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New approach to complex organic compounds mixtures analysis based on gas chromatography–atmospheric pressure photoionization–mass-spectrometry

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A B S T R A C T

The mass-spectra of a number of different hydrocarbons were obtained using atmospheric pressure photoionization (APPhI) and photochemical ionization (APPhCI) mass-spectrometry. The respective mass-spectra consisted mainly of molecular (M^+) or quasimolecular (MH^+) ion peaks or both. The composition of aromatic hydrocarbons in straight-run gasoline was investigated using standard PIONA method, based on capillary GC and retention time indexes, and GC/MS (APPhI). 56 aromatic hydrocarbons were identified using GC/MS (APPhI) and 43-using standard PIONA method. The opportunities of MS (APPHCI) for determination of impurities in pure hydrocarbons and for direct analysis of complex mixtures without separation were demonstrated when MS (APPhCI) analysis for GC standards of benzene and toluene was carried out (main component vapor was reagent gas). The targeted PAHs and phtalates were registered selectively in 44 component model mixture of semivolatiles with partial or without separation of the components, using GC/MS (APPhI).

1. Introduction

The most widely used approach to complex hydrocarbon mixtures analysis is based on capillary GC with flame ionization detector (FID) or with mass-spectrometer (GC/MS). In latter case electron ionization (EI) mode is used in most cases. For many hydrocarbons (especially n-alcanes) the intensity of molecular ion peak–most important peak in EI mass-spectra–is very low. In case of aromatic hydrocarbons this peak intensity is high but it is very often not most intensive peak of mass-spectra. In general case mass-spectra of hydrocarbons consist of a lot of ion peaks, which are not characteristic for individual compound. Molecular ion peak (or quasimolecular ion) intensity of many hydrocarbons can be increased due to use of chemical ionization mode, but detection limit in this case is about ten times higher (10^{-10}–10^{-9} g) than in case of EI mode. Due to complex EI mass-spectra composition of individual hydrocarbons their selective registration in complex mixtures is difficult or even impossible especially when mixture is only partially resolved into compounds. Besides that registration of the compounds coeluted with the main component, concentration of which is much higher than of coeluted impurities is not possible in case of EI and CI mass-spectrometry due to need to switch-off cathode current.

In case of pure organic compounds analysis for impurities the most difficult problem is recognition of the number of impurities, which are not known. It cannot be solved properly even in case of capillary GC/MS (EI, CI), as complete separation of impurities from the main component is not possible in this case also. It is well known, that complex hydrocarbon mixtures cannot be separated completely (part of the components are coeluted).

We have developed method of atmospheric pressure photoionisation (APPhI) and atmospheric pressure photochemical ionization (APPhCI) mass-spectrometry [1.2]. Unlike EI, this method enables the registering of mass-spectra for individual compounds, which consist of only molecular $[M]^+$ and/or quasimolecular $[MH]^+$ ion peaks. Such capability was demonstrated for compounds (n-alcanes, alcohols, esters, ethers and amines) EI mass-spectra which contained molecular ion peaks of very low intensity or they were absent at all. APPhI and APPhCI mass-spectra were investigated for a lot of compounds (more than 200) (normal and branched alcohols, aromatic hydrocarbons, polyaromatic hydrocarbons (PAHs), phthalates, alkyklphosphates and phosphonates, phenols, amines, nitroaromatics, polychlorbiphenyles (PCBs), tert-butyldimethylsilyl (TMDMS) derivatives of aminoacids etc.) using GC/MS (APPhI/APPhCI) [3–10].

In all cases respective mass-spectra consisted of only molecular and/or quasimolecular peaks, depending on the nature of compounds and reagent vapor (used in APPhCI MS).

Detection limits in GC/MS (APPhI) were 10^{-12}–10^{-10} g in SIM mode, depending on ionization potential of the compound and

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UV-lamp photons energy; in GC/MS (APPhCI) – 10^{-14}–10^{-13} g in the same SIM mode depending on the compound and reagent vapor.

Fast selective and high sensitive GC/MS (APPhCI) determination of phtalates in complex mixtures using short capillary columns (1.5 m) was demonstrated in [11]. Detection limits in SIM mode were 10^{-13}–10^{-12} g. In case of GC/MS (APPhCI) respective detection limits for phosphates and phosphonates [12] were about $(3–5)\times10^{-13}$ g.

In the case of mixture analysis without separation APPhI MS [11,12] as well APPhCI MS [4–9] were applied.

The number peaks, registered in respective APPhCI mass-spectra of mixtures without separation, coincided with the number of components in the mixture (in case of model mixtures) [11,12].

Every peak corresponded to respective molecular or quasimolecular ion. Detection limits in the case of solution mixtures analysis without separation by APPhCI MS were about the same as in case of GC/MS (APPhCI). It is obvious that direct mixture mass-spectrometric analysis at atmospheric or subatmospheric pressure using photoionisation described in [18–21] in reality is APPhCI MS or sub-APPhCI MS. In spite of successful coupling of APPhCI MS with micro-HPLC [22], we considered that GC/MS (APPhI/APPhCI) was preferable for analysis of GC amenable compounds due to as higher efficiency of capillary columns and higher sensitivity of GC/MS (APPhCI).

Reliable and selective determination of aromatic hydrocarbons, PAHs and phtalates in complex mixtures, as well of impurities in pure hydrocarbons (GC standards) is very important. Therefore it was interesting to investigate possibility of high selective recognition of aromatic hydrocarbons in straight-run gasoline, targeted compounds in complex mixtures and impurities in some hydrocarbon GC standards using GC/MS (APPhCI).

2. Experimental

Our investigation was carried out using Finnigan model «4021» GC/MS equipped with APPh/APPhCl ion source developed by us.

These methods of ionization are described in Refs. [1–3,11,12].

In case of straight-run gasoline analysis 100 m × 0.25 mm × 0.25μm capillary column with nonpolar (SE-30) cross-bonded stationary phase was used. The same column was used in standard PIONA method. It was connected directly to the ion source, 1 μl of gasoline was introduced into injector in split mode. Helium flow rate was about 1.5 ml/min. Split ratio was 200:1. The separation of hydrocarbon mixtures was carried out using temperature programming: isotherm 35 °C (14 min), temperature increasing rate 1.1 °C/min till 60 °C; isotherm 60 °C (19 min), heating till 250 °C with rate 2 °C/min, isotherm 250 °C (10 min).

Injector temperature was 250 °C. The internal volume of the ionization chamber was about 150 μl. Make-up gas flow was also used (about 30 ml/min). The photoionisation was carried out using krypton discharge lamp; energy of UV photons was 10.2 eV. Ion source temperature was 240 °C.

The analysis of 44 component mixture, containing PAH's and phthalates was carried out using capillary column (7 m × 0.32 mm × 0.25 μm) with cross-bonded SE-54 stationary phase.

3. Compounds

As model compounds mixtures we have used the set of mixtures of different hydrocarbons (alkanes – 11, iso-alkanes – 32, olefins – 25, naphtenes – 27 and aromatics – 36) and the mixture of hydrocarbons, containing 144 compounds, belonging to different classes (ALPHAGAS, USA). Besides that we have separated components of straight-run gasoline.

GC standards (Polyscience Corp., USA) of toluene and benzene and 44 component mixture of semivolatiles, containing PAHs and phthalates, were used in our research also.

4. Results and discussion

Total number of peaks on chromatograms of registered in total ion current (TIC) mode for sample of straight-run gasoline was about 200. Selective registration of aromatic hydrocarbons and their identification was carried out using mass-chromatograms, registered for $m/z=78$, 92, 106, 120, 134, 148, 162, 128, 142 and respective retention indexes.

APPhI mass-spectra of aromatic hydrocarbons consisted practically of one peak, corresponding to molecular ion peak.

The comparison of the GC/APPhI MS data with respective PIONA method data has allowed to identify additionally 13 aromatic hydrocarbons. Total number of reliably identified aromatic hydrocarbons with the help of GC/APPhI MS has allowed to determine more accurately their content in the sample of the straight-run gasoline in comparison with PIONA method. The content of these hydrocarbons, determined by GC/APPhI MS and PIONA method, was 8.54% and 5.96% respectively. The determination of aromatic hydrocarbons content was carried out using coefficients of relative sensitivity of Photoionisation detector (PID), determined by us before and using iso-propylbenzene as external standard. It is necessary to keep in mind that accuracy of aromatic hydrocarbons content determination is very important in gasoline quality control. The respective data are presented in the Table 1.

As it is seen from the Table 1, GC/APPhI MS has allowed to increase the reliability of components number determination and their selective identification in complex multicomponent mixture. Using short capillary column (15 m × 0.25 mm × 0.4 μ film thickness)with unpolar (SE-30) and polar (Carbowax 20M) bonded stationary phases the possibility of fast selective determination of the aromatic hydrocarbons in straight-run gasolines with the help of GC/APPhI MS was shown also. The time of analysis in this case was not more than 15 min. GC/APPhI MS has to be perspective in catalytic gasoline analysis for aromatic hydrocarbons. This type of gasoline cannot be analyzed accurately, when standard PIONA method is used, due to high concentrations of aromatics in the mixture, overloading of the capillary column and incorrect identification on the base of retention indexes.

For the demonstration of the opportunities of APPhI mass-spectrometry for the determination of the number and nature of impurities in pure organic compounds APPhI MS analysis of benzene and toluene (without separation) was carried out (specified purity degree of them was higher than 99.5%). The number and nature of impurities was not known to us. GC/MS (EI mode) of these compounds has shown that on total ion chromatogram of the former one was registered one impurity and on the respective chromatogram of the latter one – two impurities.

As to APPhI mass-spectrometry (see Tables 2 and 3) 29 impurities were registered in benzene and 40 ones – in toluene.

As it is seen from the data, presented in the Tables 2 and 3, and comparison of them with the respective data, obtained using GC/MS (EI) for the same samples of GC standards such ones as toluene and benzene, the direct APPhI MS analysis allows to determine much more impurities being present in these fine chemicals than usual approach based on GC/MS (EI) analysis and to identify them on the base of their molecular weights. To be more correct – it is APPhCI MS and reagent vapor of the main component used as reagent gas.

Table 1
Determination of aromatic hydrocarbons in straight-run gasoline by HRGC (PIONA method) and by HRGC/APPhI MS.

	Compound name	Retention index	Weight % (by PIONA)	M^+ (m/z)	Weight % (by APPhI/MS)
1	Benzene	652.70	Not ident.	78	0.008
2	Toluene	756.20	Not ident.	92	0.530
3	Ethylbenzene	853.56	0.639	106	0.805
4	m-Xylene	862.42	1.284	106	2.32(4+5)
5	p-Xylene	863.41	0.447	106	
6	o-Xylene	882.48	0.856	106	0.740
7	i-Propylbenzene	912.83	0.012	120	0.164
8	n-Propylbenzene	945.86	0.257	120	0.548
9	1-Methyl-3-Ethylbenzene	955.80	0.152	120	0.446
10	1-Methyl-4-Ethylbenzene	956.10	Not ident.	120	0.232
11	1,3,5-Trimethylbenzene	961.62	0.188	120	0.475
12	1-Methyl-2-Ethylbenzene	971.16	0.255	120	0.234
13	1,2,4-Trimethylbenzene	983.41	0.352	120	0.475
14	t-Butylbenzene	984.54	0.079	134	0.001
15	i-Butylbenzene	995.82	0.006	134	0.004
16	sec-Butylbenzene	998.00	0.045	134	0.006
17	1,2,3-Trimethylbenzene	1007.74	0.153	120	0.362
18	1-Methyl-3-i-propylbenzene	1009.86	0.054	134	0.003
19	1-Methyl-4-i-propylbenzene	1013.47	0.056	134	0.005
20	1-Methyl-2-i-propylbenzene	1027.67	0.290	134	0.001
21	1,3-Diethylbenzene	1042.70	0.081	134	0.003
22	1-Methyl-3-n-propylbenzene	1044.44	0.125	134	0.123
23	1,4-Diethylbenzene	1046.55	0.109	134	0.177
24	1-Methyl-4-n-propylbenzene	1047.70	0.033	134	0.024
25	n-Butylbenzene	1048.40	Not ident.	134	0.089
26	1,3-Dimethyl-5-Ethylbenzene	1049.70	Not ident.	134	0.067
27	1,2-Diethylbenzene	1051.60	0.026	134	0.075
28	1-Methyl-2-n-propylbenzene	1061.30	0.020	134	0.016
29	1,4-Dimethyl-2-Ethylbenzene	1068.79	0.131	134	0.018
30	sec-Pentylbenzene	1070.02	0.016	148	0.014
31	1,2-Dimethyl-4-Ethylbenzene	1075.75	Not ident.	134	0.017
32	1,3-Dimethyl-2-Ethylbenzene	1081.18	0.012	134	0.088
33	1-Methyl-4-t-Butylbenzene	1090.78	0.001	148	0.007
34	1,2-Dimethyl-3-Ethylbenzene	1093.73	0.048	134	0.059
35	1-Ethyl-2-i-propylbenzene	1096.87	0.008	148	0.012
36	1-Ethyl-4-i-propylbenzene	1103.86	0.003	148	0.006
37	1,2,4,5-Tetramethylbenzene	1105.95	0.020	134	0.045
38	1,2,3,5-Tetramethylbenzene	1108.37	0.023	134	0.004
39	2-Methylbutylbenzene	1109.74	0.001	148	0.004
40	1-t-Butyl-2-methylbenzene	1125.11	0.001	148	0.009
41	1-Ethyl-2-n-propylbenzene	1134.93	0.002	148	0.005
42	1-Methyl-3-n-butylbenzene	1141.42	0.007	148	0.005
43	1,3-Di-i-propylbenzene	1143.96	0.043	162	0.001
44	n-Pentylbenzene	1148.91	Not ident.	148	0.006
45	1,2-Di-i-propylbenzene	1158.34	0.011	162	0.001
46	1-Methyl-2-n-butylbenzene	1159.69	0.006	148	0.001
47	1,4-Di-i-propylbenzene	1159.80	Not ident.	162	0.001
48	Naphtalene	1167.46	0.100	128	0.227
49	1-t-Butyl-3,5-dimethylbenzene	1169.58	0.005	162	0.001
50	1,3-Di-n-propylbenzene	1188.25	0.001	162	0.001
51	1,3,5-Triethylbenzene	1209.32	0.004	162	0.001
52	1-t-Butyl-4-ethylbenzene	1226.42	Not ident.	162	0.001
53	1,2,4-Triethylbenzene	1231.50	Not ident.	162	0.001
54	1-Methyl-4-n-pentylbenzene	1243.00	Not ident.	162	0.001
55	n-Hexylbenzene	1253.50	Not ident.	162	0.001
56	2-Methylnaphtalene	1269.50	Not ident.	142	0.073
			Sum = 5.962		Sum = 8.543

Detection limit for iso-propyl benzene (model compound) using GC/MS (APPhI) in scan mode was about 4×10^{-11} g and in SIM mode – 4×10^{-12} g. Our experiments with GC/MS (APPhCI) (benzene vapor was used as reagent gas) have shown that respective calculated detection limit was about 100 times less than in GC/MS (APPhI).

We have investigated possibility of selective registration of the sets of targeted PAHs and phthalates in model mixture of 44 semivolatile organic compounds using GC/MS (APPhI). Many compounds were only partially resolved.

All targeted compounds being present in the mixture were registered. Respective data are presented in the Table 4.

As it is seen from the Table 4, components with very close retention times were reliably recognized due to respective molecular or quasimolecular ions.

5. Conclusion

It was shown that APPhI mass-spectra of individual compounds consist practically of one ion peak (M^+ or MH^+).

Using GC/MS (APPhI) possibility of selective recognition of aromatic hydrocarbons in straight-run gasoline was shown. The number of registered aromatics was 56. In case of standard PIONA

Table 2
Homological ion series in mass-spectrum of investigated sample of high purity degree toluene.

Item	*m*/*z* of ions	Empiric formula	Number of ion peaks	Class of organic compounds
1	96; 106; 120; 134; 148; 162; 176; 190; 218	C_nH_{2n-6}	9	Alkylbenzenes (C_7–C_{15})
2	86; 128; 142; 170; 184; 198; 212	C_nH_{2n+2}	7	n- and iso-alkanes (C_6; C_9–C_{10}; C_{12}–C_{15})
3	96; 110; 124; 166; 180; 194; 236	C_nH_{2n-2}	7	aliphatic dienes (C_7–C_9; C_{12}–C_{14}; C_{17})
4	80; 108; 136; 150	C_nH_{2n-4}	4	cyclodienes (C_6; C_8; C_{10}–C_{11})
5	144; 172; 186; 200; 214; 242	C_nH_{2n-10}	6	Dinaphtobenzenes (C_{11}; C_{13}–C_{16}; C_{18})
6	98; 112; 140; 154; 168; 182; 196	$C_nH_{2n-4}S$	7	Alkyltiophenes (C_5–C_6; C_8–C_{13}) and olefines

Table 3
Homological ion series in mass-spectrum of investigated sample of high purity degree benzene.

Item	*m*/*z* of ions	Empiric formula	Number of ion peaks	Class of organic compounds
1	96; 106; 120; 134; 148; 162; 176	C_nH_{2n-6}	7	Alkylbenzenes (C_7–C_{13})
2	114; 128; 142; 156; 170; 184;	C_nH_{2n+2}	6	n-alkanes (C_8–C_{13})
3	96; 152	C_nH_{2n-2}	2	aliphatic dienes (C_7; C_{11})
4	80; 94; 108; 122; 136; 150;164;178	C_nH_{2n-4}	8	cyclodienes (C_6–C_{13})
5	102; 116; 130; 158; 172; 186	C_nH_{2n-10}	6	Dinaphtobenzenes

Table 4
Targeted PAHs and phthalates registered in 44 component mixture of semivolatile organic compounds using GC/MS (APPhI).

No	Compound	Mol. mass	Retention time, min	*m*/*z*
1	naphthalene	128	1.65	128
2	acenaphthylene	152	2.17	152
3	dimethyl phthalate	194	2.25	195
4	acenaphthene	154	2.27	154
5	fluorene	166	2.52	166
6	diethyl phthalate	222	2.62	223
7	phenanthrene	178	3.08	178
8	fluoranthene	202	3.87	202
9	pyrene	202	3.97	202
10	Benzilbutyl phthalate	312	4.92	313
11	Benz(a)anthracene	228	5.05	228
12	chrysene	228	5.06	228
13	Di-n-oktylphtalate	390	5.67	391
14	Benz(a)pyrene	252	6.10	252
15	Bis(2-ethylhexyl) phthalate	390	6.23	391
16	Indeno (1,2,3-cd) pyrene	276	7.90	276

method, based on retention indexes use for identification, only 43 aromatics were registered.

Possibility of registering of large number of impurities in GC standards of benzene and toluene by MS (APPhCI) (the main component vapor was reagent gas) coeluted with the main component was shown too. These impurities could not be recognized by GC/MS (EI).

The detection limits for iso-propyl benzene in SIM mode were 4×10^{-12} g and 4×10^{-14} g for APPhI/MS and for APPhCI/MS, respectively.

High selective GC/MS (APPhI) and reliable recognition of the sets of targeted PAHs and phthalates in the 44 components model mixture of semivolatile organic compounds was shown. Some of them were practically coeluted.

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