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SYNCHRONOUS LUMINESCENCE TECHNIQUE IN INVESTIGATIONS OF AROMATIC FRACTION OBTAINED FROM EXTRACT OF URBAN SUSPENDED AIR DUST FROM INDUSTRIAL REGION

Summary. The qualitative fluorescence analysis was performed of aromatic fraction obtained from extract of air dust from Upper Silesia region. The synchronous luminescence technique was used for the investigations. This technique enables a direct identification of individual mixture components thanks to special conditions of measurements and on the basis of spectral characteristic of respective standards. In this manner a series of hydrocarbons was identified, mainly from groups of : naphthalenes, phenanthrenes, anthracenes, benzophenanthrenes, benz(a)anthracenes, chrysenes, pyrenes and benz(a)pyrenes.

TECHNIKA SYNCHRONICZNEJ LUMINESCENCJI W BADANIACH SKŁADU FRAKCJI AROMATYCZNEJ WYODRĘBNIONEJ Z EKSTRAKTU MIEJSKICH PYŁÓW ZAWIESZONYCH W POWIETRZU Z REGIONU UPRZEMYSŁOWIONEGO

Streszczenie. Wykonano jakościową analizę fluorescencyjną frakcji aromatycznej uzyskanej z ekstraktu pyłu z powietrza z regionu Górnego Śląska. W analizie wykorzystano technikę synchronicznej luminescencji, która umożliwia bezpośrednią identyfikację składników mieszaniny dzięki specjalnym warunkom pomiaru oraz na podstawie charakterystyki spektralnej odpowiednich wzorców.

Zidentyfikowano w ten sposób szereg węglowodorów głównie z grupy naftalenów, fenantrenów, antracenów, benzofenantrenów, benzo(a)antracenów, chryzenów, pirenów i benzo(a)pirenów.

Introduction

Carcinogenic and mutagenic properties of many aromatic compounds are a cause for investigations of environmental samples also in consideration of polycyclic aromatic compounds (PAHs). The aromatic compounds existing in environment can originate from natural sources. It was stated that PAHs form a part of metabolism products of bacteria, algae and higher plants [1,2]. Amounts of PAHs of natural origin is however insignificant and moreover, these compounds undergo natural degradation. There is a higher saturation of environment by aromatic compounds of anthropogenic origin. Also these compounds are subjected to natural degradation e.g. by action of oxygen or ultraviolet radiation [3,4] but a large contents of pollutants discriminates the self-defensive power of environment. The main source of anthropogenic PAHs is imperfect combustion of fuels in industry, transport and domestic processes. All of these emitters are especially active in industrial agglomerations, like Upper Silesia. It is a cause of large monitoring in this region. The stations of WSSE in Katowice collect among others the air dust, analysing there also PAHs as e.g. phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(a)fluoranthene, dibenz(a,h)anthracene, benz(a)pyrene, benz(e)pyrene, perylene, benz(ghi)perylene. In analysis described here the attention was paid therefore to identification of a series of these compounds in aromatic fraction of the extract of urban air dust from Upper Silesia region. During analysis in ambient conditions a technique of synchronous luminescence was used consisting in record of spectra at constant difference of position of excitation and emission monochromators ($\Delta\lambda$). The choice of effective value of $\Delta\lambda$ parameter specific for individual compound enables his identification directly in the mixture [3, 5-9]. This identification may be verified by the use of record of emission or excitation spectrum at fixed characteristic wavelength of excitation or emission respectively, specific for analysed compound. It is because the techniques mentioned was called the spectral fractionation techniques [3].

Experimental

The filter with air dust sample obtained from WSSE in Katowice (suspended dust collected in staplex type apparatus in Mysłowice) was subjected to extraction by redistilled n-hexane in Soxhlet apparatus by the period of 3 hours. Despite of non-polar character n-hexane eluates also some weakly polar compounds. The additive fractionation was made to reduction of amounts of polar compounds contents. For this purpose Merck's tlc plate was used covered by silicagel. The mobile phase was n-hexane. The fractionation has given aliphatic, aromatic and polar compounds. Aromatic fraction was recovered by elution from silikagel by n-heksane in a glass column. For the fluorescence analysis the solutions in n-hexane were prepared with concentrations of : 0.07mg/ml and 0.01mg/ml.

The spectrofluorimeter used was Fluorolog 3-12 Spex, Jobin Yvon, with xenone, ozone free lamp (45W). The analysis was performed in the ambient temperature.

Discussion of results

The investigated sample was first analysed by synchronous luminescence technique using value of parameter $\Delta\lambda=23\text{nm}$. After literature data [6] this value of $\Delta\lambda$ was here used to general estimation of range of condensation degree. The synchronous luminescence spectrum recorded (Fig.1) presents a series of peaks from 328nm to 434nm what enables to estimate that in the sample aromatics exist with 2 to 6 condensed rings. Despite of general , demonstrative character of this spectrum an attempt was made to identificate preliminarily of particular compounds or their homologs , after literature data [3,6] : naphthalenes (328,335nm), phenanthrene (345nm), chrysenes (363nm), anthracene (377), benz(a)anthracene (385nm), The band at 396nm can be attributed here probably to the presence of pyrene-3,10-quinone. The existence of quinones among air pollutants was attributed among others to progressive degradation of aromatic compounds under the influence of oxygene and ultraviolet radiation [3,4]. Other peaks may indicate the contribution of 9,10-disubstituted anthracenes (404nm), dimethylbenz(a)pyrenes (411), benzo(b)fluoranthene (425nm) and anthanthrene (432nm). For confirmation of this introductory interpretation and for development of identification a series of measurements was performed at various values of $\Delta\lambda$ parameter , characteristic for diffe-

rent compounds. Fig.2 presents a synchronous luminescence spectrum of analysed sample recorded at $\Delta\lambda=20\text{nm}$. The band at 381nm predominating here, after definition of $\Delta\lambda$ parameter, should represent a compound characterized by effective emission wavelength $\lambda_{\text{em}}=381\text{nm}$ and effective excitation wavelength $\lambda_{\text{ex}}=361\text{nm}$. These data compared with literature data for standards [3] indicate: 1-methylanthracene with effective wavelengths: $\lambda_{\text{em}}=383\text{nm}/\lambda_{\text{ex}}=361\text{nm}$. The emission band at 387nm in this spectrum (Fig.2) was attributed to 5-methylbenz(a)anthracene (after literature data [3]: $\lambda_{\text{em}}=388\text{nm}$, $\lambda_{\text{ex}}=367\text{nm}$). The next intensive band in this spectrum may be attributed to pyrene-3,10-quinone, mentioned earlier (experimental data: $\lambda_{\text{em}}/\lambda_{\text{ex}}$: 397/377, after [3]: 398/377). (The differences of results obtained and literature data are in error limits, estimated as 1-3nm). The presence of pyrene-3,10-quinone was confirmed also by the band at 397nm in the spectrum recorded at $\Delta\lambda=26\text{nm}$ (397/371; [3]: 398/370) (Fig.3).

Fig.4 shows a spectrum recorded at $\Delta\lambda=71\text{nm}$ – parameter characteristic for phenanthrene. The intense band at 356nm attest rather a predomination of phenanthrene homologs. The experimental data (356/285) indicate 9,10-dimethylphenanthrene (354/285, [3]). The band of unsubstituted phenanthrene is here marked weakly (364/293). In the spectrum recorded at $\Delta\lambda=33\text{nm}$ (Fig.5) besides the bands attributed to chrysenes (367nm) [3] and dibenz(a,c)anthracene 374/340 (374/341 [3]), the intense band exist at 395nm. The spectral characteristic of this band (395/362) is nearest to the literature data for 6-methylbenz(a)anthracene (393/362 [3]). It is also worthy of statement the presence of the band at 402nm (402/369) indicating benz(a)pyrene (403/370 [3]).

In the composition of analysed sample the presence was also stated of of 1',9-dimethylbenz(a)anthracene (401/362; 402/361 [3]) (Fig.6). The spectral data for this compound indicate two intense emission bands: at 402 and 427nm (and weaker at 455nm). These data are similar to those for benz(a)pyrene: intense band at 403nm, weaker band at 427nm (and bands of lower intensity at: 408nm and 431nm) and for 9,10-dimethylanthracene: 402nm, 428nm (weaker bands at: 407nm, 424nm, 453nm). Two stronger emission bands (about 402 and 427nm) for mentioned compounds (all of them are characteristic moreover by high fluorescence yield) give probably very intense background in all emission spectra for this sample. This analytical problem of identification of compounds with similar emission spectra is however solvable. It is possible e.g. to record the synchronous spectra at various $\Delta\lambda$ values or to record the emission or excitation spectra at respective λ_{ex} or λ_{em} values. Fig. 7 shows e.g. the well overlapping emission spectrum of benz(a)pyrene with the similar one of analysed sample

at $\lambda_{ex}=350\text{nm}$ characteristic for benz(a)pyrene. The additive band in the sample spectrum at 436nm may be attributed to 3',10-dimethylbenz(a)pyrene on the basis of the emission spectra of the sample performed at $\lambda_{ex}=388\text{nm}$ (Fig.8). The spectral characteristic obtained ($411,418,426,435,441\text{nm}$) is similar to standard one ([3]: $\lambda_{ex}=389\text{nm}$, $\lambda_{em}:412,418,436,441\text{nm}$) without 426nm band derived from earlier mentioned compounds. The band at 458nm in Fig.7 may be attributed to anthanthrene (458nm [3], 456nm [10]). The presence in analysed sample the earlier mentioned benz(a)fluorantene can be confirmed with high probability by existence of band at 424nm in the synchronous spectra recorded at $\Delta\lambda=73\text{nm}$ ($424/350$ [3]).

The excitation spectrum shown in Fig.9 ($\lambda_{ex}=426\text{nm}$) enabled to identify 9,10-dimethylantracene discussed earlier ($\lambda_{em}: 325,343,360,380,401\text{nm}$; [3]: $325,342,359,378,400\text{nm}$; [10]: $325,342,359,377, 398\text{nm}$). The presence of 1',9-dimethylbenz(a)anthracene was confirmed in turn by his emission spectrum at $\lambda_{ex}=298\text{nm}$ (Fig.10) showing characteristic, distinctive for this compound predomination of the bands at 401 and 426nm , in relation to other bands in this range.

In the analysed sample the other else, very characteristic compounds appear: pyrene and his homologs. In Fig.11 the synchronous spectrum is drawn at $\Delta\lambda=51\text{nm}$. The maximum at 374nm is an emission wavelength of pyrene ($374/322$ [3]). The confirmation was made with the use of emission spectra (Fig.12) recorded at $\lambda_{ex}=337\text{nm}$ effective for pyrene [3]. The experimental data of $\lambda_{em}: 371, 377, 382, 386, 392$ are in well accordance (in limits of error) with these from literature data: $372, 379, 384, 389,393\text{nm}$ [3] or: $377, 383, 393\text{nm}$ [10]. Other very intensive bands in Fig. 12 originate from the group of compounds mentioned above, with high fluorescence yield .

Among pyrene homologs the presence of 3-methylpyrene is distinctively marked, e.g. by emission band at 376nm in the synchronous spectrum (Fig.13) recorded at $\Delta\lambda=48\text{nm}$ ($376/328$ [3]).

Conclusions

Fluorescence spectroscopy taking advantage of the fluorescence properties of aromatic compounds gives moreover a possibility of identification of particular components of mixture without previous separation. It is because some of techniques of this method are called

"spectral separation techniques". Among these techniques the synchronous luminescence is especially worthy of use to environmental samples. The spectra obtained are highly resolved and make possible to identify particular components of mixture with the use of respective value of $\Delta\lambda$ parameter. The emission or excitation spectra recorded for solutions at ambient temperature are of worse quality because of their low resolution but may be used additively as a manner of confirmation of synchronous technique results. The techniques mentioned have enabled here identification in industrial urban dust of series aromatic compounds and their homologs mainly from following groups: naphthalenes, phenanthrenes, anthracenes, benzophenanthrenes, benz(a)anthracenes, chrysenes, pyrenes and benz(a)pyrenes.

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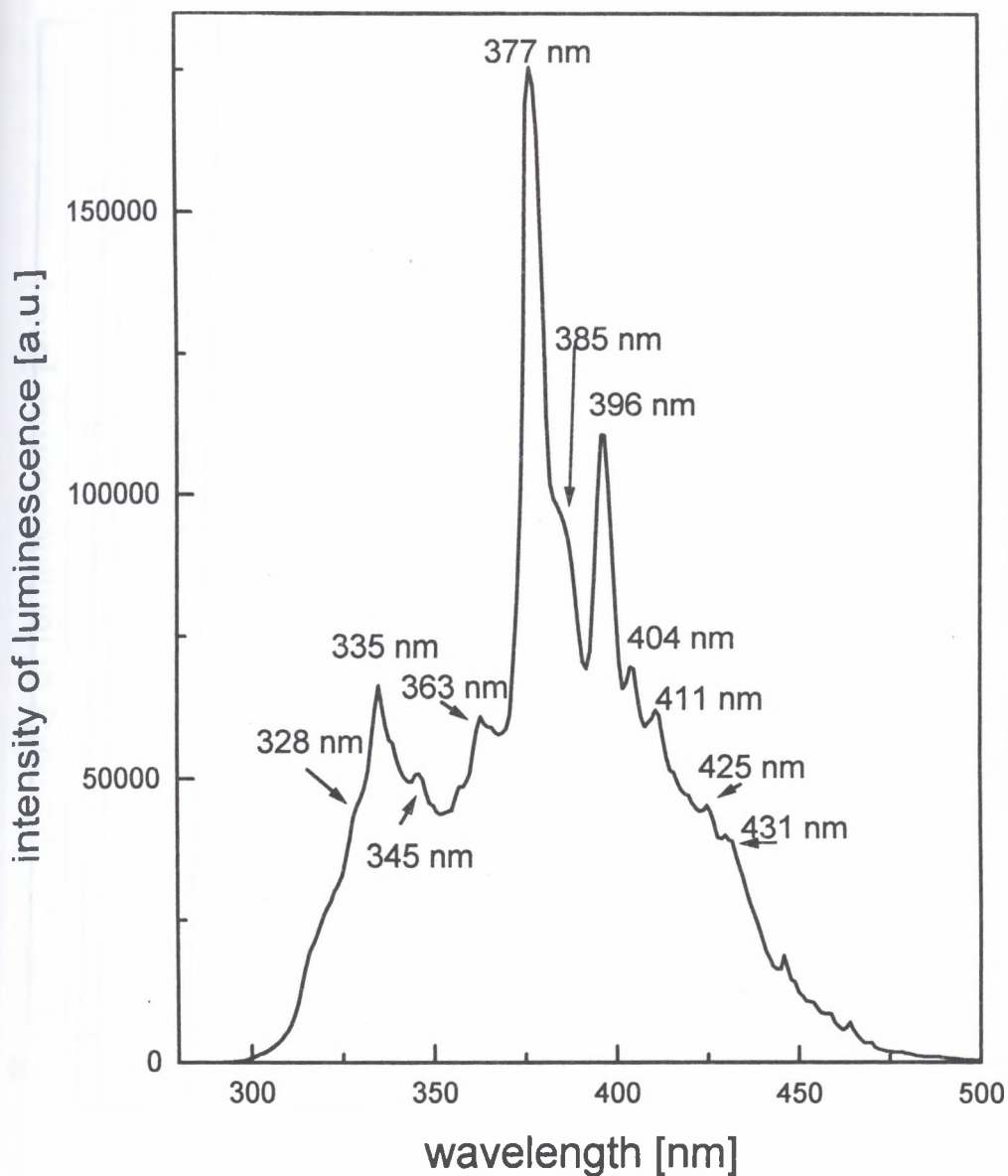
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Abstract

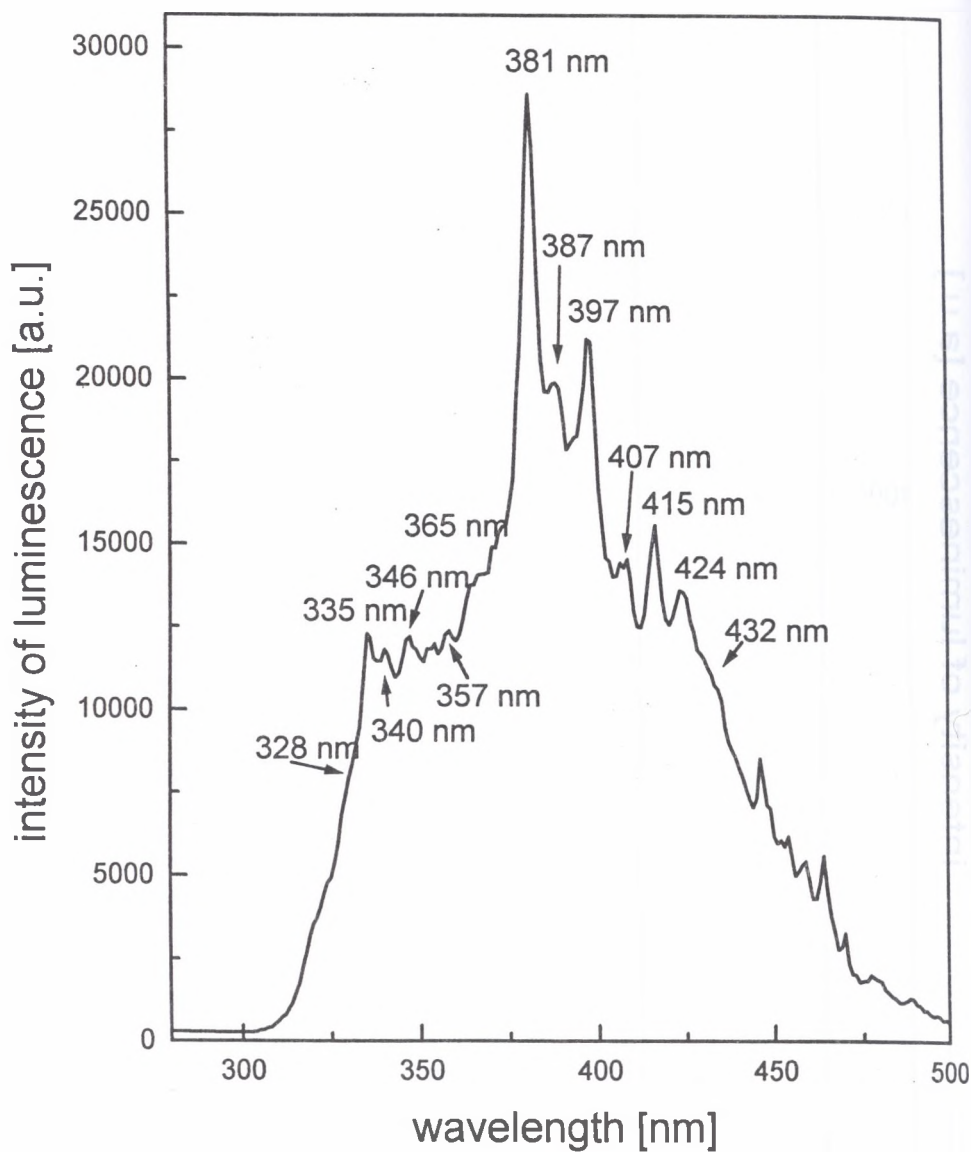
The synchronous luminescence technique was here used to analysis of individual or group components of aromatic fraction of extraction products of suspended dust from urban air from industrial region (Upper Silesia). The emission spectra obtained by this technique are simpler and better resolved than those obtained by conventional emission or excitation techniques. The sunchronous luminescence spectroscopy consists in the use of record of spectra at parameter $\Delta\lambda$ values characteristic for particular analysed compounds. This parameter has been defined as the difference between the position of emission and excitation monochromators during measurements. The value of $\Delta\lambda$ is calculated for analysed compound as a difference between his the most effective excitation and emission wavelength on the basis of the data estimated earlier for respective standard. In this work the literature data were used [3,10] to identification of compounds and comparisons with experimental results. The identification of compounds made here with the use of synchronous technique in analysed sample was verified by emission or excitation technique. It was realised by the record of spectra of investigated sample at excitation or emission wavelengths, respectively, characteristic for identified components of mixture. Thanks to the possibility of identification of individual components of the mixture without their separation the techniques mentioned have been called the techniques of spectral fractionation [3].

In this work the synchronous luminescence technique has been used to analysis of aromatic fraction of organic air pollutions adsorbed on the urban dust in industrial region. The compounds identified in this manner belong mainly to the following groups of condensed aromatics: naphthalenes, phenanthrenes, anthracenes, benzophenanthrenes, chrysenes, pyrenes, benz(a)anthracenes, dibenzoanthracenes and benz(a)pyrenes.



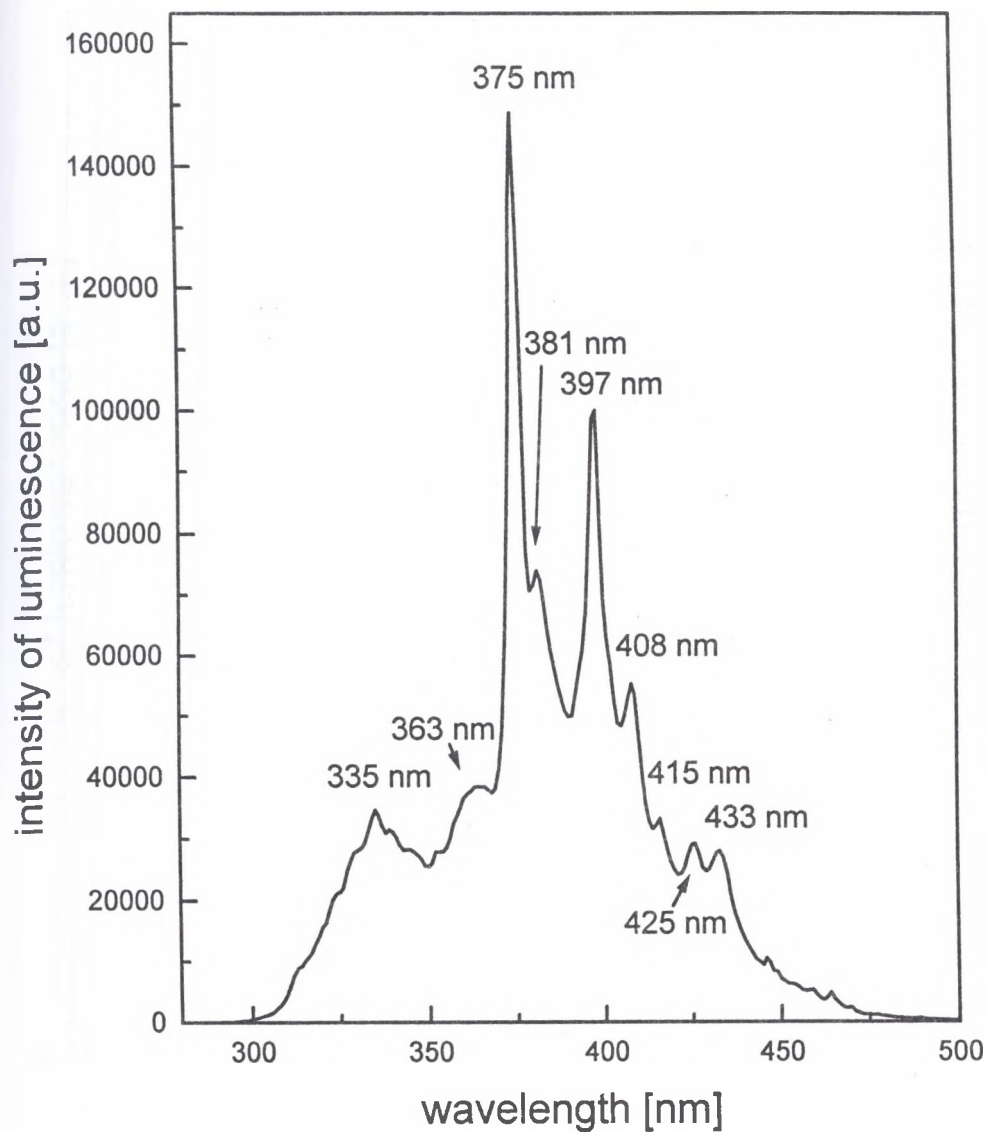
Rys.1. Widmo synchronicznej luminescencji aromatycznej frakcji zdesorbowanej z pyłu zawieszonego (Górny Śląsk); $\Delta\lambda=23\text{nm}$, $c=0.01\text{mg/ml}$

Fig.1. Synchronous luminescence spectrum of aromatic fraction desorbed from suspended dust (Upper Silesia); $\Delta\lambda=23\text{nm}$, $c=0.01\text{mg/ml}$



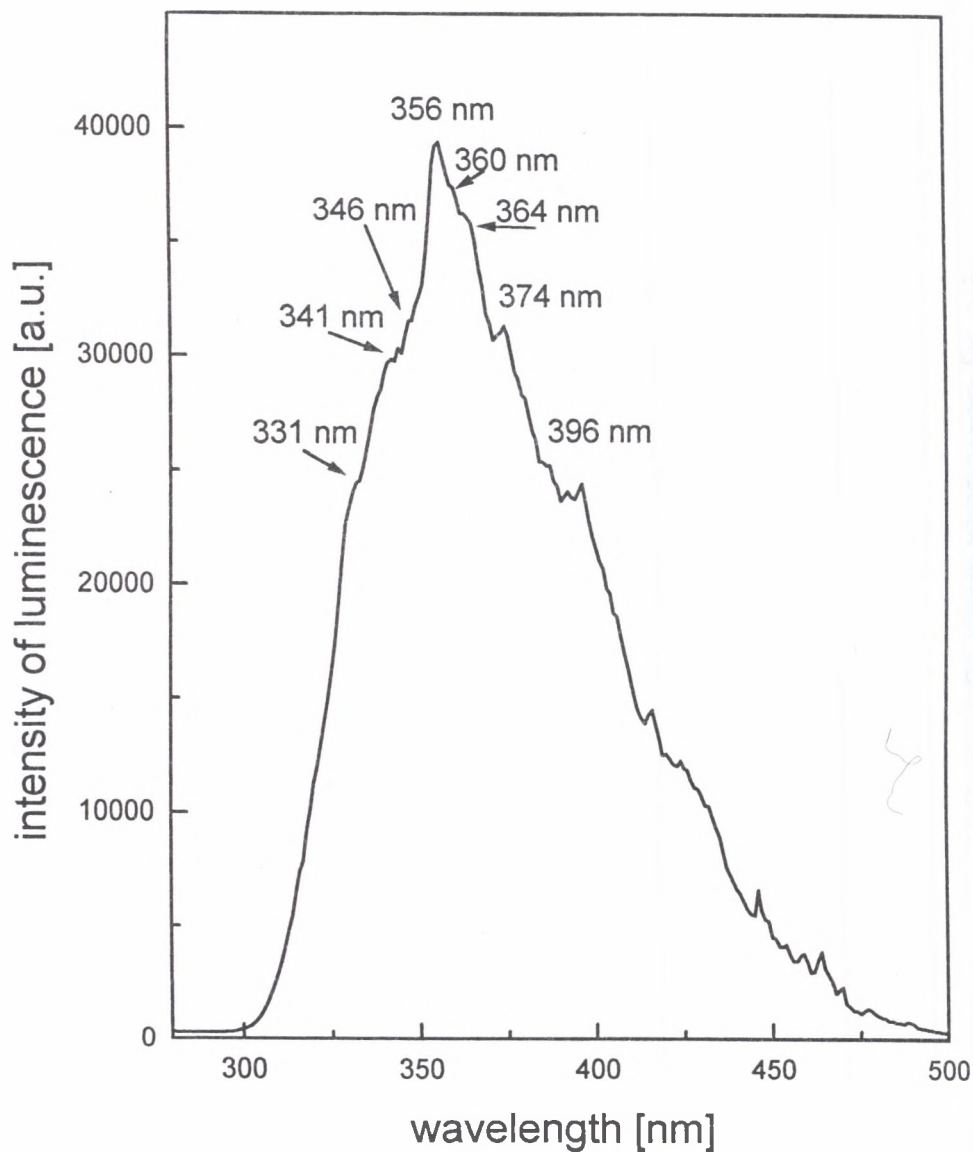
Rys.2. Widmo synchronicznej luminescencji aromatycznej frakcji zdesorbowanej z pyłu zawieszonego (Górny Śląsk); $\Delta\lambda=20\text{nm}$, $c=0.07\text{mg/ml}$

Fig. 2. Synchronous luminescence spectrum of aromatic fraction desorbed from suspended dust (Upper Silesia); $\Delta\lambda=20\text{nm}$, $c=0.07\text{mg/ml}$



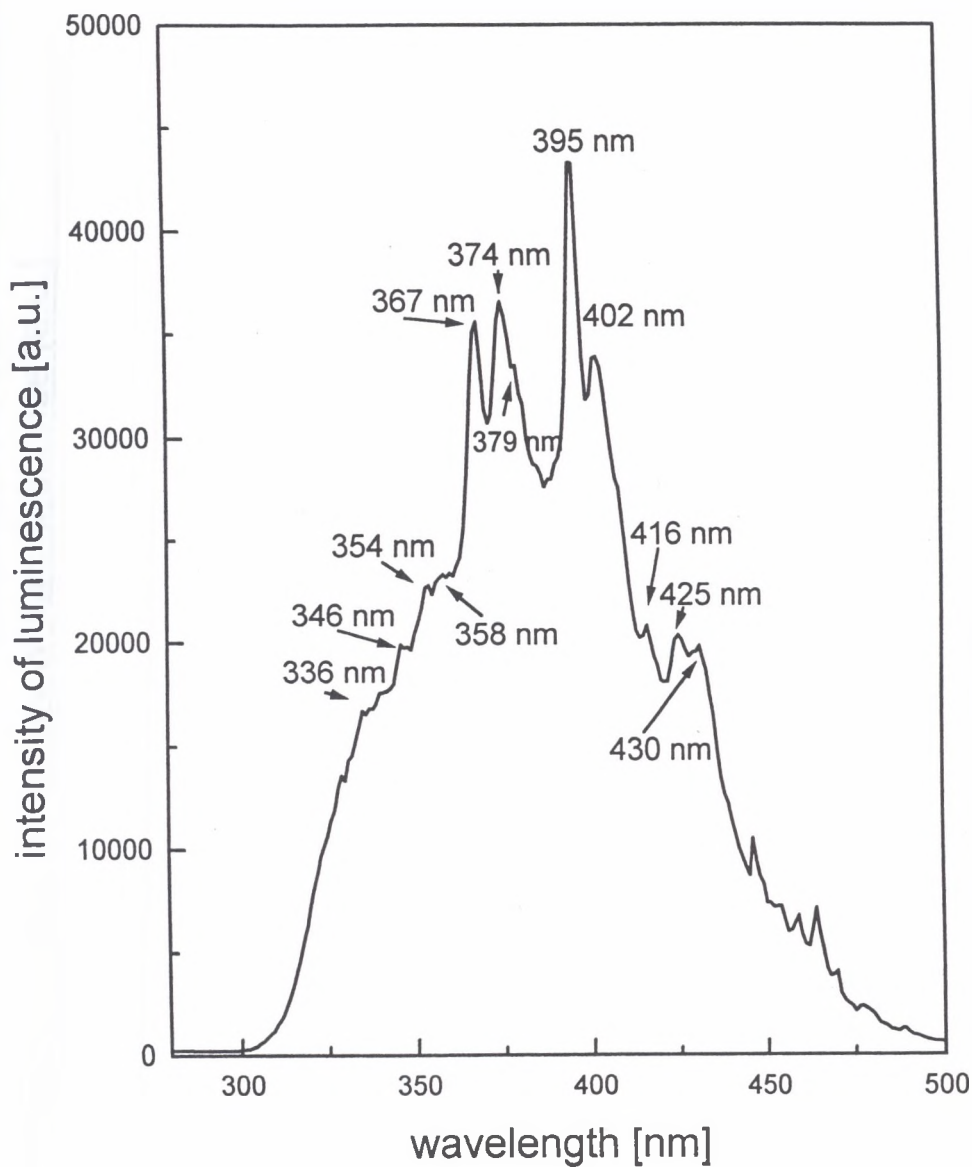
Rys.3. Widmo synchronicznej luminescencji aromatycznej frakcji zdesorbowanej z pyłu zawieszonego (Górny Śląsk); $\Delta\lambda=26\text{nm}$, $c=0.01\text{mg/ml}$

Fig. 3. Synchronous luminescence spectrum of aromatic fraction desorbed from suspended dust (Upper Silesia); $\Delta\lambda=26\text{nm}$, $c=0.01\text{mg/ml}$



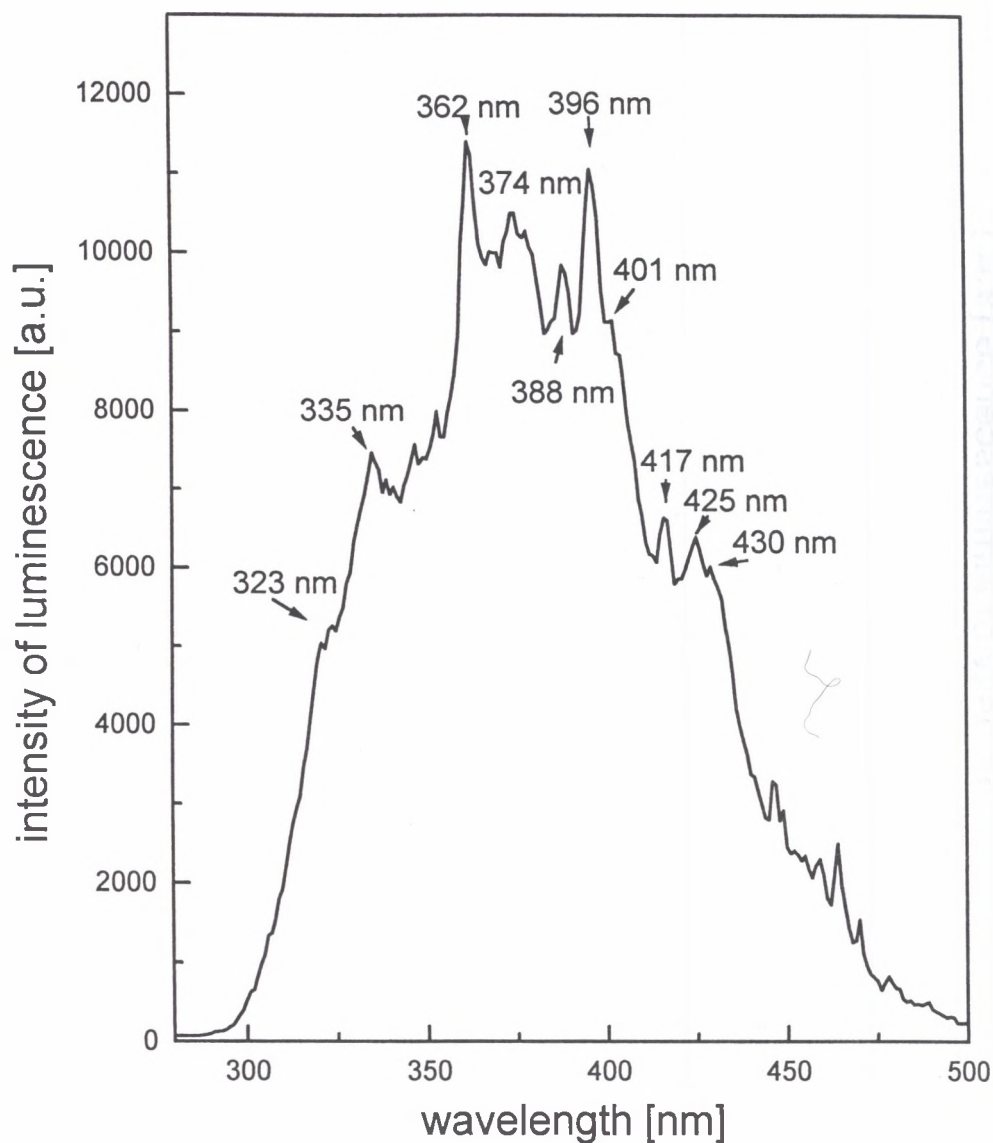
Rys.4. Widmo synchronicznej luminescencji aromatycznej frakcji zdesorbowanej z pyłu zawieszonego (Górny Śląsk); $\Delta\lambda=71\text{nm}$, $c=0.07\text{mg/ml}$

Fig. 4. Synchronous luminescence spectrum of aromatic fraction desorbed from suspended dust (Upper Silesia); $\Delta\lambda=71\text{nm}$, $c=0.07\text{mg/ml}$



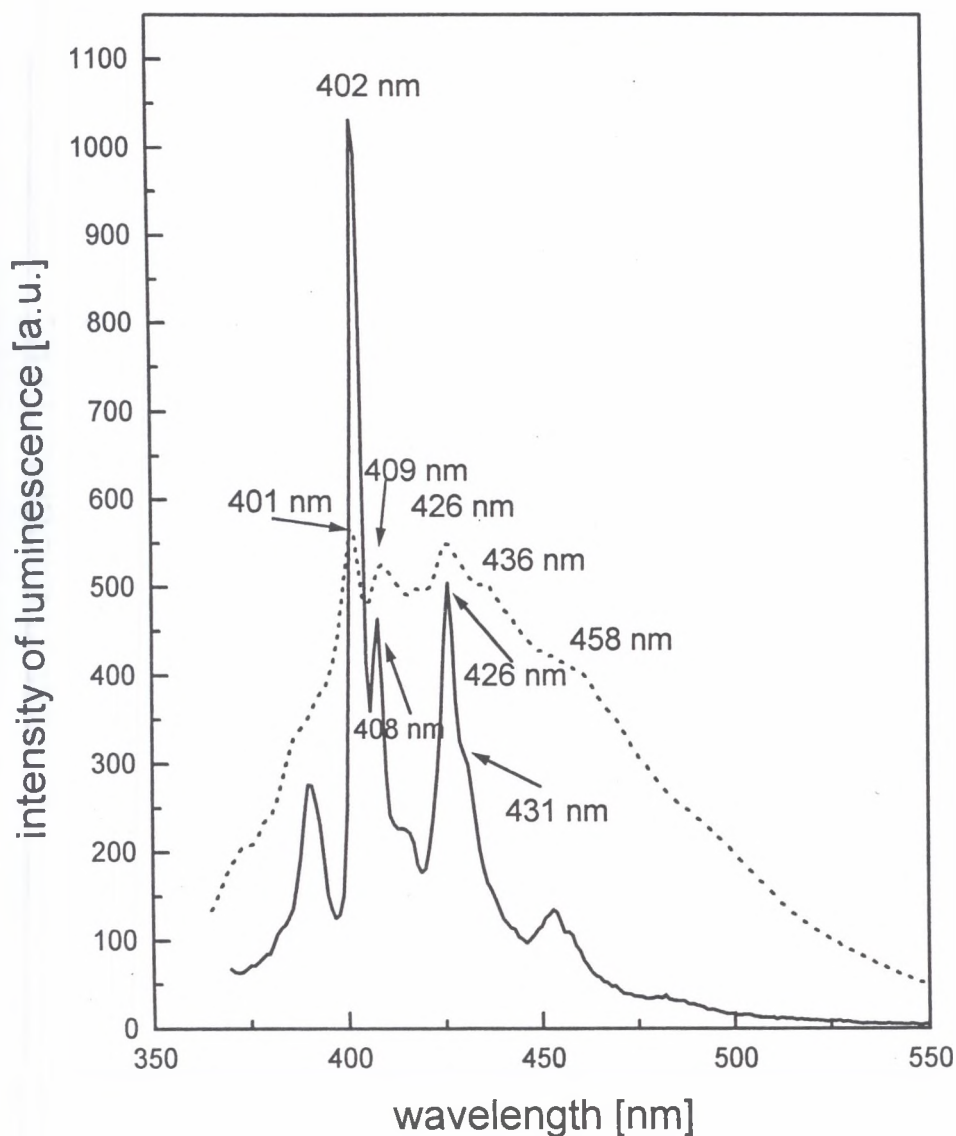
Rys.5. Widmo synchronicznej luminescencji aromatycznej frakcji zdesorbowanej z pyłu zawieszonego (Górny Śląsk); $\Delta\lambda=33\text{nm}$, $c=0.07\text{mg/ml}$

Fig. 5. Synchronous luminescence spectrum of aromatic fraction desorbed from suspended dust (Upper Silesia); $\Delta\lambda=33\text{nm}$, $c=0.07\text{mg/ml}$



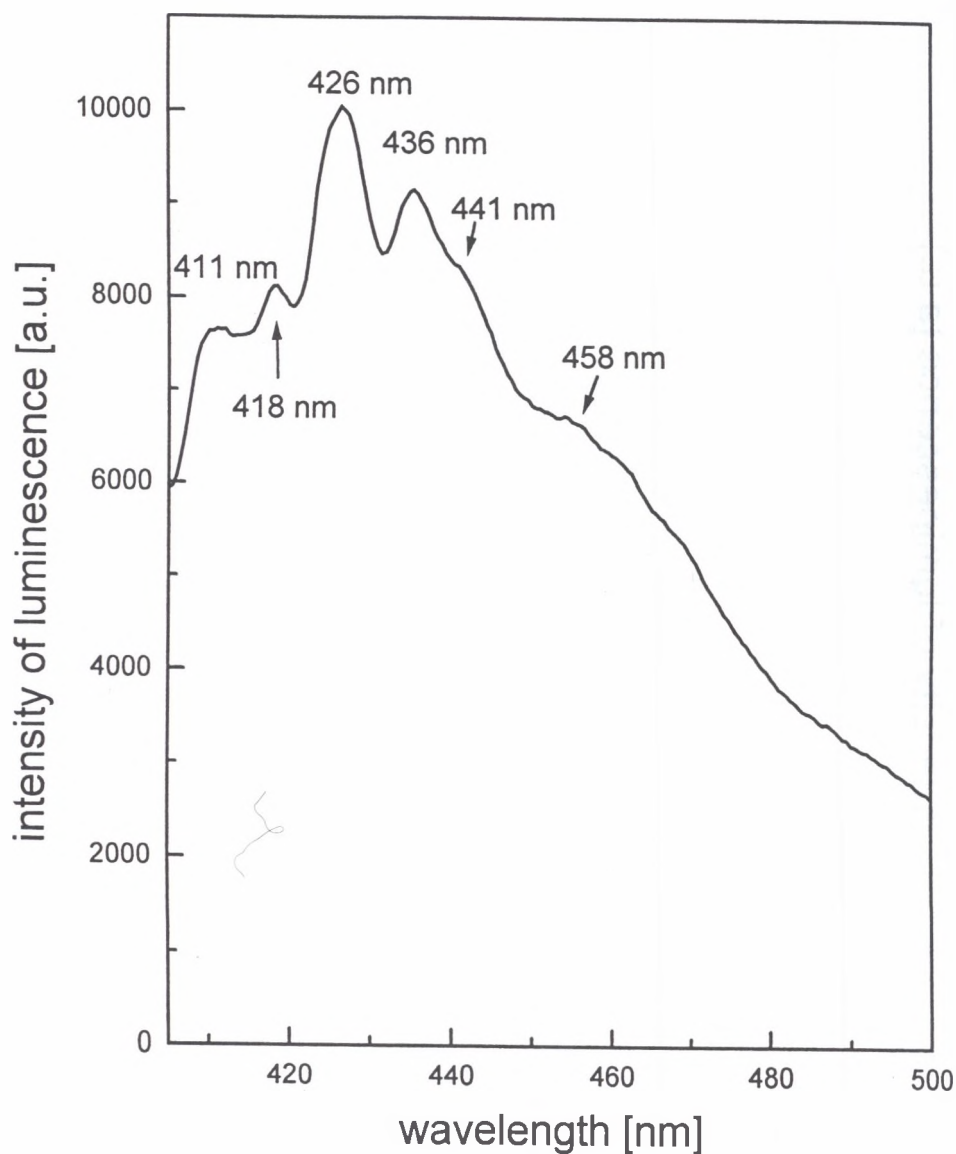
Rys.6. Widmo synchronicznej luminescencji aromatycznej frakcji zdesorbowanej z pyłu zawieszonego (Górny Śląsk); $\Delta\lambda=39\text{nm}$, $c=0.07\text{mg/ml}$

Fig. 6. Synchronous luminescence spectrum of aromatic fraction desorbed from suspended dust (Upper Silesia); $\Delta\lambda=39\text{nm}$, $c=0.07\text{mg/ml}$



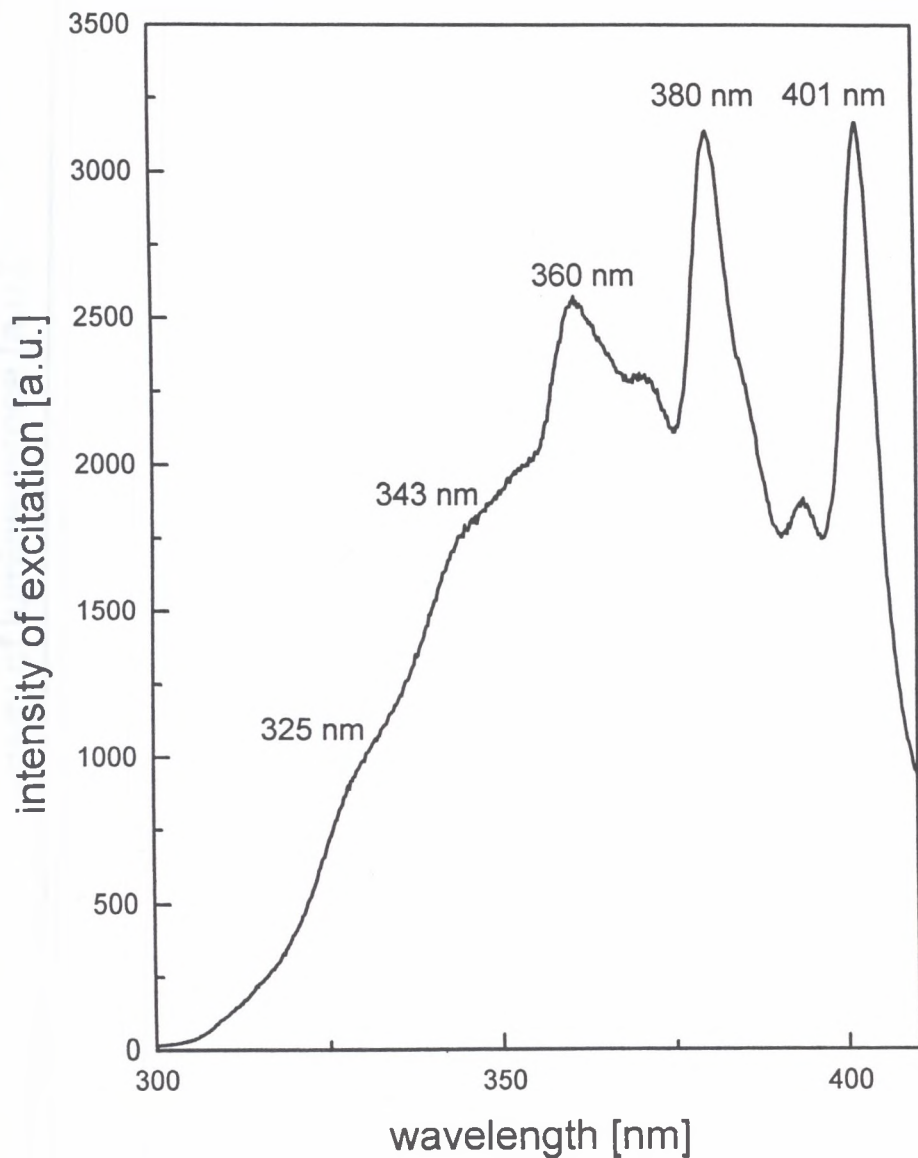
Rys.7. Widma emisyjne ($\lambda_{\text{ex}}=350\text{nm}$) benzo(a)pirenu ($c=0.00005\text{mg/ml}$) (a) oraz aromatycznej frakcji zde-sorbowanej z pyłu zawieszonego (Górny Śląsk) ($c=0.01\text{mg/ml}$) (b)

Fig.7. Emission spectra ($\lambda_{\text{ex}}=350\text{nm}$) of benz(a)pyrene ($c=0.00005\text{mg/ml}$) (a) and aromatic fraction de sorbed from suspended dust (Upper Silesia); $c=0.01\text{mg/ml}$ (b)



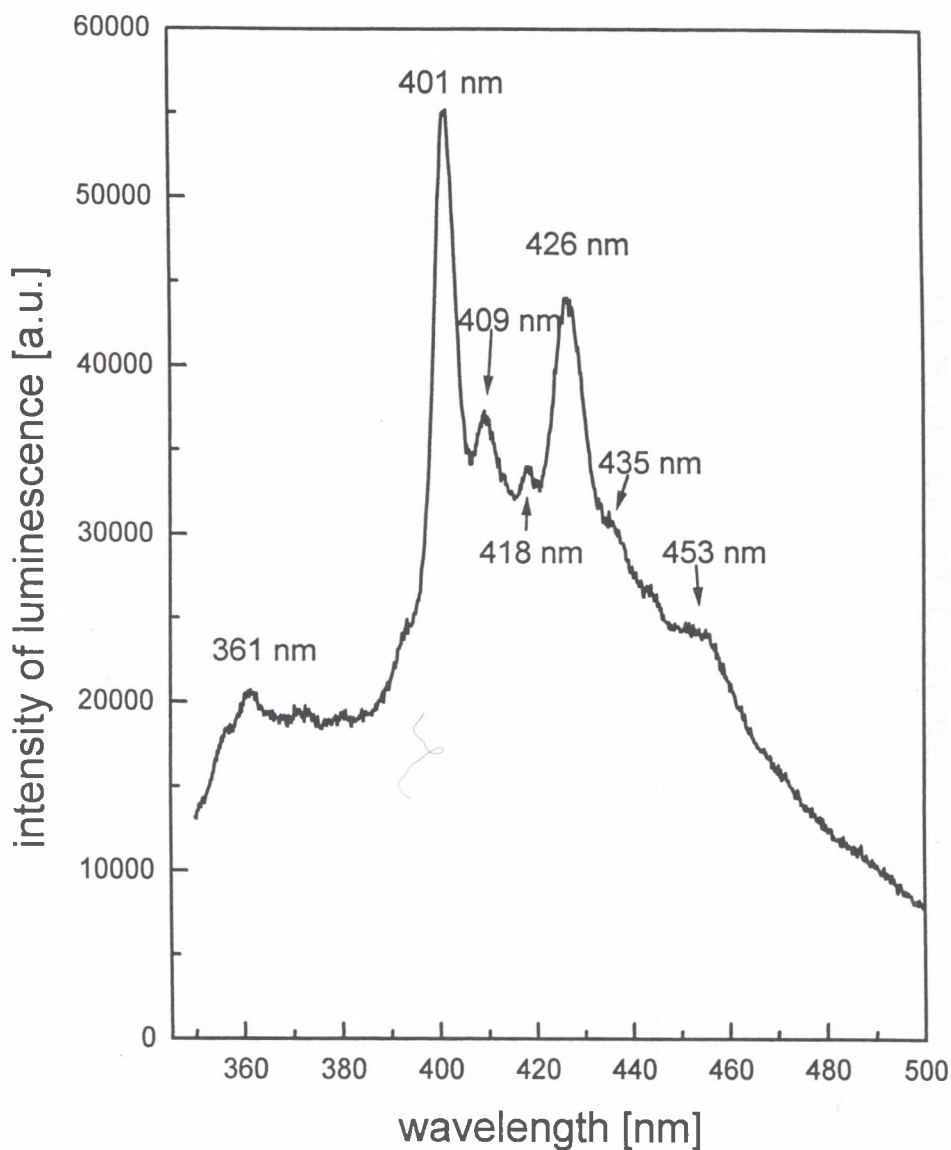
Rys.8. Widmo emisyjne aromatycznej frakcji zdesorbowanej z pyłu zawieszonego (Góry Śląsk) ($\lambda_{\text{ex}}=388\text{nm}$, $c=0.01\text{mg/ml}$)

Fig. 8. Emission spectrum of aromatic fraction desorbed from suspended dust (Upper Silesia) ($\lambda_{\text{ex}}=388\text{nm}$, $c=0.01\text{mg/ml}$)



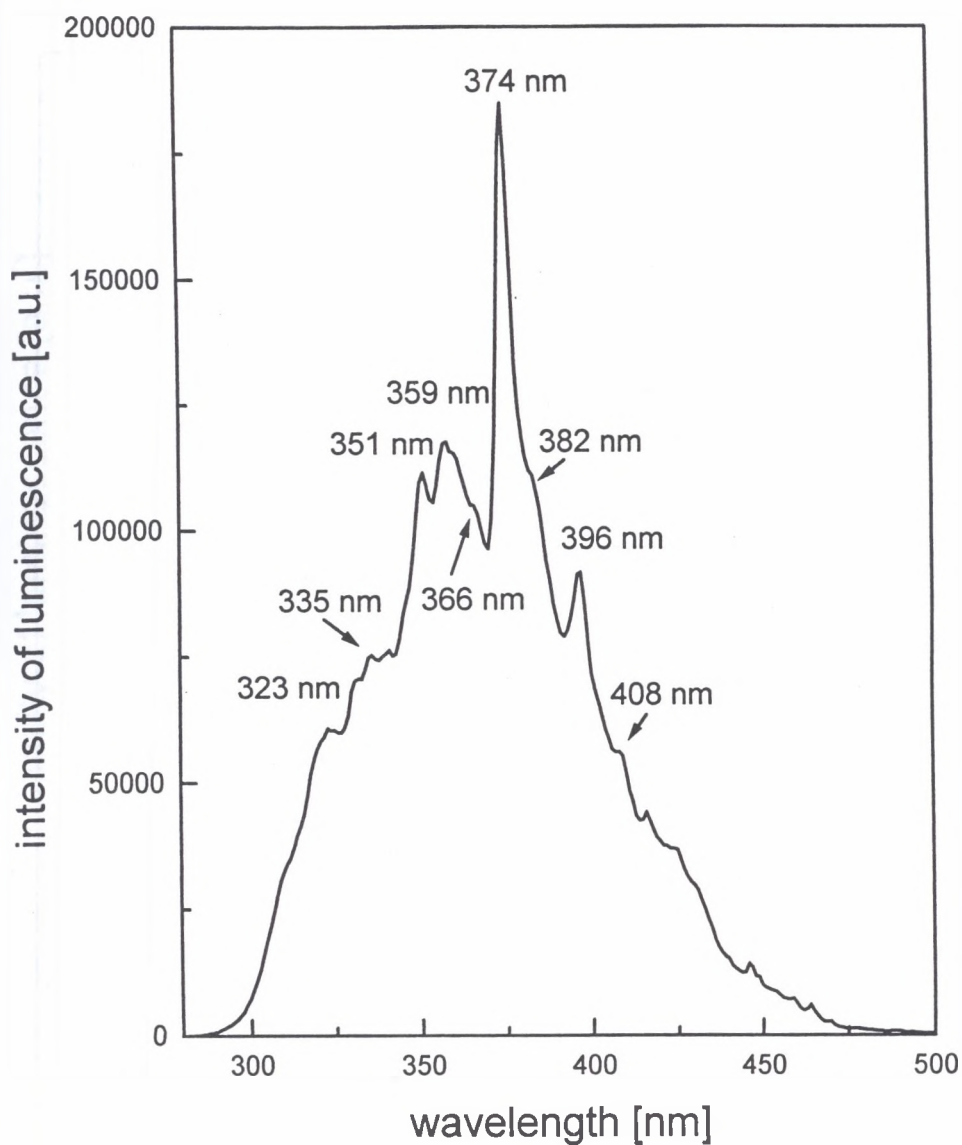
Rys. 9. Widmo wzbudzenia aromatycznej frakcji zdesorbowanej z pyłu zawieszonego (Górny Śląsk) ($\lambda_{em}=426\text{nm}$, $c=0.01\text{mg/ml}$)

Fig. 9. Excitation spectrum of aromatic fraction desorbed from suspended dust (Upper Silesia) ($\lambda_{em}=426\text{nm}$, $c=0.01\text{mg/ml}$)



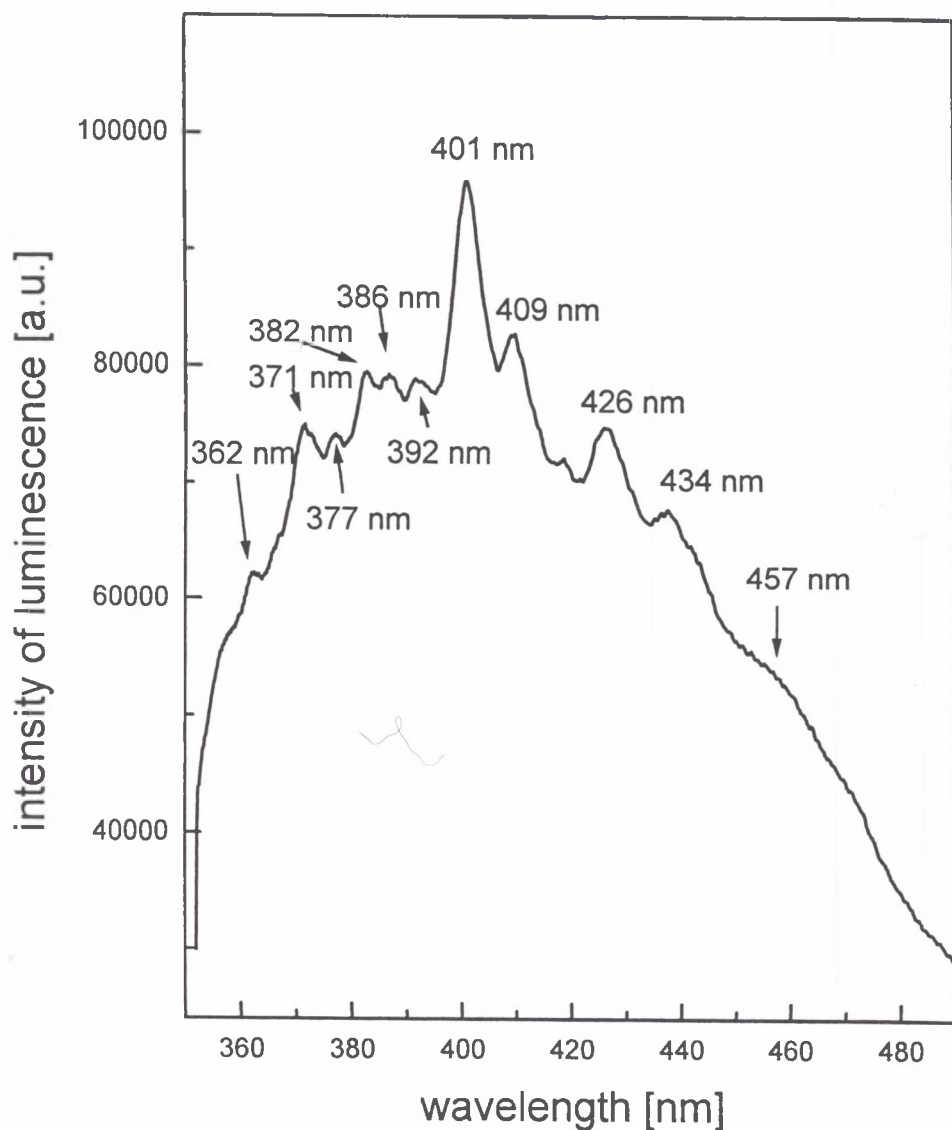
Rys.10. Widmo emisyjne aromatycznej frakcji zdesorbowanej z pyłu zawieszonego (Górny Śląsk) ($\lambda_{\text{ex}}=298\text{nm}$, $c=0.01\text{mg/ml}$)

Fig.10. Emission spectrum of aromatic fraction desorbed from suspended dust (Upper Silesia) ($\lambda_{\text{ex}}=298\text{nm}$, $c=0.01\text{mg/ml}$)



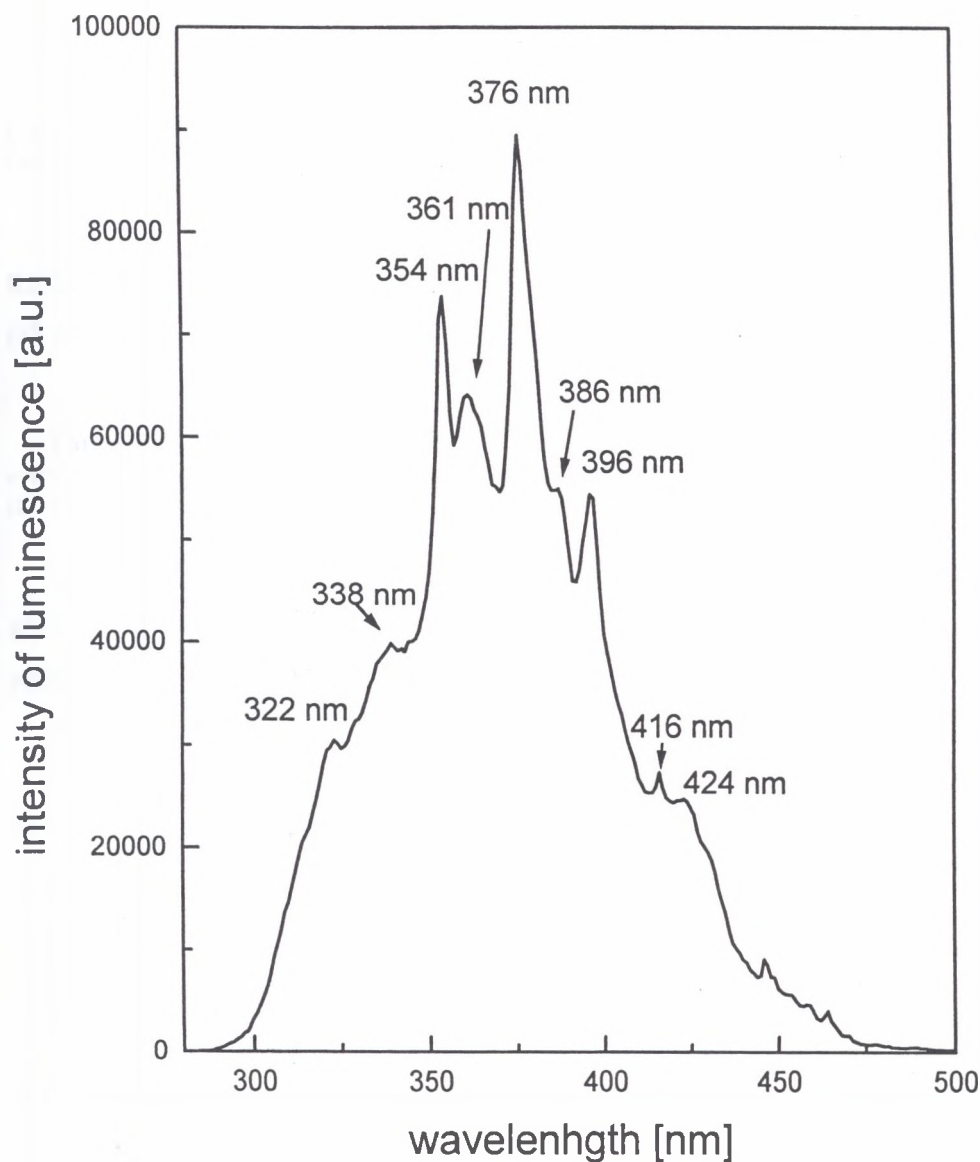
Rys.11. Widmo synchronicznej luminescencji aromatycznej frakcji zdesorbowanej z pyłu zawieszonego (Górny Śląsk); $\Delta\lambda=51\text{nm}$, $c=0.01\text{mg/ml}$

Fig. 11. Synchronous luminescence spectrum of aromatic fraction desorbed from suspended dust (Upper Silesia); $\Delta\lambda=51\text{nm}$, $c=0.01\text{mg/ml}$



Rys.12. Widmo emisyjne aromatycznej frakcji zdesorbowanej z pyłu zawieszonego (Górný Śląsk) ($\lambda_{\text{ex}}=337\text{nm}$, $c=0.002\text{mg/ml}$)

Fig.12. Emission spectrum of aromatic fraction desorbed from suspended dust (Upper Silesia) ($\lambda_{\text{ex}}=337\text{nm}$, $c=0.002\text{mg/ml}$)



Rys.13. Widmo synchronicznej luminescencji aromatycznej frakcji zdesorbowanej z pyłu zawieszonego (Górny Śląsk); $\Delta\lambda=48\text{nm}$, $c=0.01\text{mg/ml}$

Fig. 13. Synchronous luminescence spectrum of aromatic fraction desorbed from suspended dust (Upper Silesia); $\Delta\lambda=48\text{nm}$, $c=0.01\text{mg/ml}$