DEVELOPMENT OF A TRAP FOR FUEL EXHAUST PARTICULATE MATTER UNDER DRIVING CONDITIONS AND GC-MS METHOD FOR THEIR ANALYSIS*[1]

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Simple and useful GC/MS method was developed in order to analyze the toluene soluble components in particulate matter from diesel exhaust. Easily adaptable specially designed trap was built which could be mounted on exhaust pipe of different vehicles. It was filled with different materials on which particles were collected. After collection of the particles, the bare trap and different materials were washed and soaked with toluene. In some cases extraction process was speeded up with ultrasonification of the samples for 30 min. Samples were filtered and concentrated to 125–500 µl and afterwards were directly analyzed by GC/MS. The separated components were identified by Automated Mass Spectral Deconvolution and Identification System (AMDIS) using a specialized user-built library. Five of the identified components [4-methylphenol, 3,3'-dichloro-1,1'-biphenyl, diethyl phthalate, 1,2-benzenedicarboxylic acid, bis(2-methylpropyl) ester and mono(2-ethylhexyl) ester of 1,2-benzenedicarboxylic acid] were found in the European priority lists (Category 1 and Category 2) of endocrine disruptors.

Key words: vehicle exhaust; diesel motors; particulate trap; GC/MS; endocrine disruptors; European priority list.

КОНСТРУКЦИЈА НА СТАПИЦА ЗА ЧЕСТИЧКИ ОД ИЗДУВНИ ГАСОВИ НА ВОЗИЛА ВО УСЛОВИ НА ВОЗЕЊЕ И НИВНА АНАЛИЗА СО GC-MS

Разработен е едноставен метод за GC-MS со цел да се анализираат честички растворливи во толуен од издувни гасови на дизел-возила. Конструирана е специјална стапица која може да се прилагоди и монтира на различни возила. Користени се разни материјали на кои честичките се атсорбираат. По собирање на честичките, самата стапица и атсорбентот беа натопени во толуен. Процесот на екстракција може да се забрза ако се изведува во ултразвучна бања во тек од 30 min. Примероците се филтрираат и концентрираат до 125–500 µl, а потоа директно се анализираат со GC-MS. Издвоените компоненти беа идентификувани со помош на системот за автоматска деконволуција и идентификација на масени спектри. Идентификувани се пет компоненти [4-метилфенол, 3,3'-дихлоро-1,1'-бифенил, диетил фталат, 1,2-бензендикарбоксилна кислеина, бис(2-метилпропил) естер и моно(2-етоксихексил естер на 1,2-бензендикарбоксилна кислеина) од европските приоритетни листи на ендокрини нарушувачи (категорија 1 и категорија 2).

Клучни зборови: издувни гасови; дизел-возила; стапица за честички; ендокрини нарушувачи; GC-MS

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*Dedicated to Professor Svetomir Hadži Jordanov on the occasion of his 70th birthday.

1. INTRODUCTION

Endocrine disruptors (ED) are exogenous substances that cause adverse health effects in intact human or animal organisms, or their progeny. A wide variety of both man made and naturally occurring chemicals can mimic hormones and thus influence many bodily functions. It has been shown that contaminants can alter hormone production at its endocrine source, the release of stimulatory or inhibitory hormones from adrenal glands like pituitary or hypothalamus, enzymatic biotransformation of hormones, and free hormone concentrations in serum by alteration of concentrations or functioning of proteins transport. The Japanese Environmental Agency in 1998 made a list of 67 chemicals which were labeled as endocrine disruptors. The list includes mostly pesticides and related chemicals, as well as several by-products of combustion [1–3].

Vehicle exhaust fumes are complex mixtures of gaseous and particulate substances derived from unburned fuel, lubricant oil and combustion products. Their chemical composition is predetermined by the nature of the fuels and mechanical design of the engines. The main components are carbon monoxide (CO), carbon dioxide (CO_2), nitrogen oxides (NO_x), sulfur oxides (SO_x), hydrocarbons (HC), as well as particulate matter (PM). The chief constituents of exhaust fumes are elemental carbon as well as polycyclic aromatic hydrocarbons (PAH) along with their methylated, nitrated and oxygenated derivatives and substituted polycyclic aromatic compounds [4, 5]. From an environmental standpoint, the diesel engines, compared to gasoline engines, have an advantage that they emit lower concentrations of "greenhouse gases" such as CO and CO_2. However, their disadvantage is that they emit higher concentration of NO_x and PM. Studies have shown that the compound content varies with particle size. Usually larger particles contain lower mass PAH and vice versa [6]. Sulphur is a key component for one of the nucleation modes that leads to formation of exhaust PM [7]. As a prevention of PM formation, there is a tendency to reduce the sulfur content in the fuels, and presently the maximum allowed amount is 10 ppm [8, 9].

These global concerns about adverse health effects and environment concerns lead us to develop a screening method for determination of components in particulate matter from vehicle exhaust. A simple trap, adaptable to any vehicle exhaust pipe, was built in order to collect samples under driving conditions. Herein, we would like to describe the construction of the trap, the optimization of the extraction, gas chromatographic-mass spectrometric (GC-MS) analysis and the initial results from this study.

2. EXPERIMENTAL PART

2.1. *Materials and methods*

Toluene (Fluka pestanal and Merck GC quality) was used as solvent for dilution/extraction of PM [10, 11]. Rotoevaporator model RV 10C S40 (IKA) with the following default toluene programme was applied: bath – 60 ºC, rotation – 100 rpm, vacuum – 77 mBar, efficiency – 80 %, caloric value 1720 J/(kg·K), evaporation enthalpy – 427, density of toluene – 867 kg/m³ was used for the solvent evaporation.

The analysis and identification of the analytes was carried out on an Agilent GC-MS model 6890N with autosampler coupled to a mass spectrometer 5975B EI/CI. The chromatographic separation was performed on a HP-5MS column, length 30 m, internal diameter 250 μm and thickness of the stationary phase of 0.25 μm. The samples were injected in splitless mode at an injector temperature of 250 ºC. The initial column temperature was 40 ºC, maintained for 1 min, raised to 300 ºC at a rate of 10 ºC/min, then held at 300 ºC for 3 min. The whole analysis time was 30 min. The temperature of the auxiliary line to the MS was 250 ºC, MS quad at 150 ºC and electron ionization was maintained at 230 ºC.

For the purpose of this study various collection materials were tested: filter paper, cotton and glass. The cotton was cleaned in washing machine and air dried. The glass was cleaned with detergent, followed by tap water and deionized water, and dried at 200 ºC. Dry filter paper was used. The trap and its parts were cleaned with a detergent, followed by tap water and deionized water. Every part was dried at 150–200 ºC before use. The bolts were cleaned with technical toluene.

After the field test was performed the inner walls of the trap were cleaned with 30–50 mL of the solvent. Suitable solvent extraction was used for extracting the components.

In some cases, for speeding up the extraction process, ultrasonification was applied for 30 min. The default toluene method on the rotoevaporator was used for solvent reduction. Samples were reduced to 125–500 μl.

2.2. *Field tests*

The trap was set to be in a coaxial direction to the exhaust system. The distance between the last plane of the exhaust and the first plane of the trap was set to be between 0–2 cm. The chosen route of 34 km was driven in period of 30–40 min, with average speed of 80–90 km/h.

3. RESULTS AND DISCUSSION

The development of the screening method involved four steps: construction of a trap for collecting the particulate matter, optimizing the extraction procedure, optmizing the chromatographic conditions and mass spectrometric identification of the components.

The trap had to fulfill two major conditions: collect the maximum amount of exhaust particualte matter under driving conditions but at the same time not to interfere with the normal function of the engine. Furthermore, it had to be made of inert material and also adaptable to various vehicles and constructions of the exhaust pipe where it was mounted.

The trap was made from stainless steel, and contains five contact barriers. A scheme of the trap is given Figure 1, and Figure 2 illustrates it mounted on the car exhaust. Trap dimensions are 120×120×100 mm. Four of the contact barriers are fixed and the last one is removable. Fixed contact barriers are with the following dimensions, going from the inlet to the outlet of the trap: 1 (60×120×1 mm), 2 (60×120×1 mm), 3 (70×120×1 mm), 4 (50×120×1 mm). The removable fifth barrier has an opening of 70×90 mm, where glass, filter paper or cotton fabrics were used as fillers of the gap.

The fabric used was made of cotton, the paper was standard quantitative filter paper (Whatman) and the glass was common window glass (100×80×4 mm).
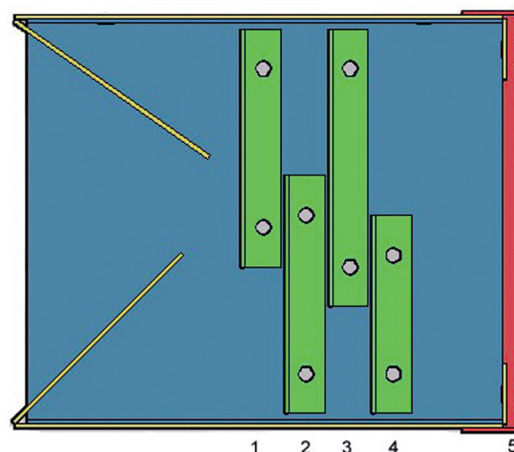

Fig. 1. Construction of the trap used for testing particulate matter (PM)

Fig. 2. The trap mounted on the exhaust pipe of a car

The optimization of the extraction and gas chromatographic conditions was done by modifying published procedures given in the literature [11, 12] and the conditions are given in the experimental part.

The identification of the large number of components by their EI mass spectra was performed by the Automated Mass Spectral Deconvolution and Identification System (AMDIS) [13] which has been shown to be very valuable for extraction of the mass spectra of superimposed peaks [14].

AMDIS allows users to build their own libraries so a special library containing 4506 mass spectra was built for the purpose of this study. Since our aim was to cover every possible component we used these starting libraries and their reference number of components: NISTCW (Chemical Weapons) – 62, NISTDRUG (Drugs) – 739, NISTEPA (Environmental Protection Agency) – 1086, NISTFDA (Food and Drug Administration) – 415, NISTFF (Flavors and Fragrances) – 991, NISTTOX (TOXIC) –1213.

An additional mass spectra library with 134 components was also built, using either the AMDIS libraries or the basic NIST library, containing endocrine disruptors. The primary list contained around 180 components and encompasses the endocrine disruptors as given by the European Union and Japan. From the European library only category 1 and category 2 components were utilized. Category 1 includes components which at least one study has provided evidence of endocrine disruption in an intact organism. Category 2 includes components that are potential endocrine disruptors, i.e. in vitro data indicate potential for endocrine disruption in intact organisms. Also, it includes effects in vivo that may, or may not, be ED-mediated and may include structural analyses and metabolic considerations [15]. There is also an available selection of components dependant on the nature of the source of pollution. Japan's list includes 73 components with the nature of components and the nature of the source of the pollution.

The analysis was performed on several diesel vehicles. All were of the common rail construction using high-pressure injection systems from different manufacturers but also of different age and wear using eurodiesel. One gasoline engine was included in this study for comparison to the diesel engines. Multiple runs were performed in order to optimize the extraction and analysis method. The vehicles used for this study, as well as relevant data for each vehicle, are given in Table 1.

T a b l e 1

Model, type, motor capacity, year of manufacture of the vehicles used for testing of particulate matter (PM)

Sample	Vehicle	Motor capacity /cm^3	Manufactured /year	Mileage /km	Fuel
1	BMW 320 D	1995	2007	65 000	Eurodiesel
2	BMW 320 D (E46)	1951	2000	180 000	Eurodiesel
3	Citroen Saxo	1527	1999	121 000	Eurodiesel
4	Peugeout 306 XND	1905	1998	132 000	B8
5	Peugeout 206 SW	1398	2003	289 000	Eurodiesel
6	Fiat Fiorino	1697	1996	197 000	Eurodiesel
10	Opel Astra	2000	1992	227 000	ES95

The GC-MS analysis on the particulate matter from the exhaust of the tested vehicles followed by a search in the custom-made AMDIS libraries revealed from 1034 to 2785 discreet components. In order to ensure greater accuracy, optimized settings were applied for the deconvolution process: high resolution, high sensitivity, medium peak requirements, and minimum match factor 95 % for component identification [16]. By applying these strict settings, only 53 components, given in Table 2, were identified. The first five are endocrine disruptors, while the rest are not classified as such by either the European or Japanese standards. Only 4-methylphenol was detected in the particulate matter of both the diesel and gasoline vehicle. It is interesting that in the particulate matter of the vehicle on B8 there was found only one endocrine disruptor. Despite all precautions, the phthalates are so omnipresent that it cannot be excluded that they have been introduced in the manipulation process. In a work supported by a Japan Automobile Research Institute, 21 endocrine disruptors were investigated in PM. Their study revealed the presence of only two endocrine disruptors (n-pentylphenol and benzo[a]pyrene) from the total list. These components were found both in the diesel and gasoline powered vehicles.

T a b l e 2

Identified components in the exhaust PM

No	Sample	CAS	Name
			Endocrine disruptors
1	1,2,3,4,5,10	106-44-5	4-methylphenol
2	1,2,3,5,6,7,8,9	2050-67-1	3,3'-dichloro-1,1'-biphenyl
3	6,7,8,9	84-66-2	diethyl phthalate
4	6,7,8,9	84-69-5	1,2-benzenedicarboxylic acid, bis(2-methyl-propyl) ester
5	6,7	4376-20-9	1,2-benzenedicarboxylic acid, mono(2-ethyl-hexyl) ester
			Other components
6	1,2,4,10	98-82-8	(1-methylethyl)benzene
7	1,2,3,4,5,10	124-18-5	decane
8	1,2,3,4,5,10	874-41-9	1-ethyl-2,4-dimethylbenzene
9	1,2,3,4,5,9,10	1120-21-4	undecane
10	1,2,3,4,5,10	527-53-7	1,2,3,5-tetramethyl-benzene
11	1,2,3,4,5,10	103-69-5	N-ethylbenzenamine
12	1-10	112-40-3	dodecane
13	2,3	629-50-5	tridecane
14	1,2	91-57-6	2-methylnaphthalene
15	1-10	629-59-4	tetradecane
16	1,2,3,4,5,10	629-62-9	pentadecane
17	1-10	544-76-3	hexadecane
18	1-10	629-78-7	heptadecane

No	Sample	CAS	Name
			Endocrine disruptors
19	2	1921-70-6	2,6,10,14-tetramethylpentadecane
20	2,5	120-51-4	benzyl benzoate
21	1-10	3622-84-2	N-butylbenzenesulfonamide
22	1-10	120-12-7	anthracene
23	1,2,3,5,6,7,9,10	112-95-8	eicosane
24	2,3,4,5,6,7,9,10	129-00-0	pyrene
25	1,2,3,4,5,10	629-94-7	heneicosane
26	1,2,3,4	646-31-1	tetracosane
27	1,3	103-65-1	propylbenzene
28	1,3,5	108-67-8	1,3,5-trimethylbenzene
29	1,3,5,10	138-86-3	limonene
30	1,7,9	59-89-2	4-nitrosomorpholine
31	1,3,4,5,10	535-77-3	1-methyl-3-(1-methylethyl)benzene
32	1	95-93-2	1,2,4,5-tetramethylbenzene
33	1,3,5,10	91-20-3	naphthalene
34	1,3,4	112-72-1	1-tetradecanol
35	3	142-62-1	hexanoic acid
36	3	934-74-7	1-ethyl-3,5-dimethylbenzene
37	3,4	123-08-0	4-hydroxybenzaldehyde
38	3,4	112-70-9	1-tridecanol
39	3	630-01-3	hexacosane
40	3	593-49-7	heptacosane
41	3	630-02-4	octacosane
42	3	638-68-6	triacontane
43	5,6,7,8	111-92-2	N-butyl-1-butanamine
44	5,10	95-50-1	1,2-dichlorobenzene
45	5	629-73-2	1-hexadecene
46	4	95-63-6	1,2,4-trimethylbenzene
47	4	112-92-5	1-octadecanol
48	6,9	85-01-8	phenanthrene
49	1	111-84-2	nonane
50	10	103-65-1	n-propylbenzene
51	10	108-67-8	1,3,5-trimethylbenzene

As expected, all extracts from the emissions particulate matter contained the saturated hydrocarbons. Vehicle 1 uses a diesel particulate filter to capture carbon particles and then intermittently burn them using extra fuel injected directly into the filter, although has a lower amount of particulate matter, the number of components is about the same as in the older types of engines. We can estimate 1.01 mg PM/cm^2, or 2.38 mg PM/km driving distance.

The limit of detection was determined on anthracene, as a representative compound of the components identified. The limit of detection was determined to be 0.125 ng/µl which is in the range with literature data [17].

It must be mentioned that the fuels used were from different providers and obtained at different periods. Manufacturers use different batches of mixtures and the variations in the results obtained probably reflect this inconsistency. Emptying the car tanks and using only one batch of diesel fuel unfortunately was not feasible for this study. However, since the purpose was to do a screening of possible endocrine disruptors and other organics, this approach gave us a cross section of the components in the exhaust particulate matter.

Tests were performed on the repeatability of the GC/MS analysis. It was found that the repeatability was acceptable considering the limitations of the mass spectrometer with only ±1 out of 36 targets and ±15 out of 1880 total number of components. This was attributed to the relatively low scan speed of the quadrupole mass spectrometer which is less than two scans per second. With scanning instruments such as quadrupole MS, a scan is initiated at one point in time. As the scan progresses, time elapses so the last data for the scan is collected at a second point in time. During the scanning process, analyte concentrations change in the source, resulting in skewed spectra. The skew is corrected by averaging spectra across the apex of the chromatographic peak. This significantly complicates the mathematics and accuracy of deconvolution in the case of overlapped spectra.

This drawback is absent in time of flight mass spectrometers [18].

Tests were also performed on the influence of the storage conditions on the collected material. For example, on one of the vehicles (sample 1) two valid tests were performed, the difference being the storage time of the collected material. One was performed immediately, while the other was kept at room temperature more than 12 h. It was interesting that in the latter case the number of components was 2289, 18 more than in the one that was analyzed immediately. In another instance (sample 2), the collected material was kept at a temperature of –18 ºC, and the results showed an increase in the number of components from 1816 to 1826. This can also be explained by the low number of data points in the mass spectra. However, all other GC analyses were performed immediately after the extraction of the particulate matter.

4. CONCLUSION

Convenient method for collection of fuel exhaust particulate matter utilizing specially designed trap was developed. A GC/MS method was developed for screening analysis of components in fuel exhaust particulate matter. The method is inexpensive, easily applicable and suitable for primary information of the identified components which can lead to further studies. It can be conveniently employed for routine qualitative analysis in any working and testing conditions. Identification of five endocrine disruptors can lead to further development of this method for quantitative analysis. Furthermore, these results revealed that PM from diesel and gasoline vehicles must be investigated in greater details.

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