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CHROMATOGRAPHIC INVESTIGATION OF EXHAUST GAS COMPOSITION SAMPLED FROM GAS STREAM USING SOLID PHASE MICROEXTRACTION

Key words

Solid phase microextraction, exhaust gases, GC/MS.

Summary

An investigation of the usefulness of a solid phase microextraction technique as a method for the separation of an analytical sample from the gas stream was performed. Due to high temperatures in the sampling area and the character of anticipated products of the combustion process, suitable fibres were chosen. Several fuel blends based on the vegetable oil were examined. Based on the GC/MS analysis, the influence of commercial additives on the composition of exhaust gases composition was assessed. It was verified that the basic condition of ecological clean vegetable oil combustion is its modification.

Introduction

During the combustion of vegetable oil, compounds that are harmful to people and the environment are formed. One of the elements of interests for the European Union agrarian policy is biofuel usage, because it is necessary to reduce the emission of hazardous compounds, i.e. acrolein, PAHs [1–3]. For the separation of compounds from the gas stream, solid phase microextraction (SPME) can be used.

Solid phase microextraction is a technique of the preparation of samples for chromatographic analyse which is increasingly applied in chemical analytics. SPME can be used for selective sampling of volatile and semi-volatile organic compounds from environmental and other samples, including samples with a complicated matrix [4]. In the case when analysed compounds are contained in a non-volatile matrix, a Headspace microextraction technique can be used.

As opposed to methods in which traps with an active solid bed (e.g. Purge and Trap) are used, and methods in which a capillary column segment to the analyte's retention from gas or liquid stream is used (e.g. Thick Film Open Tubular Trap) [5], the SPME technique is rapid, easy to automate and acceptable to use in every condition [6]. As far as the above stated technique is concerned, it is also extremely interesting, because its results are general or selective, and the solvents have a low cost and the fibres have a long service life, which can be used about 100 times.

Solid phase microextraction is mainly used for the separation of analytes that contain volatile compounds. An example of the application of this technique, apart from environmental tests (e.g. water or soil contamination), can be the valuation of aroma intensity, the analysis of oil raw materials, or the detection of the presence of drugs [7–10]. A particular area of SPME application is the sampling of volatile products of the combustion of furnace oil based on vegetable raw materials.

The objective of this study is to investigate the usefulness of the solid phase microextraction technique as a method for the separation of an analytical sample from the stream of gases, which are products of the combustion of liquid fuels based on vegetable oil. The paper also aims at the chromatographic identification of the chemical structure of toxic organic compounds in exhaust gases.

1. Characteristics of the SPME technique

The analytical procedure for microextraction to solid phase is a two-stage procedure composed of the following:

- contact between the fibre and the sample in a vapour or liquid phase (sorption of analytes),
- desorption of compounds adsorbed on the fibre in the GC injector under the influence of high temperature, and their separation in a chromatographic column.

The following types of the stationary phase are available:

- carboxen/polydimethylsiloxane (PDMS),
- polydimethylsiloxane (PDMS),
- polydimethylsiloxane/divinylbenzene (PDMS/DVB),
- polyacrylate,

- polyethylene glycol (PEG), and
- divinylbenzene/carboxen/ polydimethylsiloxane.

The efficiency of extraction and the sensitivity of the method are influenced by the following parameters: temperature, the polarity of the sample matrix, and the type of the fibre material. Characteristics of typical fibres, particularly the permissible working temperatures, stationary phase film thickness, and potential areas of application are presented in Table 1.

Table 1. Permissible working temperatures for fibres of different applicatory characters, depending on the type of stationary phase, and its thickness

Fibre coating	Thickness [μm]	Permissible temperature of work [°C]	Application
PDMS	100	280	Volatiles
PDMS	30	280	Non-polar semi-volatiles
PDMS	7	340	Non-polar high molecular weight compounds
PDMS/DVB	65	270	Volatiles, amines and nitro-aromatic compounds
Polyacrylate	85	320	Polar semi-volatiles
Carboxen/PDMS	75	320	Gases and low molecular weight compounds
DVB/CAR/PDMS	50/30	270	Flavour compounds: volatiles and semi-volatiles

The selection of a suitable fibre coating depends on the chemical character of insulated compounds, among other aspects. Compounds of non-polar character are extracted on a fibre with the same character of functional groups. The stationary phase film thickness influences the amount of sorbate. Fibres coated with a stationary phase film of greater thickness have much better sorption properties. They secure the transfer of volatile compounds to a GC injector without any loss [4].

2. Research methodology

Adsorbates sampled from the stream of gases from the combustion of vegetable oil and the enriched vegetable oil based composition were selected for further investigations. The vegetable oil was enriched with two different commercial additives that significantly improved the efficiency of the combustion process inside the 15 kW fuel boiler.

Modification of the composition of fuels by the addition of certain modifiers can drastically improve the quality of the entire combustion process

as well as the quality of exhaust gases themselves. Keeping that in mind, two modifying agents were chosen:

- Warmix (by Warter) which is an additive improving the physicochemical properties of oil (it stabilises its viscosity); preventing corrosion in an installation; dispersing sediments; facilitating elimination of water by the reduction of interfacial tension between oil and water and the breakdown of water clusters into small molecules. Warmix also has lubricating properties; it affects the post combustion of soot and reduces NO_x and CO emission to the atmosphere.
- Lubrizol 8043F (by Lubrizol) which is an additive that ensures that the fuel injector remains clean and reduces the foaming of fuel at the time the container is filled. Lubrizol neutralises water and protects the fuel system against corrosion.

Samples were adsorbed by the SPME device.

In the case of sampling gases from fuel composition combustion, it is important to choose a suitable sampling location. Because of high temperatures in the combustion chamber, reaching up to 900°C, and impossibility to sample from the last section of the chimney, it was decided that the samples would be taken from the smoke conduit, once the temperatures were checked and suitable sampling temperatures are maintained in it (sampling was realised at the temperature of about 280°C).

Due to high temperatures in the sampling area and the character of anticipated products of the combustion process, fibres coated with PDMS were chosen for fuel compositions with additives and for vegetable oil exhaust gases – fibres coated with 85 µm thick polyacrylate. The desorption of compounds, which were adsorbed on the fibre, was carried out in a chromatograph injector chamber at the temperature of 320°C. For the analysis the GC/MS Clarus 680, a gas chromatograph equipped with a mass spectrometer (by Perkin Elmer) was used. Elite-5MS capillary column (30m × 0.25mm × 0.2µm) was used. The oven temperature was programmed for 50°C for 1 min, 10°C/min to 150°C (2 min), then 10°C/min to 300°C (2 min). The carrier gas was helium with purity 99.9999%.

The MS detection was conducted in the $m/z = 29$ to $m/z = 400$ u range in electron ionisation mode. Chemical compounds were identified by comparing the mass spectrum obtained with data from the NIST database. Based on the GC/MS analysis, the influence of the additives on exhaust gases composition was also assessed.

3. Test results and their analysis

Figure 1 shows the chromatogram of sample adsorbed from the vegetable oil gas stream on polyacrylate fiber.

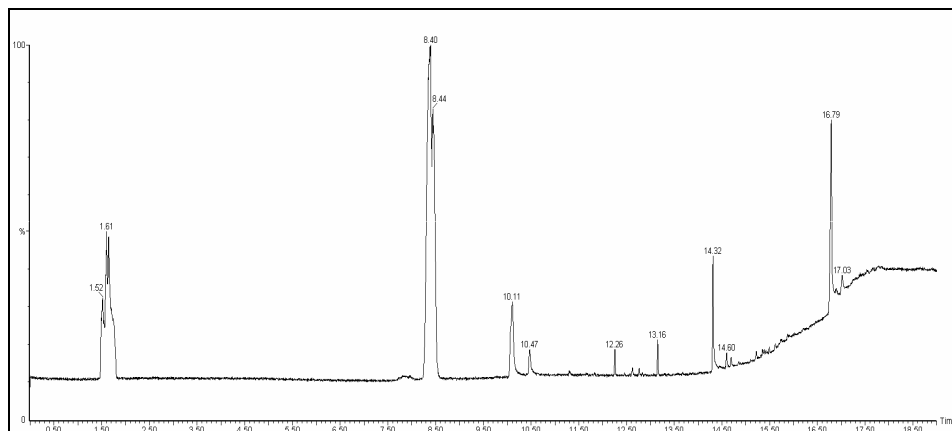
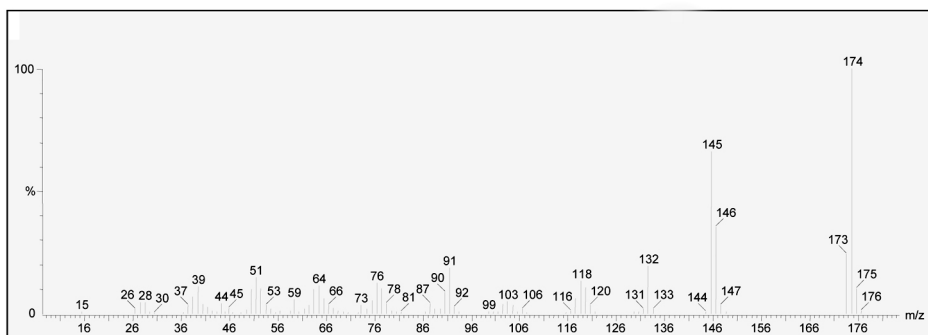


Fig. 1. Chromatogram from vegetable oil exhaust gas

The analysis of the above chromatogram indicates that the method applied for the separation of the analytical sample enables effective adsorption of emitted organic substances. The application of this technique allowed the separation of the gas products mixture and the identification of the chemical structure of the compounds, which were eluted from the tested gas sample (i. a. tacrine, 2-tridecene, 1-octadecene). The mass spectra of compounds, which were characterised by the highest toxicity in the exhaust gas sample, are shown in Fig. 2 and Fig. 3.

During the chromatographic tests, a compound from the group of aromatic isocyanates was identified. Its spectrum is shown in Fig. 2. This substance eluted from the analytical sample tested in the retention time of 8.40 min.

a)



b)

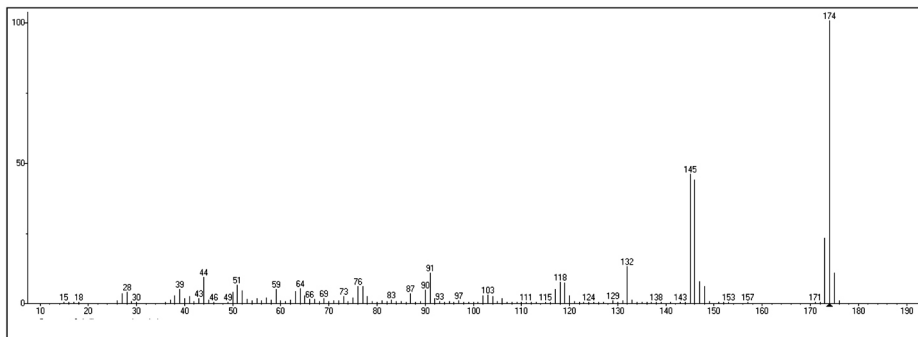
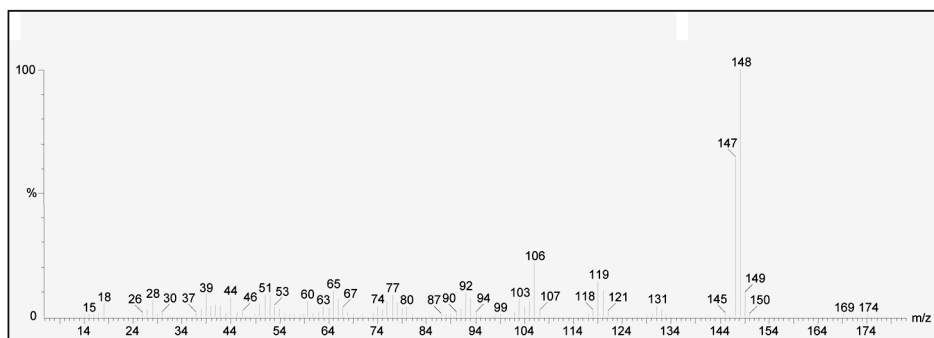


Fig. 2. Mass spectrum of the substance eluted in the retention time of 8.40 min (a) – (2,4-diisocyanato-1-methyl-benzene) and its spectrum from the NIST library – (b)

The comparison of the obtained mass spectrum with the database enabled precise identification of the chemical structure of the eluted compound, which is 2,4-diisocyanato-1-methyl-benzene. In the mass spectrum, shown in Fig. 2a, the primary ion with the mass to charge ratio ($m/z = 174$) is most visible, which means that at the time of the detection of the quadrupole, the structures that were not fragmented were prevailing. The compound identified is very toxic, irritant and allergenic, and very likely carcinogenic to humans. Its structural stability intensifies the negative environmental impact.

Figure 3 shows the mass spectrum of the compound eluted from the vegetable oil exhaust gas sample in retention time of 10.11 min.

a)



b)

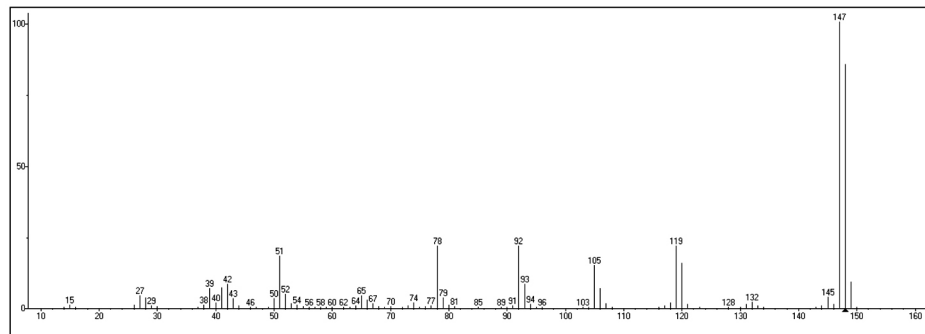


Fig. 3. Mass spectrum of the substance eluted in the retention time of 10.11 min (2,4,6- trimethylbenzaldehyde) and its spectrum from the NIST library – (b)

The analysis of the mass spectrum allowed the determination of the structure of the eluted compound, which is 2,4,6- trimethylbenzaldehyde. In the mass spectrum, shown in Fig. 3a, most visible is the parent ion $m/z = 148$, for which reason it can be said that this substance is very stable.

The developed procedure for the sampling of gases formed during the combustion of vegetable oil was modified for samples with additives. The introduction of modifiers, like Warmix or Lubrizol, into the fuel affects combustion conditions which in turn prevents the formation of toxic substances that were identified in products of vegetable oil combustion. Therefore, a fibre intended for the separation of a broad spectrum of volatile compounds (PDMS) was used which would allow for the separation of organooxygen compounds from the combustion of vegetable oil with additives.

The results of the chromatographic analysis of exhaust gases from compositions consisting of vegetable oil and Warmix modifier are shown in Fig. 4.

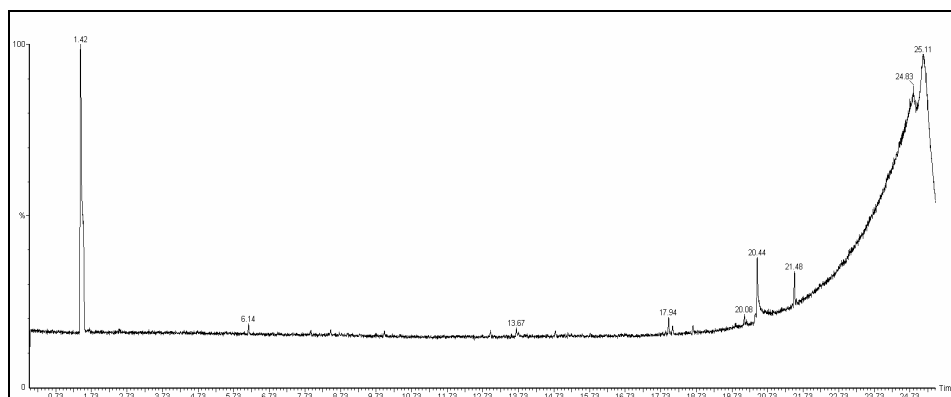
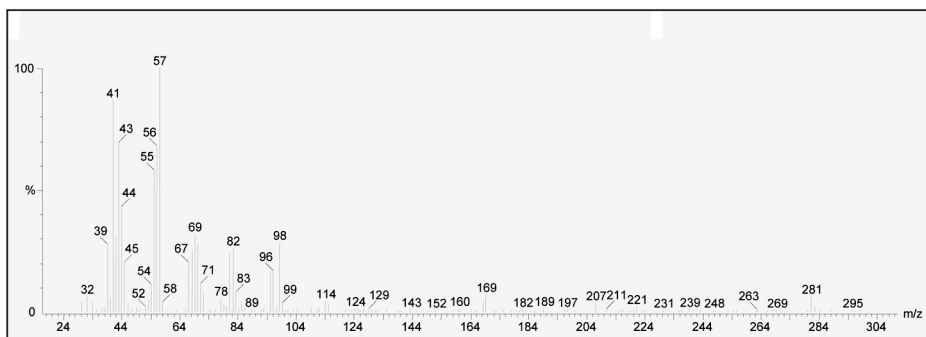


Fig. 4. Chromatogram for exhaust gases from vegetable oil with Warmix modifier

The analysis of the chromatogram allows one to conclude that the strongest signal is generated for a substance eluted in the retention time of 1.42 min. Its chemical structure is difficult to be identified due to the impossibility to assign the mass spectrum to a particular compound with sufficient probability. Mass spectra of substances characterised by remaining peaks were then analysed. The outcomes of the analyses indicated that none of these substances contained any toxic compounds, arising from the combustion of the unmodified vegetable oil.

The substance eluted in the retention time of 6.14 min was identified. Its spectrum is shown in Fig. 5.

a)



b)

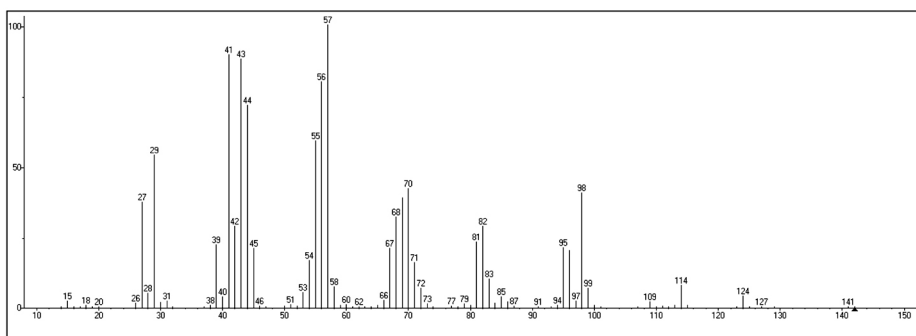


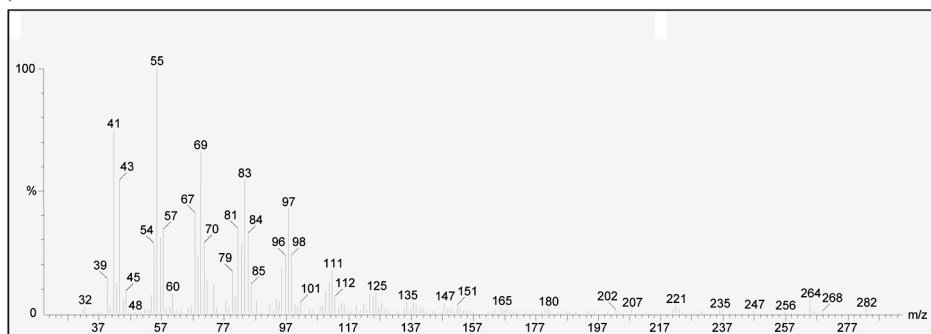
Fig. 5. Mass spectrum of the substance eluted in the retention time of 6.14 min (nonanal) and its spectrum from the NIST library – (b)

The compound eluted in the retention time of 6.14 min and two other compounds with similar chemical constitution with the retention time of 9.20 min and 17.94 min were identified as aldehydes, respectively: nonanal, 2-tridecenal and cis-9-hexadecenal. Together with the increase in the hydrocarbon chain length, the toxicity of aldehydes decreases. It means that

the compounds identified are much safer for people than highly toxic acroleine, which was expected in exhaust gases. The absence of the $m/z = 142$ peak indicates that the aldehyde was totally fragmented.

During the chromatographic analysis oleic acid eluted. This compound was identified based on the mass spectrum analysis, which is shown in the Fig. 6.

a)



b)

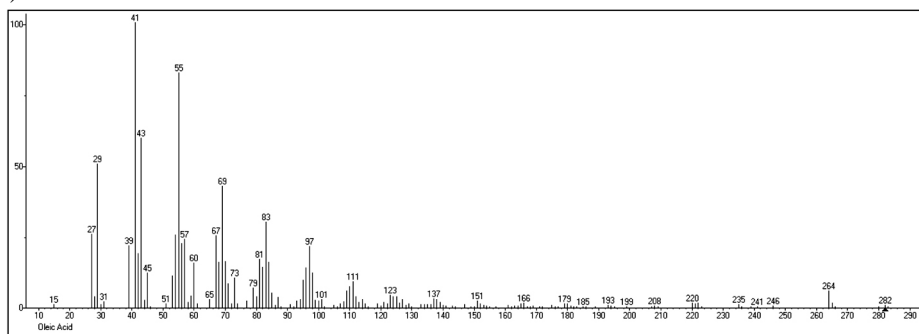


Fig. 6. Mass spectrum of the substance eluted in the retention time of 20.44 min (oleic acid) and its spectrum from the NIST library – (b)

The analysis of the mass spectrum and its comparison with the mass spectra of standard substances allowed the determination of the structure of the compound separated in the chromatographic column. It is the most common in natural fatty acid, better known as oleic acid. In the mass spectrum, a low intensive signal from a parent ion $m/z = 282$ (marked with an arrow) is visible. This signal indicates that the oleic acid has greatly undergone fragmentation during ionisation in the mass spectrometer.

Compounds formed during the combustion of vegetable oil and the commercial additive Lubrizol composition were adsorbed on a PDMS fibre. The compounds were identified based on their mass spectra.

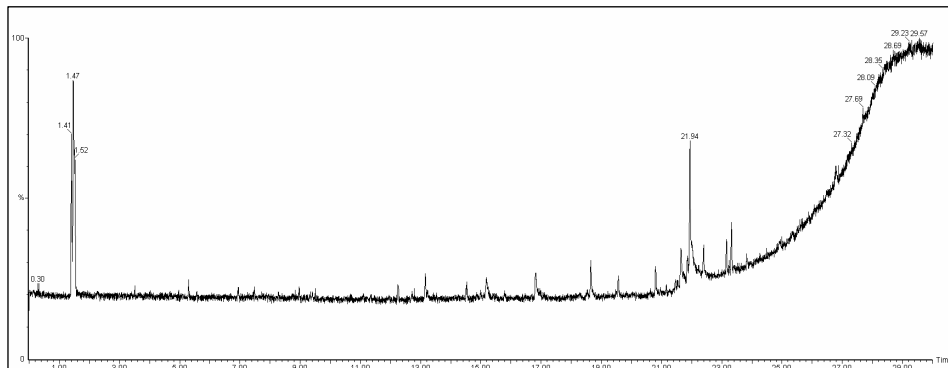
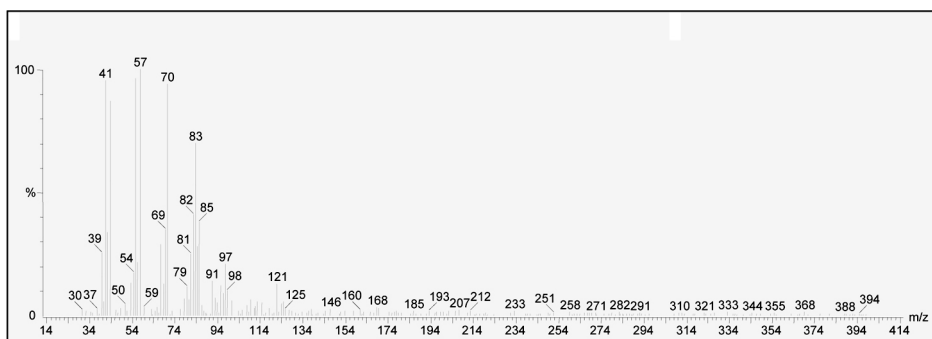


Fig. 7. Chromatogram for exhaust gases from vegetable oil and Lubrizol modifier composition

The chromatogram from vegetable oil with a Lubrizol modifier, which improves the quality of combustion process, is shown in Fig. 7. Peaks correspond to particular chemical compounds for which analysed compositions were separated. Similarly, as in the case of the chromatogram for exhaust gases from vegetable oil with a Warmix modifier composition, the most intensive signal is derived from a compound for which the identification is impossible. It may be noted that there are more products of conversion received from the combustion of Lubrizol enriched composition which is related to the different chemical composition of the additive. The mass spectra received were compared with data from the NIST spectral database. The presence of aldehydes, alkynes, and alkenes was stated.

The mass spectrum of a substance eluted from the exhaust gases from the vegetable oil composition sample in the retention time of 8.97 min is shown in Fig. 8.

a)



b)

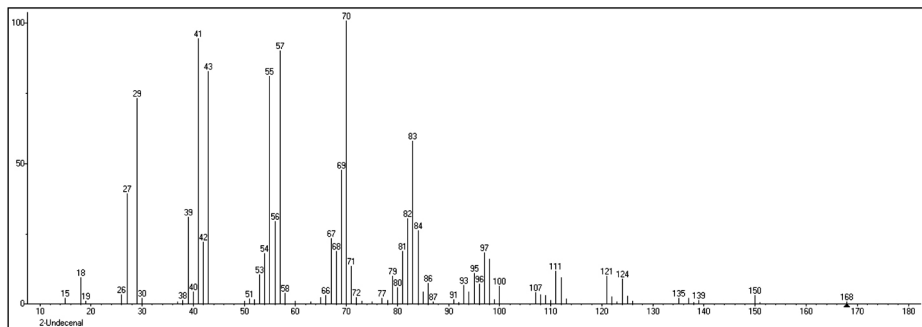
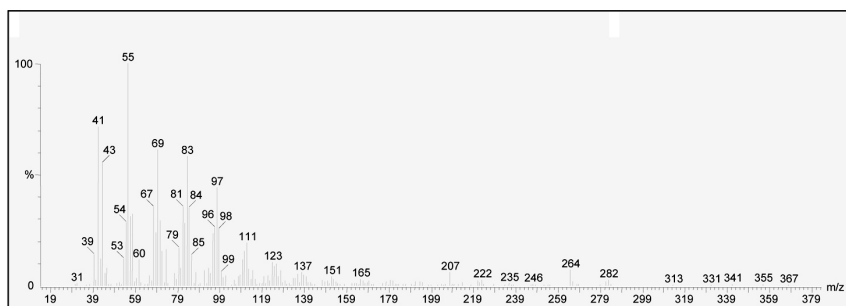


Fig. 8. Mass spectrum of the substance eluted in the retention time of 8.97 min (2-undecenal) and its spectrum from the NIST library – (b)

Based on the mass spectrum, the compound eluted in the retention time of 8.97 min was identified – 2-undecenal. It is an aldehyde whose carbon chain contains 11 carbon atoms and has a double bond in the structure. The lack

a)



b)

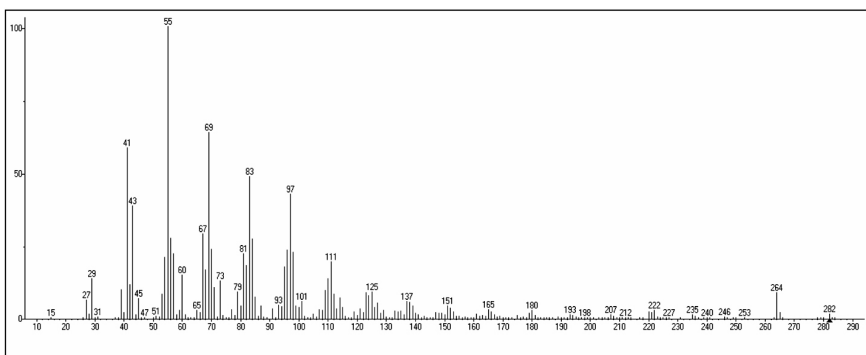


Fig. 9. Mass spectrum of the substance eluted in the retention time of 21.94 min (erucic acid) and its spectrum from the NIST library – (b)

of the $m/z = 168$ peak in the mass spectrum indicates that the compound fragmentation process has been completed.

During the GC/MS test, the compound eluted in the retention time of 21.94 min was identified. Its mass spectrum is shown in Fig. 9.

The comparison of the mass spectrum obtained with data from the NIST database indicates high conformity and it can be assumed that it is the erucic acid. The erucic acid is a long chain compound. Its molecular formula is $C_{22}H_{44}O_2$. The lack of the $m/z = 338$ peak in the mass spectrum shown in Fig. 9 indicates total completion at the fragmentation process.

Summary

Analyses with the use of the GC/MS allowed for the identification of the chemical structure of some compounds emitted in gas products of the combustion of vegetable heating oils.

The application of the polyacrylate fiber enabled the separation and identification of a few highly toxic compounds, particularly 2,4-diisocyanato-1-methyl-benzene. Another compound adsorbed on the polyacrylate fibre was 2,4,6-trimethylbenzaldehyde.

For the adsorption of the exhaust gases of vegetable oil with modifiers, PDMS fibre was used. This fibre allows for the adsorption of a wide range of volatile compounds, e.g. fatty acids and aldehydes with long chains. In addition, it was verified that the basic condition of ecological clean vegetable oil combustion is its modification. It leads to the thermal conversion and minimisation of the presence of toxic compounds in exhaust gases.

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References

1. Lin L., Cunshan Z., Vittayapadung S., Xiangqian S., Mingdong D.: Opportunities and challenges for biodiesel fuels, *Applied Energy*, 88, 4, 2011, 1020–1031.
2. Ekert K.: Analysis of hydrocarbon oil or rapeseed oil fueled diesel engine exhaust emissions of polycyclic aromatic hydrocarbons and aldehydes, *Journal of KONES*, 12, 2005, 3–4.
3. Graboski M.S., McCormick R.L. Combustions of fat and vegetable oil derived fuels in diesel engines. *Progress in Energy and Combustion Science*, 24, 2, 1998, 125–164.

4. Banel A., Zygmunt B.: Zastosowanie połączenia mikroekstrakcji do fazy stacjonarnej i chromatografii gazowej do oznaczania lotnych kwasów tłuszczowych w próbkach środowiskowych i pokrewnych, *Ecological Chemistry and Engineering*, 2008, 15, 1, 7–28.
5. Namieśnik J.: Trendy w analityce i monitoringu środowiskowym, Nowe horyzonty i wyzwania w analityce i monitoringu środowiskowym, 2003, 1–32.
6. Amorim L.C.A., Carneiro J.P., Cardeal Z.L.: An optimized method for determination of benzene in exhaled air by gas chromatography-mass spectrometry using solid phase microextraction as a sampling technique, *Journal of Chromatography B*, 2008, 865, 1-2, 141–146.
7. Andrews A.: Solid-Phase Microextraction, Environmental Applications, 2000, 3, 4170–4178.
8. Gośliński M., Zawirska-Wojtasiak R., Gajc-Wolska J.: Optymalizacja parametrów techniki SPME do oceny aromatu owoców linii transgenicznych ogórka eksprymujących gen taumatyny II, *Żywność. Nauka. Technologia. Jakość*, 2007, 5 (54), 144–154.
9. Wiergowski M., Reguła K., Szpiech B.: Szybka analiza amfetaminy w ludzkim materiale biologicznym z wykorzystaniem metody mikroekstrakcji do fazy stacjonarnej w fazie nadpowierzchniowej, *Archiwum Medycyny Sądowej i Kryminologii, Suplement 1*, 2000, L, 145–152.
10. Domeno C., Martinez-Garcia Fca, Campo L., Nerin C.: Sampling and analysis of volatile organic pollutants emitted by an industrial stack, *Analytica Chimica Acta*, 2004, 524, 1–2, 51–62.
11. Psillakis E., Kalogerakis N.: Solid-phase microextraction versus single-drop microextraction for the analysis of nitroaromatic explosives in water samples, *Journal of Chromatography A*, 2001, 938, 113–120.
12. Pawliszyn J.: Solid phase Microextraction. Theory and practice, 1997, 8–34.

Recenzent:

Andrzej BUSZEWSKI

Chromatograficzne badanie składu spalin pobranych ze strumienia gazu metodą mikroekstrakcji do fazy stacjonarnej

Słowa kluczowe

Mikroekstrakcja do fazy stałej, spaliny, chromatografia gazowa ze spektrometrią mas.

Streszczenie

Przeprowadzono analizę przydatności techniki mikroekstrakcji jako metody poboru próbki analitycznej ze strumienia gazu. Ze względu na wysokie temperatury panujące w obszarze poboru prób oraz charakter przewidywanych produktów spalania wybrano odpowiednie włókna do mikroekstrakcji. Zbadano kilka mieszanek paliwowych na bazie oleju roślinnego. Wpływ dodatków handlowych na skład spalin oceniony został na podstawie analiz chromatograficznych ze spektrometrią mas. Stwierdzono, że podstawowym warunkiem czystego ekologicznie spalania oleju roślinnego jest jego modyfikowanie.