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The Use of Synchronous Fluorescence Technique in Environmental Investigations of Polycyclic Aromatic Hydrocarbons in Airborne Particulate Matter from an Industrial Region in Poland

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Abstract

The applicability of the fluorescence techniques to identify the polycyclic aromatic hydrocarbons (PAHs) in environmental samples is presented. The technique of synchronous fluorescence enabled the identification of the PAHs series containing 2–6 condensed rings in urban airborne particulate matter from Upper Silesia industrial region in Poland. The results obtained by synchronous and conventional fluorescence measurements have been confirmed by those from gas chromatography-mass spectrometry. As the air sample was taken in summer season, the main source of pollution by PAHs component seems to be transport – the exhaust gases from motor vehicles.

Keywords: synchronous fluorescence, polycyclic aromatic hydrocarbons (PAHs), atmospheric pollutions, gas chromatography-mass spectrometry

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs), ubiquitous today in human environment, being harmful as potentially carcinogenic or mutagenic compounds, derive from various sources: natural and anthropogenic ones. Aromatic compounds generated in various natural processes can appear in the natural environment, joining the global cycle of dispersed and concentrated forms of organic matter. The dispersed forms of organic matter are, e.g., hydrocarbons existing in a small amount in rocks and minerals of various origins as well as in abyssal waters getting out on the Earth surface as natural geysers, or hydrocarbons emerging from mining shafts as well as hydrocarbons from volcanic exhalations. The hydrocarbons should be also mentioned from dispersion aureoles round about petroleum and gas deposits. There are also hydrocarbons in under waters accompanying the petroleum, coal, and ore

deposits and hydrocarbons penetrating to water reservoirs and to soil as a result of outcrop and erosion of sedimentary rocks. The concentrated forms of the hydrocarbon existence are crude oils, combustible gases, solid bitumens, coals, bituminous shales, and organic-mineral associations of various natures [1]. Among different hydrocarbon groups, there are frequently various PAHs as products of diagenetic, biological, or thermal processes [2–6]. All of these kinds of hydrocarbons occurrence form a geochemical background overlapped by the anthropogenic pollutions [1]. The main sources of anthropogenic PAHs are incomplete combustion of organic matter especially organic fuels (industry, transport, incinerating plants, domestic processes) and thermolysis of organic fossils (coke and asphalt production) [7–9]. All waste organic matter emitters are especially active in an industrial region where they spread to large areas due to various meteorological phenomena. It is because the atmosphere is a zone particularly exposed to pollution.

The permanent contact of living organisms with air makes the polluted atmosphere an especially important area of monitoring. Harmful PAH compounds that pollute the air are very susceptible to adsorption on the other else air pollutant – suspended dust, formed by mineral matter and/or by soot appeared in the air due to lack of or inappropriate protective filters on devices emitting it [10, 11].

The necessity of monitoring of PAHs in air explains the proof of the use much more effective analytical methods enabling their identification in a manner as simple and fast as possible. Among the most frequently applied modern methods of analysis of aromatic hydrocarbons in environmental samples are the chromatographic ones, particularly capillary gas chromatography, the most effective with mass spectrometry as the tool of detection (GC and GC-MS methods) [12–19].

Also high performed liquid chromatographs (HPLC method) are widely applied in these investigations (e.g., [20–22]). However, it is often not cost effective to apply these methods routinely to large numbers of samples.

In the choice of analytical method, it is always very important to take into account the specific properties of analyzed compounds. In the analyzed case, the PAH's high fluorescence efficiency and sensibility as well as simplicity of sample preparation are the reasons that fluorescent techniques are beneficial for PAHs

Figure 1.
Localization of sampling in Upper Silesia Region.

monitoring. However, the conventional fluorescent spectra of multi-component mixture of PAHs have been sometimes difficult to interpret. Now, synchronous technique of fluorescence spectroscopy (SFS) removes these difficulties (e.g., [1, 23]).

The purpose of this work is a presentation of the applicability of the technique of synchronous luminescence for qualitative analysis of aromatic fraction composition of organic substance polluting the urban air in an industrial region. The task sample was taken from Upper Silesia Metropole. This is the region of Poland with many branches of industry, such as mining, metallurgy, electric power station (coke and coal), a dense road network, and a great number of coal-fired home stoves, used sometimes also in the summer. City Mysłowice – the area where air dust was taken to investigations lies centrally in this region (**Figure 1**). The monitoring of the air state in Upper Silesia Metropole and particular cities gives not only an actual information but can also indicate the direction of changes. We believe that it also encourages the people responsible for environment for more intensive efforts to improve air quality.

2. Some remarks on PAHs fluorescence and synchronous fluorescence spectroscopy (SFS)

Fluorescence is the emission of light of wavelength generally different from that of the incident radiation. Most polycyclic aromatic hydrocarbons are fluorescent. It is caused by the fact that the delocalized electrons in the aromatic rings may be easily excited, and the stiff structure does not allow for efficient vibrational relaxation. Fluorescence spectra of each PAH are very characteristic, and they depend on the number and position of aromatic rings. With aromatic ring number increasing, the fluorescence spectrum and emission peak wavelength are all red-shifted from ultraviolet to visible range; the fluorescence emission spectra from one to four rings could be discriminated in the following wavelengths, 275–320 nm, 320–375 nm, 375–425 nm, and 425–556 nm, respectively. It can be used for distinguishing the type of the polycyclic aromatic hydrocarbons (PAHs) as it exists in single type.

The electronic states in the molecules could be singlets or triplets. Singlet state is defined when all the electron spins are paired in the molecular electronic state. The ground state is always singlet (S_0). The excited states could be singlets (S_1, S_2, …) or triplets (T_1, T_2, …) when total spin is equal 1. The most probably absorption (A) and emission transitions are singlet-singlet; their intensity is high and luminescence decay time short, 10^{-9}–10^{-7} s. Such emission transition is called fluorescence (F). Molecules in the S_1 state can undergo a spin conversion to the first triplet state T_1; energy of this triplet state is lower than of S_1 state. The emission from T_1, termed phosphorescence (P), is shifted to the longer wavelengths relatively to the fluorescence and characterized by distinctly smaller intensity and longer decay time, 10^{-6}–1 s. It was showed on the simplified Jablonski diagram (**Figure 2**) [24].

The idea of synchronous fluorescence was first suggested by Lloyd and Evett [23]. In conventional fluorescence spectrometry, an emission spectrum is measured for constant excitation wavelength (λ_{exc}). Contrary, the excitation spectrum is measured for constant emission wavelength (λ_{em}), usually to determine the energy levels (or wavelengths) that are responsible for measured emission. In some sense, excitation spectra replace the absorption spectra. In Constant-Wavelength Synchronous Fluorescence Spectroscopy, the wavelength interval $\Delta\lambda = \lambda_{exc} - \lambda_{em}$ is keeping a constant. For each PAH, the most characteristic λ_{exc} and λ_{em} and in consequence $\Delta\lambda$ values could be choose. Value of $\Delta\lambda$ parameter is so calculated as a difference between effective emission and excitation wavelength characteristic for identified compound. When the difference between the longest
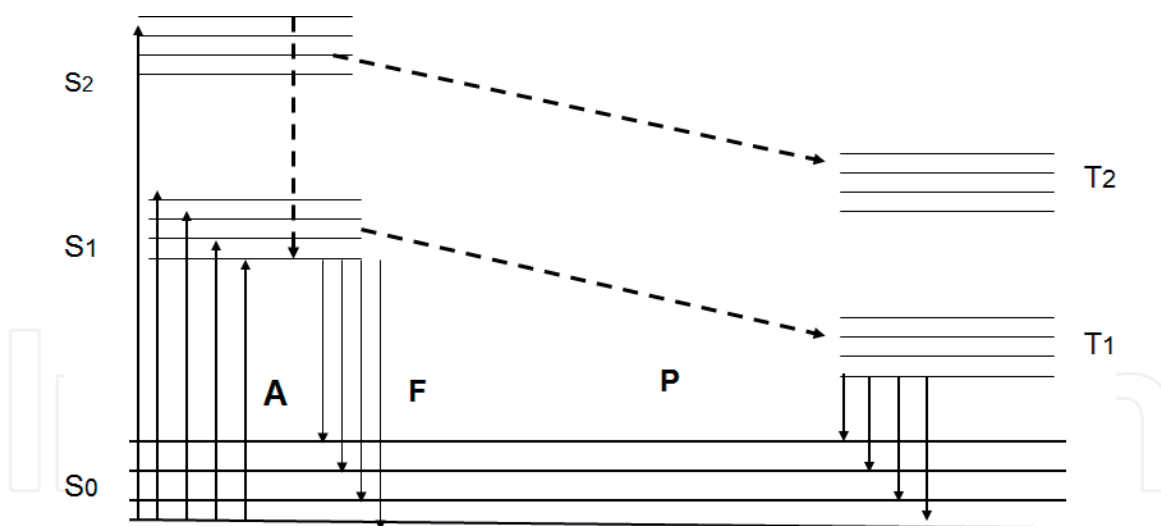
Figure 2.
The simplified Jablonski diagram.

wavelength excitation band and the shortest wavelength emission band is applied as Δλ, there is only one peak in the synchronous fluorescence spectrum [1, 25] The single peak is present at the same wavelength as the longest wavelength excitation band for a synchronous excitation spectrum or the shortest wavelength emission band for a synchronous emission spectrum [26]. The characteristic sets of λ_{exc} and λ_{em} of analyzed compounds could be known from references or obtained independently from measurements of the high purity standards. In this way, synchronous fluorescence spectra are much simpler and easier to analyze than conventional emission. Thus, synchronous fluorescence spectroscopy becomes an attractive alternative for the simultaneous determination of multiple compounds in complex samples. The analytical significance of SFS is confirmed by the fact that this technique is already relatively broadly utilized in investigations of samples of various origins [26–36].

3. Experimental

3.1 The origin and analysis of the investigation object

The analyzed airborne particulate matter derives from Mysłowice urban air (Upper Silesia industrial region, Poland; **Figure 1**). Located in an urban area, a "staplex" high volume sampler with glass fiber filter was applied as the equipment for collecting the airborne particulate matter. The collection of the sample was done in summer (non-heating season). The organic fraction was isolated from the investigated particulate matter by extraction with redistilled n-hexane for 3 hours, using a Soxhlet extractor. The choice of the solvent was substantiated by a mean to obtain nonpolar fraction because many of polar compounds fluoresce. To avoid the eventual fluorescence by traces of these compounds, the additive fractionation was made to reduce their content. For this purpose, Merck's TLC pre-coated plate was used, covered by silica gel layer (thickness of 0.2 mm). The mobile phase for thin layer chromatography process was n-hexane. This procedure enabled to obtain aromatic, aliphatic, and polar fractions. The aromatic fraction was recovered from silica gel by elution with n-hexane using the glass column. For the fluorescence analysis, the solutions of aromatic fraction were prepared with the concentrations in the range from 0.01 to 0.002 mg ml^{-1}.

The same aromatic fraction was also used for further analysis by GC-MS method.

3.2 The apparatus used and experimental conditions

Fluorescence spectra were determined at room temperature using a Jobin-Yvon (SPEX) FLUORLOG 3-12 spectrofluorimeter with a 450 W xenon lamp, a double-grating monochromator, and a Hamamatsu 928 photomultiplier. During measurements, scanning parameters were always put as 0.5 nm per 0.5 s, while the remaining parameters were for each type of measurements as follows: for synchronous measurements, excitation and emission slits have been set to 1 nm; for emission measurements, excitation slit was put to 3 nm, and emission slit – to 1 nm, while for excitation measurements, the slits settings were reversed. To verify the presence of a given PAH, the $\Delta\lambda$ parameter was chosen, according to the reference data [1, 23, 37] as well as to own earlier experimental results.

The comparative analysis of PAHs by gas chromatography-mass spectrometry (GC-MS) was performed using a HP 5890 II gas chromatograph equipped with a fused silica capillary column HP-5 (60 m length × 0.25 mm internal diameter). Helium was the carrier gas used. The GC oven was programmed from 35 to 300°C at a rate of 3°C/min. The gas chromatograph was coupled with a HP 5971A mass selective detector (MSD). The MS was operated with an ion source temperature of 200°C, an ionization energy of 70 eV, and a cycle time of 1 s in the mass range 40–600 Daltons.

4. Results

The results of the qualitative investigations performed are summarized in **Table 1**. Values λ_{ex}, λ_{em}, and $\Delta\lambda$ were collated there for individual PAHs after the experimental and literature data [1] (the limits of differences between the λ data are 1–3 nm). The presence of compounds identified by SFS technique has been confirmed by GC-MS method characterized here by the retention time. The results obtained indicate that both methods have own high research capability, but generally fluorescence analytical procedure seems to be simpler and analytical instrument cheaper in exploitation.

The results of qualitative analysis given in **Table 1** were obtained as a result of record of many synchronous spectra. Several of them are presented below.

4.1 SFS examples of application to the identification of individual aromatics in the analyzed PAH mixture

In **Figure 3**, the synchronous spectrum of analyzed PAH mixture is shown, recorded at the value of $\Delta\lambda$ = 23 nm. This value was proposed by Mille et al. [38, 39] for general characteristics of aromatics from fossil fuels, as an effective parameter to take a fair middle course between the sensitivity and resolving parameters. They used this value for estimation of PAH condensation degree range of investigated aromatic compounds in the mixture. **Figure 3** shows the distribution of emission bands of studied sample in which compounds with a number of rings from 2 to 6 can be identified, thanks to their representation by characteristic bands. The most apparent are substances with 3–5 rings. The bands in the spectrum under discussion identify the following polycyclic aromatic hydrocarbons and its alkyl, mostly methyl derivatives: acenaphthene, benzo(c)fluorene, naphthalenes

Identified compounds	Experimental data $\Delta\lambda$ [nm] $\lambda_{em}/\lambda_{ex}$ [nm/nm]		Reference data [1] $\Delta\lambda$ [nm] $\lambda_{em}/\lambda_{ex}$ [nm/nm]		GC/MS retention time [min]
2,3-Dimethyl-naphthalene	54	334/280	54	333/279	14.78
Phenanthrene	53	347/294	53	346/293	25.26
	71	365/294	71	364/293	
	105	357/252	102	356/254	
9-Methyl-phenanthrene	50	349/299	52	350/298	29.11
9,10-Dimethyl-phenanthrene	55	356/301	55	354/299	32.42
	71	355/284	69	354/285	
1-Methyl-7-isopropyl-phenanthrene	67	368/301	67	369/302	38.63
	98	358/260	100	360/260	
1-Methyl-anthracene	20	400/380	21	403/382	28.94
	37	384/347	38	383/345	
9-Methyl-anthracene	22	411/389	23	411/388	29.86
9,10-Dimethyl-anthracene	23	400/377	24	402/378	33.23
	23	424/401	24	424/400	
Fluoranthene	94	418/324	92	417/325	33.96
Benzo(b)fluorene	28	339/311	29	341/312	37.60
	46	356/310	45	357/312	
Pyrene	39	369/330	39	372/333	35.53
	46	378/332	46	379/333	
1-Methyl-pyrene	31	370/339	34	373/339	39.08
4-Methyl-pyrene	52	376/324	51	374/323	39.73
3-Methyl-pyrene	30	378/348	31	376/345	39.94
	50	377/327	48	376/328	
Benzo(c)-phenanthrene	94	376/282	93	374/281	43.37
2-Methyl-benzo-(c)-phenanthrene	66	398/332	66	399/333	43.70
	103	377/274	104	378/274	
Benz(a)-anthracene	23	384/361	23	384/361	44.88
1-Methyl-benz(a)-anthracene	47	389/342	47	389/342	48.45
2-Methyl-benz(a)-anthracene	20	385/365	19	387/368	47.91
7-Methyl-benz(a)-anthracene	17	392/375	18	392/374	48.19
8-Methyl-benz(a)-anthracene	21	387/366	21	388/367	48.77
12-Methyl-benz(a)-anthracene	35	391/356	37	393/356	47.15
1,12-Dimethyl-benz(a)-anthracene	41	404/363	41	402/361	49.35
7,12-Dimethyl-benz(a)-anthracene	53	399/346	52	399/347	51.44
Chrysene	39	362/323	39	361/322	45.16
Benzo(b)-fluoranthene	30	399/369	29	396/367	52.69
	66	430/364	63	430/367	
	94	398/304	95	396/301	

Identified compounds	Experimental data $\Delta\lambda$ [nm] $\lambda_{em}/\lambda_{ex}$ [nm/nm]		Reference data [1] $\Delta\lambda$ [nm] $\lambda_{em}/\lambda_{ex}$ [nm/nm]		GC/MS retention time [min]
Benzo(e)-pyrene	71	390/319	71	389/318	54.37
Benzo(a)-pyrene	34	400/366	33	403/370	54.69
	39	425/386	39	427/388	
Anthanthrene	25	433/408	24	434/410	61.02
	30	433/403	30	434/404	
Benzo(g,h,i)-perylene	50	420/370	50	420/370	62.85
3,4-9,10-Di-benzopyrene	34	433/399	34	432/398	69.21

The term "luminescence" is used sometimes interchangeably with "fluorescence," describing more widely the discussed phenomenon.

Table 1.
*Identification by synchronous fluorescence and GC/MS analyses of individual compounds occurring in investigated aromatic fraction of organic mixture desorbed from urban air dust collected in industrial area. Characteristic parameters of individual compounds present in studied aromatic fraction identified on the basis of luminescence * analysis ($\Delta\lambda$, $\lambda_{em}/\lambda_{exc}$) and GC-MS measurements (retention time).*
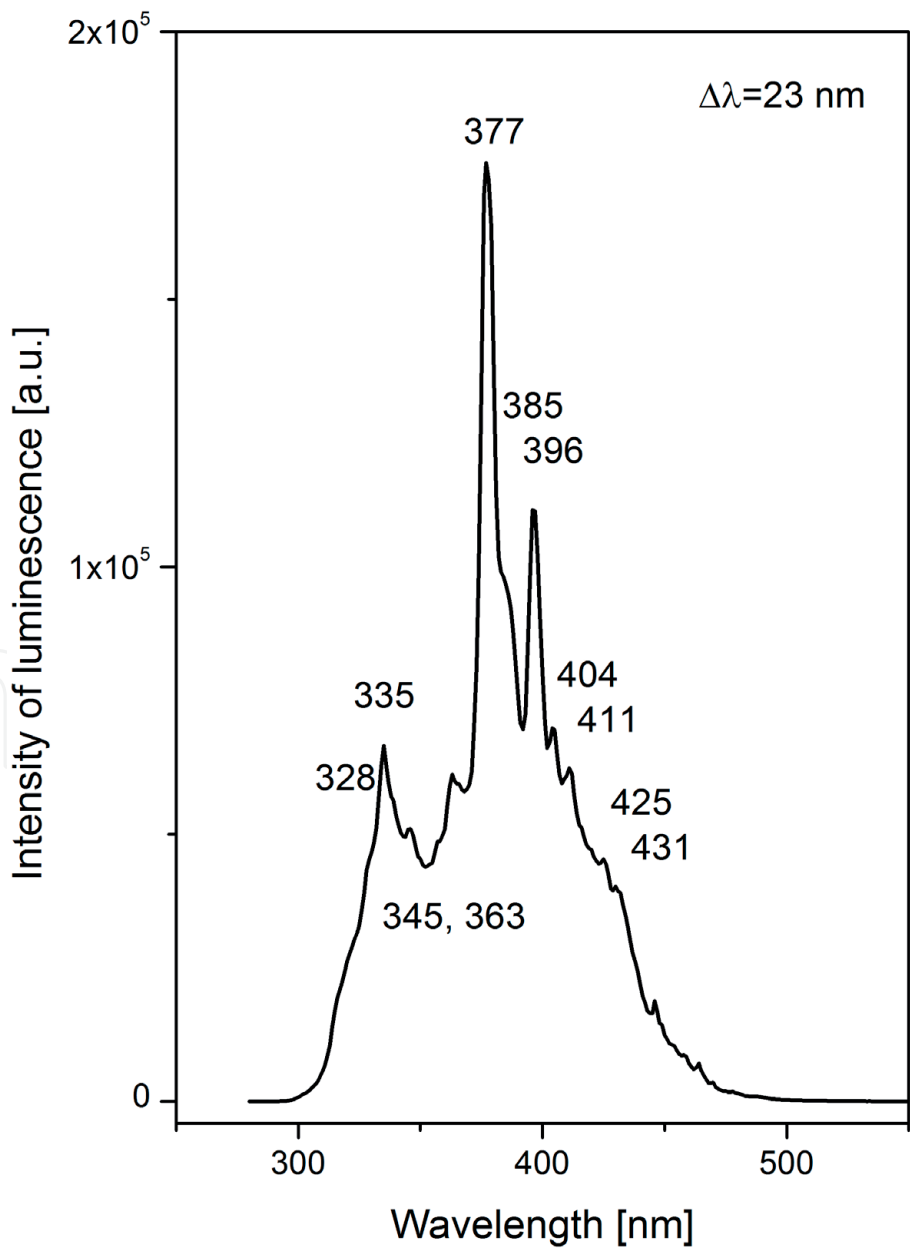

Figure 3.
Synchronous fluorescence spectrum of studied sample measured at $\Delta\lambda$ = 23 nm.

(328 and 335 nm), phenanthrene (345 nm), chrysenes (363 nm), pyrenes, anthracene (377 nm), benzo(a)anthracene (385, 411 nm), benzo(b)fluoranthene (396 and 425 nm), benzo(a)pyrene (404 nm), benzo(g,h,i)perylene (425 nm), and 3,4-9,10-dibenzopyrene (431 nm). In this way, the spectrum recorded at Δλ = 23 nm is a kind of overview spectrum for the composition of the analyzed mixture.

The use of Δλ value calculated for individual compound as it was explained earlier enables the record of a synchronous spectrum with intense band identifying analyzed compound. In **Figure 4,** the spectra are presented and recorded at Δλ = 30 nm, Δλ = 46 nm, and Δλ = 39 nm. Using Δλ = 30 nm, the presence of 3-methylpyrene and benzo(b)fluoranthene was proven on the basis of the most intense bands at 378 and 399 nm, respectively. Moreover, a distinct band of anthanthrene (433 nm) can be seen. In turn, on the spectrum recorded at Δλ = 46 nm, the presence of benzo(b)fluorene (356 nm) is evident, and other distinct bands at 378 and 399 nm correspond to pyrene and 3-methylpyrene, respectively. For chrysene identification, Δλ value equal to 39 nm was taken. In the spectrum obtained, a band at 362 nm characteristic for chrysene is very intense. The band of lower intensity at 369 nm can derive from pyrene. **Table 1** indicates parameter Δλ = 39 nm as characteristic also for benzo(a)pyrene, and in **Figure 3**, the band is seen at 425 nm
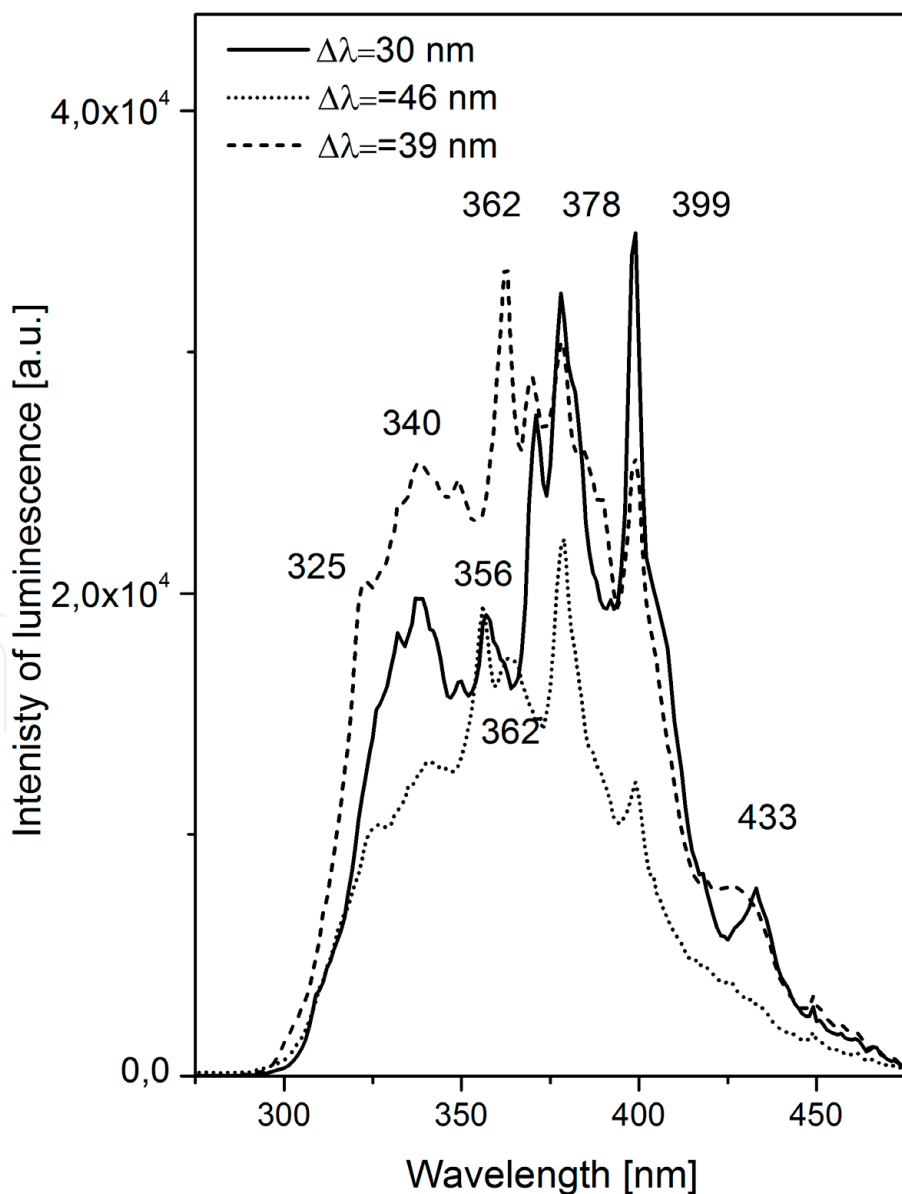

Figure 4.
Synchronous fluorescence spectra of studied sample measured at Δλ = 30 nm, Δλ = 39 nm, and Δλ = 46 nm.

deriving probably from benzo(a)pyrene. The low intensity of benzo(a)pyrene band is undoubtedly a result of low concentration of this compound (see also relatively weak benzo(a)pyrene peak on the GC-MS chromatogram presented below; **Figure 8**). However, in a complex mixture the partial quenching of the fluorescence of individual components is possible by some of other components of the mixture. This process, however, is not yet fully investigated.

Subsequent spectra in **Figure 5** show the presence of phenanthrene, thanks to the characteristic emission bands at 347 nm (at $\Delta\lambda$ = 53 nm) and 357 nm (at $\Delta\lambda$ = 105 nm). Other bands at 376 nm and 399 nm are attributed to 4-methylpyrene and 7,12-dimethylbenzo(a)anthracene.

Figure 6 is an example of verification of the results obtained by synchronous technique, using other spectral fractionation realized by conventional technique of fluorescence. For example, an emission spectrum of chrysene has been recorded at an excitation wavelength of 324 nm (close to the literature value of 322 nm; **Table 1**). Three bands at 361, 370, and 379 nm appeared distinctively complying with the literature data for chrysene: 361, 373, and 381 nm (**Table 1**). The emission spectrum of chrysene is, however, overlapped partly with group of bands at
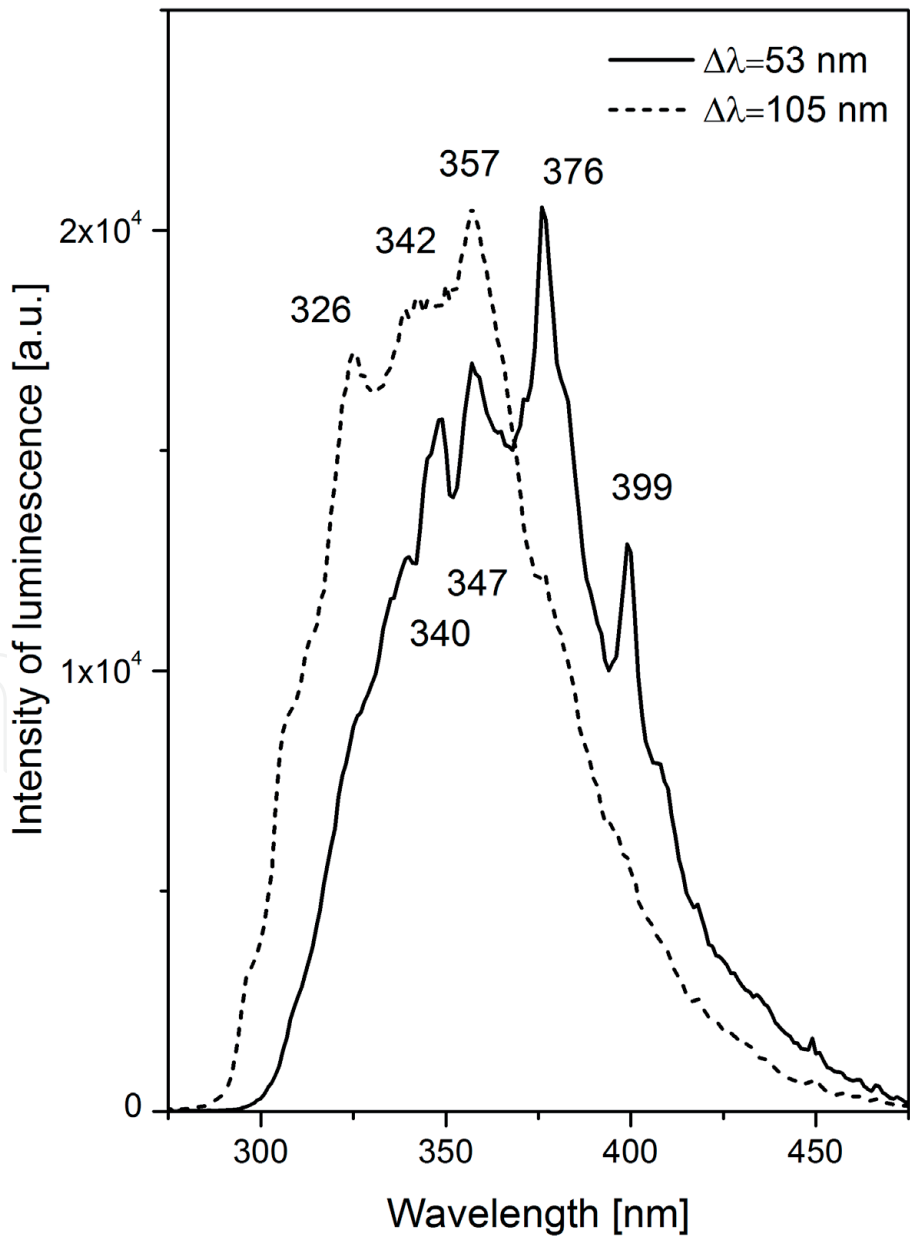

Figure 5.
Synchronous fluorescence spectra of studied sample measured at $\Delta\lambda$ = 53 nm and $\Delta\lambda$ = 105 nm.
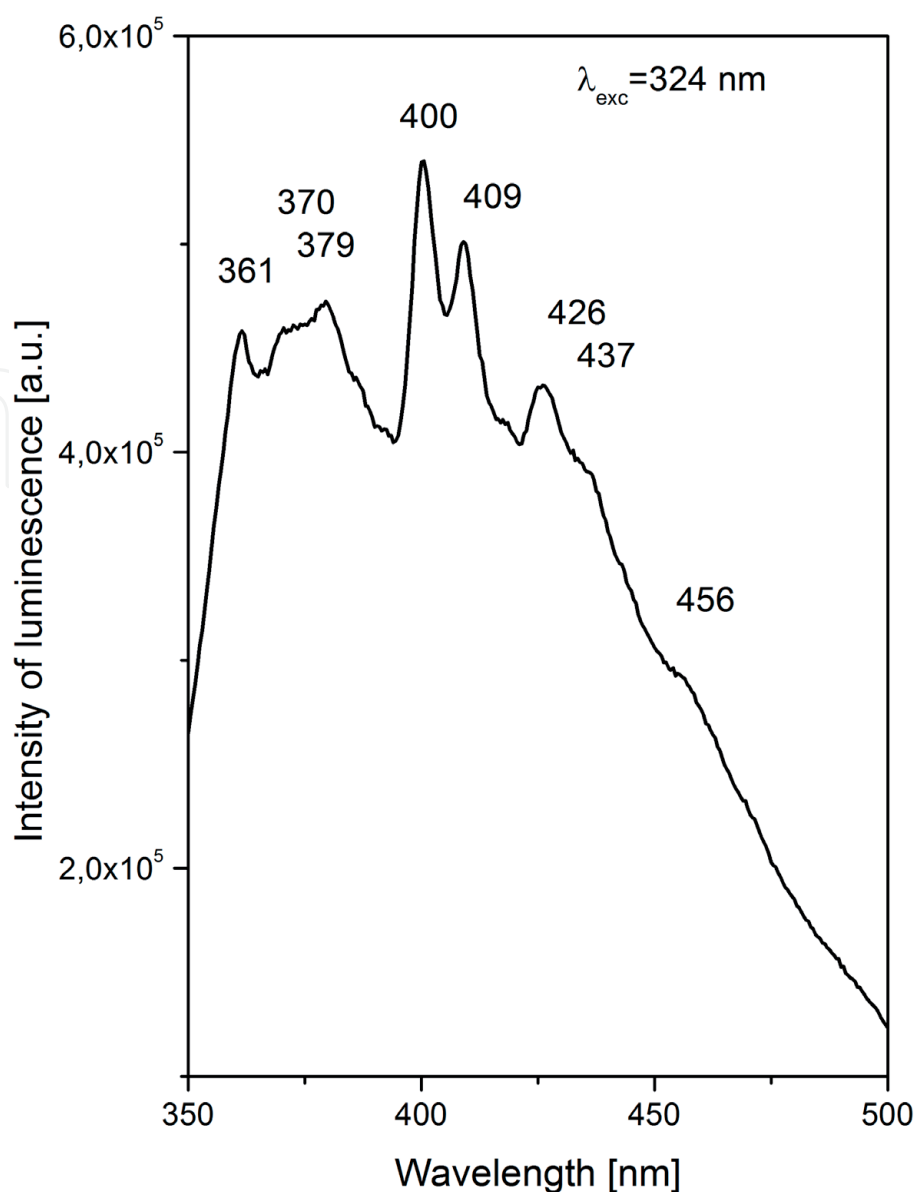
Figure 6.
Fluorescence emission spectrum of studied sample measured at λ_{exc} = 324 nm.

wavelengths: 400, 409, 426, 437, and 456 nm. The origin of these bands seems to have a complex nature. Analysis of the literature data indicates that there are probably several groups of compounds in investigated mixture characterized by similar energy levels corresponding with these emission wavelengths.

Several homologous compounds from the group of anthracene, benzo(a) anthracene, and benzo(a)pyrene can contribute to the mentioned bands. A series of tests with the record of various emission and excitation spectra using conventional techniques and also synchronous one indicated possible contribution to the bands under discussion of 9,10-dimethylanthracene (402, 407, 424, 428, and 453 nm), 1,12-dimethylbenzo(a)anthracene (402, 427, and 455 nm), and benzo(a)pyrene (403, 408, 427, and 431 nm) [1]. However, according to various premises, the benzo(a)pyrene can be the main component of the mentioned group of bands.

To validate this hypothesis, the emission spectrum of benzo(a)pyrene was recorded, using its characteristic λ_{ex} = 350 nm. **Figure 7** obtained in this manner presents emission bands (402, 409, and 426 nm) of benzo(a)pyrene, confirming contribution of this ingredient to intensity of bands under investigation. An inverse spectral process was also carried out: the spectra recorded at the positions of emission monochromator of λ_{em} = 402 nm and λ_{em} = 427 nm allowed to get characteristic
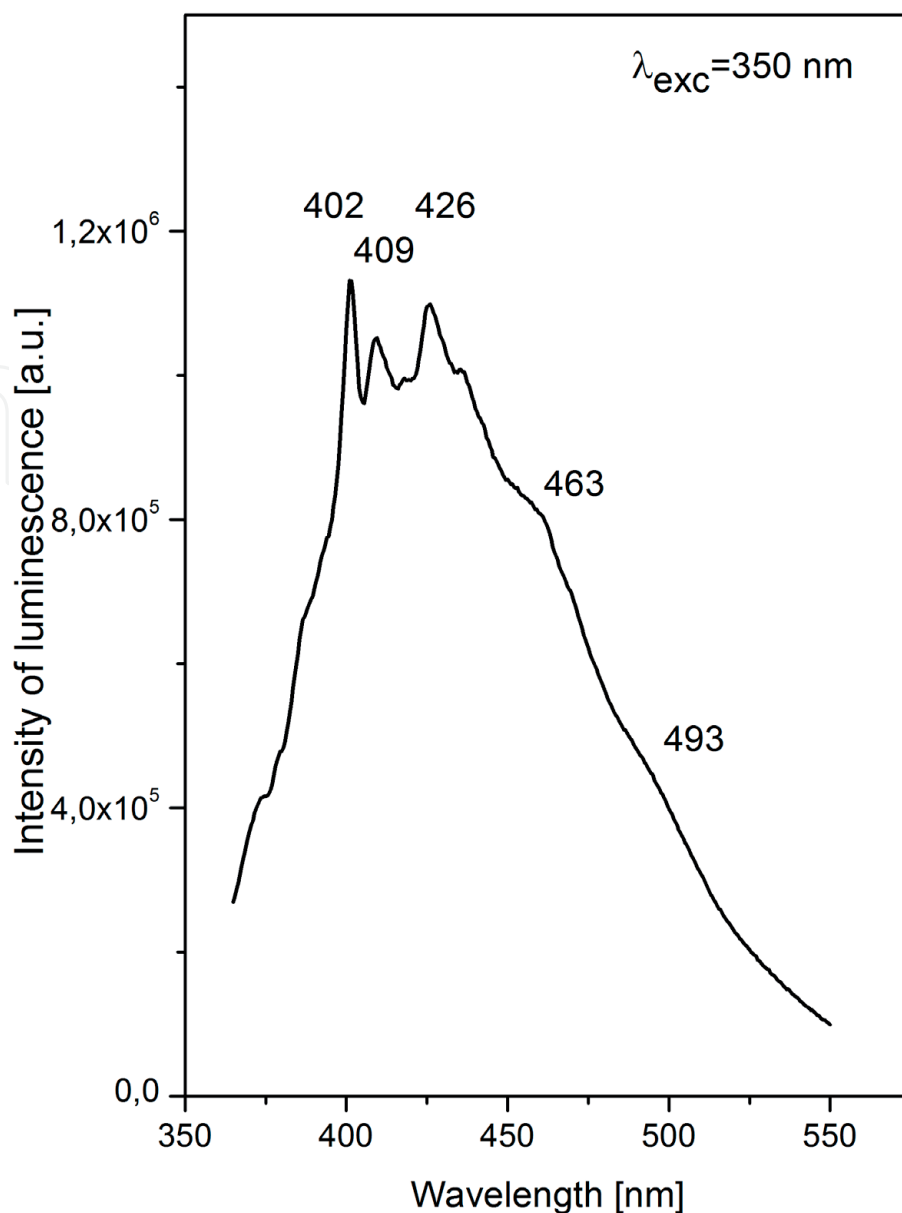
Figure 7.
Fluorescence emission spectrum of studied sample measured at λ_{exc} = 350 nm.

clearly visible excitation bands with maxima at 349 and 372 nm, close to the literature data for λ_{ex} of benzo(a)pyrene at 350 and 370 nm [1]. It is important to mention that in the emission spectrum obtained at λ_{ex} = 350 nm (**Figure 7**), there are also two weak bands at 463 and 493 nm deriving probably from indeno (1,2,3-cd)pyrene.

The high condensed aromatics as coronene were not identified by SFS technique. Lin et al. [26] also found difficulties with the use of SFS to analyze PAHs containing more than six rings. The authors emphasize at the same time that SFS technique is the most sensitive in detecting three- or four-ring PAHs. For the coronene mentioned (seven condensed rings), not identified by SFS, the additional analysis has been performed, and its strong emission band at 446 nm was obtained in the emission spectrum recorded using λ_{ex} = 300 nm.

4.2 Comparative GC-MS analysis

In **Figure 8**, total ion chromatogram (TIC, GC/MS) is presented of aromatic fraction of the extract from analyzed airborne particulate matter. The following PAHs were identified, and their characteristic peaks indicated there by consecutive numbers from 1/ to 20/:
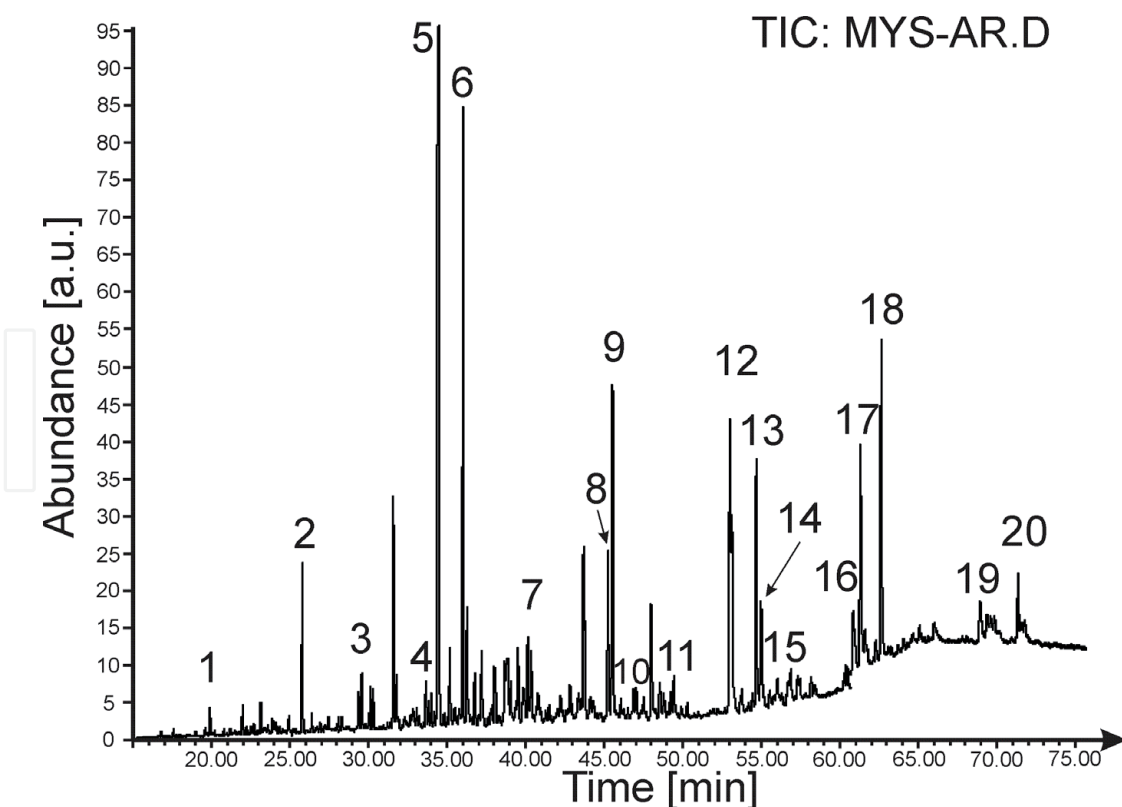
Figure 8.
Total ion-chromatogram (TIC, GC/MS) of aromatic fraction of the extract from analyzed airborne particulate matter.

1/ alkylnaphthalenes, 2/ phenanthrene, 3/ methylphenanthrenes + methylan-thracenes, 4/ dimethylphenanthrenes + dimethylanthracenes, 5/fluoranthene, 6/ pyrene, 7/ benzofluorenes + methylpyrenes + benzo(c)phenanthrenes, 8/ benzo(a) anthracene, 9/ chrysene + triphenylene, 10/ alkylbenz(a)anthracenes, 11/alkyl-chrysenes, 12/benzofluoranthenes, 13/ benzo(e)pyrene, 14/ benzo(a)pyrene, 15/ perylene, 16/ anthanthrene, 17/ indeno(1,2,3-c,d)pyrene, 18/ benzo(ghi)perylene, 19/3,4-9,10-dibenzopyrene, and 20/ coronene. Many compounds from this group seem to be typical for pollution of atmosphere of the investigated industrial region in Poland (e.g., [40]) and at the same time are basic for environmental monitoring in the European Union and the USA (e.g., [41], *loc.cit.*).

The PAHs alkylated are described here as groups of compounds, not all homo-logs being identified. In **Table 1**, the several alkyl substituted PAHs are presented, among other hydrocarbons, and identified by GC-MS and SFS methods.

5. Discussion of the results

SFS technique made possible the identification of a series of PAHs polluting urban air in the industrial region in Poland. Comparative analysis by GC-MS method has confirmed these results. Qualitative analysis of PAH mixtures by SFS is rather a fast technique and does not need many preparation steps and chemicals. However, for a complex mixture as the analyzed extract from the filter of air dust, the separation into fractions has been done (see subsection 3.1) to reduce the possibilities of mutual quenching of fluorescence by particular components of the mixture. Simplicity of SFS analysis can be shown, e.g., by the possibility of initial estimation of the condensation range of PAHs in analyzed mixture by the use of $\Delta\lambda = 23$ nm parameter as it was described earlier. However, the most important is

here the possibility of receiving the SFS spectra of particular identified PAHs, with one or several well resolved bands, characteristic for analyzed compounds. For recording these spectra, the specific values of Δλ parameters are used after calculation on the basis known spectral characteristics of identified compounds.

The possibility of the use of other analytical techniques of fluorescence method (as the record of emission or extinction conventional spectrum) can broaden the group of identified compounds as, e.g., in the case of coronene with seven condensed rings, not identified by SFS but indicated by emission spectrum as mentioned above.

Thus, the fluorescence techniques, especially SFS, can play a significant role in urban air monitoring for the identification of PAHs. The main order is the environmental impact assessment by the indication of the presence PAHs harmful to health due to toxic, carcinogenic, or mutagenic properties. The total number of PAHs in environment is estimated on about 200, and in exhaust gases, for example, of diesel motors – on over 100 [41]. It is not possible to analyze all of them during everyone monitoring process. It is because only some representative compounds are usually chosen to analyze. For example, Environmental Protection Agency of USA has selected the 16 PAHs for a basic environmental monitoring program [US EPA, Polycyclic Aromatic Hydrocarbons (PAHs)-EPA fact sheet, Washington (DC)-National Center for Environmental Assessment, Office of Research and Development; e.g., [31, 41, 42] *loc. cit.*].

These 16 PAHs are included in the US list of priority pollutants and are usually analyzed: naphthalene, acenaphthene, acenaphthylene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[b] fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, dibenzo[a,h]anthracene, and benzo[ghi]perylene. The influence of these PAHs on the human health has been there also noted. The majority of compounds from this list were identified in the samples of environmental PAHs reported by various authors [1, 12–14, 40, 43]. Their widespread occurrence in the environment causes that most of them are chosen also in European monitoring programs (including Polish programs), e.g., CONCAWE-The Oil Companies European Organization for Environment, Health, and Safety or ARC-International Agency for Research on Cancer (e.g., [41, 44] *loc. cit.*). These compounds characterize very high toxicity.

Almost all of compounds from EPA list are identified among PAHs analyzed here. Taking into account relative intensities of pollutant peaks seen clearly in the ion-chromatogram realized for this work (**Figure 8**), one can stated that the most intense peaks can be attributed to fluoranthene and pyrene, not carcinogenic after EPA. The highest carcinogenicity is attributed, in turn, to benzo(a)pyrene and dibenzo(ah)anthracene, relatively lower to benzo(b)fluoranthene and the lowest to chrysene (potentially carcinogenic) and also to benzo(a)anthracene and indeno(1,2,3-cd)pyrene. Other compounds from the EPA list are not noted as carcinogenic. Main representative of carcinogens – benzo(a)pyrene does not dominate in analyzed group of PAHs, what may be related to summer season of sampling [1], but its content in air of the Silesian industrial region is still relatively high [44].

The general similarity of own results with these ones from the world literature data can suggest that major of identified PAHs may be universal products of high chemical stability, deriving from incomplete burning of various organic fuels. It may be also possible that these compounds derive mainly from the incomplete burning of oil fuels as the result of so-called low emission from vehicle exhaust because of widespread development of automotive transport. In the case of our own results, it could be confirmed by PAH distribution of the summer season when low emission pollutions are dominated by the exhaust gases from car engines as it is suggested below.

Considerable air pollution in the investigated urban atmosphere results in undoubtedly high pollution of whole region of Silesia. This is due to the high degree of industrialism, where an emission of diverse pollutants from many sources can be expected. In the region mentioned, the certain branches of industry, such as mining, metallurgy, nonferrous metals, and coke-making industries were developed excessively. There are also electric power stations and heat generating plants. High intensification of motor transport increases additively level of pollution in this region [13, 14].

The sources of air pollution in the Mysłowice urban area create a specific character of this air compared to that in the whole industrial region. The investigated air dust was sampled in summer. In this season, industrial production using organic fuels is underway, but the low emission from home stoves is minimalized. The main sources of low emission, however, seem to be in summer the engine fumes especially these from diesel motors (despite various actions to improve them). After the literature data [43], in summer season, one can expect in Silesia the relative increasing of concentration of pollutions originating from automobile exhaust as, e.g., pyrene, chrysene, triphenylene, benzo(g,h,i)perylene, benzo(c) phenanthrene, benzo(k)fluoranthene, and indeno(1,2,3-cd)pyrene. All of these compounds have been identified in analyzed PAH mixture, and they show clear dominance over other compounds (**Figure 8**). The domination of the engine exhaust in analyzed air pollution might be caused by the intense automobile traffic on the city area. There are three great car transit lines through the city: a highway autostrada passing by the city, expressway, and national road crossing the city center (the beltway around the city is only enabled in spatial planning).

The particular identified pollutants or their groups can thus help to indicate the pollution sources and to look for ways to improve the quality of environment.

6. Conclusions

The use of synchronous fluorescence spectroscopy (SFS technique) is advantageous for qualitative monitoring of the PAHs mixtures from urban air of the industrial region because this technique is simple, fast, low time consuming, and of low costs. Simpler and better separated spectra may be obtained in this manner than in the case of conventional fluorescence analysis. The special advantage of SFS technique is the possibility of analysis of complex environmental PAHs mixtures without the need of multistage sample fractionation. In this case, the "separation" of the complex mixtures is performed spectroscopically, which may be called the "spectral fractionation technique" [1].

Technique SFS used for samples in a form of solution, applied at the ambient temperature, allows obtaining well-separated spectra, simplified to one or several bands, allowed identification of individual compounds. This analytical process is possible, thanks to the use of the parameter $\Delta\lambda$ characteristic for the particular identified compound. In this manner, the presence was stated in analyzed urban air dust of the PAHs with 2–6 condensed rings. However, the most clearly marked were aromatics from groups of anthracenes, benzo(a)anthracenes, pyrenes, and benzo(a)pyrenes. These compounds are among these PAHs, which characterize high fluorescence yield. The compounds from the group of naphthalene, benzofluorene, phenanthrene, benzophenanthrene, chrysene, fluoranthene, benzofluoranthene, and anthanthrene were also identified. The verification was performed for specific compounds, by recording of respective conventional emission or excitation spectra.

The results obtained may be a basis to discussion on the evaluation of the environmental hazards.

The harmful influence of identified PAHs is a reason why they should be of a special interest in investigations of environmental samples. Thus, the choice of the effective analytical methods and techniques is here very important. The synchronous fluorescence technique seems to be appropriate method for monitoring PAHs in air dust samples of the industrial regions, especially when combustion of organic fossils still remains the main source of energy.

Abbreviations

SFS	synchronous fluorescence spectroscopy
PAHs	polycyclic aromatic hydrocarbons
TIC	total ion-chromatogram
TLC	thin layer chromatography
GC/MS	gas chromatography-mass spectrometry
HPLC	high performed liquid chromatography
MSD	mass selective detector
EPA	Environmental Protection Agency

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