Oct. 23, 2023



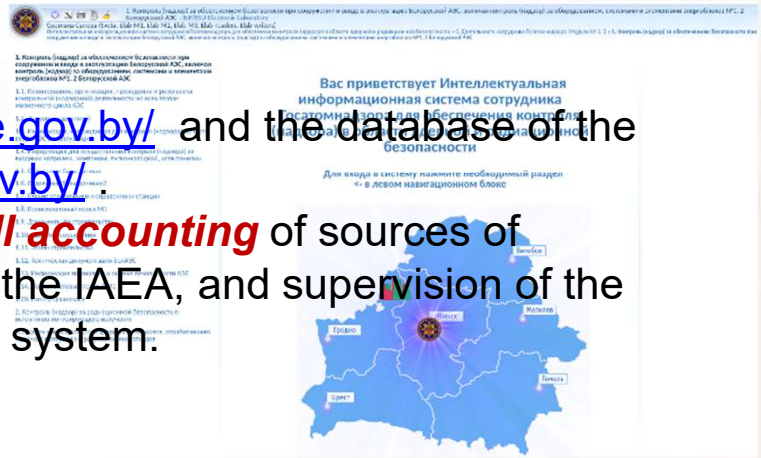
* Information technology based on free software

1. Development of electronic document management system of the testing laboratory (framework) ***eLab*** based on free software
2. Establishment of nuclear knowledge management system in the Republic of Belarus and development of Belarusian portal of nuclear knowledge BelNET (***Bel****arusian* ***N****uclear* ***E****ducation and* ***T****raining*) https://belnet.by/, https://belnet.bsu.by/, https://net.inpnet.net/

* Information technology based on free software

Intellectual information system of a Gosatomnadzor employee to ensure control (supervision) in the field of nuclear and radiation safety contains the following modules:

1. Module of control (supervision) over ensuring safety during the construction, commissioning and operation of the Belarusian NPP, including control (supervision) over the equipment, systems and elements of power units No. 1, 2 of the Belarusian NPP;
2. Module of control (supervision) over radiation safety of ionizing radiation sources;
3. Module for accounting and control of nuclear materials, radioactive waste and spent nuclear material;
4. Module "General information and auxiliary tools ".



The system is connected to the Unified Register of Licenses https://license.gov.by/ and the database of the Ministry of Taxes and Duties of the Republic of Belarus http://nalog.gov.by/ .

At present, in the Republic of Belarus at the level of the regulatory body, ***all accounting*** of sources of ionizing radiation, ***all accounting*** of nuclear material with reporting to the IAEA, and supervision of the construction of the Belarusian NPP are carried out with the help of the system.

* Information technology based on free software

Framework **eLab** is a client-server architecture system running undo Windows and Linux operating systems, based on free software:

- Debian GNU / Linux
- Apache web-server
- Firebird database server
- PHP application server.

It works through the Web interface in multi-user mode with shared access rights through any browsers: Mozilla Firefox, Google Chrome, Opera, etc.

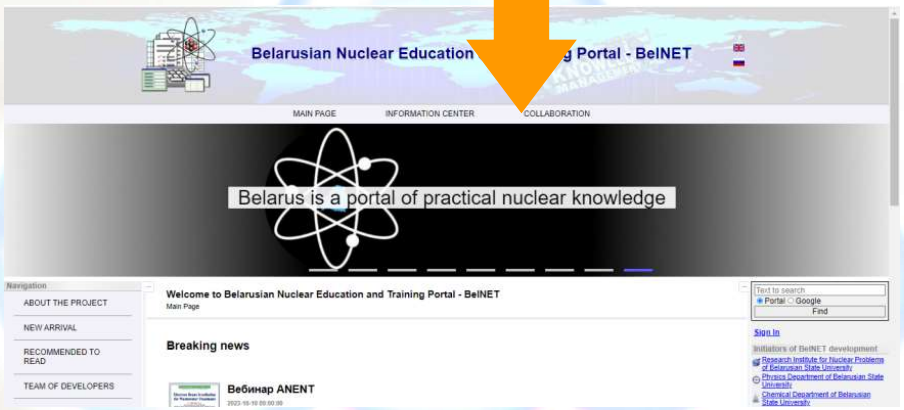
* Information technology based on free software

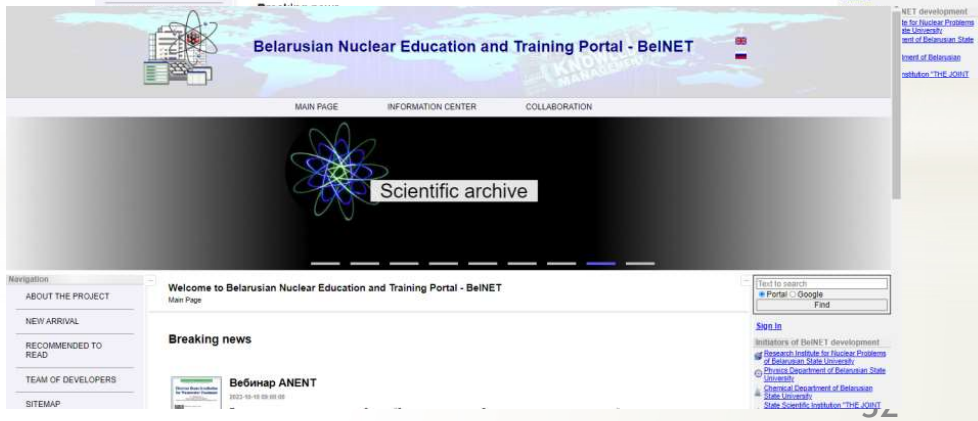
Steps in eLab development:

2010 – eLab is implemented in the educational process of Belarusian State University, Belarusian State Technological University, Belarusian National Technical University, in the Chemical-toxicological, laboratory of the Minsk Drug Treatment Clinic.
2012 – Commissioning of eLab-Fuel in 202 Chemmotology Center of the Fuel for quality monitoring and management of specimens, measurements and passports of fuels and lubricants of the Belarusian Armed Forces.
2013 – Commissioning of eLab-Fuel in Belarusian branch of company GazPromNeft.
2014 – Software eLab-Atom for control of ionizing radiation sources
2015 – Developed CMS eLab-Science
2015 – Portal of nuclear knowledge BelNET https://belnet.bsu.by,
2017 – Portal of the project of Programme Horizon2020 Coexan https://coexan.bsu.by
2018 – Software eLab-Control for Intellectual information system of the Gosatomnadzor employee to ensure control (supervision) in the field of nuclear and radiation safety
2019 – Scientific portal https://elab.bsu.by/
2021 – Start of work on development of nuclear knowledge management system in Belarus and futher development of portal BelNET https://belnet.by/

* BelNET is a repository of nuclear knowledge of Belarus

https://belnet.by/





Methods of quality control of alcohol and alcohol-containing products

Absinthe drinkers by ChatGPT

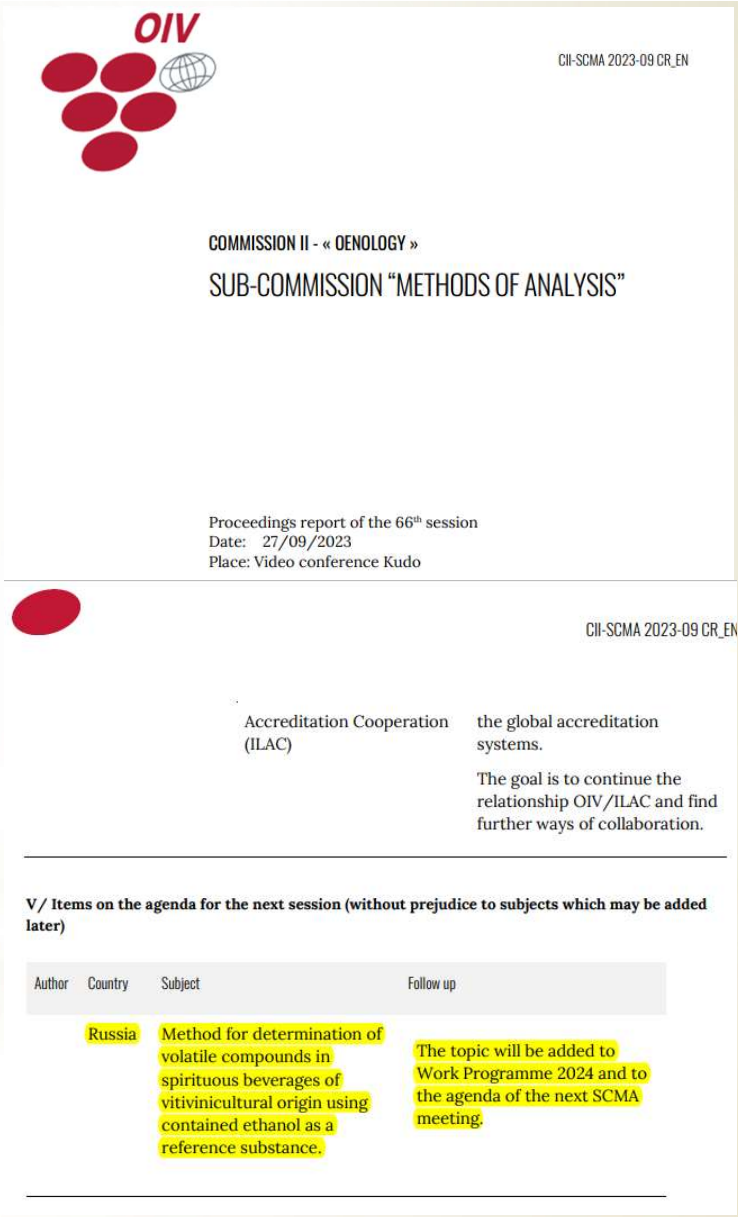
Methods of quality control of alcohol and alcohol-containing products

66th Session of the Sub-Commission Methods of Analysis

Proposal of the Russian Federation for new work on

«Method for determination of volatile compounds in spirituous beverages of vitivinicultural origin using contained ethanol as a reference substance»

Project presentation
Wednesday 27th of September 2023



OIV

CII-SCMA 2023-09 CR_EN

COMMISSION II - « OENOLOGY »

SUB-COMMISSION "METHODS OF ANALYSIS"

Proceedings report of the 66th session
Date: 27/09/2023
Place: Video conference Kudo

CII-SCMA 2023-09 CR_EN

Accreditation Cooperation (ILAC) | the global accreditation systems.

The goal is to continue the relationship OIV/ILAC and find further ways of collaboration.

V/ Items on the agenda for the next session (without prejudice to subjects which may be added later)

Author	Country	Subject	Follow up
	Russia	Method for determination of volatile compounds in spirituous beverages of vitivinicultural origin using contained ethanol as a reference substance.	The topic will be added to Work Programme 2024 and to the agenda of the next SCMA meeting.

Current status:
OIV, Regional & National Methods for the Determination of Volatile Compounds in Spirituous Beverages of vitivinicultural origin

OIV-MA-AS312-03A:R2015
OIV-MA-BS-14:R2009
OIV-MA-AS315-27:R2016

Commission Regulation (EC) No. 2870/2000

GB/T 11858-2009
GB/T 15038-2008
GB 5009.266-2016
GB/T 10781-2021

BIS IS 3752:2005(R2009)

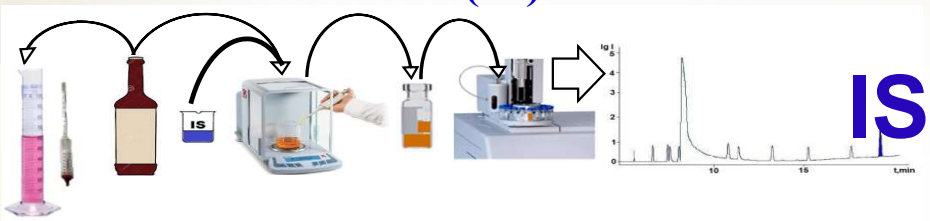
Norma Mexicana
NMX-V-005-NORMEX-2018

AOAC Official Methods
972.10/11, 2005

- In the vast majority of countries, the determination of the content of volatile components in alcoholic beverages is carried out using gas chromatographs with a flame ionization detector (GC-FID)
- Quantitative calculation of the concentrations of volatile components is carried out using the traditional internal standard (IS) method
- This method was adopted in the European Union as official EC 2870/2000 based on the results of an interlaboratory study carried out in 1999 with wide international participation
- The traditional internal standard requires a manual procedure for adding an internal standard substance to the test sample
- In order *to eliminate the manual procedure (1)* for introducing an internal standard substance into the test sample, *to increase the reliability of the experimental data obtained (2)*, *to reduce the cost (3)* and *reduce the analysis time (4)*, a new method using ethyl alcohol as a reference substance directly contained in analyzed samples, is proposed

Background & Differences

Internal Standard Method (IS)

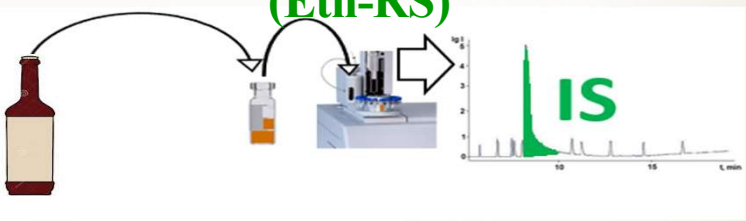


1 2 3 4 5 - operations

- In accordance with the traditional IS method the concentration of the *i*-th component in terms of mg/kg is determined by the following formula: $C_i(\text{mg/kg}) = RRF_i^{IS} \cdot \frac{A_i}{A_{IS}} \cdot C_{IS}(\text{mg/kg})$
- The values of the relative response factors RRF of the detector to the analyzed volatile compound relative to the response to the selected internal standard are calculated using the following formula: $RRF_i^{IS} = \frac{C_i^{calibr}(\text{mg/kg})}{C_{IS}^{calibr}(\text{mg/kg})} \cdot \frac{A_{IS}^{calibr}}{A_i^{calibr}}$
- To calculate the concentration of the component, expressed in mg/L AA, it is necessary to measure the density of the sample and determine its strength (volume content of ethanol):

$$C_i(\text{mg/L } AA) = RRF_i^{IS} \cdot \frac{A_i}{A_{is}} \cdot C_{IS}(\text{mg/kg}) \cdot \frac{\rho_{sample}(\text{kg/L}) \cdot 100\ \%}{\text{"Strength" } (\%,\ ABV)}$$

New method with Ethanol as a Reference Substance (Eth-RS)



2 5 - operations

- In accordance with new method «Ethanol as a reference Substance» (Eth-RS), the concentration of the *i*-th compound in the dimension mg/L of anhydrous alcohol (AA) is determined by the following formula: $C_i(\text{mg/L } AA) = RRF_i^{Eth} \cdot \frac{A_i}{A_{Eth}} \cdot \rho_{Eth}(\text{mg/L})$
- The values of the relative response factors RRF of the detector to the analyzed volatile compound relative to the response to ethanol are calculated using the following formula: $RRF_i^{Eth} = \frac{C_i^{calibr}(\text{mg/L } AA)}{\rho_{Eth}(\text{mg/L})} \cdot \frac{A_{Eth}^{calibr}}{A_i^{calibr}}$
- Ethanol is always present in alcoholic products and its concentration in mg/L AA is always known with a 100% guarantee and is equal to the density of ethanol $\rho_{Eth} = 789270$ mg/L
- There is no need to add any internal standard to the sample
- There is no need to determine density of the sample and its strength

New method – New possibilities:
Easier, cheaper, trust & robust measurements

Internal Standard Method (IS)

250 mL

determine volume ethanol content

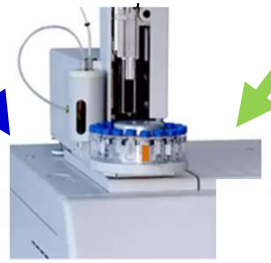
100 mL

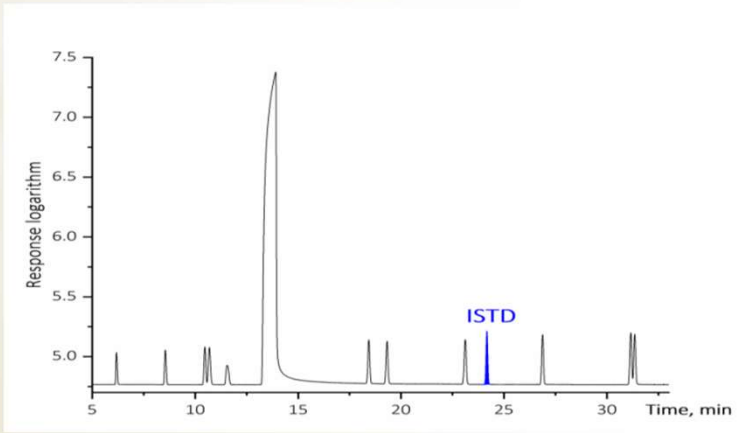
1.0 mL

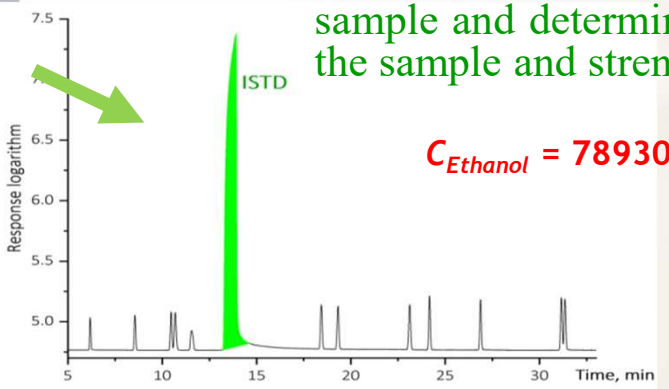
add Internal Standard

1.5 mL

1.5 mL







New Method (Eth-RS)

- The equipment and reagents for preparing calibration mixtures are the same as in the current OIV regulations and in regional & national standards of wine producing countries
- The main difference and advantage of the proposed method is that there is no need to introduce a separate reference substance into the analyzed sample and determine density of the sample and strength.

$C_{Ethanol}$ = 789300 mg/L AA

New method's application: Determination of aldehydes, esters, methanol and higher alcohols in different beverages

Result for	 40 % ABV	 40 % ABV	 43 % ABV	 40 % ABV	 40 % ABV	 40 % ABV	 40 % ABV	 47 % ABV	 45 % ABV
	Rum	Whiskey	Bourbon	Grain spirit	Brandy	Grappa	Calvados	Gin	Slivovice
IS-Method, mg/L AA	48.1 / 145 / 1043 / 22.2	162 / 589 / 6693 / 132	150 / 645 / 5546 / 88.4	44.0 / 84.7 / 4662 / 110	143 / 396 / 4801 / 297	191 / 289 / 2113 / 414	182 / 583 / 3690 / 910	1.70 / 0 / 1.54 / 4.16	210 / 907 / 6255 / 10546
Eth-RS-Method, mg/L AA	48.4 / 146 / 1051 / 22.3	160 / 584 / 6635 / 130	151 / 649 / 5580 / 88.9	44.4 / 85.4 / 4703 / 111	142 / 396 / 4794 / 297	190 / 288 / 2100 / 412	182 / 585 / 3702 / 913	1.72 / 0 / 1.55 / 4.19	211 / 912 / 6288 / 10603
Δ, %	0.7 / 0.7 / 0.7 / 0.7	-0.9 / -0.9 / -0.9 / -0.9	0.6 / 0.6 / 0.6 / 0.6	0.9 / 0.9 / 0.9 / 0.9	-0.2 / -0.2 / -0.2 / -0.2	-0.6 / -0.6 / -0.6 / -0.6	0.3 / 0.3 / 0.3 / 0.3	0.8 / - / 0.9 / 0.9	0.5 / 0.5 / 0.5/ 0.5
Result for	 38 % ABV	 14.5 % ABV	 38 % ABV	 15 % ABV	 18 % ABV	 8.5 % ABV	 70 % ABV	 27.5 % ABV	 40 % ABV
	Tsikoudia	Sake	Tequila	Vermouth	Nalewka	Mulled wine	Rectified spirit	Cocktail	Vodka
IS-Method, mg/L AA	356 / 266 / 2297 / 755	37.6 / 47.0 / 1367 / 18.2	34.8 / 126 / 2895 / 1456	30.5 / 0 / 5.94 / 17.5	47.4 / 74.4 / 10.3 / 168	22.7 / 55.9 / 871 / 25.3	4.83 / 25.2 / 0 / 6.05	61.9 / 84.0 / 728 / 77.3	0.504 / 0 / 0 / 21.8
Eth-RS-Method, mg/L AA	359 / 268 / 2316 / 761	37.2 / 46.5 / 1352 / 18.1	34.9 / 127 / 2904 / 1460	30.6 / 0 / 5.98 / 17.6	47.8 / 75.1 / 10.4 / 169	22.5 / 55.6 / 866 / 25.1	4.81 / 25.1 / 0 / 6.03	61.1 / 83.0 / 719 / 76.3	0.50 / 0 / 0 / 21.7
Δ, %	0.9 / 0.8 / 0.9 / 0.9	-1.1 / -1.1 / -1.1 / -1.1	0.4 / 0.3 / 0.3 / 0.3	0.6 / - / 0.6 / 0.6	0.9 / 0.9 / 0.9 / 0.9	-0.6 / -0.5 / -0.6 / -0.6	-0.4 / -0.4 / - / -0.4	-1.3 / -1.2 / -1.2 / -1.2	-0.7 / - / - / -0.7
Result for	 38 % ABV	 17 % ABV	 35 % ABV	 25 % ABV	 16 % ABV	 16.5 % ABV	 35 % ABV	 40 % ABV	 56 % ABV
	Liqueurs								
	Sambuca	Egg	Herbal	Limon	Cherry	Raspberry	Sloe gin	Rakia	Baijiu
IS-Method, mg/L AA	4.20 / 0 / 2.44 / 2.32	6.89 / 0 / 125 / 9.75	38.1 / 13.5 / 9.39 / 19.5	25.1 / 0 / 0 / 29.1	18.4 / 266 / 0 / 9.77	36.6 / 31.8 / 0 / 127	1.12 / 0 / 0 / 20.5	92.2 / 1334 / 6165 / 11862	63.9 / 1072 / 2114 / 115
Eth-RS-Method, mg/L AA	4.24 / 0 / 2.46 / 2.34	6.94 / 0 / 125 / 9.81	38.2 / 13.5 / 9.43 / 19.6	25.3 / 0 / 0 / 29.4	18.5 / 267 / 0 / 9.82	36.2 / 31.5 / 0 / 126	1.13 / 0 / 0 / 20.7	91.6 / 1325 / 6217 / 11791	64.3 / 1079 / 2128 / 116
Δ, %	0.8 / - / 0.8 / 0.8	0.8 / - / 0.7 / 0.7	0.4 / 0.4 / 0.4 / 0.4	0.8 / - / - / 0.8	0.5 / 0.6 / - / 0.5	-1.0 / -1.1 / - / -1.1	0.6 / - / - / 0.6	0.6 / 0.7 / 0.6 / 0.6	0.6 / 0.6 / 0.6 / 0.6

The relative difference between obtained values of concentrations (Δ, %) measured according to the IS-Method (EC 2870/2000) and new Eth-RS-Method method does not exceed 1.5 %

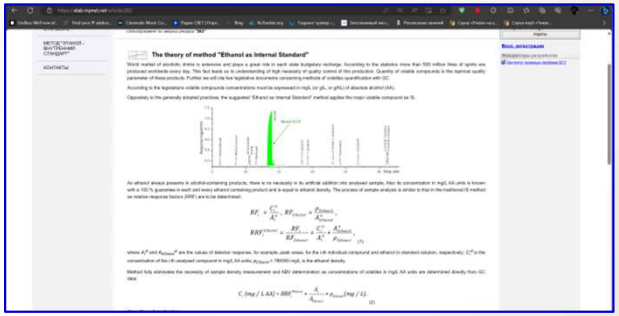
* New Method's Validations: single- and interlaboratory tests

- **Results of the single-laboratory validation** (published in Journal of AOAC International, 2019.- Vol. 102.- No. 2.- P. 669-672 (doi:10.5740/jaoacint.18-0258).
- **Short description of the validation's procedure:** ***(1) Conditions*** *- 7 standard solutions of the following volatile compounds were prepared gravimetrically in 40% (v/v) water-ethanol solution: acetaldehyde, methyl acetate, ethyl acetate, methanol, 2-propanol, 1-propanol, isobutanol, 1-butanol, and isoamylol. Each sample was measured with the proposed method 30 times in repeatability conditions;* ***(2) Results*** *- FID-response was linearly correlated with assigned concentrations at a range of 2 to 5000 mg/L of absolute alcohol (AA) with coefficients of determination (R2) more than 0.995 for all analyzed components. Repeatability (RSDr ≤ 4.5%; RSDr ≤ 2.0%), reproducibility (RSDR ≤ 5.0%; RSDR ≤ 2.0%), and trueness (relative bias ≤ 2.6%; relative bias ≤ 1.4%) were obtained for low (10-25 mg/L AA for methanol and 2-10 for other volatiles) and high (25-5000 mg/L AA for methanol and 10-5000 for other volatiles) ranges of concentrations, correspondingly;* ***(3) Conclusions*** *- the method increases the reliability of measurements and eliminates manual procedures of internal standard addition into both calibration standard solutions and spirit drinks;* ***(4) Possibilities for additional validations*** *- in addition, the following example of method validation based on interlaboratory tests can also be given. Regularly, twice a year, the Bureau National Interprofessionnel du Cognac (BNIC) carries out interlaboratory comparisons for the quality control of cognac and brandy, in which more than 15 profile laboratories take part.*
- **Results of the interlaboratory test** (published in BIO WEB of Conferences, 2019.- V. 15.- 8 pages (https://doi.org/10.1051/bioconf/20191502030).
- **Short description of the validation's procedure:** ***(1) Conditions*** *- in this study 9 laboratories from 4 different countries were supplied with standard solutions for gas chromatographic measurements. Five aqueous ethanol 40% (v/v) standard solutions containing target compounds in concentrations ranging from 10 mg/L to 400 mg/L of absolute alcohol were prepared and sent to the participants for quantification of acetaldehyde, methyl acetate, ethyl acetate, methanol, 2-propanol, 1-propanol, 2-methyl-1-propanol, 1-butanol and 3-methyl-1-butanol. The interlaboratory validation was evaluated according to the ISO 5725 standards and the Eurachem guide;* ***(2) Results & conclusions -*** *the within-laboratory precision varied between 0.4% and 7.5% for all samples and compounds, showing a sufficiently high repeatability of the method. The between-laboratory precision was found to vary within a satisfactory range of 0.5% ÷ 10.0%. Precision of the method was well within the range predicted by the Horwitz equation for all analytes. The analysis of trueness showed that the bias of the method is insignificant at the significance level a = 5%.*
- **Results of additional validations:** ILIADe 453:2021 | CLEN Method. *Determination of Isopropyl Alcohol and Methyl Ethyl Ketone in Alcoholic Products by GC-FID [Electronic resource]. - 2021 (link for download: https://taxation-customs.ec.europa.eu/system/files/2022-02/ILIADe453_IPA%26MEK_v2Feb2021.pdf).*

* New method: information support - papers, reviews, reports & communications at the OIV World Congresses, trainings videos & materials

- Journal of Agricultural and Food Chemistry, 2013. -Vol. 61. - No.12. - P. 2950-2956 (doi: 10.1021/jf3044956)
- Journal of Chemical Metrology, 2018. - Vol. 12. - No.1. - P. 59-69 (doi:10.25135/jcm.14.18.02.063)
- Food Control, 2021. - Vol. 120 - P. 107528 (doi: 10.1016/j.foodcont.2020.107528)
- Food Analytical Methods, 2021 (doi: 10.1007/s12161-021-02047-8)
- Journal of Food Composition and Analysis, 2022. - Vol. 114. - 104772 (doi: 10.1016/j.jfca.2022.104772)
- Journal of Food Composition and Analysis, 2023. - Journal of Food Measurement and Characterization (doi: 10.1007/s11694-023-01868-x)
- 42nd & 44th OIV World Congresses of Vine and Wine, 2019, 2023
- Several training materials were prepared on the official method website elab.inpnet.net: (a) https://elab.inpnet.net/article/282 -theoretical background; (b) https://elab.inpnet.net/article/430 - Development of the method for determination of volatile compounds in spirituous beverages of vitivinicultural origin using contained ethanol as a reference substance; (c) https://elab.inpnet.net/article/788 -about the method - video; (d) https://elab.inpnet.net/article/430 - practical recommendations for «Agilent Chemstation»

elab.inpnet.net



* New method: application in research

CHARLES UNIVERSITY

Faculty of Science

Study programme: Analytical chemistry

Anton Korban, M.Sc.

Development and metrological evaluation of gas chromatographic methods for quality and safety control of alcoholic products

Vývoj a metrologické hodnocení metod plynové chromatografie pro kontrolu kvality a bezpečnosti alkoholických výrobků

Doctoral thesis

Supervisor: Assoc. Prof. Radomír Čabala, Ph.D.

Prague, 2022

R. JELÍNEK

Original Czech Distilleries

Vážený pan
Prof. RNDr. Jiří Zima, CSc.
Děkan
Přírodovědecká fakulta University Karlovy
Albertov 6
128 43 PRAHA 2

Ve Vizovicích 26.11.2021

Věc: Poděkování za spolupráci – Anton Korban

Vážený pane děkane!

Chtěl bych Vás alespoň touto cestou informovat o spolupráci, kterou jsme navázali s jedním z Vašich studentů doktorského studia panem Antonem Korbanem a současně Vám moc poděkovat za podporu, kterou této spolupráci jako škola poskytujete.
Naše společnost RUDOLF JELÍNEK a.s. je největším světovým výrobcem ovocných destilátů. Jistě si dovedete představit kolik různých faktorů potřebujeme v naší závodní laboratoři analyzovat a upřímně, naše kapacity jsou omezené. Máme k dispozici plynový chromatograf, ale nemáme kapacitu na to, abychom vyvíjeli různé metodiky pro stanovení různých sloučenin v našich destilátech. A tak jsme se něco více než před rokem spojili s Vaším studentem Antonem Korbanem a domluvili se s ním, že by nám v tom mohl pomoci.
Zavedli jsme s jeho pomocí metodu na stanovení těkavých látek v našich destilátech, kterou téměř denně používáme a velmi nám usnadnila každodenní život. To, co hlavně oceňujeme na Antonovi je jeho pracovitost, cílevědomost a ohromná snaha nám vždycky pomoci. Anton byl už i u nás ve Vizovicích, a tak jsme měli možnost detailně pochopit zavedenou metodu a úspěšně ji aplikovat v praxi. Od té doby už jsme udělali jistě několik desítek či stovek analýz, což nám moc pomáhá i v kontrole naší technologie. Nyní bychom rádi ve spolupráci pokračovali, chceme vyvinout přesnější metodu na stanovení ethylkarbamátu a některých dalších, zejména aromatických látek.
Chtěl jsem Vám o všem tomto napsat, protože velice oceňuji, že jsme našli někoho, kdo nám pomáhá přímo v praxi konkrétními činy.
Ještě jednou moc děkuji a věřím, že i v budoucnu podpoříte naši spolupráci.

S úctou,

Ing. Vladimír Darebník
prokurista

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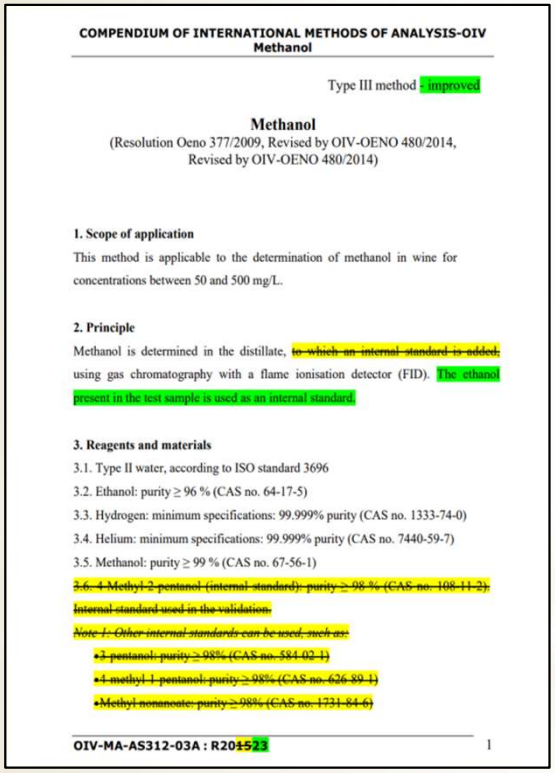
* New method: main advantages

- There is no need to purchase an internal standard reagent
- There is no need for a manual procedure for quantitative addition of an internal standard substance to the analyzed samples and standard mixtures
- A GC-chromatograph equipped with a FID-detector from any manufacturer can be used
- Uncertainty of the concentration of the reference substance is zero (concentration of ethyl alcohol expressed as *«mg per liter of anhydrous ethanol»*)
- The relative response factors RRF of the detector response to the volatile compound relative to the detector response to ethanol RRF, which determine the calibration characteristic of the GC for the proposed method, can be tabulated, which makes it possible to significantly increase the time interval between calibrations
- There is no need to determine strength of the sample
- There is no need to determine density of the sample
- General result - the determination of the quantitative content of volatile components in alcoholic products becomes *(1) more reliable*, *(2) cheaper*, *(3) faster*, *(4) simpler & (5) more robust*

OIV-MA-AS312-03A - simplification
Methanol



COMPENDIUM OF INTERNATIONAL METHODS OF ANALYSIS-OIV
Methanol

Type III method - improved

Methanol
(Resolution Oeno 377/2009, Revised by OIV-OENO 480/2014,
Revised by OIV-OENO 480/2014)

1. Scope of application

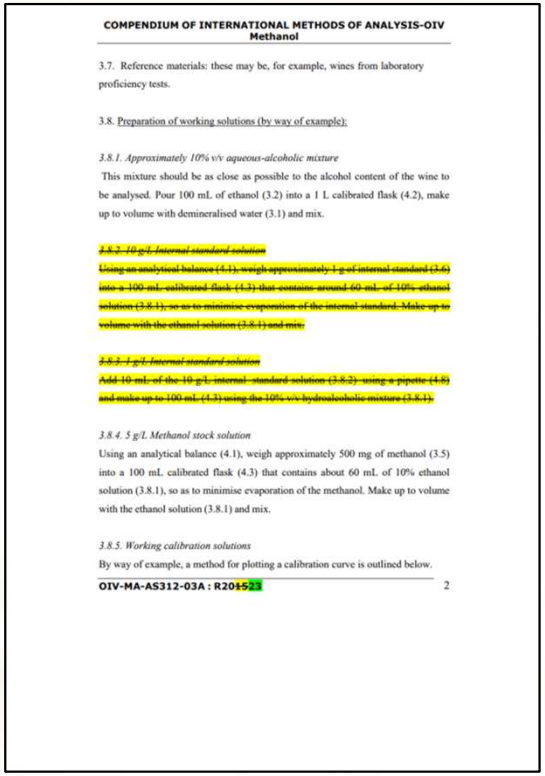
This method is applicable to the determination of methanol in wine for concentrations between 50 and 500 mg/L.

2. Principle

Methanol is determined in the distillate, ~~to which an internal standard is added,~~ using gas chromatography with a flame ionisation detector (FID). The ethanol present in the test sample is used as an internal standard.

3. Reagents and materials

3.1. Type II water, according to ISO standard 3696
3.2. Ethanol: purity ≥ 96 % (CAS no. 64-17-5)
3.3. Hydrogen: minimum specifications: 99.999% purity (CAS no. 1333-74-0)
3.4. Helium: minimum specifications: 99.999% purity (CAS no. 7440-59-7)
3.5. Methanol: purity ≥ 99 % (CAS no. 67-56-1)
~~3.6. 4-Methyl-2-pentanol (internal standard): purity ≥ 98 % (CAS no. 108-11-2), Internal standard used in the validation.~~
~~*Note 1: Other internal standards can be used, such as:*~~
- ~~2-pentanol: purity ≥ 98% (CAS no. 584-02-1)~~
- ~~4-methyl-1-pentanol: purity ≥ 98% (CAS no. 626-89-1)~~
- ~~Methyl-nonanoate: purity ≥ 98% (CAS no. 1731-84-6)~~



3.7. Reference materials: these may be, for example, wines from laboratory proficiency tests.

3.8. Preparation of working solutions (by way of example):

3.8.1. Approximately 10% v/v aqueous-alcoholic mixture

This mixture should be as close as possible to the alcohol content of the wine to be analysed. Pour 100 mL of ethanol (3.2) into a 1 L calibrated flask (4.2), make up to volume with demineralised water (3.1) and mix.

~~*3.8.2. 10 g/L Internal standard solution*~~
~~Using an analytical balance (4.1), weigh approximately 1 g of internal standard (3.6) into a 100 mL calibrated flask (4.3) that contains around 60 mL of 10% ethanol solution (3.8.1), so as to minimise evaporation of the internal standard. Make up to volume with the ethanol solution (3.8.1) and mix.~~

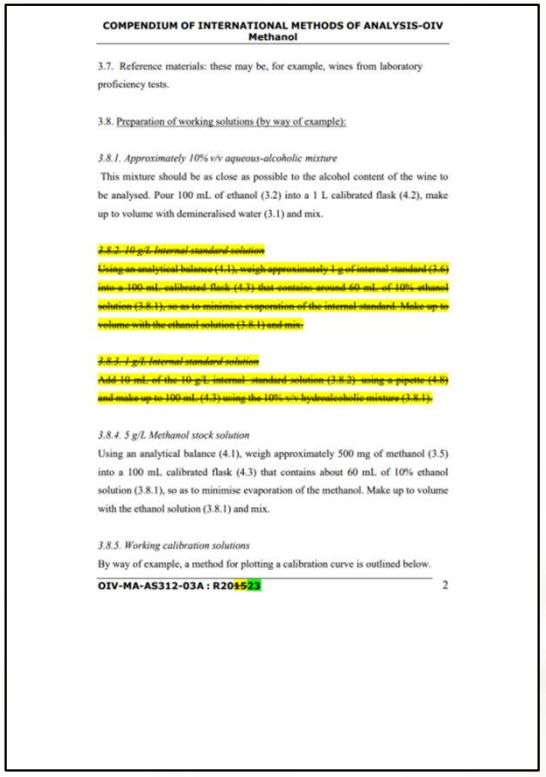
~~*3.8.3. 1 g/L Internal standard solution*~~
~~Add 10 mL of the 10 g/L internal standard solution (3.8.2) using a pipette (4.8) and make up to 100 mL (4.3) using the 10% v/v hydroalcoholic mixture (3.8.1).~~

3.8.4. 5 g/L Methanol stock solution

Using an analytical balance (4.1), weigh approximately 500 mg of methanol (3.5) into a 100 mL calibrated flask (4.3) that contains about 60 mL of 10% ethanol solution (3.8.1), so as to minimise evaporation of the methanol. Make up to volume with the ethanol solution (3.8.1) and mix.

3.8.5. Working calibration solutions

By way of example, a method for plotting a calibration curve is outlined below.



3.7. Reference materials: these may be, for example, wines from laboratory proficiency tests.

3.8. Preparation of working solutions (by way of example):

3.8.1. Approximately 10% v/v aqueous-alcoholic mixture

This mixture should be as close as possible to the alcohol content of the wine to be analysed. Pour 100 mL of ethanol (3.2) into a 1 L calibrated flask (4.2), make up to volume with demineralised water (3.1) and mix.

~~*3.8.2. 10 g/L Internal standard solution*~~
~~Using an analytical balance (4.1), weigh approximately 1 g of internal standard (3.6) into a 100 mL calibrated flask (4.3) that contains around 60 mL of 10% ethanol solution (3.8.1), so as to minimise evaporation of the internal standard. Make up to volume with the ethanol solution (3.8.1) and mix.~~

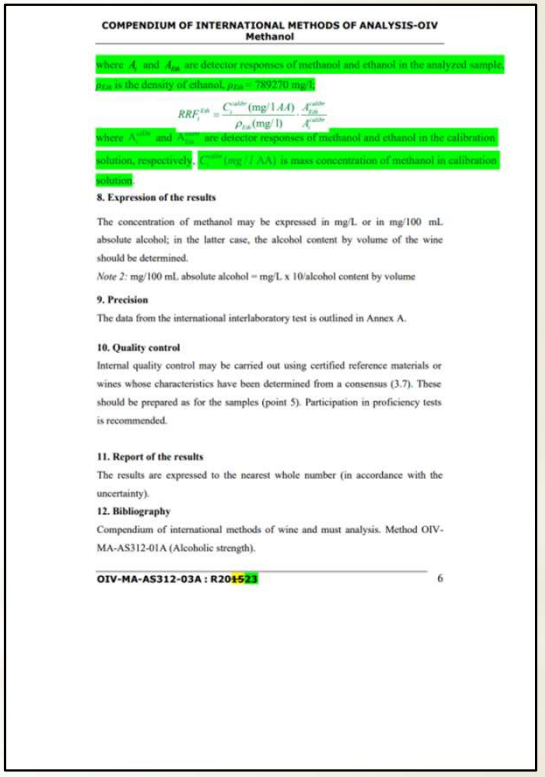
~~*3.8.3. 1 g/L Internal standard solution*~~
~~Add 10 mL of the 10 g/L internal standard solution (3.8.2) using a pipette (4.8) and make up to 100 mL (4.3) using the 10% v/v hydroalcoholic mixture (3.8.1).~~

3.8.4. 5 g/L Methanol stock solution

Using an analytical balance (4.1), weigh approximately 500 mg of methanol (3.5) into a 100 mL calibrated flask (4.3) that contains about 60 mL of 10% ethanol solution (3.8.1), so as to minimise evaporation of the methanol. Make up to volume with the ethanol solution (3.8.1) and mix.

3.8.5. Working calibration solutions

By way of example, a method for plotting a calibration curve is outlined below.



where A_i and A_{Eth} are detector responses of methanol and ethanol in the analyzed sample, ρ_{Eth} is the density of ethanol, ρ_{Eth} = 789270 mg/L

$$RRF_i^{Eth} = \frac{C_i^{calib}(\text{mg/l AA})}{\rho_{Eth}(\text{mg/l})} \cdot \frac{A_{Eth}^{calib}}{A_i^{calib}}$$

where A_i^{calib} and A_{Eth}^{calib} are detector responses of methanol and ethanol in the calibration solution, respectively, C_i^{calib} (mg / l AA) is mass concentration of methanol in calibration solution.

8. Expression of the results

The concentration of methanol may be expressed in mg/L or in mg/100 mL absolute alcohol; in the latter case, the alcohol content by volume of the wine should be determined.

Note 2: mg/100 mL absolute alcohol = mg/L x 10/alcohol content by volume

9. Precision

The data from the international interlaboratory test is outlined in Annex A.

10. Quality control

Internal quality control may be carried out using certified reference materials or wines whose characteristics have been determined from a consensus (3.7). These should be prepared as for the samples (point 5). Participation in proficiency tests is recommended.

11. Report of the results

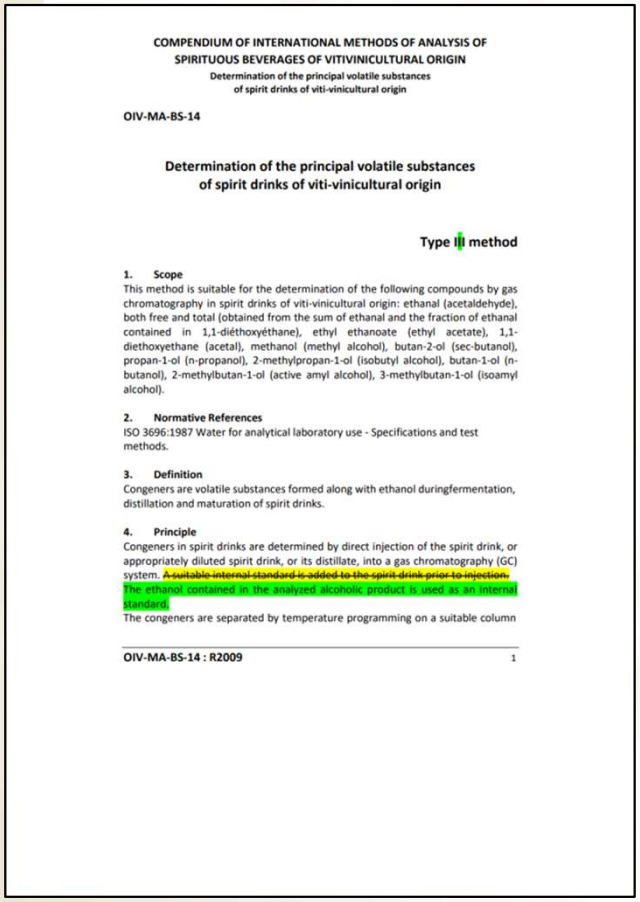
The results are expressed to the nearest whole number (in accordance with the uncertainty).

12. Bibliography

Compendium of international methods of wine and must analysis. Method OIV-MA-AS312-01A (Alcoholic strength).

OIV-MA-BS-14 - simplification

Determination of the principal volatile substances of spirit drinks of viti-vinicultural origin



COMPENDIUM OF INTERNATIONAL METHODS OF ANALYSIS OF SPIRITUOUS BEVERAGES OF VITIVINICULTURAL ORIGIN

Determination of the principal volatile substances of spirit drinks of viti-vinicultural origin

OIV-MA-BS-14

Determination of the principal volatile substances of spirit drinks of viti-vinicultural origin

Type III method

1. Scope

This method is suitable for the determination of the following compounds by gas chromatography in spirit drinks of viti-vinicultural origin: ethanal (acetaldehyde), both free and total (obtained from the sum of ethanal and the fraction of ethanal contained in 1,1-diéthoxyéthane), ethyl ethanoate (ethyl acetate), 1,1-diethoxyethane (acetal), methanol (methyl alcohol), butan-2-ol (sec-butanol), propan-1-ol (n-propanol), 2-methylpropan-1-ol (isobutyl alcohol), butan-1-ol (n-butanol), 2-methylbutan-1-ol (active amyl alcohol), 3-methylbutan-1-ol (isoamyl alcohol).

2. Normative References

ISO 3696:1987 Water for analytical laboratory use - Specifications and test methods.

3. Definition

Congeners are volatile substances formed along with ethanol duringfermentation, distillation and maturation of spirit drinks.

4. Principle

Congeners in spirit drinks are determined by direct injection of the spirit drink, or appropriately diluted spirit drink, or its distillate, into a gas chromatography (GC) system. A suitable internal standard is added to the spirit drink prior to injection. The ethanol contained in the analyzed alcoholic product is used as an internal standard.

The congeners are separated by temperature programming on a suitable column

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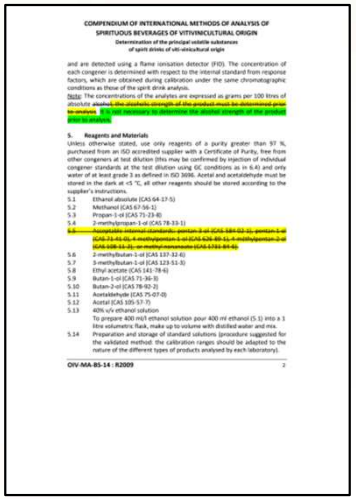

COMPENDIUM OF INTERNATIONAL METHODS OF ANALYSIS OF SPIRITUOUS BEVERAGES OF VITIVINICULTURAL ORIGIN

Determination of the principal volatile substances of spirit drinks of viti-vinicultural origin

and are detected using a flame ionisation detector (FID). The concentration of each congener is determined with respect to the internal standard from response factors, which are obtained during calibration under the same chromatographic conditions as those of the spirit drink analysis.

Note: The concentrations of the analytes are expressed as grams per 100 litres of absolute alcohol, the alcoholic strength of the product must be determined prior to analysis. It is not necessary to determine the alcohol strength of the product prior to analysis.

5. Reagents and Materials

Unless otherwise stated, use only reagents of a purity greater than 97 %, purchased from an ISO accredited supplier with a Certificate of Purity, free from other congeners at test dilution (this may be confirmed by injection of individual congener standards at the test dilution using GC conditions as in 6.4) and only water of at least grade 3 as defined in ISO 3696. Acetal and acetaldehyde must be stored in the dark at <5 °C, all other reagents should be stored according to the supplier's instructions.

5.1 Ethanol absolute (CAS 64-17-5)
5.2 Methanol (CAS 67-56-1)
5.3 Propan-1-ol (CAS 71-23-8)
5.4 2-methylpropan-1-ol (CAS 78-33-1)
5.5 3-methylbutan-1-ol (CAS 123-51-3), pentan-3-ol (CAS 584-02-1), pentan-1-ol (CAS 71-41-0), 4-methylpentan-1-ol (CAS 626-89-1), 4-methylpentan-2-ol (CAS 108-11-2), or methyl nonanoate (CAS 1731-84-6).
5.6 2-methylbutan-1-ol (CAS 137-32-6)
5.7 3-methylbutan-1-ol (CAS 123-51-3)
5.8 Ethyl acetate (CAS 141-78-6)
5.9 Butan-1-ol (CAS 71-36-3)
5.10 Butan-2-ol (CAS 78-92-2)
5.11 Acetaldehyde (CAS 75-07-0)
5.12 Acetal (CAS 105-57-7)
5.13 40% v/v ethanol solution
To prepare 400 ml/l ethanol solution pour 400 ml ethanol (5.1) into a 1 litre volumetric flask, make up to volume with distilled water and mix.
5.14 Preparation and storage of standard solutions (procedure suggested for the validated method: the calibration ranges should be adapted to the nature of the different types of products analysed by each laboratory).

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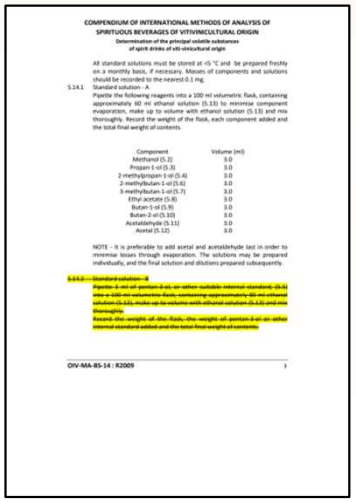

COMPENDIUM OF INTERNATIONAL METHODS OF ANALYSIS OF SPIRITUOUS BEVERAGES OF VITIVINICULTURAL ORIGIN

Determination of the principal volatile substances of spirit drinks of viti-vinicultural origin

All standard solutions must be stored at <5 °C and be prepared freshly on a monthly basis, if necessary. Masses of components and solutions should be recorded to the nearest 0.1 mg.

5.14.1 Standard solution - A
Pipette the following reagents into a 100 ml volumetric flask, containing approximately 60 ml ethanol solution (5.13) to minimise component evaporation, make up to volume with ethanol solution (5.13) and mix thoroughly. Record the weight of the flask, each component added and the total final weight of contents.

Component	Volume (ml)
Methanol (5.2)	3.0
Propan-1-ol (5.3)	3.0
2-methylpropan-1-ol (5.4)	3.0
2-methylbutan-1-ol (5.6)	3.0
3-methylbutan-1-ol (5.7)	3.0
Ethyl acetate (5.8)	3.0
Butan-1-ol (5.9)	3.0
Butan-2-ol (5.10)	3.0
Acetaldehyde (5.11)	3.0
Acetal (5.12)	3.0

NOTE - It is preferable to add acetal and acetaldehyde last in order to minimise losses through evaporation. The solutions may be prepared individually, and the final solution and dilutions prepared subsequently.

5.14.2 Standard solution - B
Pipette 3 ml of pentan-3-ol, or other suitable internal standard, (5.5) into a 100 ml volumetric flask, containing approximately 60 ml ethanol solution (5.13), make up to volume with ethanol solution (5.13) and mix thoroughly.
Record the weight of the flask, the weight of pentan-3-ol or other internal standard added and the total final weight of contents.

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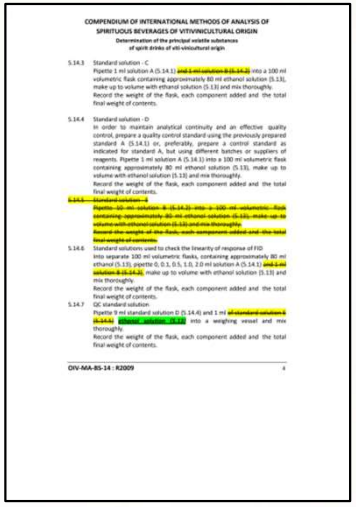


COMPENDIUM OF INTERNATIONAL METHODS OF ANALYSIS OF SPIRITUOUS BEVERAGES OF VITIVINICULTURAL ORIGIN

Determination of the principal volatile substances of spirit drinks of viti-vinicultural origin

5.14.3 Standard solution - C
Pipette 1 ml solution A (5.14.1) and 1 ml solution B (5.14.2) into a 100 ml volumetric flask containing approximately 80 ml ethanol solution (5.13), make up to volume with ethanol solution (5.13) and mix thoroughly.
Record the weight of the flask, each component added and the total final weight of contents.

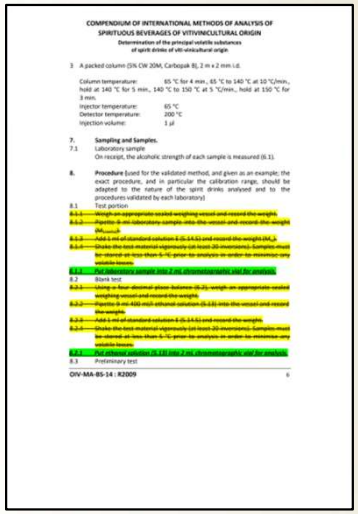
5.14.4 Standard solution - D
In order to maintain analytical continuity and an effective quality control, prepare a quality control standard using the previously prepared standard A (5.14.1) or, preferably, prepare a control standard as indicated for standard A, but using different batches or suppliers of reagents. Pipette 1 ml solution A (5.14.1) into a 100 ml volumetric flask containing approximately 80 ml ethanol solution (5.13), make up to volume with ethanol solution (5.13) and mix thoroughly.
Record the weight of the flask, each component added and the total final weight of contents.

5.14.5 Standard solution - E
Pipette 10 ml solution B (5.14.2) into a 100 ml volumetric flask containing approximately 80 ml ethanol solution (5.13), make up to volume with ethanol solution (5.13) and mix thoroughly.
Record the weight of the flask, each component added and the total final weight of contents.

5.14.6 Standard solutions used to check the linearity of response of FID
Into separate 100 ml volumetric flasks, containing approximately 80 ml ethanol (5.13), pipette 0, 0.1, 0.5, 1.0, 2.0 ml solution A (5.14.1) and 1 ml solution B (5.14.2), make up to volume with ethanol solution (5.13) and mix thoroughly.
Record the weight of the flask, each component added and the total final weight of contents.

5.14.7 QC standard solution
Pipette 5 ml standard solution D (5.14.4) and 1 ml of standard solution E (5.14.5) ethanol solution (5.13) into a weighing vessel and mix thoroughly.
Record the weight of the flask, each component added and the total final weight of contents.

OIV-MA-BS-14 : R2009 4



COMPENDIUM OF INTERNATIONAL METHODS OF ANALYSIS OF SPIRITUOUS BEVERAGES OF VITIVINICULTURAL ORIGIN

Determination of the principal volatile substances of spirit drinks of viti-vinicultural origin

3 A packed column (5% CW 20M, Carbopak B), 2 m x 2 mm i.d.

Column temperature: 65 °C for 4 min., 65 °C to 140 °C at 10 °C/min., hold at 140 °C for 5 min., 140 °C to 150 °C at 5 °C/min., hold at 150 °C for 3 min.
Injector temperature: 65 °C
Detector temperature: 200 °C
Injection volume: 1 µl

7. Sampling and Samples.

7.1 Laboratory sample
On receipt, the alcoholic strength of each sample is measured (6.1).

8. Procedure (used for the validated method, and given as an example; the exact procedure, and in particular the calibration range, should be adapted to the nature of the spirit drinks analysed and to the procedures validated by each laboratory)

8.1 Test portion
8.1.1 Weigh an appropriate sealed weighing vessel and record the weight.
8.1.2 Pipette 5 ml laboratory sample into the vessel and record the weight (M_{sample}).
8.1.3 Add 1 ml of standard solution E (5.14.5) and record the weight (M_{IS}).
8.1.4 Shake the test material vigorously (at least 20 inversions). Samples must be stored at less than 5 °C prior to analysis in order to minimise any volatile losses.
8.2 Put laboratory sample into 2 ml chromatographic vial for analysis.
8.2 Blank test
8.2.1 Using a four decimal place balance (8.2), weigh an appropriate sealed weighing vessel and record the weight.
8.2.2 Pipette 5 ml 100 ml/l ethanol solution (5.13) into the vessel and record the weight.
8.2.3 Add 1 ml of standard solution E (5.14.5) and record the weight.
8.2.4 Shake the test material vigorously (at least 20 inversions). Samples must be stored at less than 5 °C prior to analysis in order to minimise any volatile losses.
8.2.5 Put ethanol solution (8.13) into 2 ml chromatographic vial for analysis.
8.3 Preliminary test

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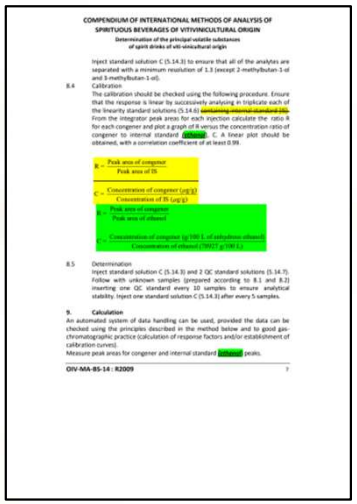

COMPENDIUM OF INTERNATIONAL METHODS OF ANALYSIS OF SPIRITUOUS BEVERAGES OF VITIVINICULTURAL ORIGIN

Determination of the principal volatile substances of spirit drinks of viti-vinicultural origin

Inject standard solution C (5.14.3) to ensure that all of the analytes are separated with a minimum resolution of 1.3 (except 2-methylbutan-1-ol and 3-methylbutan-1-ol).

8.4 Calibration
The calibration should be checked using the following procedure. Ensure that the response is linear by successively analysing in triplicate each of the linearity standard solutions (5.14.6) containing internal standard (5). From the integrator peak areas for each injection calculate the ratio R for each congener and plot a graph of R versus the concentration ratio of congener to internal standard (above). C. A linear plot should be obtained, with a correlation coefficient of at least 0.99.

$$R = \frac{\text{Peak area of congener}}{\text{Peak area of IS}}$$

$$C = \frac{\text{Concentration of congener (µg/l)}}{\text{Concentration of IS (µg/l)}}$$

$$R = \frac{\text{Peak area of congener}}{\text{Peak area of ethanol}}$$

$$C = \frac{\text{Concentration of congener (g/100 L of anhydrous ethanol)}}{\text{Concentration of ethanol (39927 g/100 L)}}$$

8.5 Determination
Inject standard solution C (5.14.3) and 2 QC standard solutions (5.14.7). Following with unknown samples (prepared according to 8.1 and 8.2) inserting one QC standard every 10 samples to ensure analytical stability. Inject one standard solution C (5.14.3) after every 5 samples.

9. Calculation

An automated system of data handling can be used, provided the data can be checked using the principles described in the method below and to good gas-chromatographic practice (calculation of response factors and/or establishment of calibration curves).
Measure peak areas for congener and internal standard (ethanol) peaks.

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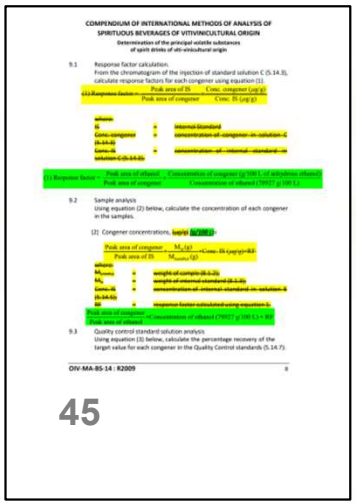

COMPENDIUM OF INTERNATIONAL METHODS OF ANALYSIS OF SPIRITUOUS BEVERAGES OF VITIVINICULTURAL ORIGIN

Determination of the principal volatile substances of spirit drinks of viti-vinicultural origin

9.1 Response factor calculation.
From the chromatogram of the injection of standard solution C (5.14.3), calculate response factors for each congener using equation (1).

(1) Response factor = $\frac{\text{Peak area of IS}}{\text{Peak area of congener}} \times \frac{\text{Conc. congener (µg/g)}}{\text{Conc. IS (µg/g)}}$

where:
IS = Internal standard
C_{cong} = concentration of congener in solution C (5.14.3)
C_{IS} = concentration of internal standard in solution C (5.14.3).

(1) Response factor = $\frac{\text{Peak area of ethanol}}{\text{Peak area of congener}} \times \frac{\text{Concentration of congener (g/100 L of anhydrous ethanol)}}{\text{Concentration of ethanol (39927 g/100 L)}}$

9.2 Sample analysis
Using equation (2) below, calculate the concentration of each congener in the samples.

(2) Congener concentration, (µg/g or g/100 g):

$$\frac{\text{Peak area of congener}}{\text{Peak area of IS}} \times \frac{M_{IS}\,(g)}{M_{sample}\,(g)} \times \text{Conc. IS (µg/g)} \times \text{RF}$$

where:
M_{sample} = weight of sample (6.1.2)
M_{IS} = weight of internal standard (5.14.5)
C_{IS} = concentration of internal standard in solution B (5.14.2)
RF = response factor calculated using equation 1.

$$\frac{\text{Peak area of congener}}{\text{Peak area of ethanol}} \times \text{concentration of ethanol (39927 g/100 L)} \times \text{RF}$$

9.3 Quality control standard solution analysis
Using equation (3) below, calculate the percentage recovery of the target value for each congener in the Quality Control standards (5.14.7).

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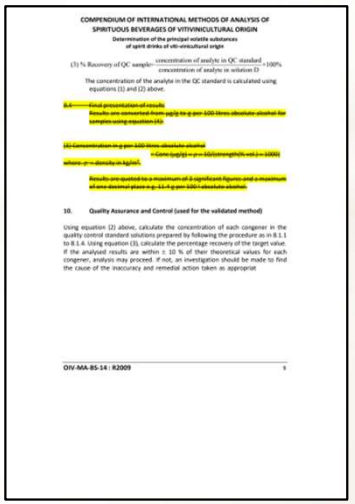


COMPENDIUM OF INTERNATIONAL METHODS OF ANALYSIS OF SPIRITUOUS BEVERAGES OF VITIVINICULTURAL ORIGIN

Determination of the principal volatile substances of spirit drinks of viti-vinicultural origin

(3) % Recovery of QC sample = $\frac{\text{concentration of analyte in QC standard}}{\text{concentration of analyte in solution D}} \times 100\%$

The concentration of the analyte in the QC standard is calculated using equations (1) and (2) above.

9.4 Final presentation of results
Results are converted from µg/g to g per 100 litres absolute alcohol for samples using equation (4).

(4) Concentration in g per 100 litres absolute alcohol = Conc (µg/g) x ρ x 10/(strength(% vol.) x 1000)

where: ρ = density in kg/m³.

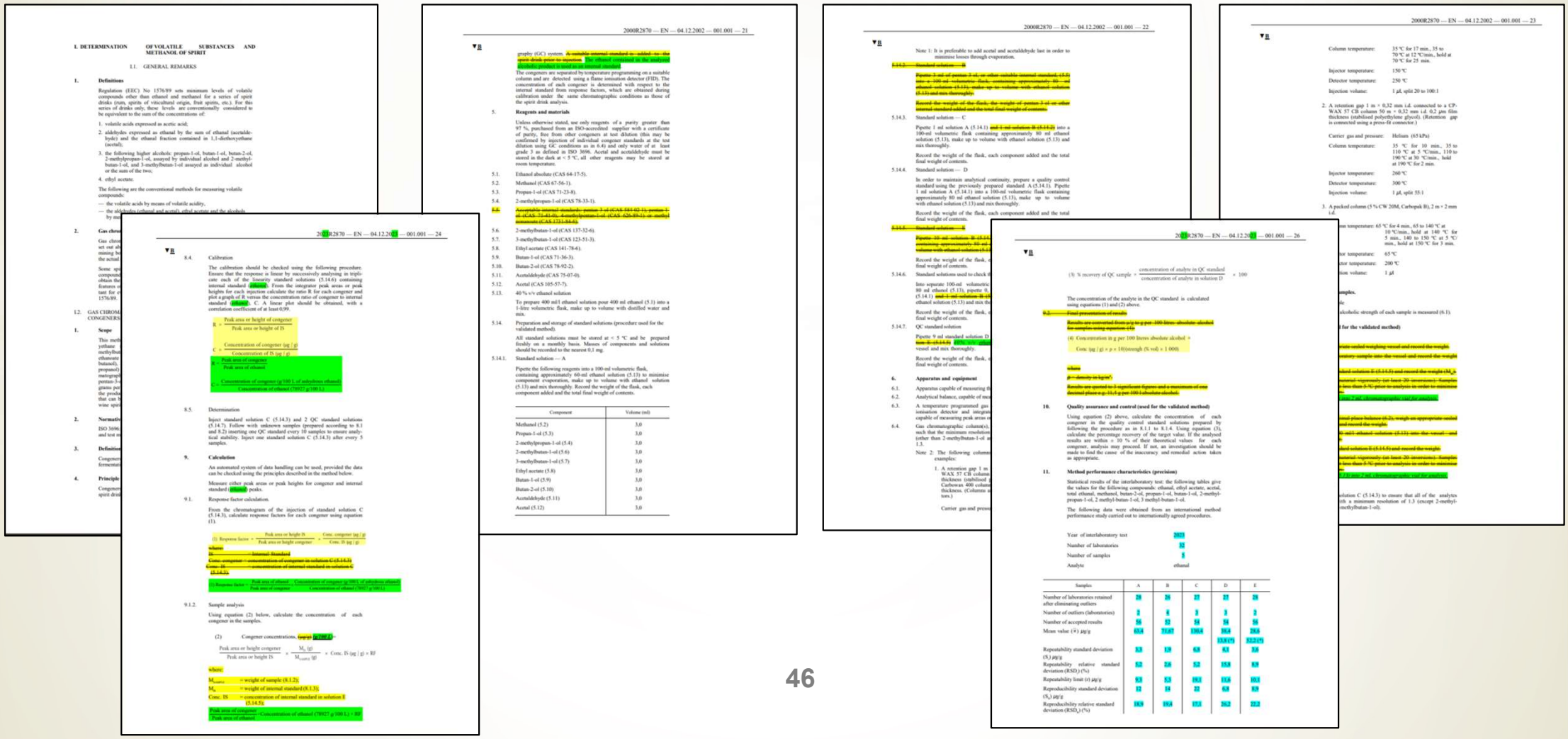
Results are quoted to a maximum of 3 significant figures and a maximum of one decimal place e.g. 11.4 g per 100 l absolute alcohol.

10. Quality Assurance and Control (used for the validated method)

Using equation (2) above, calculate the concentration of each congener in the quality control standard solutions prepared by following the procedure as in 8.1.1 to 8.1.4. Using equation (3), calculate the percentage recovery of the target value. If the analysed results are within ± 10 % of their theoretical values for each congener, analysis may proceed. If not, an investigation should be made to find the cause of the inaccuracy and remedial action taken as appropriat

OIV-MA-BS-14 : R2009 9

EC 2870/2000 – simplification
Determination of Volatile Substances and Methanol of Spirit



I. DETERMINATION OF VOLATILE SUBSTANCES AND METHANOL OF SPIRIT

1.1. GENERAL REMARKS

1. Definitions

Regulation (EEC) No 1576/89 sets minimum levels of volatile compounds other than ethanol and methanol for a series of spirit drinks (rum, spirits of viticultural origin, fruit spirits, etc.). For this series of drinks only, these levels are conventionally considered to be equivalent to the sum of the concentrations of:

1. volatile acids expressed as acetic acid;
2. aldehydes expressed as ethanal by the sum of ethanal (acetaldehyde) and the ethanal fraction contained in 1,1-diethoxyethane (acetal);
3. the following higher alcohols: propan-1-ol, butan-1-ol, butan-2-ol, 2-methylpropan-1-ol, assayed by individual alcohol and 2-methylbutan-1-ol, and 3-methylbutan-1-ol assayed as individual alcohol or the sum of the two;
4. ethyl acetate.

The following are the conventional methods for measuring volatile compounds:

— the volatile acids by means of volatile acidity,

— the aldehydes (ethanal and acetal), ethyl acetate and the alcohols by gas

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1.2. GAS CHROM
CONGENERS

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3. Definitio

Congeners
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4. Principle

Congeners
spirit drink

graphy (GC) system. A suitable internal standard is added to the spirit drink prior to injection. No ethanol contained in the analysed alcoholic product is used as an internal standard.

The congeners are separated by temperature programming on a suitable column and are detected using a flame ionisation detector (FID). The concentration of each congener is determined with respect to the internal standard from response factors, which are obtained during calibration under the same chromatographic conditions as those of the spirit drink analysis.

5. Reagents and materials

Unless otherwise stated, use only reagents of a purity greater than 97 %, purchased from an ISO-accredited supplier with a certificate of purity, free from other congeners at test dilution (this may be confirmed by injection of individual congener standards at the test dilution using GC conditions as in 6.4) and only water of at least grade 3 as defined in ISO 3696. Acetal and acetaldehyde must be stored in the dark at < 5 °C, all other reagents may be stored at room temperature.

5.1. Ethanol absolute (CAS 64-17-5).
5.2. Methanol (CAS 67-56-1).
5.3. Propan-1-ol (CAS 71-23-8).
5.4. 2-methylpropan-1-ol (CAS 78-33-1).
5.5. Acceptable internal standards: pentan-3-ol (CAS 584-02-1), pentan-1-ol (CAS 71-41-0), 4-methylpentan-1-ol (CAS 626-89-1), or methyl nonanoate (CAS 1731-84-6).
5.6. 2-methylbutan-1-ol (CAS 137-32-6).
5.7. 3-methylbutan-1-ol (CAS 123-51-3).
5.8. Ethyl acetate (CAS 141-78-6).
5.9. Butan-1-ol (CAS 71-36-3).
5.10. Butan-2-ol (CAS 78-92-2).
5.11. Acetaldehyde (CAS 75-07-0).
5.12. Acetal (CAS 105-57-7).
5.13. 40 % v/v ethanol solution

To prepare 400 ml/l ethanol solution pour 400 ml ethanol (5.1) into a 1-litre volumetric flask, make up to volume with distilled water and mix.

5.14. Preparation and storage of standard solutions (procedure used for the validated method).

All standard solutions must be stored at < 5 °C and be prepared freshly on a monthly basis. Masses of components and solutions should be recorded to the nearest 0,1 mg.

5.14.1. Standard solution — A

Pipette the following reagents into a 100-ml volumetric flask, containing approximately 60-ml ethanol solution (5.13) to minimise component evaporation, make up to volume with ethanol solution (5.13) and mix thoroughly. Record the weight of the flask, each component added and the total final weight of contents.

Component	Volume (ml)
Methanol (5.2)	3,0
Propan-1-ol (5.3)	3,0
2-methylpropan-1-ol (5.4)	3,0
2-methylbutan-1-ol (5.6)	3,0
3-methylbutan-1-ol (5.7)	3,0
Ethyl acetate (5.8)	3,0
Butan-1-ol (5.9)	3,0
Butan-2-ol (5.10)	3,0
Acetaldehyde (5.11)	3,0
Acetal (5.12)	3,0

Note 1: It is preferable to add acetal and acetaldehyde last in order to minimise losses through evaporation.

5.14.2. Standard solution — B

Pipette 3 ml of pentan-3-ol, or other suitable internal standard, (5.5) into a 100 ml volumetric flask, containing approximately 80 ml ethanol solution (5.13), make up to volume with ethanol solution (5.13) and mix thoroughly.

Record the weight of the flask, the weight of pentan-3-ol or other internal standard added and the total final weight of contents.

5.14.3. Standard solution — C

Pipette 1 ml solution A (5.14.1) and 1 ml solution B (5.14.2) into a 100-ml volumetric flask containing approximately 80 ml ethanol solution (5.13), make up to volume with ethanol solution (5.13) and mix thoroughly.

Record the weight of the flask, each component added and the total final weight of contents.

5.14.4. Standard solution — D

In order to maintain analytical continuity, prepare a quality control standard using the previously prepared standard A (5.14.1). Pipette 1 ml solution A (5.14.1) into a 100-ml volumetric flask containing approximately 80 ml ethanol solution (5.13), make up to volume with ethanol solution (5.13) and mix thoroughly.

Record the weight of the flask, each component added and the total final weight of contents.

5.14.5. Standard solution — E

Pipette 10 ml solution B (5.14.2) into a 100-ml volumetric flask containing approximately 80 ml ethanol solution (5.13), make up to volume with ethanol solution (5.13) and mix thoroughly.

Record the weight of the flask, each component added and the total final weight of contents.

5.14.6. Standard solutions used to check the

Into separate 100-ml volumetric flasks containing approximately 80 ml ethanol (5.13), pipette 0, 1, 2, 5, 10 and 20 ml solution A (5.14.1) and 1 ml solution B (5.14.2). Make up to volume with ethanol solution (5.13) and mix thoroughly.

Record the weight of the flask, each component added and the total final weight of contents.

5.14.7. QC standard solution

Pipette 9 ml standard solution D (see 5.14.4) into a 100-ml volumetric flask containing approximately 80 ml 40% v/v ethanol solution (5.13), make up to volume with ethanol solution (5.13) and mix thoroughly.

Record the weight of the flask, each component added and the total final weight of contents.

6. Apparatus and equipment

6.1. Apparatus capable of measuring the

6.2. Analytical balance, capable of mea

6.3. A temperature programmed gas ionisation detector and integrat capable of measuring peak areas o

6.4. Gas chromatographic column(s), such that the minimum resolution (other than 2-methylbutan-1-ol a 1.3.

Note 2: The following column examples:

1. A retention gap 1 m WAX 57 CB column thickness (stabilised Carbowax 400 column thickness. (Columns a tors.)

Carrier gas and pressu

8.4. Calibration

The calibration should be checked using the following procedure. Ensure that the response is linear by successively analysing in triplicate each of the linearity standard solutions (5.14.6) containing internal standard (deleted). From the integrator peak areas or peak heights for each injection calculate the ratio R for each congener and plot a graph of R versus the concentration ratio of congener to internal standard (deleted), C. A linear plot should be obtained, with a correlation coefficient of at least 0,99.

$$R = \frac{\text{Peak area or height of congener}}{\text{Peak area or height of IS}}$$

$$C = \frac{\text{Concentration of congener (µg / g)}}{\text{Concentration of IS (µg / g)}}$$

$$R = \frac{\text{Peak area of congener}}{\text{Peak area of ethanol}}$$

$$C = \frac{\text{Concentration of congener (g/100 L of anhydrous ethanol)}}{\text{Concentration of ethanol (78927 g/100 L)}}$$

8.5. Determination

Inject standard solution C (5.14.3) and 2 QC standard solutions (5.14.7). Follow with unknown samples (prepared according to 8.1 and 8.2) inserting one QC standard every 10 samples to ensure analytical stability. Inject one standard solution C (5.14.3) after every 5 samples.

9. Calculation

An automated system of data handling can be used, provided the data can be checked using the principles described in the method below.

Measure either peak areas or peak heights for congener and internal standard (deleted) peaks.

9.1. Response factor calculation.

From the chromatogram of the injection of standard solution C (5.14.3), calculate response factors for each congener using equation (1).

$$\text{(1) Response factor} = \frac{\text{Peak area or height IS}}{\text{Peak area or height congener}} \times \frac{\text{Conc. congener (µg / g}}{\text{Conc. IS (µg / g)}}$$

where:

IS = Internal Standard

Conc. congener = concentration of congener in solution C (5.14.3)

Conc. IS = concentration of internal standard in solution C (5.14.3).

$$\text{(1) Response factor} = \frac{\text{Peak area of ethanol}}{\text{Peak area of congener}} \times \frac{\text{Concentration of congener (g/100L of anhydrous ethanol)}}{\text{Concentration of ethanol (78927 g/100 L)}}$$

9.1.2. Sample analysis

Using equation (2) below, calculate the concentration of each congener in the samples.

(2) Congener concentrations, (µg/g or g/100 L):

$$\frac{\text{Peak area or height congener}}{\text{Peak area or height IS}} \times \frac{M_{is}\text{ (g)}}{M_{sample}\text{ (g)}} \times \text{Conc. IS (µg / g)} \times \text{RF}$$

where:

M_{sample} = weight of sample (8.1.2);

M_{is} = weight of internal standard (8.1.3);

Conc. IS = concentration of internal standard in solution E (5.14.5);

Peak area of congener / Concentration of ethanol (78927 g/100 L) × RF

(3) % recovery of QC sample = $\frac{\text{concentration of analyte in QC standard}}{\text{concentration of analyte in solution D}} \times 100$

The concentration of the analyte in the QC standard is calculated using equations (1) and (2) above.

9.2. Final presentation of results

Results are converted from g/g to g per 100 litres absolute alcohol for samples using equation (4):

(4) Concentration in g per 100 litres absolute alcohol = Conc (µg / g) × ρ × 10/(strength (% vol) × 1 000)

where

ρ = density in kg·m⁻³

Results are quoted to 3 significant figures and a maximum of one decimal place e.g. 11,5 g per 100 l absolute alcohol.

10. Quality assurance and control (used for the validated method)

Using equation (2) above, calculate the concentration of each congener in the quality control standard solutions prepared by following the procedure as in 8.1.1 to 8.1.4. Using equation (3), calculate the percentage recovery of the target value. If the analysed results are within ± 10 % of their theoretical values for each congener, analysis may proceed. If not, an investigation should be made to find the cause of the inaccuracy and remedial action taken as appropriate.

11. Method performance characteristics (precision)

Statistical results of the interlaboratory test: the following tables give the values for the following compounds: ethanal, ethyl acetate, acetal, total ethanol, methanol, butan-2-ol, propan-1-ol, butan-1-ol, 2-methylpropan-1-ol, 2 methyl-butan-1-ol, 3 methyl-butan-1-ol.

The following data were obtained from an international method performance study carried out to internationally agreed procedures.

Year of interlaboratory test 2023
Number of laboratories 32
Number of samples 5
Analyte ethanol

Samples	A	B	C	D	E
Number of laboratories retained after eliminating outliers	28	26	27	27	28
Number of outliers (laboratories)	3	4	3	3	3
Number of accepted results	56	52	54	54	56
Mean value ($\bar{x}$) µg/g	63,4	71,67	130,4	10,4	28,6
				13,8 (*)	52,2 (*)
Repeatability standard deviation (S_r) µg/g	3,3	1,9	6,8	4,1	3,6
Repeatability relative standard deviation (RSD$_r$) (%)	5,2	2,6	5,2	15,8	8,9
Repeatability limit (r) µg/g	9,3	5,3	19,1	11,6	10,1
Reproducibility standard deviation (S_R) µg/g	12	14	22	6,8	8,9
Reproducibility relative standard deviation (RSD$_R$) (%)	18,9	19,4	17,1	36,2	17,1

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GBT 11858-2008 Vodka

National Standards of People's Republic of China

GB/T 11858-2008

National Food Safety Standards

Vodka

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Issued by the General Administration of Supervision, Inspections and Quarantine of the People's Republic of China and National Standardization Management Committee

5.3.6 Precision

Discrepancies between the results of two independent tests conducted under iterative conditions and the average value of the test results should not exceed the 2% range.

5.4 Total Aldehyde

5.4.1 Gas Chromatography Method

5.4.1.1 Principle

Channel vaporized sample along with the carrier gas into the chromatography columns and then perform separation of individual components that are meant to be measured by the process of leveraging on the differences of partition coefficients between components while transiting between the two phases (gaseous-liquid) and the consequential discrepancies between the migration speeds of each component within the columns. Separated components will flow out of the chromatography column in a specific order into the hydrogen flame ionization detector. Conduct qualitative analysis by comparing sample standard values with the retention values of the peaks of individual components illustrated on the resultant chromatograph; quantify by internal standard method with the use of peak area (or peak height). Ethanol is used as an internal standard.

5.4.1.2 Apparatus

5.4.1.2.1 Gas Chromatography: With hydrogen flame ionization detector (FID).

5.4.1.2.2 Chromatography Columns: PEG20M cross-linked quartz capillary chromatography column, column length 25m~50m, inner diameter 0.25mm. Or any other capillary chromatography column with equal effect of analysis.

5.4.1.2.3 Micro Injector: 10 μL.

5.4.1.3 Reagents and Solutions

5.4.1.3.1 40% Ethanol Solution: Mix ethanol (chromatographically pure) with water.

5.4.1.3.2 Acetaldehyde Solution (2%): Use as standard sample. Extract 2 mL acetal (chromatographically pure) and then titrate it with 40% ethanol solution till it reaches 100 mL.

~~5.4.1.3.3 N-butanol Solution (2%): Use as internal standard. Extract 2 mL N-butyl alcohol (chromatographically pure) and then titrate it with 40% ethanol solution till it reaches 100 mL.~~

5.4.1.4 Chromatographic Conditions

... diversion ratio ~37:1; make

Column Temperature (T_C): Initial temperature at 70°C. Maintain temperature for 3 mins and then systematically increase the temperature at 5°C/min to 100°C. Maintain temperature for another 10 mins.

The flow rate of carrier gas, hydrogen and air may differ according to different chromatographic conditions between apparatus used. Experiments should be conducted to determine the best operating conditions, with the end goal of complete separation of internal standard peak and individual peaks of each component present in the alcohol sample achieved as the basis.

5.4.1.5 Analysis Procedure

5.4.1.5.1 Determination of Calibration Factor (f value)

Extract 1.00 mL acetaldehyde solution (as prepared in 5.4.1.3.2) and transfer into a 100 mL volumetric flask. Add 1.00 mL N-butanol solution (prepared as in 5.4.1.3.3) thereafter into the flask and then dilute the mixture with 40% ethanol solution to full. The concentration of acetaldehyde and N-butanol should both be 0.02%. Wait till the chromatographic basic line stabilized, then inject the sample with a micro injector, where the amount of sample injected will be dependent on the sensitivity of the apparatus. Make records of the retention time of acetaldehyde and the internal standard peak (ethanol is used as internal standard) as well as their individual peak area (or peak height). Use these values to calculate the relative calibration factor (f value) of acetaldehyde.

The relative calibration factor (f value) of acetaldehyde to N-butanol (ethanol) is according to experience value, at about 1.50.

5.4.1.5.2 Determination of Sample Solution

Extract 10.0 mL of alcohol sample directly with a 10 mL volumetric flask and then add 0.10 mL N-butanol solution (prepared as in 5.4.1.3.3), mix evenly. Inject samples in under the same conditions as the f value test and then determine the positions of acetaldehyde and N-butanol (ethanol) according to the retention time. Determine the peak area (or peak height) of the acetaldehyde (or N-butanol) and internal standard peak (ethanol), compute the difference between peak areas (or peak heights) and calculate the proportion of acetaldehyde (or N-butanol) in the sample respectively, with acetaldehyde as the basis of measurement.

5.4.1.6 Result Calculation

a) Calibration Factor (f value) can be calculated with the following formula (6).

$$f = \frac{A_1}{A_2} * \frac{d_2}{d_1} \quad \text{(6)}$$

b) Acetaldehyde (or Acetal) content in the sample can be calculated with the following formula (7).

$$X_1 = f * \frac{A_3}{A_4} * X_2$$

c) Acetaldehyde (or Acetal) content in a liter of 100% ethanol can be ... (8).

$$X_{2a} = \frac{X_2 * 100}{E}$$

4) 5 Total aldehyde (acetaldehyde) content in a liter of 100% ethanol can be calculated with the following formula (9).

$$X_3 = X_1 + X_4 * 0.37 \quad \text{(9)}$$

In the formula:

f – Relative calibration factor of acetaldehyde (or acetal);

A_1 – Peak area (or peak height) of the internal standard (ethanol) during the determination of standard sample f value;

A_2 – Peak area (or peak height) of acetal during the determination of standard sample f value;

d_2 – Relative concentration of acetal. Concentration of acetaldehyde (or acetal) in standard sample, unit is milligram per liter of 100% ethanol (mg/L AA);

d_1 – Relative concentration of internal standard. Concentration of internal standard (ethanol) in standard sample, d_1 is 789270 mg/L;

X_1 – Acetaldehyde (or Acetal) content in sample, unit is milligram per liter of 100% ethanol (mg/L AA);

A_3 – Peak area (or peak height) of acetaldehyde (or acetal) in sample;

A_4 – Peak area (or peak height) of internal standard added in the alcohol sample;

X_4 – Internal standard (added in the alcohol sample) (ethanol) content, unit is milligram per liter (mg/L), X_4 = 789270 mg/L;

X_2 – Acetaldehyde (or Acetal) content in a liter of 100% ethanol in the sample, unit is milligram per liter (mg/L);

E – Actual alcohol content of the sample;

X_3 – Total aldehyde (acetaldehyde) content in a liter of 100% ethanol in the sample, unit is milligram per liter (mg/L);

X_5 – Acetaldehyde content in a liter of 100% ethanol in the sample, unit is milligram per liter (mg/L);

X_6 – Acetal content in a liter of 100% ethanol in the sample, unit is milligram per liter (mg/L);

0.37 – Conversion coefficient of acetal to acetaldehyde.

5.4.1.7 Precision

... tests conducted under iterative conditions and the 10% range.

In the formula:

X_1 – Total acetaldehyde content, unit is milligram per liter (mg/L);

V_1 – Volume of iodine standard reagent used on the sample, unit is milliliter (mL);

V_0 – Volume of iodine standard reagent used on the control experiment, unit is milliliter (mL);

c – Concentration of the iodine standard titration reagent, unit is mol per liter (mol/L);

22 – Molar mass value of iodine, unit is mol per gram (g/mol) [M(I2) = 22];

V – Volume of sample absorbed, unit is milliliter (mL);

X_2 – Total acetaldehyde content in a liter of 100% ethanol of the sample, unit is milligram per liter (mg/L);

E – Actual alcohol content of sample determined.

Result should be presented in one decimal place format.

5.4.2.7 Precision

Discrepancies between the results of two independent tests conducted under iterative conditions and the average value of the test results should not exceed the 10% range.

5.5 Total Ester

5.5 .1 Gas Chromatography Method

5.5.1.1 Principle

Same as 5.4.1.1.

5.5.1.2 Apparatus

Same as 5.4.1.2.

5.5.1.3 Reagents and Solutions

5.5.1.3.1 40% Ethanol Solution: Mix ethanol (chromatographically pure) with water.

5.5.1.3.2 Ethyl Acetate Solution (2%): Use as standard sample. Extract 2 mL ethyl acetate (chromatographically pure), then titrate it with 40% ethanol solution till it reaches 100 mL volume.

~~5.5.1.3.3 N-butanol Solution (2%): Use as internal standard. Extract 2 mL N-butanol (chromatographically pure), then titrate it with 40% ethanol solution till it reaches 100 mL volume.~~

5.5.1.4 Chromatographic Conditions

Same as 5.4.1.4.

5.5.1.5 Analysis Procedure

Entirety of the analysis operation procedure is the same as what is described in section 5.4.1.5, with the

5.5.2.3 .7 Ethyl Acetate Series Standard Reagent: Use a micro burette to extract volumes of 0.0 mL, 0.75 mL, 1.5 mL, 2.25 mL, 3.0 mL, 4.5 mL ethyl acetate standard storage reagent (prepared as in 5.5.2.3.6) into six individual 100 mL conical flasks respectively. Dilute each solution with 40% ethanol solution till each flask is full and mix evenly. These newly formulated standard reagents should contain ethyl acetate at 0.0 mg/L, 2.50 mg/L, 5.00 mg/L, 7.50 mg/L, 10.00 mg/L and 15.00 mg/L.

5.5.2.4 Analysis Procedure

5.5.2.4.1 Preparation of Sample Solution

If alcohol sample does not contain any external substances, take sample directly during tests. Otherwise, distill the sample before any further tests.

5.5.2.4.2 Standard Curve Illustration

Extract 2.0 mL of each of the ethyl acetate series of standard reagents and place them individually in a 25 mL colorimetric tube with stopper. Add 2.0 mL hydroxylamine hydrochloride solution (prepared as in 5.5.2.3.1) and 2.0 mL sodium hydroxide solution (prepared as in 5.5.2.3.2), mix evenly and let it settle for the next 10 mins. Thereafter, add 2.0 mL hydrochloric acid solution (prepared as in 5.5.2.3.3), mix evenly. Then add 2.0 mL ferric chloride solution (prepared as in 5.5.2.3.4), mix evenly again. Use a 1 cm cuvette, recalibrate to zero with a control tube and then determine the light absorbance of each under a wavelength of 525 nm. Plot the standard curve.

5.5.2.4.3 Determination of Sample Solution

Extract 2.0 mL sample solution (prepared as in 5.5.2.4.1) into a 25 mL colorimetric tube with stopper and then operate in the same manner as in section 5.5.2.4.2. Determine the ethyl acetate content on the standard curve and that will be the total ester content. Alternatively, use linear regression to calculate the total ester content.

5.5.2.5 Precision

Discrepancies between the results of two independent tests conducted under iterative conditions and the average value of the test results should not exceed the 10% range.

5.6 Methanol

5.6.1 Principle

Same as 5.4.1.1.

5.6.2 Apparatus

Same as 5.4.1.2.

5.6.3 Reagents and Solution

5.6.3.1 40% Ethanol Solution: Mix ethanol (chromatographically pure) with water.

5.6.3.2 Methanol Solution (2%): Use as standard sample. Extract 2 mL methanol (chromatographically pure), then titrate it with 40% ethanol solution till it reaches 100 mL volume.

~~5.6.3.3 N-butanol Solution (2%): Use as internal standard. Extract 2 mL N-butanol (chromatographically pure), then titrate it with 40% ethanol solution till it reaches 100 mL volume.~~

5.6.4 Chromatographic Conditions

Same as 5.4.1.4.

5.6.5 Analysis Procedure

Entirety of the analysis operation procedure is the same as what is described in section 5.4.1.5, with the specific exception that the standard sample used will be replaced by methanol solution (prepared as in 5.6.3.2) instead.

5.6.6 Result Calculation

Same as 5.4.1.6.

5.6.7 Precision

Same as 5.4.1.7.

5.7 High Quality Alcohols

5.7.1 Principle

Same as 5.4.1.1.

5.7.2 Apparatus

Same as 5.4.1.2.

5.7.3 Reagents and Solutions

5.7.3.1 40% Ethanol Solution: Mix ethanol (chromatographically pure) with water.

5.7.3.2 Isobutanol Solution (2%): Use as standard sample. Extract 2 mL isobutanol (chromatographically pure), then titrate it with 40% ethanol solution till it reaches 100 mL volume.

~~5.6.3.3 Isoamyl Ethanol Solution (2%): Use as internal standard. Extract 2 mL isoamyl ethanol (chromatographically pure), then titrate it with 40% ethanol solution till it reaches 100 mL volume.~~

5.7.4 Chromatographic Conditions

Same as 5.4.1.4.

5.7.5 Analysis Procedure

Entirety of the analysis operation procedure is the same as what is described in section 5.4.1.5, with the specific exception that the standard sample used will be replaced by isobutanol solution (prepared as in 5.7.3.2) and internal standard used will be replaced by isoamyl ethanol solution (prepared as in 5.7.3.3) instead.

5.7.6 Result Calculation

Same as 5.4.1.6, determine total content of isobutanol and isoamyl ethanol.

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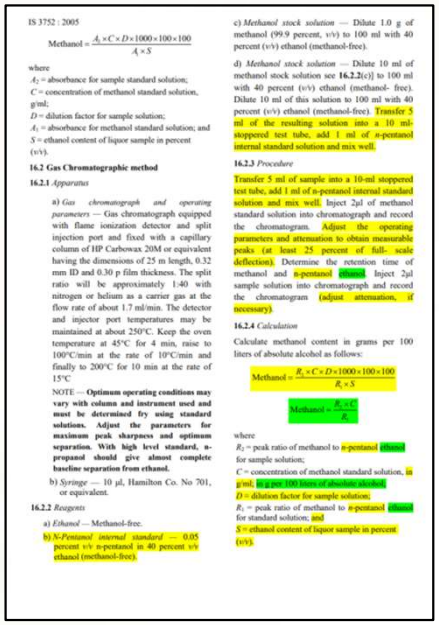
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$$\text{Methanol} = \frac{A_2 \times C \times D \times 1000 \times 100 \times 100}{A \times S}$$

where
A_2 = absorbance for sample standard solution;
C = concentration of methanol standard solution, g/ml;
D = dilution factor for sample solution;
A_1 = absorbance for methanol standard solution; and
S = ethanol content of liquor sample in percent (v/v).

16.2 Gas Chromatographic method

16.2.1 *Apparatus*

a) *Gas chromatograph and operating parameters* — Gas chromatograph equipped with flame ionization detector and split injection port and fixed with a capillary column of HP Carbowax 20M or equivalent having the dimensions of 25 m length, 0.32 mm ID and 0.30 p film thickness. The split ratio will be approximately 1:40 with nitrogen or helium as a carrier gas at the flow rate of about 1.7 ml/min. The detector and injector port temperatures may be maintained at about 250°C. Keep the oven temperature at 45°C for 4 min, raise to 100°C/min at the rate of 10°C/min and finally to 200°C for 10 min at the rate of 15°C

NOTE — **Optimum operating conditions may vary with column and instrument used and must be determined fry using standard solutions. Adjust the parameters for maximum peak sharpness and optimum separation. With high level standard, n-propanol should give almost complete baseline separation from ethanol.**

b) *Syringe* — 10 µl, Hamilton Co. No 701, or equivalent.

16.2.2 *Reagents*

a) *Ethanol* — Methanol-free.

b) *N-Pentanol internal standard* — 0.05 percent v/v n-pentanol in 40 percent v/v ethanol (methanol-free).

c) *Methanol stock solution* — Dilute 1.0 g of methanol (99.9 percent, v/v) to 100 ml with 40 percent (v/v) ethanol (methanol-free).

d) *Methanol stock solution* — Dilute 10 ml of methanol stock solution see **16.2.2**(c)] to 100 ml with 40 percent (v/v) ethanol (methanol- free). Dilute 10 ml of this solution to 100 ml with 40 percent (v/v) ethanol (methanol-free). Transfer 5 ml of the resulting solution into a 10 ml-stoppered test tube, add 1 ml of *n*-pentanol internal standard solution and mix well.

16.2.3 *Procedure*

Transfer 5 ml of sample into a 10-ml stoppered test tube, add 1 ml of n-pentanol internal standard solution and mix well. Inject 2µl of methanol standard solution into chromatograph and record the chromatogram. Adjust the operating parameters and attenuation to obtain measurable peaks (at least 25 percent of full- scale deflection). Determine the retention time of methanol and n-pentanol ethanol. Inject 2µl sample solution into chromatograph and record the chromatogram (adjust attenuation, if necessary).

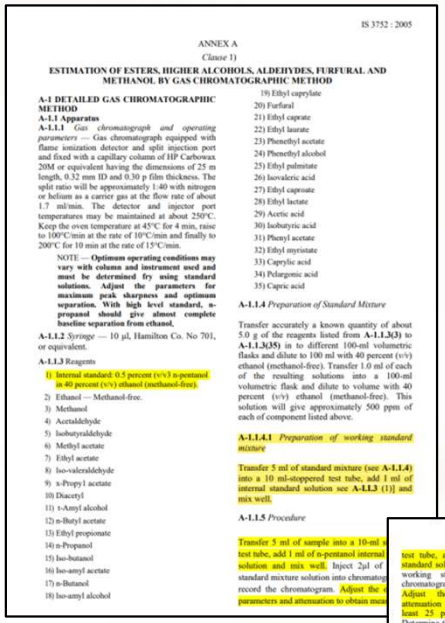
16.2.4 *Calculation*

Calculate methanol content in grams per 100 liters of absolute alcohol as follows:

$$\text{Methanol} = \frac{R_2 \times C \times D \times 1000 \times 100 \times 100}{R_1 \times S}$$

$$\text{Methanol} = \frac{R_2 \times C}{R_1}$$

where
R_2 = peak ratio of methanol to n-pentanol ethanol for sample solution;
C = concentration of methanol standard solution, in g/ml; in g per 100 liters of absolute alcohol;
D = dilution factor for sample solution;
R_1 = peak ratio of methanol to *n*-pentanol ethanol for standard solutions; and
S = ethanol content of liquor sample in percent (v/v).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ANNEX A
Clause 1)

ESTIMATION OF ESTERS, HIGHER ALCOHOLS, ALDEHYDES, FURFURAL AND METHANOL BY GAS CHROMATOGRAPHIC METHOD

A-1 DETAILED GAS CHROMATOGRAPHIC METHOD

A-1.1 Apparatus

A-1.1.1 *Gas chromatograph and operating parameters* — Gas chromatograph equipped with flame ionization detector and split injection port and fixed with a capillary column of HP Carbowax 20M or equivalent having the dimensions of 25 m length, 0.32 mm ID and 0.30 p film thickness. The split ratio will be approximately 1:40 with nitrogen or helium as a carrier gas at the flow rate of about 1.7 ml/min. The detector and injector port temperatures may be maintained at about 250°C. Keep the oven temperature at 45°C for 4 min, raise to 100°C/min at the rate of 10°C/min and finally to 200°C for 10 min at the rate of 15°C/min.

NOTE — **Optimum operating conditions may vary with column and instrument used and must be determined fry using standard solutions. Adjust the parameters for maximum peak sharpness and optimum separation. With high level standard, n-propanol should give almost complete baseline separation from ethanol.**

A-1.1.2 *Syringe* — 10 µl, Hamilton Co. No 701, or equivalent.

A-1.1.3 Reagents

1) Internal standard: 0.5 percent (v/v) n-pentanol in 40 percent (v/v) ethanol (methanol-free).
2) Ethanol — Methanol-free.
3) Methanol
4) Acetaldehyde
5) Isobutyraldehyde
6) Methyl acetate
7) Ethyl acetate
8) Iso-valeraldehyde
9) n-Propyl acetate
10) Diacetyl
11) t-Amyl alcohol
12) n-Butyl acetate
13) Ethyl propionate
14) n-Propanol
15) Iso-butanol
16) Iso-amyl acetate
17) n-Butanol
18) Iso-amyl alcohol
19) Ethyl caprylate
20) Furfural
21) Ethyl caprate
22) Ethyl laurate
23) Phenethyl acetate
24) Phenethyl alcohol
25) Ethyl palmitate
26) Isovaleric acid
27) Ethyl caproate
28) Ethyl lactate
29) Acetic acid
30) Isobutyric acid
31) Phenyl acetate
32) Ethyl myristate
33) Caprylic acid
34) Pelargonic acid
35) Capric acid

A-1.1.4 *Preparation of Standard Mixture*

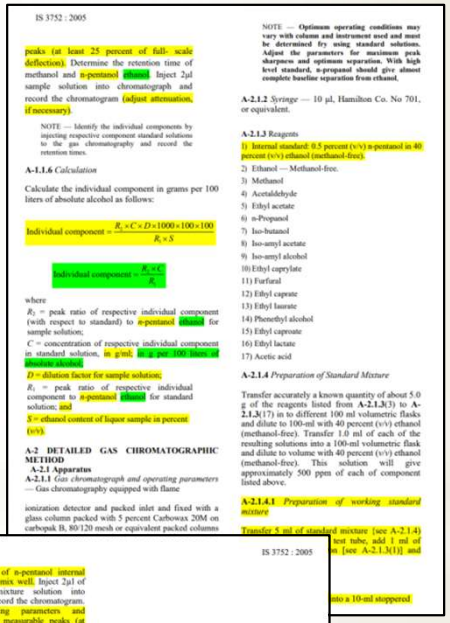
Transfer accurately a known quantity of about 5.0 g of the reagents listed from **A-1.1.3**(3) to **A-1.1.3**(35) in to different 100-ml volumetric flasks and dilute to 100 ml with 40 percent (v/v) ethanol (methanol-free). Transfer 1.0 ml of each of the resulting solutions into a 100-ml volumetric flask and dilute to volume with 40 percent (v/v) ethanol (methanol-free). This solution will give approximately 500 ppm of each of component listed above.

A-1.1.4.1 *Preparation of working standard mixture*

Transfer 5 ml of standard mixture (see **A-1.1.4**) into a 10 ml-stoppered test tube, add 1 ml of internal standard solution see **A-1.1.3** (1)] and mix well.

A-1.1.5 *Procedure*

Transfer 5 ml of sample into a 10-ml s
test tube, add 1 ml of n-pentanol internal
solution and mix well. Inject 2µl of
standard mixture solution into chromatogr
record the chromatogram. Adjust the
parameters and attenuation to obtain meas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peaks (at least 25 percent of full- scale deflection). Determine the retention time of methanol and n-pentanol ethanol. Inject 2µl sample solution into chromatograph and record the chromatogram (adjust attenuation, if necessary).

NOTE — Identify the individual components by injecting respective component standard solutions to the gas chromatography and record the retention times.

A-1.1.6 *Calculation*

Calculate the individual component in grams per 100 liters of absolute alcohol as follows:

$$\text{Individual component} = \frac{R_2 \times C \times D \times 1000 \times 100 \times 100}{R_1 \times S}$$

$$\text{Individual component} = \frac{R_2 \times C}{R_1}$$

where
R_2 = peak ratio of respective individual component (with respect to standard) to n-pentanol ethanol for sample solution;
C = concentration of respective individual component in standard solution, in g/ml; in g per 100 liters of absolute alcohol;
D = dilution factor for sample solution;
R_1 = peak ratio of respective individual component to n-pentanol ethanol for standard solution; and
S = ethanol content of liquor sample in percent (v/v).

A-2 DETAILED GAS CHROMATOGRAPHIC METHOD

A-2.1 Apparatus

A-2.1.1 *Gas chromatograph and operating parameters* — Gas chromatography equipped with flame

ionization detector and packed inlet and fixed with a glass column packed with 5 percent Carbowax 20M on carbopak B, 80/120 mesh or equivalent packed columns

NOTE — **Optimum operating conditions may vary with column and instrument used and must be determined fry using standard solutions. Adjust the parameters for maximum peak sharpness and optimum separation. With high level standard, n-propanol should give almost complete baseline separation from ethanol.**

A-2.1.2 *Syringe* — 10 µl, Hamilton Co. No 701, or equivalent.

A-2.1.3 Reagents

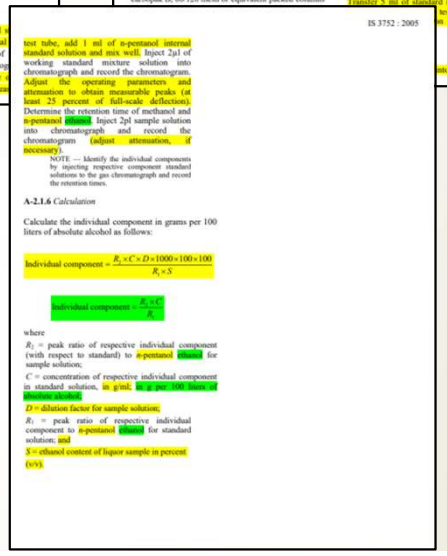
1) Internal standard: 0.5 percent (v/v) n-pentanol in 40 percent (v/v) ethanol (methanol-free).
2) Ethanol — Methanol-free.
3) Methanol
4) Acetaldehyde
5) Ethyl acetate
6) n-Propanol
7) Iso-butanol
8) Iso-amyl acetate
9) Iso-amyl alcohol
10) Ethyl caprylate
11) Furfural
12) Ethyl caprate
13) Ethyl laurate
14) Phenethyl alcohol
15) Ethyl caproate
16) Ethyl lactate
17) Acetic acid

A-2.1.4 *Preparation of Standard Mixture*

Transfer accurately a known quantity of about 5.0 g of the reagents listed from **A-2.1.3**(3) to **A-2.1.3**(17) in to different 100 ml volumetric flasks and dilute to 100-ml with 40 percent (v/v) ethanol (methanol-free). Transfer 1.0 ml of each of the resulting solutions into a 100-ml volumetric flask and dilute to volume with 40 percent (v/v) ethanol (methanol-free). This solution will give approximately 500 ppm of each of component listed above.

A-2.1.4.1 *Preparation of working standard mixture*

Transfer 5 ml of standard mixture [see A-2.1.4)
test tube, add 1 ml of
[see A-2.1.3(1)] and
into a 10-ml stoppered


IS 3752 : 2005

test tube, add 1 ml of n-pentanol internal standard solution and mix well. Inject 2µl of working standard mixture solution into chromatograph and record the chromatogram. Adjust the operating parameters and attenuation to obtain measurable peaks (at least 25 percent of full-scale deflection). Determine the retention time of methanol and n-pentanol ethanol. Inject 2µl sample solution into chromatograph and record the chromatogram (adjust attenuation, if necessary).

NOTE — Identify the individual components by injecting respective component standard solutions to the gas chromatograph and record the retention times.

A-2.1.6 *Calculation*

Calculate the individual component in grams per 100 liters of absolute alcohol as follows:

$$\text{Individual component} = \frac{R_2 \times C \times D \times 1000 \times 100 \times 100}{R_1 \times S}$$

$$\text{Individual component} = \frac{R_2 \times C}{R_1}$$

where
R_2 = peak ratio of respective individual component (with respect to standard) to n-pentanol ethanol for sample solution;
C = concentration of respective individual component in standard solution, in g/ml; in g per 100 liters of absolute alcohol;
D = dilution factor for sample solution;
R_1 = peak ratio of respective individual component to n-pentanol ethanol for standard solution; and
S = ethanol content of liquor sample in percent (v/v).

Norma Mexicana NMX-V-005-NORMEX-2013 – simplification
Determination de Aldehidos, Esters, Methanol y Alcoholes Superiores.
Metodo por cromatografia de Gases

NMX-V-005-NORMEX-2013
FECHA DE INICIO DE VIGENCIA: 24 DE MARZO DE 2014

5.0 DETERMINACION DE ALDEHIDOS, ESTERES, METANOL Y ALCOHOLES SUPERIORES. ***METODO POR CROMATOGRAFIA DE GASES***

5.1 **Fundamento**
Este método se basa en los principios de la cromatografía de gases y consiste en la inyección de una pequeña cantidad de la muestra (que contiene una mezcla de sustancias volátiles) en el inyector de un cromatógrafo de gases en el que son vaporizadas y transportadas por un gas inerte a través de una columna empacada o capilar con un líquido de partición que presenta solubilidad selectiva con los componentes de la muestra, ocasionando su separación.

Los componentes que eluyen de la columna pasan uno a uno por el "detector", el cual genera una señal eléctrica proporcional a su concentración, la que es transformada por el registrador, integrador o sistema de manejo de datos en una gráfica llamada cromatograma.

La identificación de cada componente registrado como un pico en el cromatograma, se realiza por inyección del o de los componentes en forma pura y con las mismas características y entidades que se sospecha contiene la muestra, midiendo el tiempo de retención en esas condiciones. También se puede comprobar por adición del componente a la muestra e inyectándola nuevamente para apreciar el incremento de altura o área del pico correspondiente.

La cuantificación se puede efectuar por cualquiera de estos tres métodos: normalización, estandarización externa y estandarización interna, siendo este último el único que se describe a continuación:

La cuantificación por estandarización interna consiste en obtener el cromatograma de la muestra estandarizada, adicionada de una Sustancia llamada estándar interno que debe aparecer en un sitio del cromatograma, libre de traslapes y desde luego no debe ser componente de la muestra, aunque es recomendable que sea de la misma naturaleza química y del mismo intervalo de concentración que el componente de la muestra por cuantificar. Deben obtenerse cromatogramas paralelos con soluciones de concentración conocida de cada componente por cuantificar y del estándar interno que sea adecuad muestra y trazar una curva de calibración que tenga por ordenada la relación de concentraciones correspondientes al componente por cuantificar y al estándar interno y en las abscisas la relación de áreas correspondientes al compuesto por cuantificar y a las áreas del estándar interno.

Esta curva sirve para situar en sus ordenadas la relación de áreas correspondientes al componente por cuantificar y el estándar interno del cromatograma de la muestra estandarizada y así ubicar la relación correspondiente de concentraciones.

5.2 Alcance
Este método determina la concentración de aldehídos, ésteres, alcoholes superiores y metanol en bebidas alcohólicas por cromatograma de gases.

5.3 Equipos e instrumentos
Todos los equipos e instrumentos de medición deberán ser calibrados y/o verificados.

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AOAC Official Method 972.11 - simplification

Methanol in Distilled Liquors. Gas Chromatographic Method

26.1.36

AOAC Official Method 972.11
Methanol in Distilled Liquors
Gas Chromatographic Method
First Action 1972
Final Action 1973

A. Apparatus

See 968.09A (see 26.I.30).

B. Reagents

(a) Alcohol. —Methanol-free.

(b) *Methanol stock* solution. —Dilute 10 mL methanol, 99.9 *mol* % (Fisher Scientific Co., A-936, or equivalent) to 100 mL with 40% alcohol.

~~(c) *n-Butyl alcohol internal standard stock* solution. Dilute 10 mL n-butanol, 99.9 mol % (Fisher Scientific Co., A-384, or equivalent) to 100 mL with 40% alcohol.~~ The ethanol contained in the analyzed alcoholic product is used as an internal standard

(d) *Methanol standard solution.* —0.050% methanol plus 0.030% ii-butanol internal standard. Fill 100 mL volumetric flask to ca 99 mL with 40% alcohol and add, by syringe, 500 ML mixture stock solution, (b), and 300 µL n-butanol stock solution, (c). Mix and dilute to volume with 40% alcohol. Mix again.

G. Determination

Inject 10 µL mixture of standard solution. Adjust operating parameters and attenuation to obtain measurable peak height (ca ¼, full scale deflection). Determine retention time of methanol and ~~n-butanol~~ ethanol (ca 3 and 7 min, respectively). Inject 10 µL test portion to estimate methanol, using attenuation if necessary, and to check for absence of n-butanol. ~~On basis of presence or absence of n-butanol in test portion, determine methanol content from~~

~~standard curve prepared according to (a) or (b).~~ The ethanol contained in the analyzed alcoholic product is used as an internal standard.

~~(a) *n-Butyl alcohol* absent. —On basis of estimate of methanol, prepare series of standards (4 or 5) in which range of concentration includes methanol concentration in test portion. Add internal standard to both test portion and standard solutions at concentration similar to that of methanol in test portion. Calculate peak height ratios of methanol:n-butanol, using average of duplicate injections, and plot ratios against methanol concentration.~~ Put ethanol solution into 2 mL chromatographic vial for analysis.

~~(b) *n-Butyl alcohol present.* Prepare series of methanol standards as in (a), but do *not* add n-butanol to test portion or to standards. Plot actual peak height of methanol against concentration.~~

Reference: *JAOAC* 55, 564(1972).

CAS-67-56- I (methanol)

50

26.1.36'

AOAC·Official·Method·972.11¶
Methanol·in·Distilled·Liquors¶
Gas·Chromatographic·Method·
First·Action·2023¶
·Final·Action·2025¶

A.→***Apparatus***¶

See·968.09A·(see·26.·I.·30).¶

B.→Reagents¶

(a)→Alcohol.·—Methanol-free.¶

(b)→*Methanol·stock*·solution.·—Dilute·10·mL·methanol,·99.9·*mol*·% (Fisher·Scientific·Co.,·A-936,·or·equivalent)·to·100·mL·with·40%· alcohol.¶

(c)→The·ethanol·contained·in·the·analyzed·alcoholic·product·is·used as·an·internal·standard¶

(d)→*Methanol·standard·solution.*·—0.050%·methanol·plus·0.030% ii-butanol·internal·standard.·Fill·100·mL·volumetric·flask·to·ca·99·mL with·40%·alcohol·and·add,·by·syringe,·500·ML·mixture·stock·solution, (b),·and·300·pL·n-butanol·stock·solution,·(c).·Mix·and·dilute·to·volume with·40%·alcohol.·Mix·again.¶

G.·Determination¶

·····Inject· 10· pL· mixture· of· standard· solution.· Adjust· operating parameters·and·attenuation·to·obtain·measurable·peak·height·(ca·%,·full scale·deflection).·Determine·retention·time·of·methanol·and·ethanol·(ca 3·and·7·min,·respectively).·Inject·10·pL·test·portion·to·estimate methanol,·using·attenuation·if·necessary,·and·to·check·for·absence·of n-butanol.·The·ethanol·contained·in·the·analyzed·alcoholic·product·is used·as·an·internal·standard.¶

·····Put·ethanol·solution·into·2·mL·chromatographic·vial·for·analysis.¶

¶

Reference:·JAOC·66,·555(2021)¶

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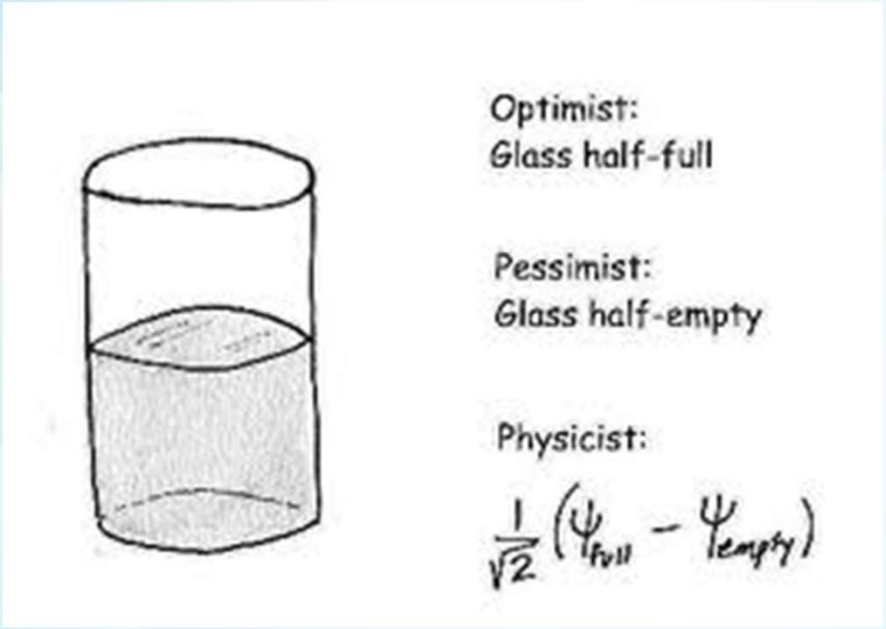
CAS-67-56-1·(methanol)·¶

* Thank You for attention!



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