Method and complex of express diagnostics of liquid packaged products

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Annotation. In order to improve the efficiency of quality control and safety of liquid packaged products, a method and model of an automated complex have been developed that allow rapid diagnostics of liquid without opening the container and sampling. The article describes the method, the results of its application in the identification of engine oil and the model of a portable automated complex with sensors-covers for continuous monitoring of bottled water. The data of experimental studies of the models are presented. The obvious result of using the method and the complex, from the point of view of energy saving and energy efficiency, is its application for continuous control of motor and transformer oils, to ensure the technical resource of motor vehicles and transformers at electrical substations, which, according to preliminary estimates, reduces the cost of selective control and losses from unscheduled repairs by 2 times.

1 Introduction

Quality and safety control of liquid packaged products is an extremely time-consuming process, since the methods and means used are costly and time-consuming, and the selective control method does not guarantee the quality of each individual packaged product in a batch [1-5], which, to prevent counterfeiting, requires a radical change in the policy of supervision and controls, i.e. it is necessary to develop and implement automated methods and means of continuous control of parameters [6].

Both industrial liquid products and household liquids, in addition to the determination of chemical compositions, can be identified by many physical and chemical parameters, for example, by kinematic and dynamic viscosity, by density by standard temperatures, electrical parameters, by characteristic frequencies, etc. [7-9].

2 Materials and methods

At manufacturing plants, liquid filling in containers is carried out on automated lines, the advantage of which is high accuracy of dosing [10]. At the same time, the standard for packaging strictly limits the maximum deviations from the nominal size and weight of the

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container [11]. Thus, knowing the mass of empty container, it is possible to weigh, without breaking the tightness of the container, to determine the density of the liquid inside it according to the following formula [4, 5]:

$$\rho_i = \left(P_i - P_j\right)/V_{ij}, \tag{1}$$

where are:

P_i – measured weight of the *i*-th sample in a packed container, kg;

P_j – weight of the *j*-th reference container, kg;

V_{ij}=0.5,1.5…*N* – reference container volume, l.

and the values of densities at different temperatures are calculated by the formula [4, 5]:

$$\rho(t) = \rho_{20℃} - \Delta t \cdot (t - 20℃), \tag{2}$$

where are:

$\rho_{20℃}$ – the density of the liquid at 20℃, g/cm^3;

$\Delta t = (18{,}31 - 13{,}233 \cdot \rho_{20℃}) \cdot 10^{-4}$ – temperature correction to density by one degree;

t – the desired temperature, ℃;

Also, the dependence of the kinematic viscosity on the temperature is expressed by the formula [4, 5]:

$$lglg(v + 0{,}8) = a + b\ lgT, \tag{3}$$

where the empirical coefficients a and b are determined from the known pairs of values v and T by the formulas:

$$a = lglg(v_1 + 0{,}8) - b\ lgT_1, \qquad b = \frac{\lg\left(\left.lg(v_1 + 0{,}8)\right/lg(v_1 + 0{,}8)\right)}{lg\frac{T_1}{T_2}}. \tag{4}$$

On the other hand, the simplest method for determining the transport function in the study of an electrochemical system is to excite it with a signal in the form of a sinusoidal wave [12, 13]. This method uses the conductivity relations in liquids, which are described by Ohm's laws (Z, G, R, I). In addition to determining the specific parameters of samples and standards, the main equation of the characteristic impedance can be used [4, 5]:

$$Z_i = \sqrt{\frac{R_i + i\omega L_i}{G_i + i\omega C_i}}, \tag{5}$$

where are:

Z_i – complex resistance;

$\omega = 2\pi f$ – cyclic frequency;

i – imaginary unit;

R_i – resistance;

L_i – inductance;

G_i – conductivity;

C_i – capacitance.

By solving the impedance equation (5), additional parameters can be obtained for sample identification, in particular, for determining the magnetic permeability of a liquid using the formula [4, 5]:

$$\mu = \frac{Z^2 \cdot 2l}{S \cdot G \cdot (1 + i)^2 \cdot \mu_0 \cdot \omega}, \tag{6}$$

where are:

μ_0 – magnetic constant;

S – surface area of the electrode, m^2;

l – distance between measuring electrodes, m.

In turn, the permittivity can be determined by changing the tangent of the loss angle and the conductivity [4, 5]:

$$\varepsilon = \varepsilon' - i\varepsilon'' \;\rightarrow\; tg\delta = \frac{\varepsilon''}{\varepsilon'} = \frac{\sigma}{\omega\varepsilon'^{\varepsilon_0}}, \tag{7}$$

where are:

ε – relative dielectric permittivity;

ε'' – imaginary part of the permittivity;

ε' – real part of the permittivity;

σ – active conductivity, taking into account both types of losses;

ε_0 – permittivity of vacuum.

Then, using the Debye formula [4, 5], the relaxation times are determined: macroscopic and microscopic:

$$\varepsilon'' = \frac{(\varepsilon - \varepsilon_\infty)\omega\tau}{1 + \omega^2\tau^2}, \;\; \varepsilon' = \varepsilon_\infty + \frac{\varepsilon - \varepsilon_\infty}{1 - \omega^2\tau^2}, \qquad tg\delta = \frac{\varepsilon''}{\varepsilon'} = \frac{(\varepsilon - \varepsilon_\infty)\omega\tau}{\varepsilon + \varepsilon_\infty\omega^2\tau^2}, \tag{8}$$

where are:

τ – macroscopic relaxation time.

The complex part of the permittivity ε'' tends to zero, both at small and large values of $w\tau$, and reaches a maximum at $\omega_m\tau = 1$ [4, 5], in which

$$\varepsilon''_m = \frac{\varepsilon - \varepsilon_\infty}{2}, \;\; \varepsilon'_m = \frac{\varepsilon + \varepsilon_\infty}{2}, \tag{9}$$

and the complex dielectric conductivity is equal to

$$\varepsilon^* = \varepsilon_m + \frac{(\varepsilon - \varepsilon_\infty)}{1 + i\omega\left(\frac{\varepsilon + 2}{\varepsilon_\infty + 2}\right)\tau_\mu}, \tag{10}$$

where are:

τ_μ – microscopic relaxation time.

The relation of the microscopic relaxation time to the macroscopic time is expressed by the Pauls equation [4, 5]:

$$\tau = \frac{3\varepsilon\tau_\mu}{2\varepsilon + 1}, \tag{11}$$

then, from the point of view of comparing any reference liquid with the one under study, we can use the ratio of the specified times, which according to Debye are related to their viscosity coefficients - η_i, by a simple ratio [4, 5]:

$$\tau_{\mu 2} = \tau_{\mu 1}\left(\frac{\eta_2}{\eta_1}\right). \tag{12}$$

Thus, instead of determining the kinematic viscosity of the liquid product (ν) using a viscometer, and then calculating the dynamic viscosity (η) by determining its density (ρ), one can first determine the dynamic viscosity from the change in dielectric constant and from the ratio of microscopic relaxation times with the reference liquid product, including taking into account the temperature and frequency, and then calculate the kinematic viscosity of the liquid by the formula [4, 5]:

$$\nu = \frac{\eta}{\rho}. \tag{13}$$

3 Results and discussion

The developed method was used to create "reference images" (Table 1), and then to detect and identify counterfeit products in 3 batches of Castrol Magnatec engine oil, with a total volume of 3,500 cans, as follows:

Table 1. Reference images of Castrol Magnatec engine oil.

T, °C	m, g	ρ, g/cm^3	η, Pa•s	ν, m^2/s	ε	tgσ	Cp, pF	τ, s	τ_μ, s
SW-30 A3/B4 4L									
22	3643	0,8520	130,52	153,19	2,9344	0,01510	26,3	0,009578	0,007473
15		0,8541	187,73	219,79	2,8858	0,01474		0,009583	0,012252
40		0,8365	58,55	69,50	3,0593	0,01608		0,009535	0,012293
100		0,7942	9,61	12,15	3,4758	0,02000		0,009121	0,011961
-30		0,8859	5900,70	6660,16	2,5735	0,01267		0,009443	0,011861
-45		0,8964	8964,45	10000,00	2,4694	0,01206		0,009330	0,011638
5W-30 AP 4L									
22	3629	0,8483	122,80	144,76	2,8718	0,01660	25,9	0,008558	0,006698
15		0,8504	178,24	209,60	2,8381	0,01633		0,000274	0,000214
40		0,8326	49,96	60,59	2,9588	0,17310		0,000077	0,000060
100		0,7900	8,69	11,10	3,2486	0,02000		0,000013	0,000010
-30		0,8824	6344,70	7189,87	2,6207	0,14760		0,009738	0,007622
-36		0,8866	8866,15	10000,00	2,5918	0,01456		0,008472	0,010652
5W-30 A5 4L									
22	3627	0,8490	123,60	145,58	2,7394	0,15000	25,7	0,008819	0,006952
15		0,8411	182,69	217,20	2,7086	0,01460		0,008881	0,007001
40		0,8334	45,00	54,36	2,8188	0,01600		0,008644	0,006784
100		0,7908	7,59	9,65	3,0833	0,02000		0,007936	0,006148
-30		0,8831	9600,70	10871,35	2,5102	0,01260		0,009186	0,007343
-39		0,8894	8894,39	10000,00	2,4705	0,01220		0,009225	0,007394
5W-40 A3/B4 4L									
22	3625	0,8490	136,38	160,63	3,2445	0,01700	29	0,009757	0,007507
15		0,8511	194,42	228,42	3,1768	0,01676		0,009629	0,007429
40		0,8334	66,59	80,09	3,4185	0,01765		0,010062	0,007689
100		0,7908	10,44	13,30	3,9987	0,02000		0,010824	0,008118
-30		0,8831	5440,70	6160,43	2,7417	0,01528		0,008690	0,006849
-48		0,8958	8958,24	10000,00	2,5677	0,01473		0,008344	0,006645

- each oil canister was weighed with an ambient temperature measurement, after which the oil densities were calculated for the current and for the standards temperatures (15°C, 40°C, 100°C);
- each oil canister was opened, the electrical parameters of the oil and the sensor capacity were measured, and their dynamic viscosities were calculated at ambient temperature and at standard temperatures;
- based on the obtained densities and dynamic viscosities, the kinematic viscosities of oils were calculated;
- according to the Walter formulas, the indices of the viscosity of oils and their pour point were calculated.

Thus, in 3 batches with a total volume of 3,500 canisters (1 and 3 liters), a fake of Castrol Magnatec engine oil was determined by Rosneft engine oil [5].

Further studies of packaged non-alcoholic products showed the effectiveness of the developed method and the possibility of its implementation, through the development and production of sensor caps (Fig. 1), as well as portable automated express control systems [3].

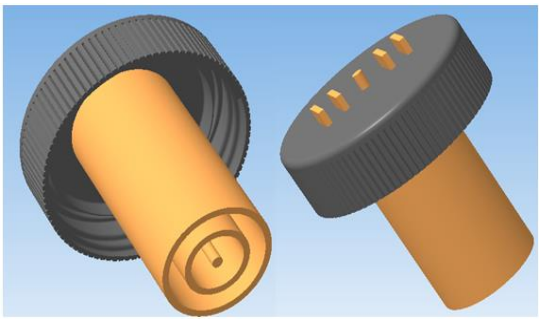

Fig. 1. 3D model of the prototype sensor-cover

Under the control of a computer, the immitance meter is connected to the contact pad of the sensor-cover of the packed liquid product, which is placed on the scale, to determine the mass of the liquid (P) and its density (ρ), first the parameters of the gas medium (air with liquid vapor) inside the container are measured, and after turning and installing the packed liquid product with the contact plate on the electronic scale - again, the mass and density, as well as the parameters of liquid: sensor-cover capacitance (Cp), resistance (Rp), electrical conductivity (Gp), loss angle tangent ($tg\delta$), and leakage current (I) at fixed frequencies from 10 to 1,000,000 Hz. In this case, the obtained data form the spectra of values that are used for the subsequent calculation of the relative permittivity (ε), macroscopic relaxation time (τ), molecular relaxation time (τ_μ), dynamic (η) and kinematic viscosity (ν) [3-5].

The key elements of the portable automated complex (Fig. 2) are an immitance meter, an electronic scale with a temperature sensor, a laptop and special software (SPO) that implements control and computational algorithms [3-5].

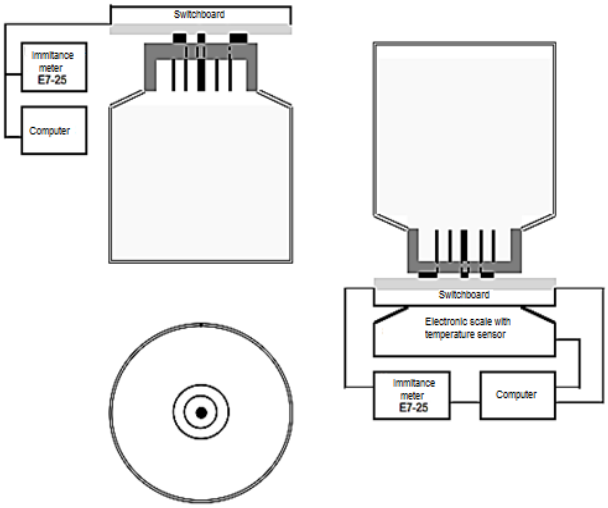

Fig. 2. Structure of the complex

Table 2. Measured parameters of the gas medium at 22°C

f, Hz	MEASURED PARAMETERS				
	Cp, pF	*Rp, Om*	*Gp, nS*	*tgd*	*I, mA (DC)*
60	1050	458483	2171	5,5	0,0000143011
120	545	424537	2352	5,72	
240	281	395422	2520	5,95	
480	148	369647	2710	6,08	
960	81	345962	2892	5,93	
2000	46	325017	3079	5,27	
4000	32	306603	3263	4,11	
8000	24	289248	3457	2,9	
16000	20	270317	3691	1,86	
32000	17	244983	4106	1,16	
64000	15	232983	4289	0,71	
125000	15	211783	4745	0,4	
250000	14	182267	5485	0,24	
500000	14	151500	6621	0,15	
1000000	14	101183	9893	0,11	

Table 3. Measured water parameters at 22 and 44°C

f, Hz	MEASURED PARAMETERS									
	Cp, pF		*Rp, Om*		*Gp, nS*		*tgσ*		*I, mA (DC)*	
	22°C	44°C	22°C	44°C	22°C	44°C	22°C	44°C	22°C	44°C
60	221383	594733	8906	1664	110810	590440	1,32	2,67	0,0002965970	0,0026630000
120	171282	388265	6268	1418	150438	709043	1,22	2,39		
240	128470	261712	4159	1187	236390	836245	1,23	2,13		
480	85062	174217	2745	965	360074	1038300	1,41	1,97		
960	49005	109500	1878	760	527272	1316483	1,79	1,99		
2000	21971	57982	1407	587	504576	1659775	2,56	2,34		
4000	9082	27388	1178	480	841530	2080550	3,7	3,02		
8000	3582	11190	1055	419	941214	2386550	5,25	4,24		
16000	1477	4186	980	386	1012640	2588960	6,84	6,15		
32000	707	1572	927	370	1071500	2704500	7,56	8,55		
64000	426	687	888	362	1121300	2765250	6,55	10		
125000	328	404	857	359	1161300	2790920	4,51	8,78		
250000	292	311	819	358	1212700	2808467	2,65	5,74		
500000	280	281	775	352	1283920	2842250	1,46	3,22		
1000000	260	275	726	335	1372720	2988220	0,84	1,72		

Table 4. Calculated water parameters at 22°C

f, Hz	CALCULATED PARAMETERS				
	e	*τ, s*	τ_μ, *s*	$\eta 0 \cdot 10^6$, *Pa•s*	$v \cdot 10^6$, m^2/s
60	210,7	0,4176088	0,27906633	36094898	36159,99
120	314,2	0,3394552	0,22666354	61070598	61180,72
240	457,3	0,2445432	0,16320705	91458807	91623,73
480	575,7	0,1344113	0,08968538	102656627	102841,74
960	606,3	0,0556805	0,03715096	82918423	83067,95
2000	472,5	0,0144325	0,00963185	39830990	39902,82
4000	287,8	0,002926	0,00195408	12602933	12625,66
8000	150,8	0,0004291	0,00028702	2607721	2612,42
16000	74,98	0,0000537	0,00003609	422004	422,77
32000	40,43	0,0000129	0,00000876	127500	127,73
64000	28,26	0,0000051	0,00000351	62418	62,53
125000	21,78	0,0000029	0,000002	38858	38,93
250000	20,15	0,0000023	0,00000157	37058	37,13
500000	19,66	0,0000034	0,00000238	69045	69,17
1000000	17,94	0,000003	0,0000021	89094	89,25

Table 5. Calculated water parameters at 44°C

f, Hz	CALCULATED PARAMETERS				
	e	*τ, s*	τ_μ, *s*	$\eta 0 \cdot 10^6$, *Pa•s*	$v \cdot 10^6$, m^2/s
60	656,05	0,4539641	0,3028734	39174143	39244,78
120	846,89	0,32216979	0,21490666	57902911	58007,32
240	1139,13	0,23926722	0,15958149	89427098	89588,36
480	1475,69	0,3377767	0,22526076	257840369	258305,32
960	1795,42	0,20884705	0,13927014	310841543	311402,07
2000	1848,5	0,09147687	0,06100107	252260232	252715,12
4000	1504,12	0,03097409	0,02065626	133223406	133463,64
8000	983,3	0,00789306	0,00526472	47833328	47919,58
16000	531,04	0,00158892	0,00106028	12397765	12420,12
32000	253,17	0,00014513	0,00009694	1411317	1413,86
64000	123,47	0,00002727	0,00001825	324259	324,84
125000	57,1	0,00000549	0,00000369	71802	71,93
250000	32,53	0,00000164	0,00000111	26134	26,18
500000	23,76	0,00000083	0,00000056	16295	16,33
1000000	20,68	0,0000006	0,00000041	17518	17,55

According to the control program, 6 parameter measurements were made at the following frequencies: 60, 120, 240, 480, 960, 2000, 4000, 8000, 16000, 32000, 64000,

125000, 250000, 500000 and 1000000 Hz. Distilled water was used as the test liquid. The measurements were carried out at 22 and 44°C. Table 2, 3, 4, and 5 show the data averaged for each frequency.

The set of measured and calculated parameters forms an "image"of the liquid under study, which is subsequently compared with the" image " of the reference.

The final identification of bottled water, as well as its compliance with the established quality and quantity parameters, is carried out taking into account the permissible deviations established by the relevant standards and specifications for packaged liquid products and their containers.

4 Conclusion

To carry out continuous control of liquid packaged products and, thereby, to prevent 100% counterfeit products, it is necessary, first, to develop and put into production sensors-covers on the packaging in which the product is produced, second, at the packaging stage, to install sensors-covers and perform express diagnostics of each product using a portable automated complex, third, to form a base of "reference images" of the packaged liquid products produced (according to manufacturers), fourth, "arm" all chain stores with portable automated systems, for mandatory input control of each packaged product (bottles, cans, etc.), and fifth, organize a subsystem of state and public supervision. [3, 4].

It should be noted that the portable automated system significantly reduces the time of diagnosis, has high mobility, takes into account the conditions of identification, does not require highly qualified personnel, and also for the analysis it is not necessary to withdraw the product from sale, open the container and take a sample, which will favorably affect the overall efficiency, as it will reduce the cost of laboratory control, increasing its frequency.

The obvious result of energy saving and energy efficiency of using the method and the complex is its application for continuous control of motor and transformer oils, to ensure the technical resource of motor vehicles and transformers at electrical substations, which, according to preliminary estimates, reduces the cost of selective control and losses from unscheduled repairs by 2 times.

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