CHEMICAL ENGINEERING TRANSACTIONS

VOL. 57, 2017

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Sauro Pierucci, Jiří Jaromír Klemeš, Laura Piazza, Serafim Bakalis
Copyright © 2017, AIDIC Servizi S.r.l.
ISBN 978-88-95608- 48-8; **ISSN** 2283-9216
DOI: 10.3303/CET1757242

Fast Analysis of PAH in Complex Organic Carbon Mixtures by Reconstruction of UV-Visible Spectra

Antonio Tregrossi*, Barbara Apicella, Anna Ciajolo, Carmela Russo

Istituto di Ricerche sulla Combustione, C.N.R, Naples, Italy
a.tregrossi@irc.cnr.it

Polycyclic aromatic hydrocarbons (PAH) are components of complex organic mixtures featuring liquid and solid fossil fuels as well as tars derived from combustion and/or pyrolysis of coal and hydrocarbon fuels. PAH can also be detected at the exhaust of combustion systems, often associated to carbon particulate matter emissions. Due to their high toxicological potential the concentration levels of PAH detection should be very low (order of ppm) to meet the limits provided by the regulation on combustion emissions and atmosphere quality control. The PAH detection is mainly achieved by conventional, mainly chromatographic, analytical techniques applied to the fuel or to the organic carbon extracted from carbon particulate matter. Preliminary extraction, purification and pre-separation methods are the time-consuming methods necessary to isolate the PAH-rich mixtures from whichever organic matrix for further analysis with liquid or gas-chromatography.

In this paper an alternative method based on the UV-Visible spectroscopic technique has been used for the qualification of PAH into the organic carbon associated to particulate matter sampled in fuel-rich sooting flames. In particular, a computing methodology able to solve nonlinearly constrained problems has been implemented on the UV-Visible absorption spectra of the organic material sampled in the soot-forming region of a laminar premixed rich ethylene-oxygen flame. The procedure allowed the good fitting of measured spectra with the spectra reconstructed by a suitable composition of PAH spectra. The methodology considers and evaluates the contribution of individual PAH which altogether better reproduces the fine structure overcoming the absorption background typically observed in the UV-Visible spectra of complex organic mixtures.

1. Introduction

Polycyclic Aromatic Hydrocarbons (PAH) constitute a class of organic species featuring liquid and solid fossil fuels, tars derived from combustion and/or pyrolysis of gas, aerosol produced and emitted from combustion sources. PAH from two- to seven-rings are the individual species recognized as environmental pollutants dangerous for human health (Freudenthal and Jones, 1976) which have customarily been identified by means of condensation and/or filtration of the combustion effluents followed by laborious analytical procedures. Generally, extraction, purification and pre-separation are the preliminary time-consuming methods necessary to isolate the PAH-rich mixtures from whichever organic matrix for further analysis with liquid- or gas-chromatography.

Alternatively, methods based on absorption and fluorescence spectroscopy are promising as fast methods for in-situ and real-time identification of PAH, due to the specific light absorption and fluorescence properties of PAH. The set up of such methods requires the knowledge of the PAH composition and spectroscopic behaviour for the interpretation of complex spectra that are the result of the overlapping of many spectra of individual PAH molecules. In the meanwhile, the study of the spectroscopic behaviour of PAH-loaded mixtures is also useful for getting information about the aromatic nature of that significant fraction of these matrices which usually remains unidentified because constituted of high molecular weight aromatic species not amenable to be analyzed by conventional chromatographic techniques (Ciajolo et al., 1996).To this regard, it is noteworthy that such high molecular weight (unidentified) material could have both a pollutant effect as high or even higher than that of PAH, and could be important in soot formation. In fact, in previous work, the trend of the concentration profiles of these species and of their UV-Visible (UV-Vis) absorptivity indicated a relationship with soot inception in premixed fuel-rich flames (Ciajolo et al., 1996).

Please cite this article as: Tregrossi A., Apicella B., Ciajolo A., Russo C., 2017, Fast analysis of pah in complex organic carbon mixtures by reconstruction of uv-visible spectra, Chemical Engineering Transactions, 57, 1447-1452 DOI: 10.3303/CET1757242

In this framework, the methodology presented in this work is useful for both the evaluation of single PAH as well as for the discrimination of the PAH contribution to the background absorption in the complex UV-Visible (UV-Vis) absorption spectra of PAH-loaded mixtures sampled in sooting flames

2. Methods and Procedures

2.1 Sample preparation

In order to check the reliability of the method developed in this work a dichloromethane (DCM) solution with a mixture of a dozen of standard PAH was prepared by weighting the single species. The list of PAH constituting the mixture is reported in Table 1.

The sample of flame formed PAH-loaded mixture was obtained by isokinetic sampling in the soot-forming region of an ethylene-oxygen atmospheric premixed laminar flame (C/O=0.8 and cold gas velocity, v_o=4cm/s) and by selecting only the DCM-soluble part of the sampled material (Ciajolo et al., 1996).

2.2 Spectra reconstruction of PAH mixtures

The measured UV- spectrum of PAH mixtures can be reconstructed by a linear combination of the single PAH spectra, measured one by one, weighted by the single PAH mass contribution in the mixture according to Eq(1):

$$\varepsilon_{mix}(\lambda) = \sum_{i=1}^{n_{PAH}} \varepsilon_i(\lambda) \cdot x_i^w \qquad (1)$$

where $\varepsilon_{mix}(\lambda)$ is the mass specific absorptivity (l cm^{-1} g^{-1}) of the mixture at wavelength λ, $\varepsilon_i(\lambda)$ is the mass specific absorptivity of the PAH *i* at wavelength λ, x_i^w is the mass fraction of the PAH *i* and n_{PAH} is the total number of PAH in the mixture. This reconstruction works quite well when carried out on a synthetic PAH standard mixture by adding the UV-Vis spectra of individual PAH scaled by their weight fraction.

2.3 Spectra reconstruction of PAH-loaded flame formed mixtures

The reconstruction procedure described in previous paragraph failed when applied to PAH-loaded mixtures collected in rich premixed ethylene flames and the reconstructed PAH spectrum resulted to contribute partially to the measured spectrum (Ciajolo et al., 1996). This was attributed to the absorption of an unidentified high molecular weight fraction whose presence was confirmed by the fact that the gaschromatographically-measured PAH contribute only partially to the total weight of the mixture.

The PAH fraction, separated as a single class from the rest of the mixture by liquid chromatography, showed a very structured absorption spectrum with a main large peak located in the UV. and a relevant number of minor peaks located in the visible portion of the spectrum. On the contrary, the absorption spectrum of the unidentified rest presented a broader shape peaked in the UV. without the presence of a fine structure in the visible region (Ciajolo et al., 1998).

On the basis of this information, the reconstruction of the UV-Vis spectrum of PAH-loaded mixtures, here reported, has been done assuming the additivity of the components absorptivities taking into account for the weight contribution of the analyzed PAH and considering the unidentified rest as a single component. Moreover, the absorption of this component has been described by a power law, according to the dispersion exponent equation ($\varepsilon(\lambda) = a \cdot \lambda^{-n}$, Millikan, 1961) and its weight contribution is the difference between the total weight and the weight of the identified PAH.

Summing up, the total absorptivity can be considered as the sum of two contributions: the first one due to identified PAH absorption and the second one due to background absorption.

On this basis the Eq(1) was modified to the Eq(2):

$$\varepsilon_{mix}(\lambda) = y_{pah} \cdot \sum_{i=1}^{n_{PAH}} \varepsilon_i(\lambda) \cdot x_i^w + (1 - y_{pah}) \cdot a \cdot \lambda^{-n} \qquad (2)$$

where y_{pah} is the total weight fraction of identified PAH, *a* and *n* are a constant and the dispersion exponent, respectively.

3. Results and Discussion

As regards the reconstruction of the spectrum of the PAH synthetic mixture, the output of the computing procedure, according to Eq(1), was the set of x_i^w. Table 1 reports the mass fractions used for preparing the 12 PAHs mixture components in comparison with the mass fractions as come out from the computing procedure.

Table 1: Measured and computed mass fraction of PAH species in the standard mixture.

PAH Species	x_i^w, measured	x_i^w, computed	Δ_{abs}, %
Acenaphthylene	0.303	0.314	3.8
Benzo*(a)*pyrene	0.012	0.013	7.3
Benzo*(e)*pyrene	0.012	0.012	0.9
Benzo*(g,h,i)*perylene	0.030	0.014	15.3
Ciclopenta*(d,e,f)*phenantrene	0.061	0.027	12.4
Ciclopenta*(cd)*pyrene	0.012	0.064	4.9
Coronene	0.303	0.012	0.9
Fluoranthene	0.061	0.063	3.5
Indeno*(1,2,3,-cd)*pyrene	0.012	0.013	4.6
Naphthalene	0.303	0.304	0.3
Phenanthrene	0.061	0.055	9.2
Pyrene	0.121	0.110	9.4

Table 1 also reports the absolute percentage difference between the measured and computed values. The UV-Vis absorption spectrum of a two-, seven- ring PAH syntetic mixture (12 standard PAH) can be reconstructed by the computer methodology above described as shown in Fig.1 where the measured and the computed specific absorptivity coefficients are reported in the 250-400 nm wavelength range.

The computed PAH spectrum fits very well the measured one (Fig.1) and the set of the mass fraction evaluated by the computing procedure shows a satisfactory agreement with the measured ones, allowing to assess the described procedure as a good semi-quantitative method for the measurement of the PAH content of a mixture. To compute the PAH contribution in PAH-loaded mixtures collected in rich premixed ethylene flames, the UV-Vis spectra of the twenty-six predominant PAH detected in these mixtures (Tregrossi et al., 1999, Allouis et al., 2002) were measured on PAH standards, or recovered from open literature (Clar, 1964, Karcher et al., 1983, Karcher, 1988). All of these spectra were digitized and stored in a database.

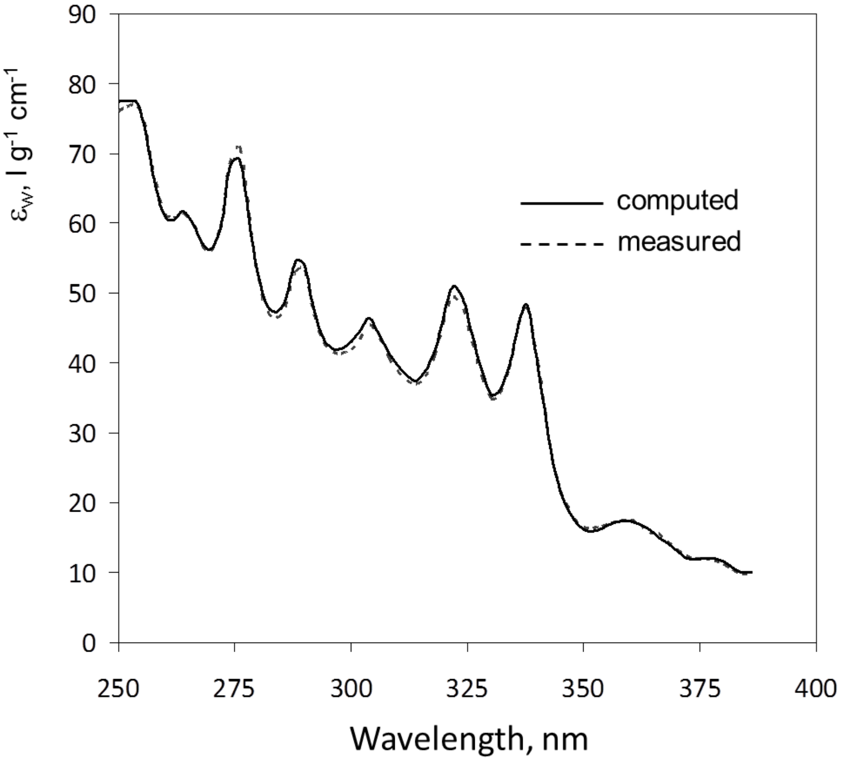

Figure 1: Measured and computed UV-Vis spectra of a synthetic mixture of PAH.

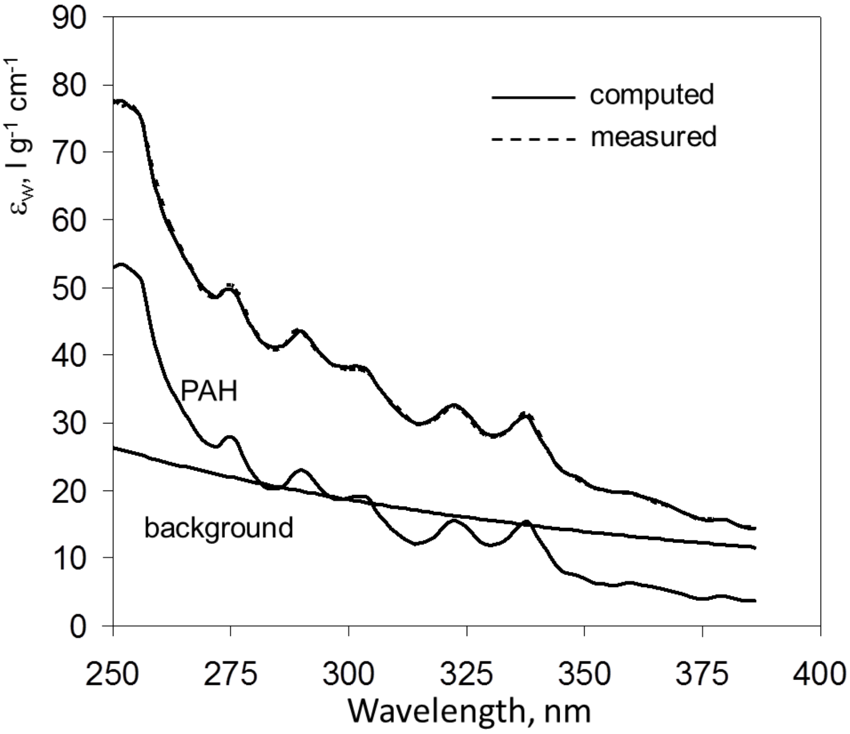

Figure 2: Measured and computed UV-Vis spectra of a PAH-loaded flame formed mixture. The computed spectra of the PAH fraction and of the unidentified high molecular weight fraction are also reported.

Table 2: Measured and computed mass fraction of PAH species in the PAH-loaded flame formed mixture.

PAH Species	x_i^w, measured	x_i^w, computed
2-phenyl-naphthalene	0.000	0.000
Acenaphthene	0.006	0.006
Acenaphthylene	0.206	0.183
Acephenantrylene	0.039	0.060
Anthracene	0.012	0.016
Benzo*(a)*anthracene	0.005	0.004
Benzo*(a)*pyrene	0.020	0.019
Benzo*(b)*fluoranthene	0.006	0.007
Benzo*(e)*pyrene	0.011	0.003
Benzo*(g,h,i)*Fluoranthene	0.042	0.087
Benzo*(g,h,i)*perylene	0.031	0.013
Benzo*(k)*fluoranthene	0.008	0.017
Biphenyle	0.010	0.011
Biphenylene	0.042	0.018
Ciclopenta*(d,e,f)*phenantrene	0.028	0.048
Ciclopenta*(cd)*pyrene	0.094	0.024
Coronene	0.006	0.015
Crisene	0.006	0.006
Dibenz*(a,h)*anthracene	0.000	0.000
Fluoranthene	0.047	0.030
Fluorene	0.032	0.043
Indeno*(1,2,3,-cd)*pyrene	0.020	0.003
Naphthalene	0.168	0.241
Phenanthrene	0.050	0.067
Phenol	0.000	0.003
Pyrene	0.054	0.074

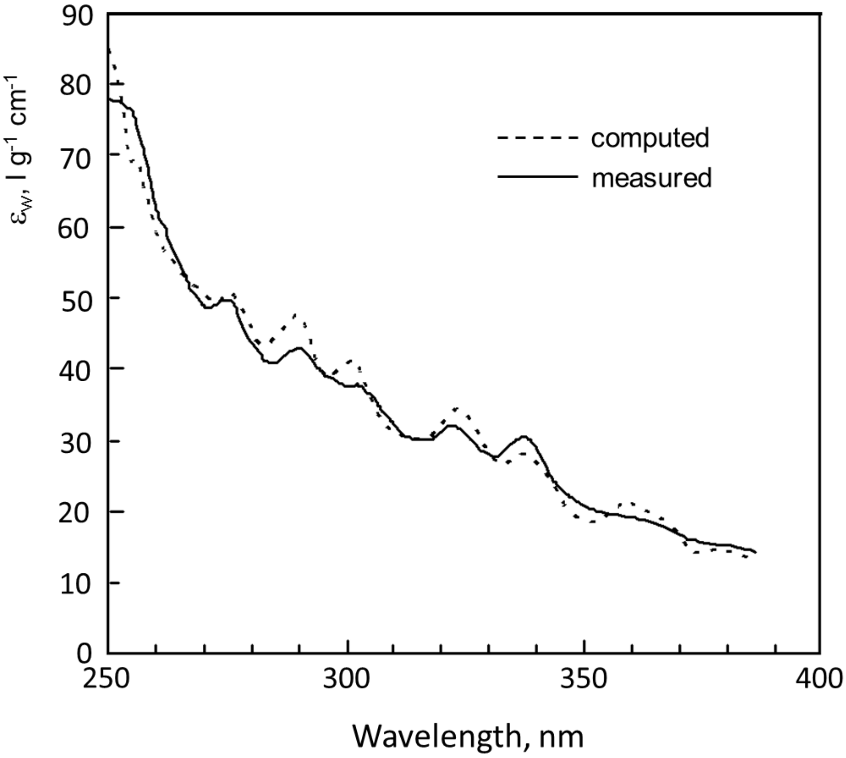

Figure 3: Measured and computed (according to Eq(1)) UV-Vis spectra of a PAH-loaded flame formed mixture.

The PAH composition, as measured by gas-chromatography, was also inserted in the program as starting set of PAH weight fractions. The output of the reconstruction procedure, accordingly to the Eq(2), were the set of x_i^w, the PAH fraction y_{pah}, and the two parameters of the power dispersion law, *a* and *n*. It is noteworthy that the value of *n* was about 1.9 that is a typical value for these materials (D'Alessio et al., 1973).

The absorption spectrum of a PAH-loaded mixture collected in a premixed rich ethylene flame is partially justified by the computed spectrum of identified PAH even though the fine structure of the spectra of computed PAH reproduces quite well the fine structure of the measured spectrum. Consequently, a background contribution has been added (Eq. (2)) to recompose the measured spectrum as shown in Fig.2 where the measured and computed absorption profiles of a typical PAH-loaded mixture are reported together with the relative contributions of identified PAH and background.

Table 2 reports the set of mass fractions of the PAH species as results from the calculations for the PAH-loaded flame formed mixture. The value of the total weight fraction of identified PAH, y_{pah}, was around 0.5, in agreement with gas-chromatography measurements (Ciajolo et al., 1998).It is evident that the absorption profile, computed taking into account the presence of a background absorption, fits quite well the measured absorption profile whereas an attempt of reconstructing the measured spectrum by considering only the identified PAH contribution did not perfectly reproduce the fine structure of the spectrum. This is shown in Fig.3 where the measured absorption spectrum and the spectrum computed considering, according to Eq(1), only PAH as absorbing species are reported. More importantly, the reconstruction by using only the absorption of identified PAH has to be discarded because the program gave out a set of PAH weight fractions too different from that measured by gas-chromatographic analysis.

4. Conclusions

A computing methodology solving nonlinearly constrained problems has been used to reconstruct UV-Vis absorption spectra of PAH-loaded mixtures sampled along a laminar premixed rich ethylene-oxygen flame. This procedure allowed to discriminate between the various contributions to the total absorption, quantifying the weight concentration of predominant PAH present in a synthetic PAH-loaded mixture. A calibration performed on a mixture of a dozen of PAH has demonstrated that the program well reconstructs the UV-Vis absorption spectrum of the mixture, by introducing small variations to the set of initial weight fractions, allowing to assess the described procedure as a good semi-quantitative method for the measurement of the PAH content of a mixture.

The same computer methodology, applied to a flame-derived PAH-loaded mixture, showed the need of adding a background contribution in order to give a good reconstruction of the UV-Vis spectrum. This supports the hypothesis of the contribution of heavier aromatic species not identifiable by conventional techniques accompanying the formation/emission of PAH from combustion processes.

Acknowledgments

The authors accomplish this work with funding of the Ricerca di Sistema Elettrico MSE-CNR project.

References

Allouis C., Apicella B., Barbella R., Tregrossi A., Beretta F., Ciajolo A.; 2002, Soot and PAH formation in the rapeseed oil spray combustion; Clean Air, 3, 53-68.

Ciajolo, A., D'Anna, A., Barbella, R., Tregrossi, A. and Violi, A., 1996, The Effect of Temperature on Soot Inception in Premixed Ethylene Flames, Twenty-Sixth Symposium (International) on Combustion/The Combustion Institute, 2327–2333.

Ciajolo, A., Barbella, R., Tregrossi, A. and Bonfanti, L., 1998, Spectroscopic and Compositional Signatures of PAH-loaded mixtures in the soot inception region of a premixed ethylene flame, Twenty-Seventh Symposium (International) on Combustion/The Combustion Institute, 1481–1487.

Clar, E., 1964, Polycyclic Hydrocarbons, Academic Press Inc.

D'Alessio, A., Di Lorenzo, A., Beretta, F., Venitozzi, C., 1973, Optical and chemical investigations on fuel-rich methane-oxygen premixed flames at atmospheric pressure, 14, 1, 941-953.

Freudenthal, R.I., Jones, P.W., Eds., 1976, Polynuclear aromatic hydrocarbons: Chemistry, metabolism, and carcinogenesis. New York: Raven Press.

Karcher, W., Fordham, R.J., Dubois, J.J., Glaude, P.G.J.M. and Lighart, J.A.M., 1983, Spectral Atlas of Polycyclic Aromatic Compounds, vol.1, D.Reidel Publishing Company.

Karcher, W.,1988, Spectral Atlas of Polycyclic Aromatic Compounds, vol.2, Kluwer Academic Publishers.

Millikan, R.C., 1961, Optical Properties of Soot, Journal of the Optical Society of America, 51, 6, 698-699.

Tregrossi, A., Ciajolo, A., Barbella, R., 1999, The combustion of benzene in rich premixed flames at atmospheric pressure, Combustion and Flame, 117, 553–561.