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Monitoring of PAHs in simulated natural and artificial fires by HPLC-DAD-FLD with the application of Multi-Component Integrated Calibration Method to improve quality of analytical results

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Abstract Modifications of integrated calibration method (ICM) in its basic variant and complementary dilution method version (CDM) were adapted to multi-component (MC) analysis to obtain novel calibration approaches improving the accuracy of analytical results. Methods were developed conceptually and their performance was assessed on the basis of polycyclic aromatic hydrocarbons (PAHs) determination in air samples. The natural (thuja needles) and synthetic (polymer) materials were combusted simulating fires or home users' combustion. Analytical method for determination EPA PAHs was developed using HPLC-DAD-FLD. It has been confirmed that the improved analytical results accuracy obtained in MC-ICM and MC-ICM/CDM was described by relative error <1.5%. Multiplicative effects due to the coelution of other substances were detected by comparing the individual estimations of the analytical results. The results free from this effect were determined. According to RGB Additive Color Model, the proposed approach is White – method is a good candidate of choice for all applications.

Keywords: Polycyclic aromatic hydrocarbons (PAHs), Integrated Calibration Method, Multi-component analysis, HPLC, Air analysis

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Abstract Modifications of integrated calibration method (ICM) in its basic variant and complementary dilution method version (CDM) were adapted to multi-component (MC) analysis to obtain novel calibration approaches improving the accuracy of analytical results. Methods were developed conceptually and their performance was assessed on the basis of polycyclic aromatic hydrocarbons (PAHs) determination in air samples. The natural (thuja needles) and synthetic (polymer) materials were combusted simulating fires or home users' combustion. Analytical method for determination EPA PAHs was developed using HPLC-DAD-FLD. It has been confirmed that the improved analytical results accuracy obtained in MC-ICM and MC-ICM/CDM was described by relative error $<1.5\%$. Multiplicative effects due to the coelution of other substances were detected by comparing the individual estimations of the analytical results. The results free from this effect were determined. According to RGB Additive Color Model, the proposed approach is White – method is a good candidate of choice for all applications.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of over 10,000 organic compounds that are ubiquitous and considered pollutants of the environment, food, air, water, and soils. PAHs consist of two or more aromatic rings. These hazardous compounds vary by a different mutual position of the benzene rings in the molecule. PAHs show strong genotoxic, mutagenic, and carcinogenic properties [1-6]. They have always been present in the environment. Still, civilization and technological development resulted in increased exposure to these compounds and their negative impact on the environment and harmful short- and long-term health effects. In 1976 the US Environmental Protection Agency (EPA) classified a list of 16 compounds from the PAH group as a priority pollutant – 16 EPA-PAHs (Method 610 [7], Method 550.1 [8], Method 8310 [9], and method for air analysis – Method TO-13A [10]), the presence of which indicates hazards. The European Union (EU) also indicates methods for the determination of PAH [11,12]. Special attention should be paid for the selected group of compounds during exposure studies for assessing risks to human health [13,14].

PAHs are produced mainly in the processes of incomplete combustion of organic compounds. The process occurs in natural conditions (e.g., during a forest fire) and the areas of human residence (waste incineration, exhaust fumes from motor vehicles, industrial activities). The amount of PAH emissions to the environment definitely derived from anthropogenic sources [1].

In the context of PAH emissions, outdoor air pollution can lead to more than 3 million premature death per year worldwide [15]. It has been estimated that a 45-95% of total PAH emission is caused by residential wood and coal burning [16,17]. A huge problem is the increasing number of fires related to climate change [18,19] and the burning of plastics [20-24]. This causes a high exposure of local residents [25,26] and firefighters fighting with natural and within human activities fires [27]. Few recent studies indicate the possibility of PAH formation during the combustion of plastics [28,29]. Three main mechanisms of PAH formation during combustion have been postulated [30]. The first one is slow Diels-Alder condensations, and the second is rapid, radical reactions and the last is the ionic reaction mechanism. The second of these processes seem to be the most probably due to the high rate of compound formation. The third is a fast reorganization of hydrocarbon radicals, which enable the formation of PAH. On the basis of low-molecular PAHs, when hydrocarbon radicals are added via the alkyl group, PAHs hydrocarbons of greater mass are produced. In the case of combustion of pulverized coal and tire crumbs, pyrosynthesis was the major mechanism for PAH formation. The cause of PAH may be the existing ring structure of cyclic compounds. Among other methods of PAH

formation, the following can be distinguished: the use of unsaturated compounds and pyrolysis process of higher alkenes present in, i.e., fuels and plant material [30,31]. The mechanism for the formation of PAH beyond the second aromatic ring has been also proposed [32]. The most possible mechanism is the process of organic radical recombination causing PAH formation [33]. However, this topic requires further research. However, the topic requires further research. Taking into account environmental considerations as well as concern for the health and life of animals and, above all, humans, it is very important to use methods that facilitate reliable determination of EPA-PAHs compounds in the air, e.g., if they are products of natural materials (from the natural environment such as needles, leaves, biomass, and others) and plastics combustion. The limitations in this type of research are other compounds formed as a result of combustion (playing the role of interferences) of the materials mentioned above and the process of air sampling, in which the analysed analytes are present in low concentrations.

Determination of PAHs in samples requires the use of chromatographic methods that enable the separation and identification of individual compounds. The two most commonly used methods are gas chromatography (GC) and high-performance liquid chromatography (HPLC). The resolving power and the ability to identify compounds of the mass spectrometry (MS) detector are much greater than the standard flame ionization detector FID in the case of GC. Whereas, in the application of HPLC chromatography, the most commonly used measurement devices are diode array detectors (DAD) and fluorescence detectors (FLD) [34,35]. The analysis of PAH in the air is carried out in several different ways; however, the most popular is adsorption of PAH on the XAD-2 sorbent, extraction with a suitable solvent, and chromatographic analysis [36,37]. The development of a reliable method of EPA-PAHs analysis requires an assessment of the accuracy and influence of interferences on the recorded analytical signal and, consequently, on the information of the individual components concentrations.

Various types of interference effects can occur in laboratory practice: proportional (multiplicative) - changing the slope of the calibration plot, constant (additive) - making a constant contribution to the signal measured for the analyte, and non-linear - described by various mathematical functions. In addition, combinations of these effects can also occur during chemical analysis [38-41]. Compensation of the interfering substances for analytes may be done by applying an appropriate methodological approach to determine accurate results, e.g., using a Good Methodology Practice approach [41].

Among the two the most commonly used methods: external calibration (EC) and standard addition method (SAM), only the second method allows to compensate for the occurring interference effects. However, it should be emphasized that these effects are proportional [42,43]. Over the years, new approaches providing new possibilities for the elimination of interference effects as well as for the accuracy assessment have been developed. Integrated calibration method (ICM) in its basic variant as well as in the complementary dilution method (ICM/CDM) version is an example of such approaches [44-46]. Comparison of the results obtained by interpolation and extrapolation allows for the elimination of multiplicative effects. Simultaneously, the dilution in the ICM/CDM version partially compensates for the non-linear calibration dependence. On this basis, the consecutive version (C-ICM) was developed and used for the determination of glutamate and aspartate by HPLC with electrochemical detection [47]. The extension of these methods to the use of gradual dilutions (both sample and standard) led to the development of the generalized calibration strategy (GCS) [48-50]. The gradual dilution treatment applied in this strategy enables compensation for non-linear effects. In the case of additive interference effects in the absence of the use of separation techniques, other methodological approaches such as H-point standard addition method (HPSAM) [51] or its modifications [52-54] should be applied. An essential aspect is that the developed methodological approaches, in addition to improving the accuracy of the results, also comply with the principles of green analytical chemistry [55].

In the present article, we adapt two calibration approaches: ICM and ICM/CDM, to realization in multi-component (MC) analysis to determine 16 EPA-PAHs with the use of HPLC-DAD-FLD. The developed MC-ICM and MC-ICM/CDM methods were tested on the example of synthetic and air samples. The study investigated the effect of fires on the type and amount of polycyclic aromatic hydrocarbons produced by simulated combustion of plastics and natural needles from coniferous trees. An air sampling scheme was developed using the properties of the XAD-2 sorbent. A procedure for the extraction and preparation of samples before the analysis was proposed. Based on a series of result estimations, the final results with increased accuracy were determined. In addition, a diagram showing the type of PAH formed from the combustion of the given material was proposed. The complete method was assessed in accordance with the RGB additive color model to analytical method evaluation presented in recent years.

2. Principle of the MC-ICM and MC-ICM/CDM methods

Developed in recent years, the ICM and the ICM/CDM are approaches that enable improvement of analytical results accuracy and diagnosis of the occurrence of the systematic errors, and especially compensation of interference effects. Both methods were adapted to multi-component analysis (MCA), resulting in the MC-ICM and MC-ICM/CDM approaches. Figure 1 presents a diagram of the preparation of calibration solutions for both methods and exemplary calibration graphs obtained for a single analyte in a multi-component analysis. The most significant change, compared to the previous versions of the methods, is the use of the standard mix of all analysed substances at the stage of preparation of the calibration solutions.

The required calibration solutions consist of three necessary components: a diluent (D), a sample (S) – most often as a solution after an appropriate sample preparation procedure, and a mix standard solution of analysed substances (ST_{mix}). Each solution consists of two components, one in volume p and one in volume q . In this way, the sample or multi-component standard is diluted with a diluent or with each other once to the P degree of dilution ($P=p/(p+q)$) and once to the Q degree ($Q=q/(p+q)$). Both degrees of dilution P and Q must be complementary ($P+Q=1$). The MC-ICM requires the preparation of four calibration solutions according to the above requirements. In comparison, the MC-ICM/CDM method involves the preparation of six solutions due to the use of the CDM approach.

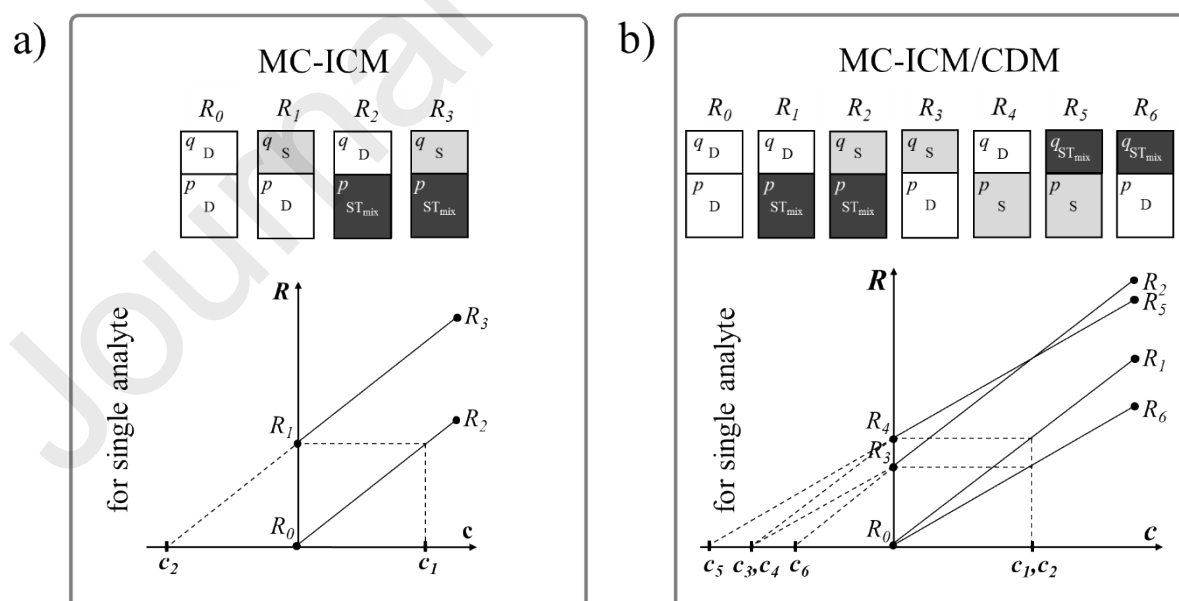


Fig. 1. A diagram showing the calibration solutions preparation process (top) and an example calibration curves for one component (bottom) for (a) MC-ICM and (b) MC-ICM/CDM. The following abbreviations were used: D – diluent, S – sample, ST_{mix} – the standard of analysed

substances, p and q – volumes, R_i – analytical signals, c_j - estimations of analytical result, i and $j = 0, 1, 2, 3, 4, 5$, and 6 .

Then, for prepared calibration solutions, measurements of analytical signals are performed under constant conditions. In the case of the MC-ICM approach, considering a single analyte, two calibration plots are obtained, one according to the EC, and the second according to the SAM. Based on these lines, estimations of the analytical result c_1 and c_2 are calculated using the following formulas (1) and (2):

$$c_1 = \frac{R_1 - R_0}{R_2 - R_0} \cdot c_{ST_{mix}} \quad (1)$$

$$c_2 = \frac{R_1 - R_0}{R_3 - R_1} \cdot c_{ST_{mix}} \quad (2)$$

where: R_0, R_1, R_2, R_3 means analytical signals, but $c_{ST_{mix}}$ denotes the concentration of the analytes in standard solution.

Four two-point calibration plots are obtained after plotting the measured analytical signals (R_0 - R_6) on a calibration coordinate system in the MC-ICM/CDM method. Two plots are in line with the EC, while the other two are following the SAM approach. The six estimations (c_1 - c_6) of the analytical result are calculated with the use of the constructed calibration lines in various ways: c_1, c_2 by interpolation following EC, c_3, c_4 by semi-extrapolation, and c_5, c_6 by extrapolation in accordance with SAM. The calculation of these estimations is based on the use of appropriate mathematical formulas:

$$c_1 = \frac{R_4 - R_0}{R_1 - R_0} \cdot c_{ST_{mix}} \quad (3)$$

$$c_2 = \frac{R_3 - R_0}{R_6 - R_0} \cdot c_{ST_{mix}} \quad (4)$$

$$c_3 = \frac{R_4 - R_0}{R_2 - R_3} \cdot c_{ST_{mix}} \quad (5)$$

$$c_4 = \frac{R_3 - R_0}{R_5 - R_4} \cdot c_{ST_{mix}} \quad (6)$$

$$c_5 = \frac{R_4 - R_0}{R_5 - R_4} \cdot \frac{R_6 - R_0}{R_1 - R_0} \cdot c_{ST_{mix}} \quad (7)$$

$$c_6 = \frac{R_3 - R_0}{R_2 - R_3} \cdot \frac{R_1 - R_0}{R_6 - R_0} \cdot c_{ST_{mix}} \quad (8)$$

For both MC-ICM and MC-ICM/CDM, a complete set of analytical result estimations is obtained for each analyte in multi-component analysis.

The developed methods allow for the following interpretation of the results in the context of compensation of interference effects:

1. In a situation when all estimations of the analytical result are statistically equal (c_1 - c_2 for MC-ICM, c_1 - c_6 for MC-ICM/CDM), it can be assumed that there are no interference effects, and the final result will be calculated as the arithmetic mean.
2. If the estimations satisfy the relation: for MC-ICM $c_1 \neq c_2$, for MC-ICM/CDM $c_1 \neq c_2 \neq (c_3+c_4)/2 = c_5 = c_6$, there is a multiplicative effect, and the mean of the extrapolative estimations should be considered as the final result (c_2 for MC-ICM, and c_3 - c_6 for MC-ICM/CDM).
3. An additive effect should be eliminated by chromatographic separation. If other measurement techniques are used, it will not be possible to compensate for this kind of interference effect.
4. If none of the above conditions are fulfilled, non-linear effects are most likely to occur. In this case, a gradual dilution process should be carried out to obtain one of the above situations. To simplify the interpretative stage in this paper, we propose to compare c_1 with c_2 for MC-ICM and for MC-ICM/CDM compare mean from all estimations (c_1 - c_6) and mean of extrapolative estimations (c_3 - c_6). Additionally, we recommend checking the homogeneity of the variance for normal distribution before comparing estimations with Student's t-test.

3. Experimental

3.1. Reagents, samples, and solutions

All necessary chemicals for HPLC analysis were of the highest purity. Water HPLC Plus (H₂O), acetonitrile for HPLC, gradient grade, $\geq 99.9\%$ (ACN), dichloromethane for HPLC, $\geq 99.8\%$ (CH₂Cl₂), contains amylene as stabilizer purchased from Sigma-Aldrich (USA) and LiChrosolv[®] methanol hypergrade for LC-MS (MeOH) (Supelco, Merck, Germany) were used for dilution of standards and synthetic samples. Standard stock solution of 16 PAH mix at concentration of 20 $\mu\text{g/mL}$ was prepared by dilution of a 0.2 mg/mL PAH Solution mix (AccuStandard[®], USA) with CH₂Cl₂:MeOH (1:1). The individual standards of 16 PAH (naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenz[a,h]anthracene, benzo[g,h,i]perylene, indeno[1,2,3-cd]pyrene) from the Polycyclic Aromatic Hydrocarbon Kit (AccuStandard[®], USA) were treated in the same

way. Working solutions of standard (16 PAH mix), as well as synthetic samples contained all analysed PAHs in the mixture, were prepared by dilution of the stock solutions in with ACN:water (1:1).

The composition of the mobile phase required the use of the following solvents: water HPLC Plus (Sigma-Aldrich, USA) and LiChrosolv[®] Acetonitrile hypergrade for LC-MS (Supelco, Merck, Germany).

For the calibration curve preparation following external calibration (EC) and for validation of HPLC-DAD method, several calibration solutions (contained 16 PAHs) at concentration of: 0, 0.5, 1.0 and 1.5 µg/mL were prepared in ACN:H₂O (1:1). Eight mix standards of all 16 PAHs (0, 5, 10, 25, 50, 100, 250 and 500 ng/mL in ACN:H₂O (1:1)) were used for validation of chromatographic method based on fluorescence detection – HPLC-FLD.

To investigate the most optimal excitation and emission conditions tests were carried out with the standards of individual substances and a mix of 16 PAH with 100 ng/mL concentrations in ACN:H₂O (1:1) using fluorescence spectrophotometer.

Synthetic sample prepared in ACN:H₂O at a concentration of 25 ng/mL was used in all experiments. Mix standard solution at the concentration of 50 ng/mL was applied in the case of MC-ICM and MC-ICM/CDM.

Dilution degrees applied in preparation of calibration solutions in MC-ICM method were equal $P=Q=0.5$ (volumes: $p=q=50$ µL), while in MC-ICM/CDM method were $P=0.6$ and $Q=0.4$ (volumes: $p=60$ µL and $q=40$ µL). The process of preparation of the calibration solutions was in accordance with the principles presented in Figure 1. Synthetic, natural and polymers samples were analysed in triplicates.

In order to investigate the type and amount of PAHs released into the air during natural and landfill fires, it was decided to verify by simulating the tests performed for the following tested samples (ts): ts1 - outside air in Katowice region (as reference sample), ts2 - thuja needles (*Thuja occidentalis*) (m=5.263 g), ts3 - polystyrene from yogurt cups (m=10.393 g), ts4 - expanded polystyrene (m=14.165 g), ts5 - PET, polyethylene terephthalate from mineral water bottles (m=16.134 g), ts6 - polyurethane foam (m=5.949 g), ts7 - Styrene-butadiene rubber 80%, Ker 80 000 (m=4.793 g), ts8 - polycarbonate from DVDs (m=7.244 g), ts9 - plywood board, and ts10 - synthetic mineral oil, gear Hipol 15 (v=5 mL).

Individual standards were used to identify substances appearing on the chromatograms.

3.2. Air sampling and extraction

The sampling stage consisted in extracting PAHs from the air by using the sorption properties of the XAD-2 resin in relation to PAH. A unique system, shown in Figure 2, was built to collect air samples.

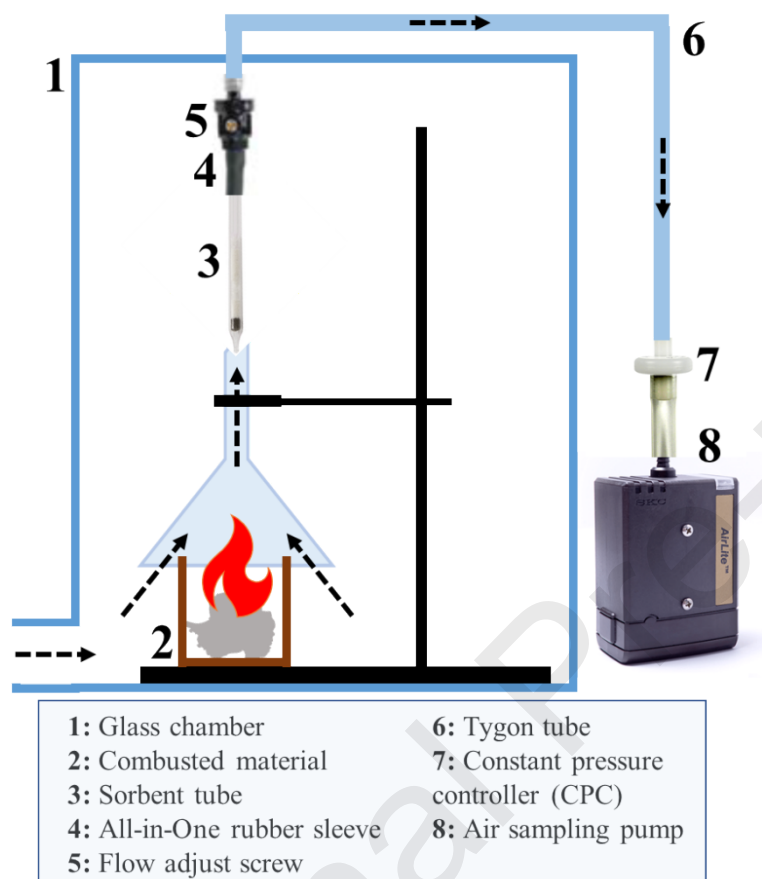


Fig. 2. Schematic diagram of the system used to collect PAHs from the air during combustion of the tested samples. The arrows indicate the air flow direction.

The constructed sampling system consisted of the following elements: AirLite sampler pump, model 110-11 (SKC Inc., USA) with 3 x AA alkaline batteries, 1 m length of Tygon tubing Saint-Gobain Tygon S3™ E-3603 NSF®-51, 1/4" ID, 3/8" OD (SKC Europe, UK), single adjustable tube holder, constant pressure controller (CPC) for low flow (SKC Inc., USA), protective tube cover type A 6 mm × 70 mm (SKC Europe, UK), single adjustable flow holder (SKC Inc., USA), low flow Adapter Kit (5 to 500 mL/min) includes All-in-One low flow holder and Type A tube cover. PAHs were adsorbed onto the tube (tube cover = B) with sorbent (coating) XAD-2 (SKC Ltd., USA) at size 8 mm × 100 mm with two sections of sorbent (100 and 50 mg) with GC ends. The system was configured to collect all combustion products. This

system was placed in a glass chamber (additional external factors was limited). The air flow generated by the pump allowed only combustion products to be collected.

The flow rate through the XAD-2 tube was experimentally established at 1 L/min using a field rotameter, 0.4-5.0 L/min (SKC Inc., USA). With the use of the constructed system, the air was collected from above the burning materials, and the tube was positioned at a distance of 30 cm from the material. The time of air passing through the tube for the reference sample ts1 (outside air) was 24 hours (due to the low concentrations), while for the remaining samples (ts2-ts10), the sampling time was 10 minutes (10 L of air samples). Sampling took place during the middle burn period. Samples with adsorbed hydrocarbons were protected against air and light and were stored at 4-8 °C before the extraction process.

The second step in pre-sample preparation was the extraction stage. A one-step extraction was used to isolate PAH adsorbed on the XAD-2 resin. After cutting the tubes with the sorbent, the protective high purity glass wool and foam separators were removed. Both layers of XAD-2 resin were poured into clear glass sample vials with white screw cap and EPE joint, 26 mL (Labbox Labware, S.L., Spain). 1 mL of acetonitrile was added to the vials, and extraction was performed for 60 min in an ultrasonic bath RK 52 H (BANDELIN electronic GmbH & Co., Germany) with 35 kHz frequency at room temperature. After this step, the samples were filtered through syringe filters with nylon membrane, diameter 13 mm, pore size 0.45 µm (Chrom4 GmbH, Germany), and the use of 2 mL Luer-Lok plastic disposable syringes (Polygen, Poland). The samples prepared in this way were ready for chromatographic analysis.

3.3. Instrumentation and procedure

The determination of EPA-PAHs in synthetic, natural and plastic material samples was conducted using Varian 920-LC high performance - liquid chromatography (HPLC) system with diode array detector (DAD) (Varian, Inc., Australia) and using Varian ProStar fluorescence detector (FLD) (Varian, Inc., Australia), model: 363. The DAD detector was equipped with a xenon lamp 150 W and flow cell 12 µL. This detector registered signals from 200 to 400 nm every 1 nm and allowed to extract chromatograms at selected wavelengths: 210, 215, 230, 254, 265, and 290 nm. The slit width was set to 8 nm, and the threshold to 10.000 mAU.

In the case of the FLD detector, the timing program including excitation and emission wavelengths (Ex/Em) [nm] was as follows: 0.0 min – 280/330, 10.0 min – 300/415, 13.0 min – 300/320, 16.0 min – 210/365, 17.5 min – 210/380, 19.0 min – 280/465, 20.2 min – 280/400, 22.0 min – 230/390, 25.0 min – 310/450, 26.0 min – 318/450, 27.2 min – 310/405, 28.6 min –

310/395, 30.8 min – 310/420, and 32.4 min – 300/500. During the analyses, the remaining parameters were set at a constant level: sensitivity – 1 V, time constant – 0.6 s, PMT voltage – medium, emission bandwidth – 15 nm, and signal offset – 9 mV.

The Galaxie Chromatography Data System version 1.9.302.952 (Varian, Inc., Australia) software was used to operate the HPLC system, register and collect data as an analytical signals from the DAD and FLD detector.

The polycyclic aromatic hydrocarbons were separated on the reversed-phase HPLC Column Hypersil GREEN PAH 250 × 4.6 mm with particle size equal to 5 μm and pore size equal to 120 Å (Thermo Fisher Scientific, Germany). A stainless guard column holder 4.6/4.0mm (Thermo Fisher Scientific, Germany) was mounted directly to the inlet of the analytical column. Dedicated reversed-phase pre-columns with the size of 10 × 4 mm and particle size 5 μm Hypersil Green PAH Guard (Thermo Fisher Scientific, Germany) were placed in this holder. The mobile phase was composed of ACN and water. During the research, gradient elution was used. The total gradient elution program is presented in Table 1.

Table 1. Mobile phase gradient program for developed method with the use of HPLC-DAD-FLD.

Time [min]	Flow [mL/min]	% H ₂ O	% ACN
Prerun	1.0	40	60
5.0		40	60
10.0		40	60
20.0		0	100
30.0		5	95
35.0		10	90

The mobile phase flow rate during all analyses was constant and was set to 1.0 mL/min. Calibration solutions and investigated samples were injected into the HPLC system in a volume equal to 10 μL. The column temperature was set to 30 °C and the total time of a single chromatogram was 35 min. The analytical signals (DAD: absorbance [mAV] and FLD: signal [mV]) were represented as a value of the area under the peak corresponding to the individual analyte from the considered EPA-PAHs group.

Varian Cary Eclipse Fluorescence Spectrophotometer (Varian, Inc., Australia) was used in experiments consisting in determining the optimal excitation and emission wavelengths for individual compounds to give the most intense analytical signals in the HPLC-FLD application. The obtained spectra were registered for individual standards of each substance (100 ng/mL in ACN:water (1:1)) as excitation-emission fluorescence matrices (EEMs). The following

parameters were used: excitation in the range of 210-450 nm (with a step $\Delta=10$ nm) and emission in the range of 215-601 nm, with a step $\Delta=2$ nm. Quartz cuvette with a 1 cm path was used for measuring fluorescence properties of liquid standards. Scan software (Varian, Inc., Australia) was used to operate the instrument and collect data.

The obtained EEMs are presented in Figure S1. These data were processed and modeled in MATLAB R2019a (MathWorks, Natick, MA, USA). Scattering correction was applied - in place of scattering, NaN (values that are not real or complex numbers with a special value) was inserted. The EEMs were used to determine the optimal excitation and emission conditions to obtain the maximum signal for each substance. These conditions were verified in HPLC-FLD tests, based on which the final excitation and emission wavelengths were selected.

Calculation of the area under peaks of individual substances on the recorded chromatograms was performed with the use of the OriginPro 2021 software (OriginLab Corporation, US). In contrast, a Microsoft Excel spreadsheet was applied for further computation of estimations of analytical results and constructions of calibration lines with considered methodological approaches.

The limit of detection (*LOD*) and limit of quantification (*LOQ*) were calculated based on the parameters of the calibration line according to equations (9) and (10), respectively.

$$LOD = \frac{3.3 \cdot s}{b} \quad (9)$$

$$LOQ = \frac{10 \cdot s}{b} \quad (10)$$

where: *s* means the intercept's standard deviation (*SD*) and *b* denotes a calibration curve slope. The accuracy of the obtained results was determined on the basis of the relative error (*RE*) expressed as a percentage. However, the precision of the obtained results was described by the coefficient of variation (*CV*) [%]. Estimations of analytical results were statistically assessed using the Student's t-test ($\alpha=0.05$). First, the normal distribution and homogeneity of the variance were checked.

The repeatability studies were carried out with the same material (ts5 – PET). Combustion was carried out under the same conditions at the same time (10 min.). There were no statistically significant differences in the obtained concentration values of individual PAHs in both experiments.

4. Results and discussion

4.1. Development and validation of a method for PAHs determination

In the first step, the developed analytical method for EPA-PAHs determination using high-performance liquid chromatography with diode array and fluorescence detection (HPLC-DAD-FL) was validated. Figure 3a presents an example of a DAD map registered for the standard of EPA-PAHs at a concentration of 20 $\mu\text{g/mL}$. On its basis, it is possible to notice places where signals from individual compounds of the PAHs group appear. Based on the characteristic areas, six wavelengths (210 nm, 215 nm, 230 nm, 254 nm, 265 nm, and 290 nm) were selected, for which the method was validated. Validation parameters for DAD detection for individual wavelengths are summarized in Tables S1-S6.

In most cases, the linear range for each compound was from 0 to 1.5 $\mu\text{g/mL}$ with R^2 higher than 0.999. The limit of detection varies depending on the wavelength considered and ranges from 0.01 to 0.09 $\mu\text{g/mL}$. Due to the lower concentrations present in air samples, a fluorescence measurement method was developed and validated (parameters determined in DAD detection can be helpful in other analytical systems). Details on the validation parameters are included in Table 2.

Table 2. Summary of validation parameters of the developed method with fluorescence detection. The considered range of concentrations was 0-500 ng/mL.

Analyte	Slope	Intercept [ng/mL]	R^2	LOD [ng/mL]	LOQ [ng/mL]
Naphthalene	0.0828	-2.83	0.9998	0.08	0.23
Acenaphthylene*	-	-	-	-	-
Acenaphthene	0.1278	-4.30	0.9997	0.15	0.45
Fluorene	0.4899	-2.70	0.9998	0.17	0.51
Phenanthrene	0.2223	-2.98	0.9970	0.21	0.64
Anthracene	0.2436	-3.64	0.9995	0.14	0.41
Fluoranthene	0.2168	-1.06	1.0000	0.20	0.62
Pyrene	0.0526	-0.96	1.0000	0.09	0.27
Benz[a]anthracene	0.1879	-2.55	0.9998	0.16	0.49
Chrysene	0.0842	-4.15	0.9996	0.16	0.47
Benzo[b]fluoranthene	0.1162	-1.30	0.9999	0.05	0.14
Benzo[k]fluoranthene	0.3592	-3.89	0.9991	0.13	0.40
Benzo[a]pyrene	0.0997	-3.01	0.9993	0.18	0.54
Dibenz[a,h]anthracene	0.1200	-3.60	0.9991	0.15	0.47
Benzo[g,h,i]perylene	0.0421	-2.06	0.9993	0.10	0.30
Indeno[1,2,3-cd]pyrene	0.0884	-2.62	0.9989	0.23	0.68

* Not detectable by fluorescence

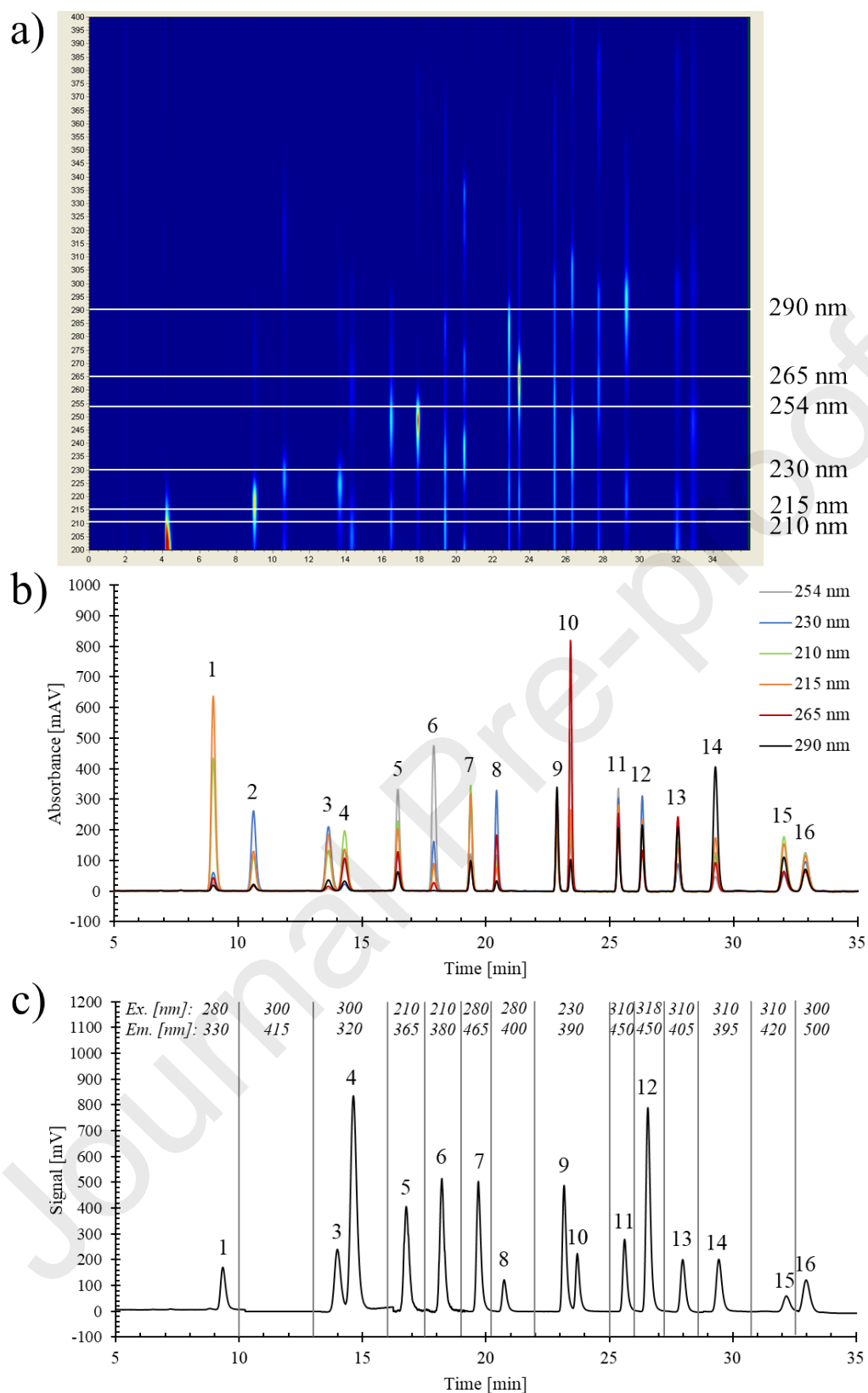


Fig. 3. Exemplary data obtained using the developed method (a) DAD map recorded for the standard of 16 PAHs (20 $\mu\text{g/mL}$ in $\text{CH}_2\text{Cl}_2\text{:MeOH}$ (50:50)) with selected wavelengths for the validation of the HPLC-DAD method, (b) exemplary DAD chromatograms at selected

wavelengths for the standard of 16 PAHs (20 $\mu\text{g/mL}$ in $\text{CH}_2\text{Cl}_2:\text{MeOH}$ (50:50)) and (c) exemplary FLD chromatogram with selected excitation and emission conditions for the standard of 16 PAHs (500 ng/mL in $\text{ACN}:\text{H}_2\text{O}$ (50:50)). Elution order: 1 – naphthalene, 2 – acenaphthylene, 3 – acenaphthene, 4 – fluorene, 5 – phenanthrene, 6 – anthracene, 7 – fluoranthene, 8 – pyrene, 9 – benz[a]anthracene, 10 – chrysene, 11 – benzo[b]fluoranthene, 12 – benzo[k]fluoranthene, 13 – benzo[a]pyrene, 14 – dibenz[a,h]anthracene, 15 – benzo[g,h,i]perylene, 16 – indeno[1,2,3-cd]pyrene.

This type of measurement allowed the PAHs detection at a concentration level between 0.05 ng/mL and 0.23 ng/mL (according to LOD) and determination of all analytes in the range of 0.23-0.68 ng/mL (according to the LOQ value). A very good fit to the measurement points was obtained, reaching more than 0.999 presented as the coefficient of determination R^2 for most cases, while the linear range for each substance was from 0 to 500 ng/mL . Obtained parameters fully support the use of a developed method for the analysis of air samples in the presence of compounds from the EPA-PAHs group. Replicate injections of the PAH mix showed the production of stable and reproducible results. Unfortunately, the acenaphthylene was not detectable in any of the considered combinations of excitation and emission wavelengths.

Figures 3b and 3c show exemplary chromatograms registered with DAD and FLD, respectively. The first one, Figure 3b, presents the composite of signals recorded for six wavelengths (210, 215, 230, 254, 265, and 290 nm) for the mix EPA-PAHs standard with a concentration of 20 $\mu\text{g/mL}$. Such a combination of signals allows for a better presentation of the separation in the analysed analytical system than the standard recommended wavelength - 254 nm. Signals for some substances invisible at this wavelength are exposed by signals collected under different measurement conditions. An exemplary chromatogram for FLD detection was measured for mix standard at 500 ng/mL in $\text{ACN}:\text{H}_2\text{O}$ (50:50). Excitation/emission setting was used to enhance signals registered for considered compounds and the setting was presented at the chromatogram to simplify the interpretation of the applied procedure. In both cases, the time needed to record the full chromatogram was equal to 35 minutes. The order of elution of the compounds was as follows: 1 – naphthalene, 2 – acenaphthylene, 3 – acenaphthene, 4 – fluorene, 5 – phenanthrene, 6 – anthracene, 7 – fluoranthene, 8 – pyrene, 9 – benz[a]anthracene, 10 – chrysene, 11 – benzo[b]fluoranthene, 12 – benzo[k]fluoranthene, 13 – benzo[a]pyrene, 14 – dibenz[a,h]anthracene, 15 – benzo[g,h,i]perylene, 16 – indeno[1,2,3-cd]pyrene. The retention

time (RT) values for each substance with both detection methods were collected and reported in Table S7. The developed method was used for further research.

4.2. Measurement of PAHs in synthetic samples

In the next stage, the performance of the developed methods (MC-ICM and MC-ICM/CDM) was checked on the basis of the analysis of the results for the synthetic sample with a given concentration (25 ng/mL). Tables ts8 and ts9 show the results obtained with both approaches for one selected substance - naphthalene.

For the MC-ICM method, two estimations of c_1 (by interpolation) and c_2 (by extrapolation) are calculated. Based on the data collected in Table S8, it can be concluded that both estimations are statistically equal to each other and are also equal to the expected value. This confirms there are no interference effects. If there were a multiplicative effect, it would be compensated by calculating the concentration c_2 . Based on this method, very good accuracy ($RE < 1\%$) and precision of the obtained results ($CV < 1\%$) were obtained.

The developed method in the CDM version allowed to obtain six estimations of the analytical result by interpolation, extrapolation, and semi-extrapolation. Also, in this case, there was no situation indicating the occurrence of interference effects. If a multiplicative effect occurs, then the exact result is defined as the mean of the semi- and purely- extrapolation estimations. Comparing the means of the c_1 - c_6 and c_3 - c_6 , very good accuracy and precision were also shown ($RE < 0.3\%$, $CV < 0.3\%$).

Assuming that it is more reliable to use extrapolation values in analytical systems with unknown interferences, the results for each substance were determined using both methods (Table 3).

Relative error values for the MC-ICM method ranged from -0.41% to 1.27%, while for the MC-ICM/CDM method, they were between -0.21-0.56%. This proves the comparable accuracy of the results as well as the correct operation of both calibration approaches. Due to the greater possibilities of data interpretation of the approach in the CDM version (especially in multiplicative and non-linear effects), it was decided to use it for measurements of air samples collected after the combustion of selected natural and synthetic (polymer) materials.

Table 3. Final results obtained for the determination of 16 PAHs in the synthetic sample with both methods MC-ICM and MC-ICM/CDM.

Analyte	MC-ICM			MC-ICM/CDM		
	c_2 [ng/mL]	RE [%]	CV [%]	c_{3-6} [ng/mL]	RE [%]	CV [%]
Naphthalene	25.01±0.10	0.06	0.39	25.08±0.07	0.30	0.26
Acenaphthylene*	-	-	-	-	-	-
Acenaphthene	25.14±0.22	0.57	0.88	25.06±0.08	0.26	0.31
Fluorene	25.21±0.16	0.85	0.62	25.14±0.02	0.56	0.07
Phenanthrene	25.00±0.35	-0.01	1.39	25.11±0.08	0.42	0.34
Anthracene	24.90±0.08	-0.41	0.32	25.09±0.08	0.35	0.33
Fluoranthene	25.23±0.21	0.91	0.82	25.08±0.08	0.32	0.31
Pyrene	25.03±0.03	0.12	0.11	25.12±0.06	0.46	0.25
Benz[a]anthracene	25.10±0.42	0.38	1.65	24.95±0.04	-0.21	0.16
Chrysene	25.17±0.14	0.67	0.54	24.92±0.02	-0.10	0.08
Benzo[b]fluoranthene	25.29±0.37	1.18	1.45	25.03±0.06	0.14	0.25
Benzo[k]fluoranthene	25.32±0.44	1.27	1.74	25.11±0.07	0.46	0.28
Benzo[a]pyrene	25.20±0.15	0.80	0.59	25.02±0.03	0.10	0.14
Dibenz[a,h]anthracene	25.23±0.15	0.93	0.65	25.04±0.05	0.18	0.18
Benzo[g,h,i]perylene	25.10±0.15	0.41	0.60	24.99±0.02	-0.03	0.09
Indeno[1,2,3-cd]pyrene	15.10±0.21	0.40	0.83	25.00±0.01	0.00	0.06

* Not detectable by fluorescence

Expected value: 25.00 ng/mL.

4.3. PAHs determination in air samples

Types and amounts of EPA-PAHs released during the combustion of natural and synthetic materials were investigated with the use of the MC-ICM/CDM approach. As a reference sample (ts1), the air from outside in Katowice (Poland) region during the summer was collected and analysed. Natural forest fires were simulated by burning thuja needles (ts2) as the main component responsible for PAHs formation. In order to show the incineration of garbage by household users or landfill fires, several materials representing the greatest risk were tested. The following synthetic materials were considered: polystyrene (ts3), expanded polystyrene (ts4), PET (ts5), polyurethane foam (ts6), styrene-butadiene rubber (ts7), polycarbonate (ts8), plywood board (ts9), and synthetic mineral oil (ts10).

The obtained results were analysed in accordance with the principles of the method described in the conceptual part. After the calculation of six estimations for each substance within each sample, the means of all estimations (c_1-c_6) were compared with the mean of the extrapolated values (c_3-c_6). Table ts10 shows exemplary data obtained for anthracene with a PET sample. In this, as well as in most cases, statistically significant differences were observed during the

comparison of the two means. Such differences indicate the occurrence of multiplicative interference effects. As the final result, the mean of the extrapolation estimations should be taken into account.

Additionally, in some cases, there were differences between the results obtained with the same calculation method, e.g., between c_1 and c_2 determined by interpolation, which indicates the occurrence of small non-linear effects. Exemplary calibration graphs for two selected compounds for different samples have been collected in Figure 4. While analysing the results, another arrangement of the calibration plots was observed. Calibration lines obtained by extrapolation overlapped the interpolation lines if there were small analytes concentrations in the analysed sample. If a higher concentration of PAH compounds were present, these curves were shifted to higher values of analytical signals along the y axis.

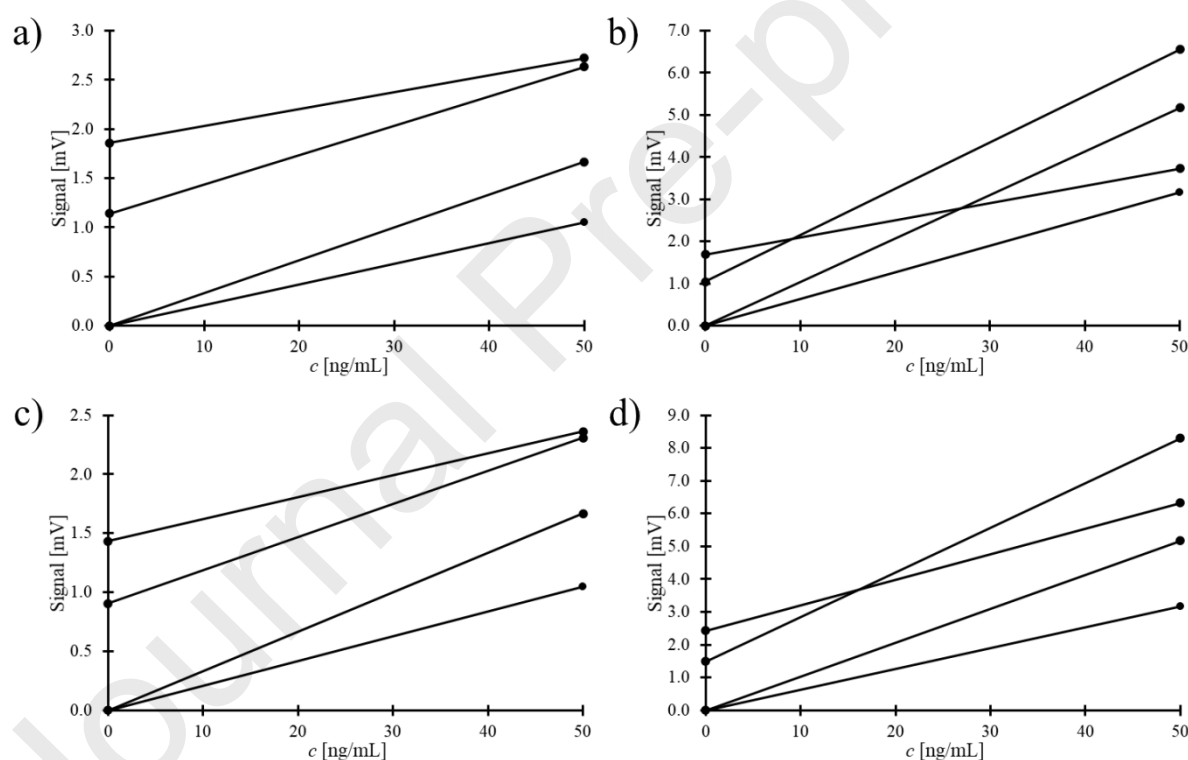


Fig. 4. Exemplary calibration curves according to MC-ICM/CDM method for (a) pyrene in sample ts2 (thuja needles), (b) benz[a]anthracene in sample ts2 (thuja needles), (c) pyrene in sample ts5 (PET, mineral water bottles), and (d) benz[a]anthracene in sample ts5 (PET, mineral water bottles).

In addition, in some cases, the lack of intersection of the extrapolation diagrams in the considered range was observed, as shown in Figures 4a and 4c, which may be due to the presence of slight non-linearities generated by other compounds formed during combustion.

According to the procedure described above, the performed analysis for all considered compounds within each material was used to determine the final results as the mean of c_3 - c_6 . The summary of the results is presented in Table 4 and Figure S2 for visual interpretation. For each sample, the concentrations of the analysed substances were above the LOQ.

Natural needles from conifers (ts2) were recognized as the most harmful and hazardous material combusted in the experiment. Its smoke sample contained naphthalene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, and chrysene in very high concentrations. They were several times higher than the other samples considered, which shows how significant a threat is forest fires, especially coniferous forests, for the lives of humans, animals, and the environment. Naphthalene, phenanthrene, and anthracene are compounds found in each of the plastic samples. Additionally, in the case of polystyrene (samples ts3 and ts4), the presence of acenaphthene, fluorene, and anthracene was noticed. PET (ts5), widespread in everyday life, used for the production of fibers, dishes, food packaging, small fittings and housings for electronic devices, also turned out to be a harmful material. Its smoke contained the same hydrocarbons that are produced during fires in coniferous forests. A similar risk is generated by the combustion of polycarbonate (ts8) products (present in layers that make glass panes resistant to breaking, information carriers such as CDs and DVDs), and in furniture boards (ts9) impregnated with various chemicals and varnishes. On the basis of results obtained for samples ts1-ts9 it can be concluded large amounts of PAH will be released when mixed waste consisting of many different plastics are combusted.

To facilitate the interpretation of the processes taking place, tabular and diagrammatic presentation of results for studied samples are included in Table 4 and Figure S3, respectively. The test samples ts2 to ts10 are placed in the middle of the diagram. The hydrocarbons formed in the amount exceeding 10 ng/mL were identified in the upper and lower parts. Then, the given sample was combined with the compound generated in an amount consistent with the above assumption. On this basis, a complex map was created showing what type of sample causes a given compound. Such a map may be helpful for further studies on the combination of simulated combustion conditions for the formed compounds when extended to other materials and their mixtures.

This work is the first article on PAH determination, which, in addition to an important environmental goal, focuses on reliable results. In the case of studies on the formation of PAHs

as a result of the combustion of various materials and their detection in the air [21,28,29], no analysis of the accuracy and precision of the results was carried out, and even more so, no discussion was made regarding the interferences. PAHs are usually determined using one technique without carrying out any reference method analyses. In the case of the determination of these compounds by chromatographic techniques, there are no reports on methodological approaches to improve the quality of analytical results. The increase in accuracy is related to the possibility of obtaining six estimations of the analytical result in various ways (interpolation, semi-extrapolation, and extrapolation in MC-ICM/CDM). On this basis, it is also possible to fully compensate for interference effects of a multiplicative nature. The comparison between interpolation and extrapolation estimations allowed accurate values to be determined. Such comparisons are not made in standard analyses presented in the literature (most often external calibration). Without access to other analytical techniques, it is possible to increase the reliability of the results obtained by comparing results calculated in various ways.

Based on a comparison of several estimations of the analytical result, it is possible to eliminate errors resulting from the coelution of other substances, reaching even a dozen percent, for which no information is obtained based on the results only of the EC method.

The advantage of the research described in this paper is also the comparison of various plastic materials with natural sources, such as coniferous plant material in the context of PAH formation during combustion. It would seem that the combustion of plant material (conifers) is relatively safe; however, it causes the formation of large amounts of PAH compounds. Particular attention should be paid to the type and amount of PAHs generated in the case of combustion of materials mixed with various kinds of plastic as well as various natural materials.

Table 4. Final results for tested samples as the mean of the c_3 - c_6 estimations.

Analyte	Final results [ng/mL] (CV [%])									
	ts1	ts2	ts3	ts4	ts5	ts6	ts7	ts8	ts9	ts10
Naphthalene	84.98±1.96 (2.30)	916.87±37.56 (4.10)	232.20±5.81 (2.50)	113.45±1.16 (1.02)	279.11±2.08 (0.74)	8.94±0.14 (1.55)	68.31±1.20 (1.75)	53.89±1.34 (2.49)	106.39±1.01 (0.95)	94.18±1.33 (1.41)
Acenaphthylene*	-	-	-	-	-	-	-	-	-	-
Acenaphthene	16.57±0.11 (0.66)	38.96±0.92 (2.37)	6.65±0.06 (0.90)	22.62±0.69 (3.06)	7.78±0.25 (3.18)	18.29±0.32 (1.75)	9.49±0.20 (2.06)	11.33±0.21 (1.88)	28.77±0.49 (1.69)	9.64±0.06 (0.62)
Fluorene	10.72±0.09 (0.82)	132.52±1.14 (0.86)	62.82±0.44 (0.70)	8.26±0.03 (0.35)	126.23±0.82 (0.65)	6.19±0.05 (0.87)	44.07±0.31 (0.70)	16.64±0.22 (1.34)	19.82±0.19 (0.95)	16.53±0.28 (1.70)
Phenanthrene	12.12±0.42 (3.49)	384.72±5.34 (1.39)	111.06±3.08 (2.77)	64.02±0.29 (0.45)	165.09±1.50 (0.91)	24.39±0.47 (1.92)	37.99±0.51 (1.33)	67.04±0.30 (0.44)	42.80±0.08 (0.19)	44.18±0.06 (0.15)
Anthracene	12.87±0.17 (1.33)	366.26±3.63 (0.99)	27.51±1.41 (5.11)	59.31±0.46 (0.78)	118.79±0.84 (0.71)	66.71±1.27 (1.90)	55.28±0.21 (0.38)	63.40±1.59 (2.51)	66.94±1.67 (2.50)	71.85±1.16 (1.62)
Fluoranthene	2.71±0.07 (2.48)	51.43±0.45 (0.87)	6.62±0.08 (1.18)	10.60±0.32 (3.06)	49.97±0.40 (0.81)	4.63±0.03 (0.61)	4.08±0.04 (0.93)	13.96±0.01 (0.04)	10.73±0.21 (1.95)	8.95±0.20 (2.22)
Pyrene	1.06±0.04 (4.00)	64.25±0.83 (1.29)	9.71±0.17 (1.73)	7.67±0.05 (0.60)	50.00±0.70 (1.40)	10.43±0.41 (3.94)	4.19±0.04 (1.01)	16.93±0.26 (1.55)	34.96±0.49 (1.40)	9.27±0.08 (0.83)
Benz[a]anthracene	1.45±0.02 (1.23)	20.50±0.34 (1.67)	5.03±0.06 (1.10)	2.01±0.09 (4.46)	18.50±0.47 (2.56)	2.70±0.06 (2.27)	6.25±0.05 (0.73)	9.49±0.03 (0.36)	5.76±0.09 (1.62)	4.68±0.08 (1.80)
Chrysene	3.52±0.05 (1.37)	35.43±0.88 (2.48)	10.33±0.11 (1.05)	11.07±0.50 (4.49)	12.20±0.17 (1.39)	7.61±0.08 (1.06)	10.72±0.07 (0.65)	16.54±0.10 (0.60)	14.46±0.18 (1.27)	9.72±0.14 (1.43)
Benzo[b]fluoranthene	0.73±0.03 (4.08)	2.51±0.03 (1.26)	1.29±0.02 (1.23)	1.19±0.04 (3.61)	5.62±0.07 (1.20)	0.89±0.03 (3.18)	1.10±0.03 (2.46)	1.27±0.02 (1.66)	1.16±0.02 (1.50)	0.57±0.02 (2.66)
Benzo[k]fluoranthene	0.57±0.01 (1.67)	1.61±0.03 (1.58)	0.53±0.01 (2.81)	1.03±0.03 (2.47)	3.03±0.00 (0.16)	0.37±0.01 (1.91)	0.53±0.01 (2.18)	0.82±0.02 (2.56)	0.77±0.01 (1.46)	0.35±0.01 (3.87)
Benzo[a]pyrene	0.43±0.03 (6.40)	3.61±0.10 (2.76)	0.90±0.02 (1.71)	0.82±0.01 (1.19)	7.46±0.07 (0.93)	0.89±0.01 (1.06)	1.03±0.01 (1.32)	2.09±0.03 (1.38)	1.03±0.01 (0.85)	0.89±0.02 (1.91)
Dibenz[a,h]anthracene	0.39±0.06 (16.60)	0.97±0.01 (1.22)	0.65±0.01 (1.82)	0.73±0.05 (7.31)	0.98±0.02 (2.16)	0.97±0.02 (1.67)	1.14±0.05 (4.48)	2.29±0.02 (1.04)	1.56±0.02 (1.14)	0.78±0.01 (1.09)
Benzo[g,h,i]perylene	1.37±0.02 (1.52)	3.01±0.25 (8.44)	0.87±0.04 (4.32)	1.29±0.07 (5.23)	5.04±0.05 (1.03)	3.81±0.14 (3.65)	5.51±0.17 (3.02)	6.57±0.11 (1.67)	5.95±0.14 (2.30)	3.39±0.04 (1.17)
Indeno[1,2,3-cd]pyrene	1.80±0.05 (2.83)	1.50±0.04 (2.96)	0.95±0.06 (6.15)	2.07±0.01 (0.44)	2.23±0.06 (2.79)	1.25±0.05 (4.29)	1.50±0.04 (2.37)	1.95±0.05 (2.41)	2.09±0.05 (2.63)	1.63±0.02 (0.93)

* Not detectable by fluorescence

4.4. Evaluation of the developed method in the context of the RGB model

The developed chromatographic method (HPLC-DAD-FLD) for EPA-PAHs determination in the air supported by the MC-ICM/CDM approach was assessed in terms of analytical utility using the RGB model [56]. The model is an extension of the concept of green analytical chemistry (GAC) and takes into account the assessment of the method in terms of three parameters: analytical performance - Red, compliance with the “green” chemistry principles - Green, and productivity/practical effectiveness - Blue.

The assessment of the method was performed using a standard Excel worksheet adjustable to the particular method specifications (published in SI of [56]). The evaluation procedure of the analytical method was carried out in accordance with the algorithm in several steps (from 1 to 8):

1. Rank the primary attributes: R (analytical performance), G (safety/eco-friendliness), and B (productivity/practical effectiveness) by assignment of individual W values (according to their subjective meaning). Template worksheet: it can be done by removing all excess rows.
2. Select the criteria by which the method will be assessed for R, G, and B attributes. Template worksheet: it is recommended to select at least three criteria (for keeping a simple format and considering the method's various aspects).
3. Rank the importance of the chosen criteria (by assignation w values in R, G, and B attributes). Template worksheet: the sum of w values should be 10. It can be done by merging rows and columns (every criterion should be represented by one cell at size given by W values and w values, vertical and horizontal dimensions, respectively).
4. Specify the “lowest acceptable value - LAV ” and “lowest satisfactory value - LSV ” for each criterion and the stipulated thresholds useful in a critical method evaluation.
5. Enter the values (determined experimentally or calculated with high accuracy; possible approximations/predictions should be clearly defined in the description) obtained by the method in each criterion in the “Result” cells.
6. Evaluate critically the method by ascription the values from 0 to 100 in each criterion in “Score” cells. LAV and LSV should be used as a reference. If a result is equal to LAV or LSV , 33.3 or 66.6 should be used.
7. Color the individual rectangles (black for <33.3 ; gray for <66.6 and ≥ 33.3 ; red, green, or blue for ≥ 66.6).
8. Read the algorithm results - method brilliance (MB), including the final color and color score (CS) values for each attribute.

The final color of the method is selected based on the following criteria:

- White - method is a good candidate of choice for all applications ($R \geq 66.6$, $G \geq 66.6$, $B \geq 66.6$).
- Magenta - it may be the method of choice if no “greener” alternatives are available ($R \geq 66.6$, $G < 66.6 \geq 33.3$, $B \geq 66.6$).
- Yellow - it may be the method of choice if the number of planned analyses is relatively low ($R \geq 66.6$, $G \geq 66.6$, $B < 66.6 \geq 33.3$).
- Cyan - it may be the method of choice if the requirements concerning quality of analytical result are less stringent ($R < 66.6 \geq 33.3$, $G \geq 66.6$, $B \geq 66.6$).
- Red - it may be the method of choice if the number of planned analyses is relatively low, and if no “greener” alternatives are available ($R \geq 66.6$, $G < 66.6 \geq 33.3$, $B < 66.6 \geq 33.3$).
- Blue - it may be the method of choice if the requirements concerning quality of analytical result are less stringent, and if no “greener” alternatives are available ($R < 66.6 \geq 33.3$, $G < 66.6 \geq 33.3$, $B \geq 66.6$).
- Green - it may be the method of choice if the number of planned analyses is relatively low, and if the requirements concerning quality of analytical result are less stringent ($R < 66.6 \geq 33.3$, $G \geq 66.6$, $B < 66.6 \geq 33.3$).
- Colorless (Gray) - method utilization may be conditionally considered, if no better methods are available ($R < 66.6 \geq 33.3$, $G < 66.6 \geq 33.3$, $B < 66.6 \geq 33.3$).
- Black - appropriate method utilization is doubtful, it is defective on account of one or more primary attributes ($R < 33.3$, $G < 33.3$, $B < 33.3$).

The individual parameters for the evaluation of the method were selected in to make a reliable assessment, especially in the context of the accuracy of the results obtained, which was the main goal of the work. Other aspects, in line with the assumptions of the model, were also taken into account. First, individual W parameters were assigned to primary attributes: R (analytical performance, assessed typically by a classical validation process) – $W=4$, G (safety/eco friendless, which includes aspects of GAC) – $W=3$, and B (productivity/practical effectiveness) – $W=3$. The first scenario was red due to considering the quality of analytical results as the most important. Then, the criteria according to which the method will be evaluated for three primary attributes were selected. There were ranked using individual w values of each characteristic (for R: Accuracy (RE) $w=4$, Precision (CV) $w=2$, Linearity range $w=2$, LOD $w=2$; for G: Amounts of chemicals $w=4$, Chemical safety/hazards $w=4$, Other hazards $w=2$; for B: Cost-effectiveness $w=3$, Time-effectiveness $w=3$, Malfunction risk $w=2$, Sample material consumption $w=2$). In the next step, the lowest acceptable value (LAV), which corresponds to score 33.3, and the lowest satisfactory value (LSV) corresponding to the score 66.6 were defined for each criterion. The experimental values obtained from the method were written. The score 0 points out the

total distortion of the method and is the opposite of the score 100, representing no better method with similar good results. The most crucial element was the critical value of the developed method in the range of 0-100 in relation to the selected *LAV* and *LSV* values. The outcomes of the analysis are presented in Table S11.

The obtained parameters points out that the developed method is satisfactory in red, green, and blue areas. Color scores (*CS*), ranging from 0% to 100%, for R, G and B were equal to 79.8%, 72.7%, and 67.9% ($\geq 66.6\%$ is named satisfactory range, $\geq 33.3\%$ is tolerance range), respectively. Particularly important is to obtain the highest value for analytical performance (R), which is consistent with the aim of the article - obtaining results with increased accuracy. The final parameter – method brilliance (*MB*), a quantitative parameter integration of all three scales, was 73.9%, and the obtained color method is White. This indicates that the proposed method is complete and coherent and is a good candidate for other/different applications. In other words methods is satisfactory in three considered parameters: Red (analytical performance), Green (compliance with the GAC), and Blue (productivity/practical effectiveness). Short annotation of the method is 73.9white, but long annotation is 73.9white(79.8/4red-72.7/3green-67.9/3blue). A particular contribution to the value of *MB* is made by the method's ability to produce results with increased accuracy and precision. The increase in the accuracy of the results obtained in the present method is related to the self-verification of several estimations obtained for the sample, which was confirmed in the analysis with the use of the RGB model.

5. Conclusion

This work describes an HPLC method validation with DAD and fluorescence detection for rapid and sensitive determination of EPA-PAHs in different air matrices. On the basis of conducted studies, it can be concluded that developed integrated calibration method adapted to multi-component analysis, especially in complementary dilution method, can be a helpful and effective analytical tool. In comparison to commonly used methods (external calibration, standard addition method), the proposed approach enables improvement of accuracy of analytical results, achieving a relative error rate of less than 1%, with a precision of less than 3%. The most important advantage of this method is the ability to eliminate multiplicative interference effects from additional substances present in the sample.

In this work, the proposed methodological approach was tested on the example of determining EPA-PAHs in air samples with the use of HPLC-DAD-FLD, obtaining low limits of detection and quantification and a very good linear range. Simulated combustion processes of selected

natural and plastic materials were carried out to investigate the risks posed by natural forest fires, landfill fires, or waste incineration by household users. It has been proven that coniferous forest fires cause the greatest risk. At the same time, the impact on the formation of EPA-PAHs in plastics is varied and plays a significant role in producing these harmful substances. It has been proven that the greatest amounts of such compounds as naphthalene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, and chrysene are formed. From the point of view of usability as well as compliance with the principles of green analytical chemistry, the developed method was assessed using the RGB Additive Color Model for Analytical Method Evaluation proposed in recent years. On this basis, it was found that the method can be described as the White – method is a good candidate of choice for all applications. The proposed methodological approach can be successfully adapted to routine laboratory practice, where samples with a complex matrix influence the recorded signals. Also, the measurement technique can be extended to many others commonly used in analytical chemistry, e.g., mass spectrometry, atomic techniques, spectroscopy, or electrochemistry – due to relatively simple calibration solution preparation step, through easy calculation and interpretation stages.

In the case of biological and medical research, due to the very small number of samples, we suggest using the integrated calibration method in the basic version, which also allows comparing the estimations of analytical results obtained by interpolation and extrapolation. In other cases, however, it seems more sensible to use the methods in the CDM version because of obtaining more information from the analytical point of view. We believe that the implementation of these approaches will enable to solve many problems occurring in analytical practice.

Despite the significant advantages of the developed approach, it does not solve all problems from an analytical point of view. Further research will include extension by gradual dilution method to eliminate non-linear effects and by combining with (Chemical-)H-point standard addition method ((C-)HPSAM) in order to eliminate interference effect of an additive character. Defining the way of calculating the uncertainty budget for estimations of analytical results obtained with the application of the proposed method is an urgent matter. The reason for this situation is the nature of the obtained estimations calculated in interpolative, semi-extrapolative, and extrapolative ways. The most promising direction of future research seems to be the application of chemometric methods (e.g., parallel factor analysis (PARAFAC), multilinear partial least squares (N-PLS), multivariate curve resolution-alternating least-squares (MCR-ALS)) to the proposed calibration approaches. This type of direction can be particularly useful

in the case of incomplete separation in the recorded chromatograms. Integrated calibration method applied to analytical calibration based on second-, third-, and higher-order data may become a universal tool in analytical work in the future.

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Competing interests

The authors declare no competing interests.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Author contribution

PŚ. Designing and performing the experiments, data collection and analysis, writing the paper, supervising all aspects of the project. **JO.** EEM experimental and data handling. **SM.** Sample collection, investigation.

CRediT author statement

PŚ: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Resources, Writing - Original Draft, Writing - Review & Editing, Visualization, Supervision, Project administration, Funding acquisition.

JO: Investigation, Writing - Review & Editing, Visualization.

SM: Investigation, Resources, Writing - Original Draft.

Supplementary materials

Supplementary materials associated with this article can be found, in the online version, at doi:

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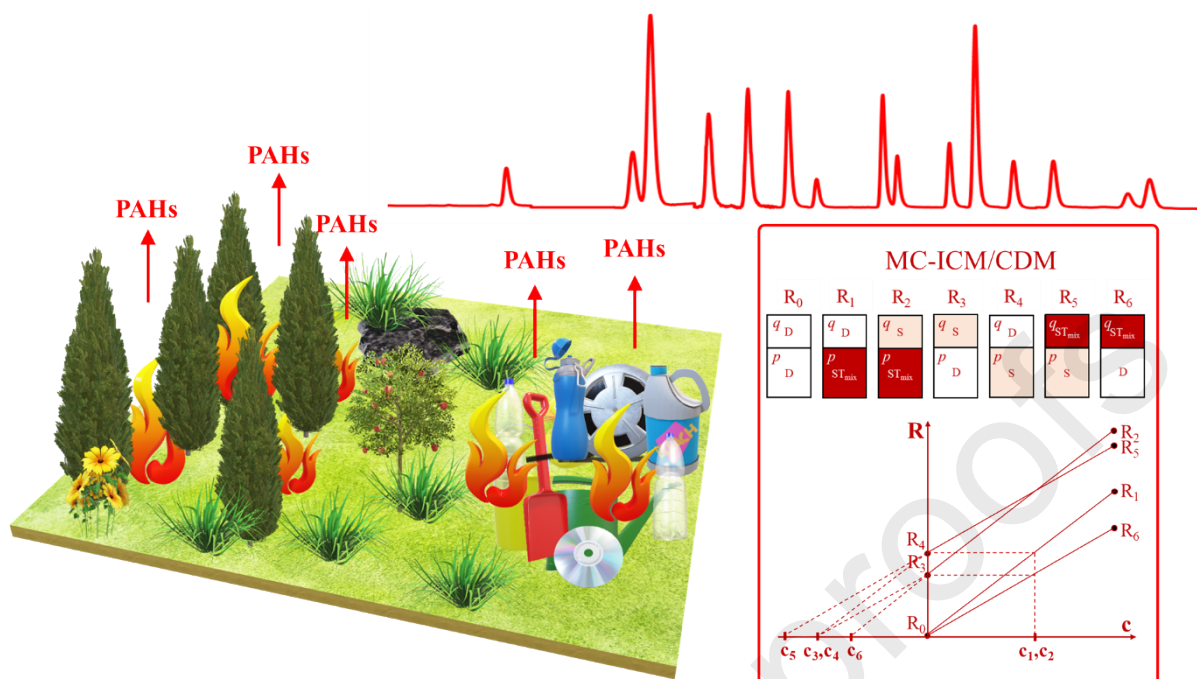
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Graphical abstract



Highlights

1. Novel calibration approach for monitoring of hazardous materials is proposed.
2. Integrated calibration method was adapted to multicomponent analysis.
3. Method is applied to the determination of polycyclic aromatic hydrocarbons.
4. Utility of the method is confirmed by analysis of air samples in simulated fires.
5. Method is White (RGB model) – is a good candidate of choice for all applications.

CRedit author statement

PŚ: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Resources, Writing - Original Draft, Writing - Review & Editing, Visualization, Supervision, Project administration, Funding acquisition.

JO: Investigation, Writing - Review & Editing, Visualization.

SM: Investigation, Resources, Writing - Original Draft.

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