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Application of Normal and Derivative Ultraviolet Absorption Spectroscopy for the Determination of Six Polyaromatic Hydrocarbons in Tigris River

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Abdul Latif M. Raouf, Kafa Kh. Hammud, Hadi K. Dahaam, Jassim M. Mohammed, Mohammed Khalil, Issam Shakir, Salwan S. Ibrahim
Ministry of Science and Technology, Baghdad, Iraq

Abstract

The aim of this study is to find a suitable analytical method for determination of some polyaromatic hydrocarbons (PAHs) in different locations in Tigris river. Six of PAHs are studied according to Environment Protection Agency, which are Naphthalene, Anthracene, Acenaphthene, Acenaphthylene, Phenanthrene, and Fluorene. Ultraviolet - Visible technique is applied by using normal and derivative spectra to find a suitable wavelength for qualitative and quantitative measurements for each compound. The calibration curve for the standard solution for the six PAHs (0.1-100) ppm gave linearity (0.979-0.999).

The proposed method was applied on different samples from Tigris river. High level of contamination caused by PAHs was detected in these samples in comparison with a previous study.

Keywords: polyaromatic hydrocarbons, derivative spectroscopy, Tigris river, pollution

Introduction

Polyaromatic Hydrocarbons PAHs, an important group of organic micropollutants (xenobiotics) due to their widespread distribution in the environment (atmosphere, water and soil) [1-3], have received considerable attention because of their documented carcinogenic and mutagenic properties [4, 5] in experimental animals of several species [6]. They are produced by incomplete combustion of fuels as well as by diagenetic processes during fuel formation and possibly microbiological synthesis.

Due to their chemical and physical properties PAHs, especially the higher molecular weights, are hardly degradable and tend to accumulate in the different environmental compartments [7]. Several analytical methods are applied for PAHs studies, such as capillary gas chromatography with mass spectrometric detection [8], thin – layer chromatography in combination with fluorescence detection scan techniques [9], supercritical fluid chromatography with ultraviolet detection [10], capillary electrophoresis with fluorescence detection [11], and high performance liquid chromatography coupled with fluorescence detection [12].

Water pollution by organic compounds, many of which are known to be toxic or carcinogenic, has caused considerable concern worldwide. Because streams, rivers, lakes, and ponds are frequently used for potable water supplies, the contamination of water source is particularly undesirable. The limit of the maximum concentration of PAHs in drinking water is 0.2 ppb [13-15], and in raw water is 1 ppb [16], so the determination of PAHs in environmental samples has become an important topic.

Several techniques have been reported for the extraction and concentration of PAHs from water and other phase materials such as soxhlet extraction, ultrasonic extraction, liquid – liquid extraction, solid phase extraction, supercritical fluid extraction and cloud point extraction [17-22]. The first three methods require high concentration of toxic organic solvents and are time – consuming. But the latter two methods require considerably less solvent with expensive and complicated procedures.

Derivative spectrophotometry is an analytical technique of great utility for extracting both qualitative and quantitative information from spectra composed of unresolved bands by using the first or higher derivatives of absorbance with respect to wavelength. It offers an alternative approach to the enhancement of sensitivity and specificity in mixture analysis [23]. Several typical PAHs are determinated in diesel fuel [24], in various gas oils and their separated fractions [25] and in suspended solid and sediments of water [26] by using derivative spectrophotometry.

The aim of the present work was to optimize and validate the ultraviolet – visible method after the extraction of six PAHs (Naphthalene, Anthracene, Acenaphthene, Acenaphthylene, Phenanthrene, and Fluorene) from water samples.

Experimental:

- **Chemicals:** Naphthalene, Anthracene, Acenaphthene, Acenaphthylene, Phenanthrene, Fluorene were from BDH chemicals Ltd Poole, England, while anhydrous calcium chloride and Dichloromethane were from (Fluka Chemicals, Switzerland.
- **Apparatus:** Ultraviolet – Visible spectrophotometer (UV- 1650 PC- Shimadzu, Japan).
- **Environmental Sampling:** During the first ten days of May 2009, nine water samples were collected in clear plastic bottles from several locations of Tigris River in Baghdad City, Iraq.
- **Extraction [27]:** Aliquots of the samples were filtered. To 40 mL of the filtered water was added 5 mL Dichloromethane in the separating funnel. The mixture was shaken vigorously for 2 min. and allowed to separate and settle. The organic layer was removed then dried by passage through anhydrous calcium chloride and the process repeated with same aqueous layer for another time.
- **Preparation of Standard solution and Calibration:** The stock standard solution was prepared by dissolving 0.1gm of each PAHs in 100 mL dichloromethane, and calibration standard of (0.1-100) ppm were prepared from the stock solution for normal, first, and second derivative spectra.

Results and Discussion:

- **Linearity, Precision, and Detection Limits**

The linearity of the suggested method was tested by ultraviolet spectrophotometer for normal, 1st, and 2nd derivative spectra by determining standard solutions with increasing concentration, a calibration range (0.1-100) ppm of PAHs standards.

Table -1- gives calibration plots and analytical features for determination of PAHs using normal, 1st, and 2nd derivative spectra and linearity of them.

- **PAHs concentration in Tigris River raw and drinking water**

Nine real samples were sampled from Tigris River in five different locations in Baghdad city (capital of Iraq) before and after the water treatment process done. The monitored results for real samples by normal ultraviolet spectra, as an example, listed in table -2-.

The results in table -2- show that:

I. High pollution limits of these six PAHs are found in Tigris River that has been used by human, animal, and plant and they were out of allowed limits which increase the risk of cancer cases.
II. Phenanthrene was undetectable in all locations with this method, but it can be detected with other extraction and determining methods.
III. The purification method which is applied in Dura electric power station and Dura refinery is not only ineffective but also increases the concentration of these PAHs.
IV. Total concentration in all location is out of allowed limits.

In comparison with the results in a previous study [28]that showed the concentration of all 16 PAHs in Iraq environment, especially the 6 PAHs in Tigris River, Baghdad city, it is easy to recognize the increase of concentration from the time of that study (2003) and this study (2009) because of many known reasons.(see table-3-)

To explore the efficiency of this method, three hypothetical polluted samples with these six PAHs prepared and tested. The first was prepared by adding 0.5 gm of each six PAHs in 1.5 L of tap water in clear plastic bottle (tap water from our lab, organic research department, ministry of science and technology, Jadriyia, Baghdad, Iraq) then extracted and analyzed with ultraviolet spectrophotometer after 13 days.

The second hypothetical sample was 10 mL of gas oil (used in the same location to generate electricity) in 1.5 L of the same tap water in clear plastic bottle then extracted and analyzed after 13 days.

The third sample was 0.5 gm of each six individual PAHs in 1.5 L tap water in clear plastic bottles from the lab extracted and analyzed after 10 days. Table -4- listed the results as normal ultraviolet spectra determining the six PAHs in the hypothetical samples.

Table -4- summarizes the concentration of all six PAHs in tap water after /or more than 10 days in a clear plastic bottle in open environment affected with changing in temperature, time, and light. The main reason to prepare these hypothesized samples was to observe the effect of these parameters on changing on concentration of PAHs especially the effect of 10 mL of gas oil in 1.5 L tap water can be noticed in increasing the concentration then increasing the pollution in Iraqi water.

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Table -1-: Calibration plots and analytical features for determination of PAHs using normal, 1st, and 2nd derivative spectra and linearity of them.

PAH	Normal ultraviolet spectra		1st derivative ultraviolet spectra		2nd derivative ultraviolet spectra	
	λ_{max}, nm	Linearity,R^2	λ_{max}, nm	Linearity,R^2	λ_{max}, nm	Linearity,R^2
Acenaphthene	290.0	0.994	295.8	0998	321.4	0.999
Acenaphthylene	339.6	0.999	292.4	0.999	326,6	0.994
Anthracene	358.4	0.999	380.0	0.999	358.6	0.999
Fluorene	300.5	0.996	304.0	0.992	305.5	0.997
Naphthalene	287.0	0.999	291.5	0.986	293.5	1.000
Phenanthrene	294.5	0.979	298	0.990	294.5	0.986

Table-2-: The concentration of the six PAHs determined by normal ultraviolet spectra for the collected samples from Tigris River (in ppm).

Location	Acenaphthene	Acenaphthylene	Anthracene	Fluorene	Naphthalene	Phenanthrene	total
A1	6.31	5.15	2.23	8.29	10.26	*	32.24
A2	*	0.68	*	1.89	*	*	2.57
A3	*	*	*	0.65	*	*	0.65
A4	0.13	o.65	*	2.44	0.45	*	3.67
A5	*	*	*	0.58	*	*	0.58
A6	*	0.68	*	2.04	*	*	2.72
A7	*	1.35	0.46	2.00	*	*	3.81
A8	*	0.76	*	1.46	*	*	2.22
A9	*	*	*	0.31	*	*	0.31

*: not detected with this method, A1: refinement station Kreeat area- before purification, A2: refinement station Kreeat area- after purification, A3: Dura electric power station- before purification, A4: Dura electric power station- after purification, A5: Dura refinery- before purification, A6: Dura refinery – after purification, A7: Diyala River- old bridge, A8: Tigris – Diyala coming together, A9: our lab- organic research department, ministry of science and technology, Jadriyia, Baghdad, Iraq

Table -3-: Concentration of the six PAHs determining in raw and drinking water in Tigris River (µg/L) by using rapid phase high performance liquid chromatography#.

PAH	Dura refinery	Dura electric power station	Diyala River, Rustamia
Acenaphthylene	*	*	*
Anthracene	0.17	*	*
Fluorene	2.12	*	*
Naphthalene	*	*	*
Phenanthrene	*	1.7	7.8

#condition of rapid phase high performance liquid chromatography: column (supelcosil LC-PAH, 150.0x4.6 mm ID), mobile phase: Acetonitrile –water, gradient elution, flow rate: 1mL/min., temperature: 35°C, wavelength: 254 nm.

Table -4-: The Concentration of the six PAHs determining by normal Ultraviolet spectra in the hypothetical samples (in ppm).

Hypothetical sample	Acenaphthene	Acenaphthylene	Anthracene	Fluorene	Naphthalene	Phenanthrene
First	47.85	15.18	3.79	36.77	76.03	31.36
Second	57.69	12.15	3.51	54.06	85.74	46.61
Third	49.94	7.32	29.05	56.96	81.39	45.59

تطبيق مطيافية النموذجية والاشتقاقية للأشعة فوق البنفسجية في تقدير ست مركبات هيدروكاربونية أروماتية متعددة الحلقات في نهر دجلة

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عبد اللطيف محمد رؤوف ، كفاء خلف حمود ،هادي كريم دحام، جاسم مهدي محمد، محمد خليل، عصام شاكر، سلوان سفيان إبراهيم
وزارة العلوم والتكنولوجيا – بغداد – العراق

الخلاصة

يهدف البحث إلى إيجاد أفضل الطرائق التحليلية المناسبة لقياس تراكيز بعض المركبات الهيدروكاربونية الاروماتية متعددة الحلقات في مواقع مختلفة من نهر دجلة. تم اختيار ست مركبات هيدروكاربونية أروماتية متعددة الحلقات والمصنفة ضمن وكالة البيئة الأمريكية وهي Naphthalene, Anthracene, Acenaphthene, Acenaphthylene, Phenanthrene, Fluorene كما تم تثبيت طريقة تحليلية لغرض تحديد تراكيزها باستخدام طريقة المشتقة الطيفية لتقنية امتصاص الأشعة فوق البنفسجية لاختيار الأطوال الموجية المناسبة للمركبات ومن ثم التقدير الكمي لها.

أعطت هذه المركبات منحنيات معاير قياسية لتراكيز (0.1-100) جزء من المليون انحدارا خطيا بمدى (0.979-0.999) للطريقة النموذجية والاشتقاقية بالمرتبة الأولى والثانية .طبقت هذه الطرائق على نماذج مائية لمواقع مختلفة من نهر دجلة وتبين وجود تراكيز عالية من التلوث بهذه المركبات العضوية وبمقدار يزيد عن الحد المسموح به ومقارنة مع دراسة سابقة استخدمت تقنية تحليلية مختلفة.