ISSN 0020-1685, Inorganic Materials, 2018, Vol. 54, No. 14, pp. 1387–1391. © Pleiades Publishing, Ltd., 2018.
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ANALYSIS OF SUBSTANCES

Use of Piezoelectric Sensors for the Determination of Oleic and Palmitic Acids in Vegetable Oils

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Received May 25, 2016

Abstract—Piezoelectric sensors based on molecularly imprinted polymers (MIPs) for sensing oleic (MIP-Oleic) and palmitic (MIP-Palmitic) acids were tested in the analysis of vegetable oils. When creating the MIP sensors, electrodes were modified with the PM polyimide (dianhydride of 1,2,4,5-benzenetetracarboxylic acid and 4,4'-diaminodiphenyl oxide). Values of the imprinting factor and selectivity coefficients of the molecularly imprinted polymers for sensing fatty acids were compared. Chromatography mass spectrometry was used as a comparison method. The difference between the results of the determination of acids by using a piezoelectric sensor and by chromatography mass spectrometry does not exceed 10%. It is established that sensors modified with molecularly imprinted polymers are selective to the acid that served as a template for the polymer synthesis.

Keywords: molecularly imprinted polymers, oleic acid, palmitic acid, polyimide PM, piezoelectric sensor, vegetable oils

DOI: 10.1134/S002016851814008X

INTRODUCTION

Triglycerides (triacylglycerols) play a significant chemical and biological role: they are the starting material for obtaining various classes of surfactants and emulsifiers [1–3] and the core component of vegetable oils, which acts as the primary source of energy for the cells. The content of fatty acids (in particular, oleic and palmitic acids), which are part of triglycerides, is the main indicator of the naturalness of fat-and-oil products. The fatty acid composition is determined by various methods [4–9] that require complicated sample preparation techniques and expensive equipment and also differ in the duration of the analysis. These factors limit their use in cases where it is necessary to perform on-line control of the fatty acid composition or express determination of individual fatty acids directly in the course of the processing of oils. In this regard, it is promising to use selective piezoelectric sensors with their low cost, small size, and an ability to be adapted to different technological solutions. To create selective sensors, their electrode surfaces are modified with various sorbents [10–11]. Molecularly imprinted polymers (MIPs) are one of such materials. These polymers are a new generation of sorbents whose important property is the ability to selectively bind those organic molecules in the presence of which the sorbents were synthesized and to retain them in the polymer via interactions of different nature [12–14].

The study aimed to test piezoelectric sensors based on molecularly imprinted polymers for the determination of oleic and palmitic acids in vegetable oils.

EXPERIMENTAL

The determination of fatty acids in liquids was carried out using the setup shown in Fig. 1. The setup includes a piezoelectric sensor and a system for collecting and transmitting analytical signals to a personal computer (an AKTACOM-8322 frequency meter and the AKTAKOM FCounter software).

To create selective sensors, we used piezoelectric AT-cut resonators with silver electrodes having a diameter of 5 mm and a thickness of 0.3 mm (manufactured by OAO Piezoquartz, Moscow) and a nominal resonance frequency of 4.607 MHz. The surface of the electrodes was modified with molecularly imprinted polymers. The starting material in the synthesis of MIPs was the AD-9103 product (prepolymerization mixture), TU-6-19-283-85, produced by OAO MIPP NPO Plastik (Moscow). AD-9103 is a

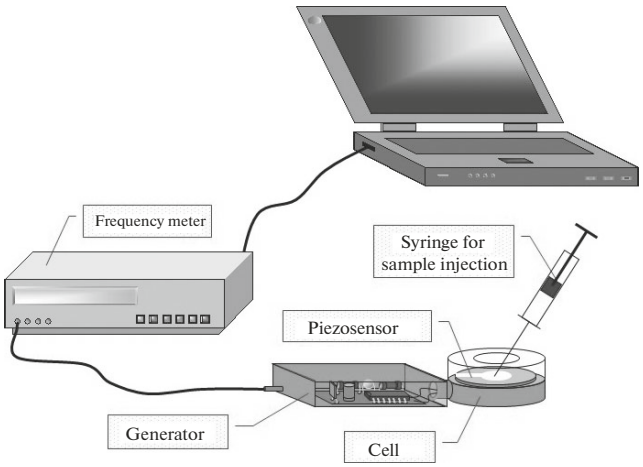

Fig. 1. Setup for the determination of substances in the solutions using piezoelectric sensors.

mixture of initial monomers 1,2,4,5-benzenetetracarboxylic acid and 4,4'-diaminodiphenyl oxide. Their polymerization leads to the formation of polyimide (PM) [15, 16].

In the preparation of molecularly imprinted polymers (MIPs), a template (oleic or palmitic acid) was added to the prepolymerization mixture. Polymerization was carried out directly on the electrode surface of the sensor at 453 K. The samples were then cooled to room temperature and placed in a water–alcohol mixture for 24 h to remove the template. The removal of the template occurs without destroying the polymer and without deforming the sensor. The control polymer (CP) was obtained simultaneously with MIPs under identical conditions but in the absence of the template [17–19]. The procedure for obtaining sensors with a selective coating using molecularly imprinted polymers is presented in more detail in patents [20, 21].

The following sensors were used in the study: a sensor modified with a pure polymer (CP) (with no molecular imprints of fatty acids), a sensor modified with a molecularly imprinted polymer for sensing oleic acid (MIP-Oleic), and a sensor modified with a molecularly imprinted polymer for sensing palmitic acid (MIP-Palmitic). The sensors obtained were tested on refined oils: sunflower oil (Sloboda), corn oil (Svetlitsa), olive oil (Maestro de Oliva), linen oil, and rapeseed oil.

Determination of the content of fatty acids using the calibration curve. For this purpose, we prepared model solutions of oleic and palmitic acids in butanol using accurately weighed quantities of high-purity grade reagents (ZAO Voronezhreaktiv). The content ranges were as follows: 0.16–0.86 g/dm^3 for oleic acid and 0.14–0.34 g/dm^3 for palmitic acid. Since the viscosity of the oils was high, they were first diluted in a ratio of 1 : 10 in the most suitable solvent (butanol) [22].

The measurement procedure was as follows. The sensor was fixed in a horizontal position, the setup was switched on, and the sensor readings were recorded without load (in air) by the frequency counter. After that, the "blank sample" (butanol) was applied with a microsyringe on the electrode surface ($V = 1$ μL) and the signal (f_1) was recorded. After the measurement, the blank sample was removed with a filter paper strip. After five to ten seconds, when the sensor readings corresponded to the initial value measured in air, the same volume of the test solution was applied, and the corresponding signal was recorded (f_2). The signal was measured every second to obtain ten values. The relative frequency shift Δf was calculated from the equation

$$\Delta f = f_1 - f_2,$$

where f_1 and f_2 are the oscillation frequencies (kHz) of the sensor in the "blank sample" and the test solution, respectively [10].

The measurements were performed moving from dilute solutions to more concentrated ones. After the experiment, the sensor was washed with a water–butanol mixture and dried in an oven at 50°C for 1 h to return the oscillation frequency of the piezoelectric sensor to the starting values.

When evaluating the properties of the MIPs, we compared the values of the imprinting factor (IF): $IF = \Delta f_{MIP}/\Delta f_{CP}$, where Δf_{MIP} and Δf_{CP} are the signals (Hz) from the piezosensor with the molecularly imprinted polymer and with the control polymer, respectively, to the given acid. We also compared the selectivity coefficients (k) of the sensor designed for the detection of the given acid to related compounds: $k = S_{fa}/S_{targ.fa}$, where S_{fa} and $S_{det.fa}$ are the sensitivity coefficients of the MIP to the foreign fatty acid and the target fatty acid, respectively. The sensitivity of the sensors was calculated as the ratio of the difference frequency of the sensor oscillations to the concentration of the detected component [23].

The correctness of the determination of fatty acids in oils by piezoelectric sensors was verified by using an Agilent Technologies 7890B GC Systems chromatography mass spectrometry complex equipped with an Agilent Technologies 5977A MSD mass selective detector (according to GOST 30418-96) and comparing the results obtained by the two methods.

Table 1. Imprinting factors and selectivity coefficients for MIP-based sensors

Sensors	Oleic acid		Palmitic acid	
	IF	k	IF	k
MIP-Oleic	6.7	1	0.1	0.19
MIP-Palmitic	0.03	0.23	7.8	1

RESULTS AND DISCUSSION

It was shown earlier [24, 25] that the synthesis of molecularly imprinted polymers results in the formation of cavities complementary to the template molecule in size, shape, and arrangement of the functional groups. Therefore, the essential expected property of a MIP is the ability to recognize target molecules in solution, which is indicated by the high values of IF and k observed for MIP sensors in the determination of the fatty acid used as a template for their synthesis (Table 1).

Calibration curves obtained using MIP sensors are described by the following equations: $\Delta f_{MIP} = -0.198c + 0.321$, $R^2 = 0.98$ for MIP-Oleic and $\Delta f_{MIP} = -0.476c + 0.553$, $R^2 = 0.97$ for MIP-Palmitic (Fig. 2).

An attempt was made to construct similar dependences for a sensor modified by the control polymer. Figure 2 shows that such a sensor cannot be used to determine oleic and palmitic acids.

The metrological characteristics of the determination of oleic and palmitic acids by piezoelectric MIP-modified sensors are presented in Table 2. The correctness of the determination in model solutions is confirmed by the spiking tests (Table 3).

The modified piezoelectric sensors were tested in the analysis of various types of vegetable oils (Table 4) to establish the triglyceride composition, an indicator of the naturalness of the oil.

It was found that the results obtained by using a piezoelectric sensor and by chromatography mass spectrometry for the determination of acids in model solutions and vegetable oils differ by no more than 10%.

CONCLUSIONS

On the basis of the comparison of the experimental data obtained by chromatography mass spectrometry and sensory methods, it was established that MIP-modified piezoelectric sensors for oleic and palmitic acids could be used to determine the corresponding template acids. The proposed piezoelectric sensors modified with PM-polyimide-based molecularly imprinted polymers for sensing oleic and palmitic acids can be used as small-sized analytical devices for the rapid determination of these fatty acids in triglycerides of vegetable oils.

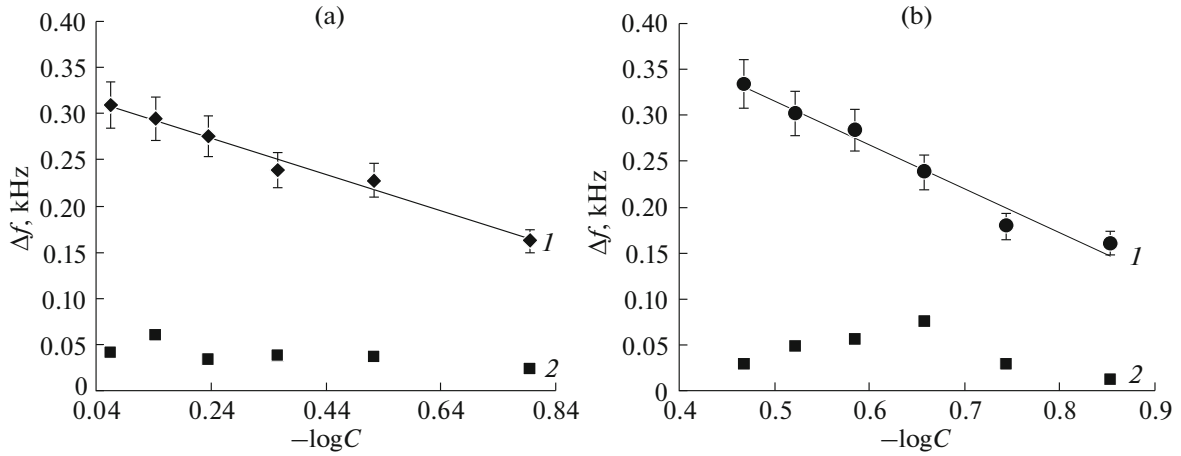

Fig. 2. Dependence of the difference frequency of the piezoelectric sensor on the logarithm of the concentration of (a) oleic acid in an alcohol solution and (b) palmitic acid in an alcohol solution (*1*—MIP and *2*—PS).

Table 2. Metrological characteristics of the determination of fatty acids in model solutions performed using modified piezoelectric sensors

Sensor	Test substance	Range of determined contents, g/dm^3	C_{min}, g/dm^3	S_r, %
MIP-Oleic	Oleic acid	0.16–0.86	0.14	5.8
MIP-Palmitic	Palmitic acid	0.14–0.34	0.12	3.2

Table 3. Results of determination of oleic and palmitic acids in model solutions by spiking tests

Analyte	Sensor with MIP_{PM}-Oleic			Sensor with MIP_{PM}- Palmitic		
	C, g/dm^3		S_r, %	C, g/dm^3		S_r, %
	introduced	found		introduced	found	
Oleic acid	0.86	0.81 ± 0.04	4.9	0.86	–	–
	0.72	0.77 ± 0.05	6.5	0.72	–	–
	0.58	0.56 ± 0.02	3.6	0.58	–	–
Palmitic acid	0.34	–		0.34	0.33 ± 0.02	6.1
	0.30	–		0.30	0.32 ± 0.02	6.3
	0.26	–		0.26	0.24 ± 0.01	4.2

Table 4. Results of the determination of oleic and palmitic acids in vegetable oils by piezoelectric sensors and by chromatography mass spectrometry (CMS)

Test object	Oleic acid, g/dm^3		S_r, %	Palmitic acid, g/dm^3		S_r, %
	CMS	MIP sensor		CMS	MIP sensor	
Sloboda sunflower oil	0.28	0.26 ± 0.02	6.5	0.10	0.09 ± 0.01	7.8
Svetlitsa corn oil	0.31	0.33 ± 0.03	9.1	0.12	0.11 ± 0.01	9.6
Maestro de Oliva olive oil	0.60	0.57 ± 0.02	3.5	0.14	0.14 ± 0.01	7.1
Linseed oil	0.22	0.23 ± 0.01	4.3	0.07	0.06 ± 0.02	3.3
Rapeseed oil	0.46	0.44 ± 0.02	4.5	0.07	0.07 ± 0.03	4.3

ACKNOWLEDGMENTS

This study was supported by the Federal Target Program "Research and Development in the Priority Areas of Development of the Russian Scientific and Technological Complex for 2014–2020" (agreement no. 14.577.21.0182, the unique identifier for applied scientific research is RFMEFI57715X0182).

REFERENCES

1. De, S., Malik, S., Ghosh, A., et al., A review on natural surfactants, *RSC Adv.*, 2015, vol. 5, pp. 65757–65767.
2. Avelino, C., Iborra, S., and Velty, A., Chemical routes for the transformation of biomass into chemicals, *Chem. Rev.*, 2007, vol. 107, pp. 2411–2502.
3. Singh, D., Bhoi, R., Ganesh, A., and Mahajani, S., Synthesis of biodiesel from vegetable oil using sup-

ported metal oxide catalysts, *Energy Fuels*, 2014, vol. 28, no. 4, pp. 2743–2753.

4. Prudnikov, S.M., Naumov, N.N., Ukraintseva, I.I., and Zhirova, E.V., Determination of the content of oleic acid in triacylglycerols of sunflower seed oil, *Izv. Vyssh. Uchebn. Zaved., Pishch. Tekhnol.*, 2006, nos. 2–3, pp. 96–97.
5. Selichev, V.E., Modern equipment and analysis methods for quality control, *Masla Zhiry*, 2009, no. 5, pp. 8–9.
6. Pershakova, T.V. and Naumov, N.N., Express test of oleic acid mass fraction in sunflower-seed oil, *Nauch. Zh. Kuban. Gos. Agrar. Univ.*, 2011, no. 5 (69), pp. 238–247.
7. *GOST (State Standard) 30418-96: Vegetable Oils. Method for Determination of Fatty Acid Content*, Moscow: Standartinform, 1998.
8. *GOST (State Standard) R 51483-99: Vegetable Oils and Animal Fats. Determination by Gas Chromatography of Constituent Contents of Methyl Esters of Total Fatty Acid Content*, Moscow: Standartinform, 2000.
9. *GOST (State Standard) 30623-98: Vegetable Oils and Margarine. Detection of Falsification*, Moscow: Standartinform, 2010.
10. Kalach, A.V., Zyablov, A.N., and Selemenev, V.F., *Sensory v analize gazov i zhidkostei* (Use of Sensors in the Analysis of Gases and Liquids), Voronezh: LIO, 2011.
11. Zyablov, A.N., Kalach, A.V., Zhibrova, Yu.A., et al., Determination of glycine in aqueous solutions using a molecularly imprinted polymermodified piezosensor, *J. Anal. Chem.*, 2010, vol. 65, no. 1, pp. 91–93.
12. Dmitrienko, S.G., Irkha, V.V., Duisebaeva, T.B., et al., Synthesis and study of the sorption properties of 4-hydroxybenzoic acid-imprinted polymers, *J. Anal. Chem.*, 2006, vol. 61, no. 1, pp. 14–19.
13. Gendrikson, O.D., Zherdev, A.V., and Dzantiev, B.B., Molecularly imprinted polymers and their use in biochemical analysis, *Usp. Biol. Khim.*, 2006, vol. 46, pp. 149–192.
14. Lisichkin, G.V. and Krutyakov, Yu.A., Molecularly imprinted materials: synthesis, properties, applications, *Russ. Chem. Rev.*, 2006, vol. 75, no. 10, pp. 998–1016.
15. Zyablov, A.N., Govorukhin, S.I., Duvanova, O.V., et al., Flow-injection determination of valine by piezoelectric sensors modified by molecularly imprinted polymers, *Anal. Kontrol'*, 2014, vol. 18, no. 4, pp. 438–441.
16. Semiletova, E.S., Zyablov, A.N., Selemenev, V.F., et al., Thermogravimetric analysis of the polymers, *Sorbtsionnye Khromatogr. Protsessy*, 2012, vol. 12, no. 5, pp. 734–738.
17. Duvanova, O.V., Volodina, L.V., Zyablov, A.N., et al., Analysis of the morphology of the surface of polymers with molecular imprints of oleic and palmitic acids, *Sorbtsionnye Khromatogr. Protsessy*, 2013, vol. 13, no. 6, pp. 884–890.
18. Volodina, L.V., Duvanova, O.V., Zyablov, A.N., et al., Analysis of the structure and composition of polymers using molecular imprints of oleic and palmitic acids, *Sorbtsionnye Khromatogr. Protsessy*, 2014, vol. 14, no. 1, pp. 111–120.
19. Duvanova, O.V., Dashina, A.I., Zyablov, A.N., et al., Evaluation of the properties of molecularly imprinted polymers for analysis the fatty acid in fluids by piezoelectric sensors, *Vestn. Voronezh. Gos. Agrar. Univ.*, 2014, no. 3 (42), pp. 147–157.
20. Zyablov, A.N., Duvanova, O.V., et al., RF Patent 137946, *Byull. Izobret.*, 2014, no. 6.
21. Zyablov, A.N., Duvanova, O.V., et al., RF Patent 138636, *Byull. Izobret.*, 2014, no. 8.
22. *Svoistva organicheskikh soedinenii: spravochnik* (Properties of Organic Compounds: A Handbook), Potekhin, A.A., Ed., Leningrad: Khimiya, 1984.
23. *Osnovy analiticheskoi khimii* (Fundamentals of Analytical Chemistry), Zolotov, Yu.A., Ed., Moscow: Akademiya, 2012, vol. 1.
24. Stepycheva, N.V. and Fud'ko, A.A., Blended oils with optimized fatty acid composition, *Khim. Rastit. Syr'ya*, 2011, no. 2, pp. 27–33.
25. Zyablov, A.N., Monicheva, T.S., and Selemenev, V.F., Detection of amino acids in VSAA preparation using piezoquartz sensors modified by molecularly imprinted polymers, *Anal. Kontrol'*, 2012, vol. 16, no. 4, pp. 406–409.

Translated by Yu. Modestova