ANALYSIS OF AROMATIC FRACTIONS OF LOW-TEMPERATURE COAL TARS WITH THE USE OF SYNCHRONOUS LUMINESCENCE TECHNIQUE

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A b s t r a c t . The qualitative analysis by synchronous luminescence technique was performed on aromatic fractions of primary tars obtained from humic and sapropelic coals (from Upper Silesia Basin). The synchronous luminescence technique, called also the technique of spectral fractionation, consists in the record of a spectrum at the constant difference between the positions of emission and excitation monochromators ($\Delta\lambda$). This difference is calculated as a result of subtraction of effective emission and excitation wavelengths characterising compounds identified in investigated mixture. In relation with conventional luminescence technique, giving broad, low resolved bands in the conditions of ambient temperature, the synchronous luminescence technique enables to obtain well resolved and simplified spectra that facilitate the identification of individual components of the mixture. The application of this technique to analysis of aromatic fractions composition of primary tars from coals of various genesis and technological properties (sapropelic and humic coals) has shown a general similarity of composition with predomination of aromatic compounds containing 2–4 condensed rings.

In the sample derived from sapropelic coal, a markedly higher intensity of bands is observed, attributed to aromatics of lower condensation degree (2–3 condensed rings), in relation with the bands of aromatics with higher intensity (3–4 condensed rings). The reverse relation is observed for sample from humic coal. In both analysed samples, a series of the following individual compounds has been identified from groups of aromatics: naphthalenes, acenaphthenes, benzofluorenes, anthracenes, pyrenes, and benz(a)anthracenes. Smaller amounts of benz(a)pyrenes, benz(ghi)perylene, and 3, 4–9, 10-dibenzopyrene were also encountered.

The technique of synchronous luminescence made possible, therefore, the identification of individual components of complex mixture of aromatic compounds in coal derived products. This technique is thus of great value for the characteristics of aromatic compounds in thermolysis products of coal, in the cognitive aspect, as well as in monitoring of environment.

K e y w o r d s : synchronous luminescence, coal primary tar, aromatics.

INTRODUCTION

Investigations of aromatic compounds are carried largely in the aspect of application (analysis of industrial products and wastes, being a potential carcinogenic imminence for environment) as well as in cognitive aspect, e.g. in consideration of conclusions resulting from observation of natural aromatization process of sedimentary organic matter). Among the spectroscopic methods, beside mass spectrometry (used as a detector in analysis by gas chromatographic method), the spectroscopy in uv–vis range is valuable in the analysis of aromatic compounds, especially the luminescence techniques.

The record of conventional luminescence spectra at ambient temperature gives, however, the low-resolved spectra. More effective is synchronous luminescence technique enabling the identification of individual components of complex mixture. It is why this technique was called also a technique of spectral fractionation (Alekseyeva, Tieplickaya, 1981). This technique was already used in the broad range to analysis of aromatic mixtures of various origin (e.g. Lloyd, 1971, 1980; Vo-Dinh, 1978, 1982; Warzecha et al., 1988; Matuszewska, Czaja, 1999a, b, 2000).

The synchronous luminescence technique consists in the use of values of $\Delta\lambda$ parameter characteristic for individual compounds. This parameter is fixed as a constant difference between the position of emission and excitation monochromators during the recording a spectrum.

For general characteristics of analysed mixtures, the value of $\Delta\lambda = 23$ nm was proposed by Mille et al.(1985,1988) as an

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effective parameter to take a fair middle course between the sensitivity and resolving parameters. They used this value for estimation of the condensation degree range of investigated aromatic compounds in the mixture. For identification of the individual compounds, the various values of $\Delta\lambda$ should be used, calculated as a difference between effective emission and excitation wavelengths, characteristic for standards of compounds under investigation.

In this work, the synchronous luminescence technique was used for comparison of aromatic fractions composition of low-temperature tars obtained from both humic and sapropelic coals (Upper Silesia Basin, Poland). The sapropelic and humic coal differ from one another with regard to the aspect of genesis and technological properties. Humus coals have been formed as a result of terrestrial plant decay. The plant residues have been deposited in peat — bog and submitted to processes of humolysis. Sapropelic coals are products of organic matter sedimentation derived from aquatic, terrestrial or mixed plant sources. These organic sediments, contaminated markedly by mineral substances, were submitted in water reservoirs to anaerobic digestion processes (Tertil, 1956). The different sources, sedimentary conditions, and transformation processes are the cause of various composition and properties of final products. The predomination of aliphatic components, high amount of hydrogen, and primary tar yield are the very distinctive examples of features in which sapropelic coals differ from the humic ones. In this work, a difference in composition of aromatic fractions of primary tars from these two coal types was examined using synchronous luminescence technique. After literature data (Grant, Vaughan, 1957; Lowry, 1963; Karr *et al.*, 1967), the 2–3-rings aromatics should be expected mainly as naphthalene, acenaphthene, anthracene, phenanthrene, and their alkyl derivatives.

EXPERIMENTAL

The parent coals were of humic and sapropelic (boghead) types, derived from Upper Silesia Basin. Their characteristics is presented in Table 1.

The analysed coal samples were submitted to the standard process of low-temperature carbonisation at normal pressure and at temperature range from 20 to 520°C. The obtained primary tars were distilled to temperature of 270°C under normal pressure. The residues after distillation were object of further investigations. This procedure has simplified a very complex composition of obtained primary tars. Other fractionation procedures were also made: two stages of separation of residues with the use of thin layer chromatography method (tlc). The pre-coated Merck's plate with silica gel layer of 0.2 mm thick was used for separation of the residues into three fractions: aliphatic, aromatic, and polar.

The mobile phase was n-hexane. Aromatic fraction was then isolated and prepared for luminescence analysis as a solution in n-hexane. This fractionation process was repeated. The aromatic fraction, developed on the tlc plate, was visualised under uv-lamp (254 nm), and shown two main bands: with violet and yellow colour of fluorescence. Each of these bands was isolated separately and prepared as a solution in n-hexane for luminescence analysis.

Three aromatic fraction of each analysed primary tar were, therefore, an object of analysis by synchronic luminescence spectroscopy: total aromatic fraction as well as fractions with violet and yellow colour of fluorescence. The solutions of these fractions of various concentrations were prepared for comparisons, but all concentrations were in the range: 0.02–0.1 mg/ml (mainly 0.04 mg/ml). The measurements were carried at ambient temperature.

The spectrofluorimeter used was Fluorolog 3-12 Spex from Jobin Yvon. The light source was a Xe-ozone-free lamp (45 W).

Table 1

Characteristics of parent coals: sapropelic (S) and humic (H) by the results of ultimate analysis and yields of low-temperature carbonisation products

Sample	A^a [%]	C^{daf} [%]	H^{daf} [%]	N^{daf} [%]	S^{daf} [%]	C/H	primary tar [%]	semi-coke [%]
S	16.10	80.70	8.97	1.36	1.43	8.98	38.10	48.00
H	3.68	84.97	5.53	1.36	0.74	15.37	10.20	75.40

RESULTS AND DISCUSSION

Data presented in Table 1 show a distinct difference between humic and sapropelic coal. The last is boghead coal, composed mainly from algae, rich in compounds containing aliphatic carbon skeleton. The result of specific structure of sapropelic coal is a high amount of hydrogen and primary tar, and also a considerable predomination of aliphatic compounds with relation to aromatic ones (Matuszewska, unpublished). Estimated by i.r. and [1]H n.m.r. methods, the ratio of hydrogen content in ar-

Identification of a series of individual compounds in analysed aromatic fractions obtained from primary tars from humic and sapropelic coals

Δλ [nm]	Experimental data: λem/λex* [nm/nm]	Identified compound	Literature data**: λem/λex* [nm/nm]
Humic coals			
23	347/324	1,2-benzofluorene	346/322
	379/356	anthracene	377/357
	384/361	1-methylanthracene	383/361
	394/371	9-methylbenz(a)anthracene	397/373
26	375/349	3-ethylpyrene	374/350
	392/366	9-ethylanthracene	392/367
	401/375	anthracene	402/376
33	324/291	1-methylnaphthalene	322/291
	336/303	acenaphthene	337/302
	356/323	acenaphthene	354/321
	375/342	3-methylpyrene	376/345
	396/363	3'-methylbenz(a)anthracene	396/362
	401/368	benz(a)pyrene	403/370
	416/383	5,8-dimethylbenz(a)pyrene	415/382
	425/392	benzo(ghi)perylene	420/390
	433/400	3,4-9,10-dibenzopyrene	432/398
36	337/301	acenaphthene	337/302
	354/321	acenaphthene	354/321
	374/338	4-methylpyrene	374/337
	392/356	9-methylbenz(a)anthracene	393/356
47	323/276	2,6-dimethylnaphthalene	324/275
	332/285	acenaphthene	331/284
	354/307	acenaphthene	354/307
	379/332	pyrene	379/333
	416/369	9-propylanthracene	417/368
	425/378	1`,9-dimethylbenz(a)anthracene	427/378
48	353/305	9,10-dibutylphenanthrene	352/304
	376/328	3-methylpyrene	376/328
53	326/273	2,6-dimethylnaphthalene	324/275
	336/283	1-methylnaphthalene	337/283
	344/291	phenanthrene	346/293
	349/296	9-heptylphenanthrene	349/296
	355/302	9,10-diisoamylphenanthrene	353/303
	372/319	pyrene	372/322
	393/340	9-methylbenz(a)anthracene	393/339
	356/285	2-cyclohexylphenanthrene	357/283
	364/293	phenanthrene	364/293
	351/253	9-isobutylphenanthrene	349/255

Δλ [nm]	Experimental data: λem/λex* [nm/nm]	Identified compound	Literature data**: λem/λex* [nm/nm]
Sapropelic coals			
15	392/377	10-methylbenz(a)anthracene	392/374
23	327/304	acenaphthene	327/302
	345/322	1,2-benzofluorene	346/322
	378/356	anthracene	377/357
	381/358	2,3-dimethylanthracene	381/359
	384/361	1-methylanthracene	383/361
33 (identification generally the same as for sample from humic coal)			
37	376/339	4-methylpyrene	374/337
	424/387	9,10-dimethylbenz(a)anthracene	424/386
47	336/289	naphthalene	337/289
	378/331	pyrene	379/333
53	326/273	2,6-dimethylnaphthalene	324/275
	344/291	phenanthrene	346/293
	372/319	pyrene	372/322
71	329/258	2,3-dimethylnaphthalene	328/259
	356/285	9,10-dimethylphenanthrene	354/285
	359/288	retene	360/288
	364/293	phenanthrene	364/293

* λem, λex — efective emission and excitation wavelengths, respectively
** after Aleksyeva, Tieplickaya, 1981

omatic compounds of sapropelic, with relation to humic primary tars under analysis, is equal 0.3. In the residues after primary tars distillation (up to temperature 270°C), this ratio was 0.6 indicating distinctive relative increase of aromatic compounds as a result of removing of light fractions during distillation (e.g. benzene derivatives and phenols abundant in humic coal).

The residues obtained were fractionated on tlc plates. The fractionation process was performed for isolation of total aromatic fraction and also to obtain two narrower fractions with violet or yellow fluorescence colour. All aromatic fractions were then analysed by synchronous luminescence technique. The results of individual compounds identification were presented separately for aromatic fractions obtained from sapropelic and humic coal primary tars (Table 2). The identification was made using literature data for standards (Alekseyeva, Tieplickaya, 1981) because of considerable difficulties in obtaining own standards of high fluorescent purity. Table 3 presents several examples taken from literature (*op. cit.*) of spectral characteristics of chosen standards. Figure 1 show, instead, by way of example, a series of synchronous luminescence spectra made for analysed samples with the use of different values of Δλ parameter.

On Figure 1A, there are shown spectra of synchronous luminescence of non separated aromatic fractions from primary tars obtained from both analysed coals. The value of Δλ = 23 nm was applied here (according to Mille *et al*., 1985, 1988) to estimate, from range of emission observed, the degree of condensation of aromatic rings. This range is generally similar for both analysed samples and indicates the predominance of aromatic compounds containing 2–4 condensed rings. The difference is, however, distinct in relative intensity of two main peaks in the

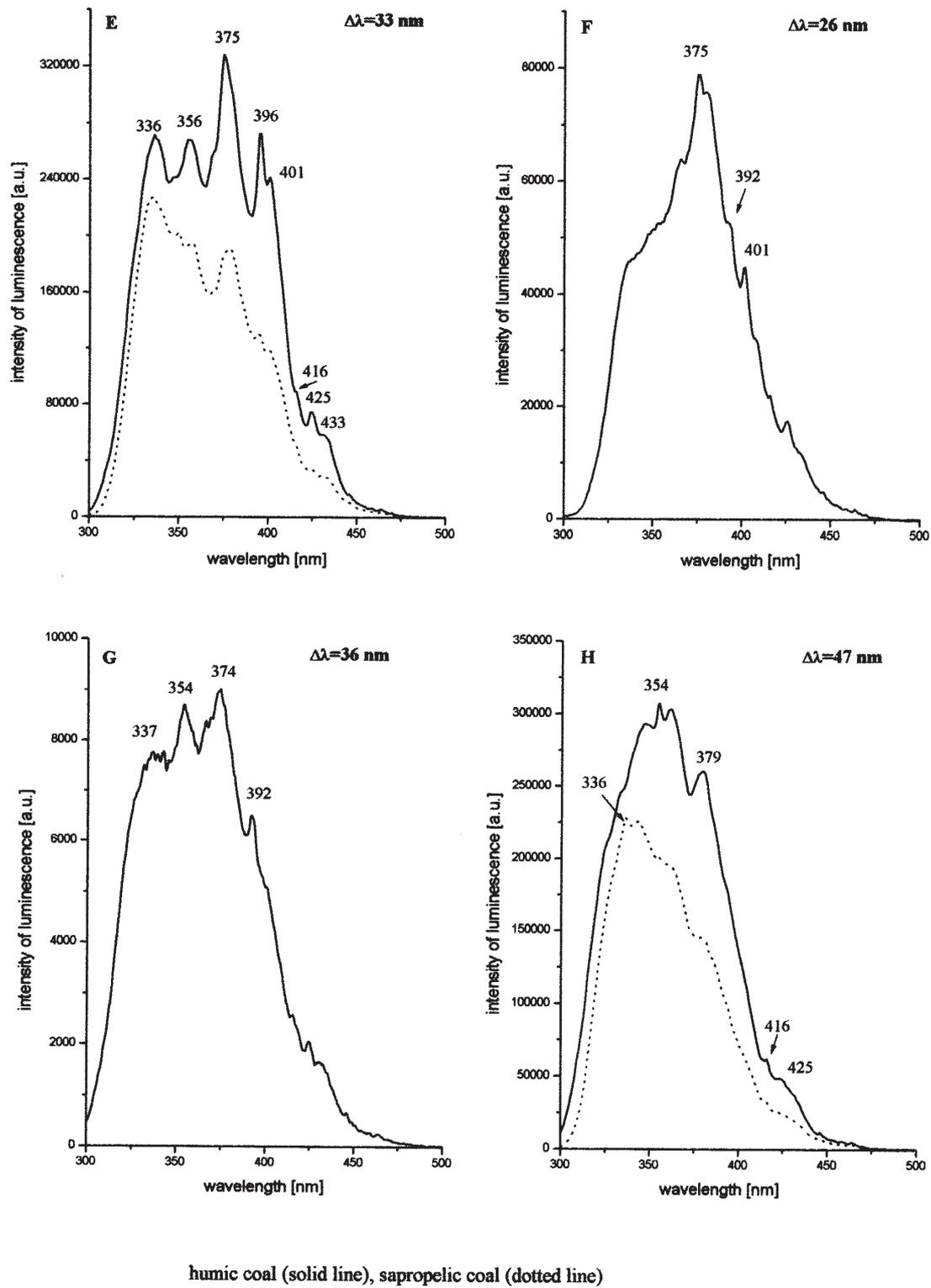humic coal (solid line), sapropelic coal (dotted line)
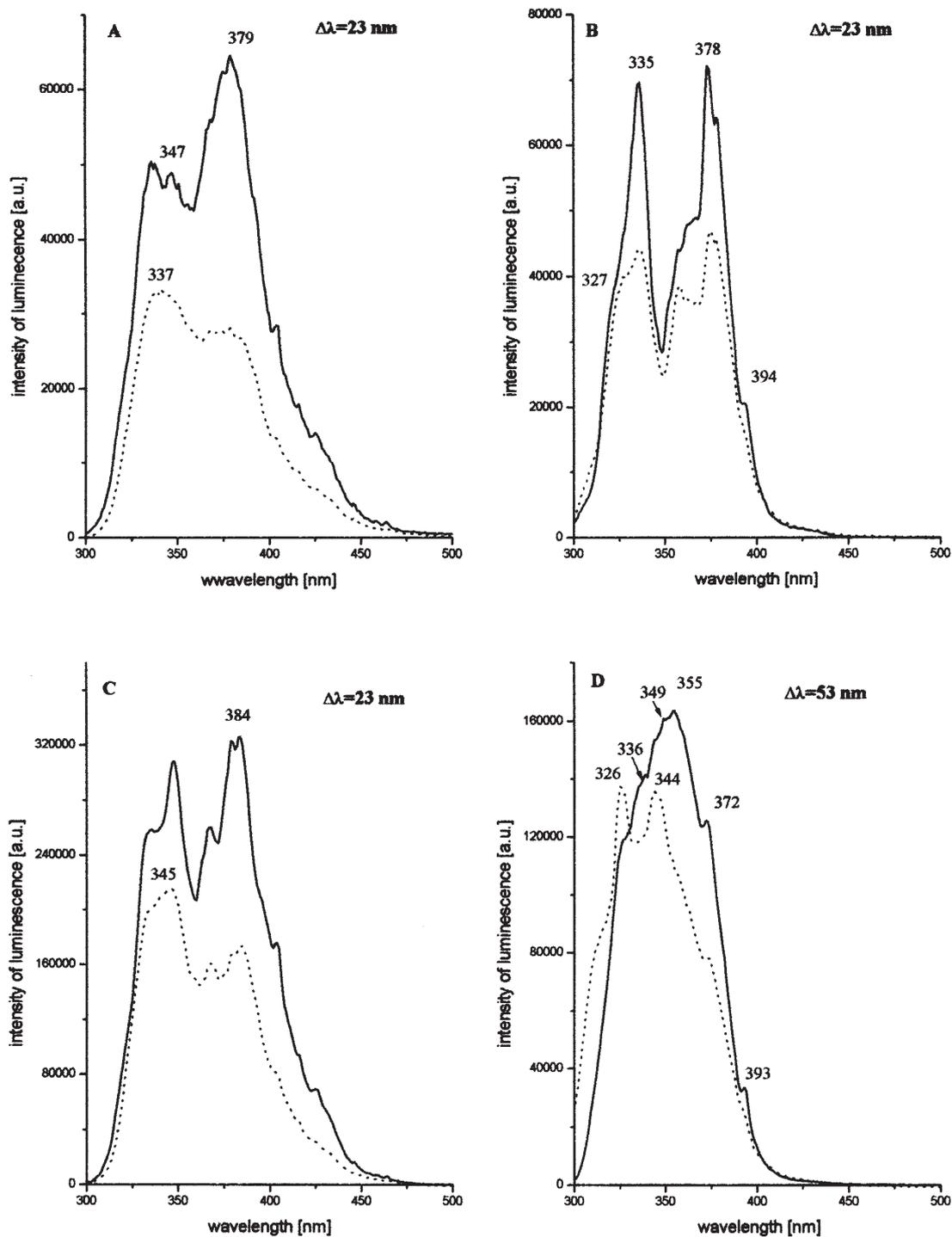
humic coal (solid line), sapropelic coal (dotted line)

Fig. 1. Synchronous luminescence spectra of aromatic fractions of primary tars from humic and sapropelic coals

**Emission (λem) and excitation (λex) wavelengths characteristic for chosen standard compounds
(after Aleksyeva, Tieplickaya, 1981)**

Compound	λex [nm]	λem [nm]	Compound	λex [nm]	λem [nm]
naphthalene	**278*** **289**	**322** 326 332 **337** 342	phenanthrene	254 274 282 **293**	**346** 356 364 384
anthracene	253 340 357 **376**	**377** 383 399 402 425	4-methylpyre-ne	275 323 333 **337**	**374** 383 388 391 394
3,4-9,10-dibenzopyrene	295 374 **398**	**432** 447 459 490	benzo[ghi]pe-rylene	287 299 350 370 **390**	406 417 **420** 423 432

* numbers recorded in bold-face signify the most effective wavelengths

rings in aromatic fraction from sapropelic coal primary tar, whereas in the sample from humic coal, the 3–4-ring condensed systems predominate.

The violet fractions isolated from both samples under discussion have shown generally similar shape of synchronous spectra recorded at $\Delta\lambda$ = 23 nm (Fig. 1B). However, also in this case, a higher content of smaller, condensed systems (as acenaphthenes — Table 2, and probably naphthalenes) is present in sample from sapropelic coal. The spectra of respective fractions of analysed samples with yellow fluorescence (Fig. 1C) are shifted to higher wavelengths, indicating a presence of aromatics with higher condensation degree than in violet fraction, as it was expected. The appearance in these spectra also of bands attributed to smaller ring systems, testify to the impurity of fractionation. However, it was not the purpose here to obtain a pure fractions but only fractions of lower complexity. This experiment has shown at the same time, however, that this measurements technique could be used also for verification of fractionation effectiveness of aromatic mixtures.

Generally, the spectra presented on Figures 1A–C indicate the existence of aromatic compounds in analysed samples, mainly of the following types: naphthalenes, acenaphthenes, benzofluorenes (the bands in the range of about 310 to 360 nm), phenanthrenes, anthracenes, chrysenes, pyrenes, and benz(a)anthracenes (from about 350 to about 380 nm). A series of individual compounds was identified also at this conditions of measurements ($\Delta\lambda$ = 23 nm) but a greater number of compounds was identified in the spectra of analysed fractions recorded at other values of $\Delta\lambda$ parameter (Table 2).

Figure 1D presents the synchronous spectra (recorded at $\Delta\lambda$ = 53 nm) of aromatic fractions (with violet fluorescence) de-rived from both analysed parent coals. As it was previously mentioned, also in this case the fraction obtained from primary tar of sapropelic coal indicates relatively higher amount of lower condensed aromatics than in the case of sample from humic coal, where e.g. relatively more abundant is four-ring system of the pyrene type (Table 2). It should be emphasised here that parameter $\Delta\lambda$ = 53 nm is very characteristic for phenanthrene; as a result of subtraction of effective values of λem (346 nm) – λex (293 nm) (Table 3), and were found among identified compounds the phenanthrene as well as his alkyl derivatives (Table 2). The parameter $\Delta\lambda$ = 33 nm proved to be advantageous for distinctive manifestation of a series of compounds (Fig. 1E, Table 2) present in both analysed fractions. A maintenance is here also stated of observed earlier proportions indicating generally lower degree of condensation of aromatics in sample from sapropelic sample in relation with the one from humic parent coal.

The distinctive simplification of spectrum was observed, instead, in the case of parameter used of $\Delta\lambda$ = 26 nm, giving a strong maximum at 375 nm attributed to 3-ethylpyrene (Fig. 1F, Table 2). The pyrenes appear very markedly in the spectra of analysed samples, especially for the ones from humic coals. Figures 1G and H also present a confirmation of this fact, showing peaks at 374 nm and 379 nm respectively, attributed to 4-methylpyrene in the spectrum recorded at $\Delta\lambda$ = 36 nm, and to pyrene in the spectrum recorded at 47 nm. In this last spectrum, a distinctive peak is shown at 362 nm, derived probably from alkylchrysene system but the exact spectral data for this group of compounds were unachievable in the literature.

CONCLUSIONS

The technique of synchronous luminescence presented in this work accomplished a task as a technique of spectral fractionation, enabling to identify a series of components of complex mixtures of aromatic compounds in fractions obtained from analysed primary tars. This technique made also possible to compare the aromatic fractions derived from sapropelic and humic coals. The difference noted consisted rather in various proportion of the same groups of aromatic compounds than in a considerable difference of condensation degree of aromatics. In samples under investigations, the aromatic compounds predominated with 2–4 condensed rings. The considerably smaller amounts of compounds with higher degree of condensation were also identified as benz(a)pyrenes, benzo(ghi)perylene, and 3, 4–9, 10-dibenzopyrene.

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