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Quartz Crystal Microbalance Detection Usage for Study of Permeation of Hydrocarbons in a Homological Line

P. Otrisal* and S. Florus

NBC Defence Institute of University of Defence, Brno

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Abstract:

The deflection from classical Chemical Warfare Agents in military use has been currently noticed. That is why questions' solution concerning contamination after their use importantly decreases. On the other hand, a possibility of contamination development after both military and terroristic Toxic Industrial Chemicals usage is very high. Despite these very important facts, necessity of solutions of questions concerning study of suits' protective properties used for specialists' isolative protection increases. In this way, the gained results principally affect the evaluation of effectivity of accepted protective measurements in all kinds of military operations conducted by both Czech Armed Forces Chemical Corps specialists and specialists from Fire Rescue Brigades. The main aim of the article is to point to some properties of butyl-rubber polymer mixture coated on polyamide fabric considering selected liquid aliphatic saturated hydrocarbons in a homological line with the use of the PIEZOTEST method which uses a QCM detector.

Keywords:

PIEZOTEST, QCM detector, Toxic Industrial Chemicals, Chemical Warfare Agents, butyl-rubber, aliphatic liquid saturated hydrocarbons.

1. Introduction

Study of traditional materials used for a relatively long time for construction of protective suits of isolative type is not a new matter. Butyl-rubber and its protective properties were researched in the sixties. In that time, the implementation of protective suit named as OPCH-70 was prepared. Then both military and civilian norms

* *Corresponding author: NBC Defence Institute, University of Defence, Sídliště Víta Nejedlého, 682 01 Vyškov, Czech Republic, phone: +420 973 452 335, +420 973 452 330, E-mail: Pavel.Otrisal@unob.cz*

demanded testing of the breakthrough time (BT) within a scope of Chemical Warfare Agents (CWAs). An ideal one for these purposes was sulphur mustard. From the results measured for this CWA, approximate values of BTs for other CWAs were derived. It did not guarantee gaining exact results.

Specification of current world security threats shows that it is not possible to make do with results which are set only for one particular CWA within keeping exactly defined conditions. A wide spectrum of operations in which Czech Armed Forces (CAF) Chemical Corps' (CCs) specialists can be deployed brings a potential chance to contact Toxic Industrial Materials (TIMs) in all kinds of their phases. Mainly affection of military CCs specialists in operations within the Czech Republic Integrated Rescue System brings a solution of relatively new tasks connected with hazard management of created chemical contamination after the Toxic Industrial Chemicals (TICs) release into the environment.

2. Determination of Breakthrough Time with the Help of PIEZOTEST Method

To be able to study barrier materials' protective properties used for people's isolative protection not only in relation to CWAs but also to TICs, it was necessary to develop qualitatively a new method which will not be selectively focused on a particular type of CWA only. A new device named as PIEZOTEST based on usage of QCM (Quartz Crystal Microbalance) detector was developed within the Military Technical Institute of Protection located in Brno. This device eliminates disadvantages of so far used selective methods. The method of QCM detection is simple, unpretentious for service personnel and relatively cheap. Moreover, it is possible to use it in both stationary and mobile laboratories, it means in field conditions. This method provides sufficiently conclusive values for evaluation of materials' protective properties. Breakthrough time results show that this method is very good for usage in the future and it is applicable for the whole spectrum of both persistent CWAs and liquid TICs.

2.1. Principle of the Method

QCM detectors, very often marked as quartz resonators, register a change of weight with the help of a piezoelectric cut. Quartz Crystal Microbalances are piezoelectric devices which are able to very sensitively measure weight changes with nanogram accuracy. It is ensured that a crystal oscillates mechanically in a resonant-cut mode with the application of a high-frequency field with the help of metal electrodes located on both sides of a quartz crystal AT-cut circle disc [1].

An incurred electric charge is directly proportional to effective force which takes effects increasing concentration of permeating chemical compound on the quartz crystal. A pressure change thus provokes the change of electric voltage whose size corresponds to the created charge. The created charge is drawn from electrodes conducted directly on the crystal. It is necessary to emphasize that within high temperatures happens to loss of piezoelectric properties from the reason of ions' formation breaking. This change occurs in leaps and bounds, similarly as the change of the state of matter. A transient temperature is characteristic for particular material and it is called the Curie point (T_c). This temperature is a characteristic property of both ferromagnetic and piezoelectric compounds. It has been described by a French physician Pierre Curie. He found out that the quartz crystal loses its either ferromagnetic or piezoelectric properties above T_c. Vysloužil [2] has informed that temperatures T_c in relation to quartz crystals are in the scope of 800 – 1 400 K.

A crystal lattice is deformed in such a way that the dipole moment increases in a molecule of a crystal. It leads to the electric potential development. Alternate mechanical deformation happens within crystals which become a part of an oscillating circuit. These deformations cause crystals' vibrating movement and lead to creation of permanent acoustic wave. The piezoelectric crystal oscillates in a regime of an angle wide cut, simultaneously with its main axe. Piezoelectric crystals made in a variation of the AT-cut use a type of quartz cut under an angle of 35°15'. It is visible in Fig. 1 [3].

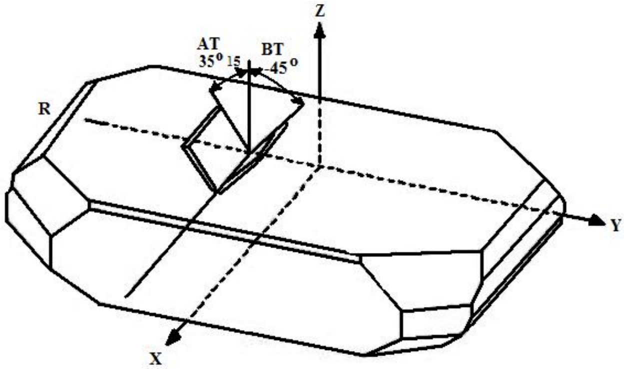

Fig. 1 A quartz crystal with cuts

Sensors of a size from 10 to 15 mm and a thickness from 0.1 to 0.2 mm are used for QCM detectors construction. Harsynyi [4] claims that resonant frequencies are moved in a scope from 6 to 20 MHz while keeping conditions of high stability. A weight sensitivity of oscillating frequency depends on a sum of weight of the crystal, used electrodes and constructive materials on their surface. An application of a suitable detection layer on electrode surface enables either temporary or permanent weight linkage of the crystal with a tested compound which causes a detectable change of the crystal weight. For QCM sensors, it is typical to use the above mentioned AT-cut quartz crystal with basic frequency of 9 MHz. This frequency is easily measurable thereby that 1 ng of an analyte which sticks in on a surface of crystal detection layer can be immediately detected as a decrease of crystal frequency in 1 Hz [5-10]. Thus, quantity of chemical compound caught on suitable either adsorbent or absorbent is determined. In principle, it is a gravimetric setting. The resonator from α modification of SiO2 is used in the case of used QCM detectors. They are very rigid, relatively chemically resistant and low temperature extensible.

An either tin or slide cut from the crystal and subsequently emended into an exact shape is a main part of piezoelectric resonator (see Fig. 2). Properties of the resonator are significantly affected with either tin or slide orientation toward crystallography axis. Metal electrodes with outlets and sorbent surface are coated on a cut surface. With the help of suitable adjustment is reached the state that after connection of the oscillator's electric circuit a piezoelectric resonator vibrates on resonant frequency. This frequency is kept with big accuracy. Mounted and set piezoelectric quartz resonator in a suitable holder creates a piezoelectric crystal unit. [11].

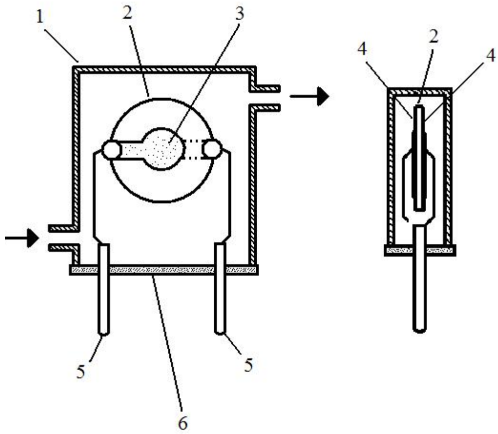

Fig 2 An example of setting of crystal resonator: 1 – measure chamber, 2 – quartz cut, 3 – electrode, 4 – layer of sorbent, 5 – electric leads in, 6 – isolative base

The crystal resonator has in a spare circuit 4 components:

- self capacity C_0 which is created on the crystal between metal contact electrodes;
- "parasite" resistor which is parallel to the first circuit R_h;
- inductivity L_h;
- capacity C_h.

Quantities Rh, Lh, Ch are concerned mostly with incoming leading which results from a scheme in Fig. 3.

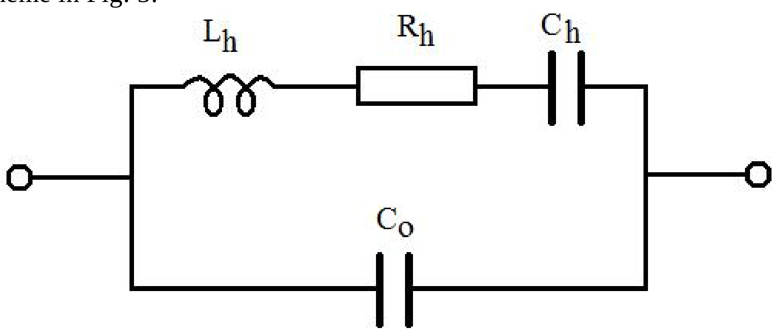

Fig 3 A spare circuit of crystal resonator

In such a case it is possible to observe two resonant frequencies:

- serial f_s determined with values L_h, C_h – equation (1) and
- parallel f_p determined with values L_h, C_h – equation (2).

Both resonant frequencies approve themselves as extremes of dependence of impedance $|Z|$ size on frequency of the measured signal (Fig. 4)

$$f_s = \frac{1}{2\pi\sqrt{L_h C_h}} \qquad (1)$$

$$f_p = \frac{1}{2\pi\sqrt{L_h C_h C_0 /(C_h + C_0)}} \tag{2}$$

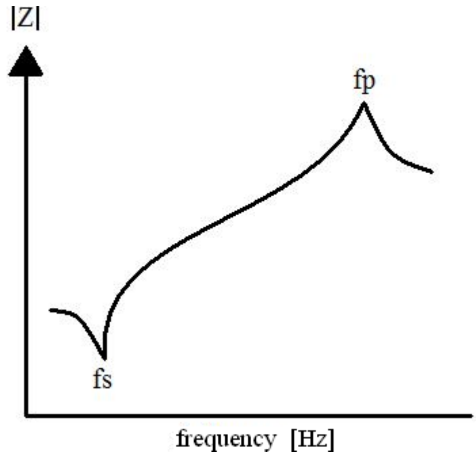

Fig 4 Frequency dependency of resonator impedance with marked vibration f_s, respectively f_p

If a sorbent layer catches a detect gas during which a weight of vibrating set is changed, the displacement of resonant frequency occurs in accordance with a formula (3). A practical application is demonstrated in Fig. 5:

$$\Delta f = const.\ f^2 \frac{\Delta m}{A} \tag{3}$$

where:

Δf - change of frequency [Hz];

F - basic frequency [Hz];

Δm - addition of weight [g];

A - area of cut [cm^2].

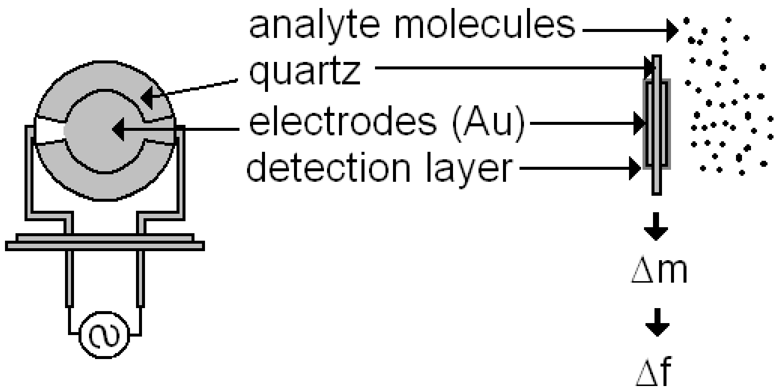

Fig 5 Working principle of QCM sensor

2.2. Fundamentals of the Measurement

A sample of tested isolative protective folio is located in a teflon permeation cell (see Fig. 6). The sample hermetically divided the permeation cell in two parts – the first one, where the contamination with a researched harmful substance occurs and the second one, where QCM detector with the polymer layer is. The harmful substance which permeates through the polymer folio and whose concentration increases in a close area around the detector, follows by diffusion procedures whose rate is ordinarily in cm/min to the crystal. The harmful substance is caught in the detector's polymer layer which causes a change of its working frequency.

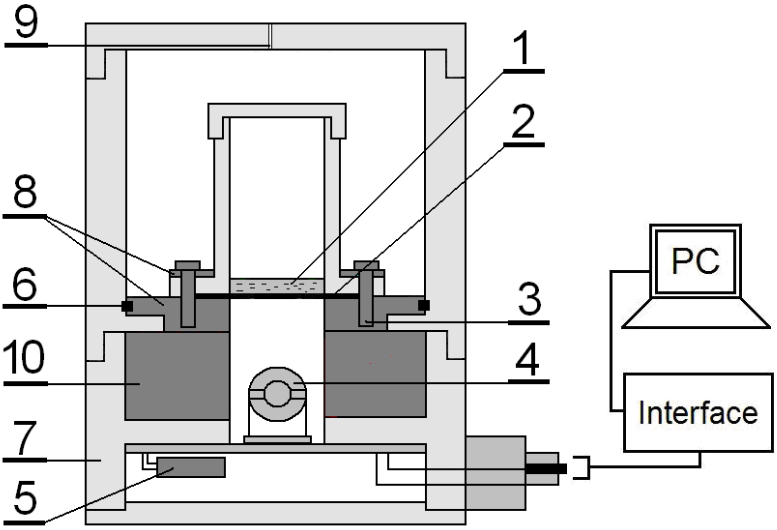

Fig 6 A scheme of permeation cell of PIEZOTEST device

1 – test substance, 2 – tested material, 3 – tightening screws, 4 – measuring crystal,5 – reference crystal, 6 – tightening ring, 7 – body of permeation cell, 8 – collars, 9 – air hole, 10 – teflon pad

Dependence of piezoelectric crystal's working frequency addition on time can be constructed for quick evaluation of tested material of resistance. With the prolongation of a linear part of dependency and its cross on a time axis it is possible to obtain values of BT for a couple folio – researched chemical compound, so called Lag Time (see Fig. 7).

3. Used Devices and Chemicals and their Basic Physical and Chemical Properties

PIEZOTEST device has been used for measurement of OPCH-05 isolative protective fabric's resistance (produced by Gryf Ltd, Havlíčkův Brod, Czech Republic). The main part of this device is the above-mentioned QCM detector. A press (produced by Polymertest, Zlín, Czech Republic) with a cutter tool in accordance with own choice (Marbach, Brno, Czech Republic) for cutting of researched samples have been used for preparation of isolative protective folio samples. Biological incubator Friocell 111 (BMT Brno, Czech Republic) has been used for tempering of permeation cells within the process of measurement. This device has been little bit conformed. A hole for elongation of PIEZOTEST device wires has been made on a glass door. As the tested material, an isolative protective folio used for OPCH-05 protective suit production has been used. This material has been delivered by ECOPROTECT Company Zlín. This company is an OPCH-05 producer. The width of samples has been measured with the help of a quick thickness meter of the type of 542-401 (Mitutoyo, Japan) with the accuracy of 1 μm.

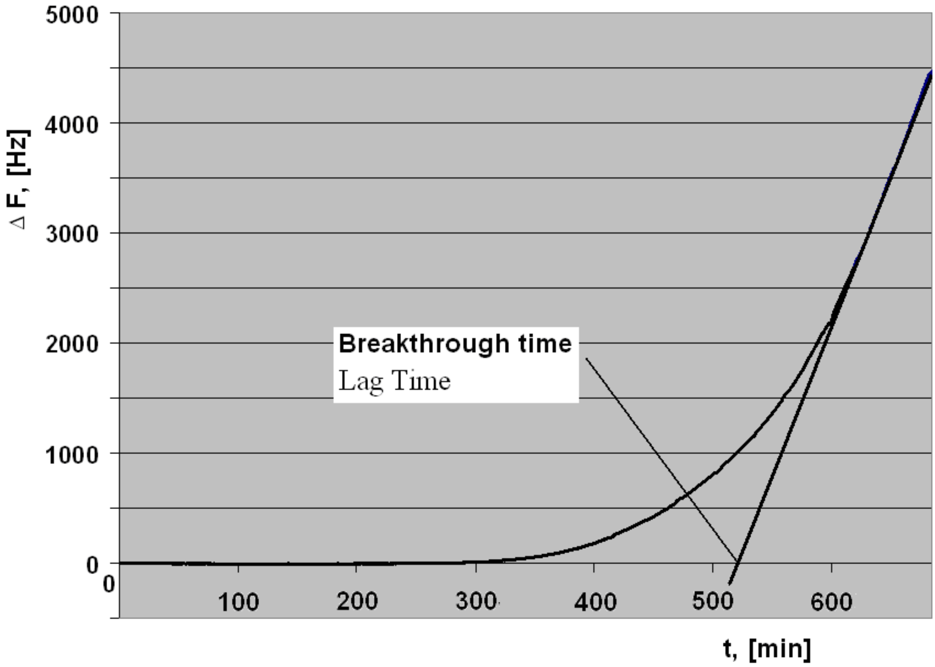

Fig 7 Scheme of quick evaluation of constructive materials resistance from dependency of QCM detector's working frequency change on time

OPCH-05's BT has been tested for aliphatic saturated liquid hydrocarbons from C5 to C10, thus, in a line from pentane to decane. Experimental work has not been performed with nonane. Data concerning both purity of used chemicals and their producers are introduced in Table 1.

Tab 1 Purity and producers of chemicals

Hydrocarbon/property	Purity	Producer
Pentane (C5)	98 %	Aldrich-Chemie, Germany
Hexane (C6)	for pesticide residue analysis, PESTAPUR	Chromservis, Czech Republic
Heptane (C7)	p.a.	LOBA – Chemie, Austria
Octane (C8)	More than 99 %	Fluka Chemie, GmbH, Switzerland
Decane (C10)	Zur Synthese	MERCK, Germany

4. Measurement Results and Discussion

Measurements have shown that material of isolative protective folio for OPCH-05 construction is homogenous from the point of view of its thicknesses. The middle value of more than 160 measured samples was about 0.350 mm and the smallest value of the thickness 0.348 mm (Table 2). Material has not embodied any disruptions in an integrity caused by either mechanical damage or damage resulted from rubber corrosion.

Measurements of OPCH-05 isolative protective folio's chemical resistance have shown high reproducibility of measurements performed with PIEZOTEST device. With regard to sufficient time for tempering and exactness of used tempering device, diversions could be caused only by different thickness of the isolative protective folio samples in permeation cells. It has been found out that the isolative protective folio BT is shorter and the differences of thickness of isolative protective folio samples can be neglected. This fact has not been proved in particular cases only, however, it is valid generally. At the same time, it has been proved that regardless QCM detector working frequency in permeation cells, results of OPCH-05 isolative protective folio chemical resistance expressed by so called Lag Time for the same folios were basically the same. This fact has been confirmed after the forced exchanging of QCM detector as a consequence of its damage.

Verification of effects of contaminant's chemical structure on chemical resistance of OPCH-05's isolative protective fabric has been done with the help of the line of aliphatic saturated C5-C10 excepting nonane. This line has been used because of its simple chemical structure and the constant change of chemical structure within a methyl group. It has been found that the change of the chemical structure in the homological line has lead to the OPCH-05 isolative protective folio BT prolongation. How it is shown in Fig. 8 and in Table 2, with addition of the methyl group comes to increasing of resistance of OPCH-05´s folio. Resistance of the OPCH-05's fabric has been 4.6 times longer for decane in comparison with Pentane. With regard to the time expression, the OPCH-05's folio has had longer BT for decane. The difference equals 17.5 minutes. It is probably connected with the increasing of molar volume of the chemical substance, which rises in the same line (see Table 3).

It is understandable that resulted isolative protective folios resistance of constructive materials used for protective fabrics construction, will depend on more factors. The most important is perhaps a character of a dissolution reagent which affects material, temperature or thickness of a barrier layer. Probably the first most important sign of possible resistance is either a rate or a degree of swelling of these materials in certain chemical compound.

Practical measurements of OPCH-05 folio's resistance for the homological line of liquid aliphatic hydrocarbons showed that PIEZOTEST device is suitable for these purposes. Measurements are reproducible enough and embody low scatter of measurement values. It is the basic presumption to use this device for the study of dependence of constructive materials resistance on chemical compound structure.

5. Conclusion

To identify the values which characterize the protective properties of materials used in individual protection is very important for assessment of their usability in all kinds of military operations. Based on the values measured for liquid hydrocarbons C5-C10, it is possible to make a conclusion that with growing chains' lines, growing molar values and, finally, with growing boiling points of concerning saturated hydrocarbons the values of resistance of OPCH-05's isolative protective folio will grow as well. It is understandable that similar dependencies have to be verified not only for this homological line but also for other categories of chemical substances. These gained values of resistance can enable to either predict constructive materials behaviour compared with interested harmful substances or to define demands for researching of more resistant constructive materials for protective means.

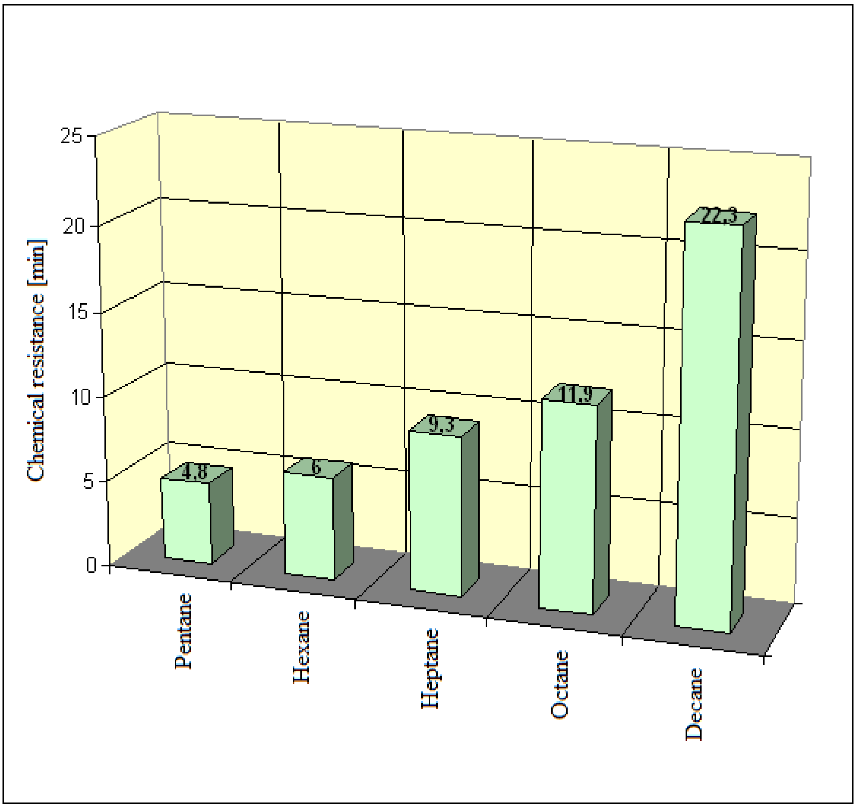

Fig 8 Resistance of OPCH-05's isolative protective folio for selected liquid aliphatic saturated hydrocarbons

Tab. 2 Statistical evaluation of tested OPCH-05 isolative protective samples' thicknesses and their chemical resistance for selected hydrocarbons expressed via the value of Lag Time [min] for temperature 30 °C

Statistical value	*Tested chemical compound*			
	Pentane		*Hexane*	
	Sample thickness [mm]	*Lag-Time [min]*	*Sample thickness [mm]*	*Lag-Time [min]*
Mean value	0.358	5.1	0.349	6.2
Mean value error	0.006	0.15	0.0003	0.098
Median	0.353	5	0.348	6
Standard deviation	0.033	0.91	0.002	0.591
Variance	0.001	0.82	0.000004	0.349
Kurtosis	36.071	4.21	1.538	1.576
Skewness	5.971	1.67	–0.981	0.799
Minimum	0.346	4	0.343	5
Maximum	0.552	8	0.351	8
Valid Number	37	37	36	36
Reliability level (95,0%)	0.011	0.30	0.001	0.199
Minimal value	0.347	4.8	0.348	6,0
Testing conditions: *temperature 30 °C, dosed – 2 ml tested substances, warmth source – biological incubator FRIOCELL*				

Continuing of Tab. 2

Statistical value	*Tested chemical compound*			
	Heptane		*Octane*	
	Sample thickness [mm]	*Lag-Time [min]*	*Sample thickness [mm]*	*Lag-Time [min]*
Mean value	0.352	9.6	0.354	12.3
Mean value error	0.001	0.131	0.0012	0.171
Median	0.352	10	0.354	12
Standard deviation	0.005	0.798	0.005	0.683
Variance	0.00003	0.637	0.00002	0.467
Kurtosis	3.772	2.887	–1.184	–0.592
Skewness	–1.344	1.234	–0.016	–0.358
Minimum	0.333	8	0.347	11
Maximum	0.361	12	0.361	13
Valid Number	37	37	16	16
Reliability level (95,0%)	0.002	0.266	0.003	0.364
Minimal value	0.350	9.3	0.351	11.9
Testing conditions: *temperature 30 °C, dosed – 2 ml tested substances, warmth source – biological incubator FRIOCELL*				

Continuing of Tab. 2

Statistical value	*Tested chemical compound*	
	Decane	
	Sample thickness [mm]	*Lag-Time [min]*
Mean value	0.350	23.2
Mean value error	0.002	0.405
Median	0.354	24
Standard deviation	0.010	2.462
Variance	0.0001	6.063
Kurtosis	0.615	0.021
Skewness	–1.389	–0.511
Minimum	0.325	17
Maximum	0.359	28
Valid Number	37	37
Reliability level (95.0%)	0.003	0.821
Minimal value	0.347	22.3
Testing conditions: *temperature 30 °C, dosed – 2 ml tested substances, warmth source – biological incubator FRIOCELL*		

Tab. 3 Selected characteristic properties of hydrocarbons C5-C10

Hydrocarbons/ property	*Molecular weight [g/mol]*	*Melting point [°C]*	*Boiling point [°C]*
Pentane (C5)	72.15	–129.8	36.1
Hexane (C6)	86.18	–95.0	69.0
Heptane (C7)	100.21	–90.6	98.4
Octane (C8)	114.22	–57.0	125.5
Decane (C10)	142.29	–27.9	174.1

Continuing of Tab. 3

Hydrocarbons/property	*Density [g/cm^3]*	*Viscosity [Pa·s]*	*Molar volume [cm^3/mol]*	*Water solubility (20 °C) [g/dm^3]*
Pentane (C5)	0.626	0.240	115.255	0.004
Hexane (C6)	0.655	0.294	131.612	0.013
Heptane (C7)	0.684	0.386	154.645	none
Octane (C8)	0.703	0.542	162.487	none
Decane (C10)	0.730	0.920	194.917	none

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