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Study the effect of positively charged natural ions on analytical figures of Merits of fluorometric analysis of Naphthalene and Anthracene in aqueous solution

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Keywords: PAHs, fluoresces, AFOM, LOD, Natural ions

Abstract:
The effect of natural ions on the fluorescence signal of different PAHs has been studied. the analytical figures of merits have been measured without presence of natural ions, the values of maximum excitation and emission values were determined and the values of LOD and LOQ also measured. The Values of LOD and LOQ were in ppt levels. The second part of the work was determine the analytical figures of merits in the presence of natural ions (calcium, magnesium, potassium and sodium). And the values of LOD and LOQ were measured and a quenching in the fluorescence signal was spotted. Thereby, in the analysis of PAHs in drinking water that include natural ions, have to take in consideration that a higher value of LOD and LOQ will be seen.

KEYWORDS: PAHs, fluorescence, AFOM, LOD, Natural ions, LOQ

1-Introduction: -

PAH (Polycyclic aromatic hydrocarbon) levels in drinking water were found to be around 0.001 mg.ml^{-1}[1-3]. And in ground water more than 0.2 mg.ml$^{-1.}$[4-6]. higher levels of PAHs were found in the industrial areas in ppm levels due to the incomplete composition of hydrocarbons[7-11]. Despite the confirmedprecision and simplicity of the measurement of pg.L^{-1} levels, the pollutant concentrations measurements in gas phase (air) by the fluorescence technique, the wide application of this technique to the quantification of PAHs in drinking water has not been studied[12-14].. Naphthalene, anthracenewere selected as representative PAHs ranging the number of rings[15-20]The selected PAHS were known to be carcinogenic[21-24]. The fluorescence intensityof the selected PAHs in water were measured along with their fluorescence concentration dependency (calibration curve). The fluorescence LOD and LOQ in water were determined in order to compare the sensitivity of the fluorescence technique to its sensitivity in the presence of natural ions.

The approach we present here is based on the collection of excitation emission fluorescence spectra of Naphthalene and Anthracene in aqueous solution in the presence of natural ions. The analytical figures of merits were collected in using fluorophotometer. The obtained results show that fluorescence intensity in the presence of natural ions will be quenched and hence higher value ofLOD and LOQ.

2-Experimental part

Materials and Chemicals

All solvents were Sigma-Aldrich high purity grade. All chemicals were analyticalreagent grade and used without additional purification., Nanopure water was used throughout. Naphthalene and Anthracene were purchased from Sigma–Aldrich. All other chemicals were purchased from commercial sources.

2.1-Preparation of stock solution of PAHs

Stock solutions of Naphthalene and Anthracene were prepared by dissolving 2.0 mg of standards in 20 mL of methanol. All stock solutions were saved in the dark at 5°C. before using, stock solutions were monitored via Room

(

3-Results and Discussion: -

3.1 Fluorescence Spectroscopic Study (no natural ions): -

3.1.1. Ex-Em spectra

Excitation (Ex) and emission (Em) spectra have been obtained by using commercial spectrofluorometer (Shimadzu RF-5301pc). The instrument use Xenon as an excitation source (150W), with wavelength measurement range from 220 to 900 nm.

The Ex and Em spectra were measured for each PAHs by dissolving each compound separately in Nanopure water. And the obtained results were below: -

1. Naphthalene: -

A concentration (75 µg / L) was prepared by dilution of 2.5µL of the 9.9975 mL solution in nanopure water. Then the Ex-Em spectrum of the Naphthalene compoundwere obtained as shown in figure (1).

individual) standard solutions containing each PAH using several concentrations.

Natural ions concentrations: -

Natural ions with different concentrations have been used by adding measured amount of the selected ion to the working solution of PAHs.

temperature fluorescence spectroscopy for possible photo-degradation of the PAHs. All stock solutions were used within 6 months of preparation. Working solutions of PAHs were prepared daily by serial dilution of stock solutions.

4.Anthracene: -

A concentration (5 µg / L) was prepared by dilution of 0.16 µL of the 9.9975 mL solution in Nano-pure water. Then the Ex-Em spectrum of the Anthracene compound were obtained as shown in figure (2).

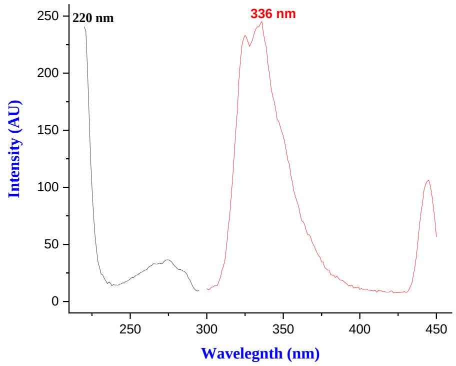

Figure (1) Ex-Em spectrum of Naphthalene

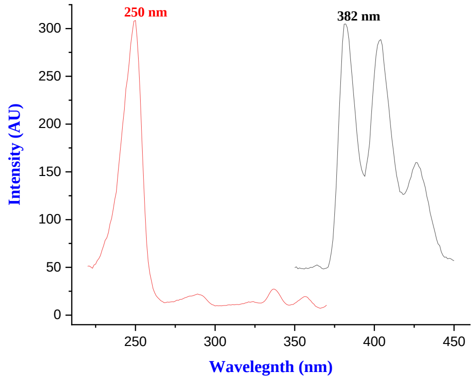

Figure (2) Ex-Em spectrum of Anthracene

2-2. Calibration curve: -

Certain concentrations of each compound were prepared innanopure water using the serial dilution method and the calibration curves were obtained for these compounds by plotting the intensity vs concentration and the obtained results were below: -

The value of the emission intensity was found. Five standard concentrationsof each PAH (Naphthalene and Anthracene) were used and the relationship between the emission intensity and concentration were shown in figure 3 and4 for Naphthalene and Anthracene respectively.

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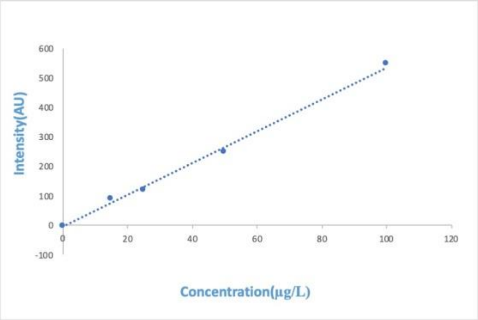

Figure (3) Calibration curve of Naphthalene

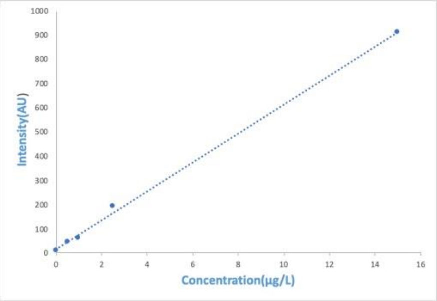

Figure (4) Calibration curve of Anthracene

4.1 analytical figures of Merits (AFOM) of fluorescence detection No natural ions

The analytical figure of merits for the detection of Naphthalene and Anthracene in aqueous solution (free from natural ions) has been measure and the values were in table below: -

Table (1) AFOM for PAHs in aqueous solution (no natural ions)

Name of compound	LOD µg/L	LOQ µg/L	R^2	RSD%	Ex-Em nm
			-		
Naphthalene	0.773	2.57	0.9955	2.3	249 – 382
Anthracene	0.0161	0.0539	0.9981	2.8	220 – 336

1. Fluorescence Spectroscopic Study (with natural ions): -

The Ex-Em spectra of the selected PAHs has been measured after adding a known concentration from natural ions which reflect the normal natural concentration in drinking bottled water. The figure 5 and6 represent a comparison between the signal obtained before and after adding natural ions for Naphthalene and Anthracene respectively using Sodium ion. The obtained results show that there is a significant reduction in signal after adding the natural ions.

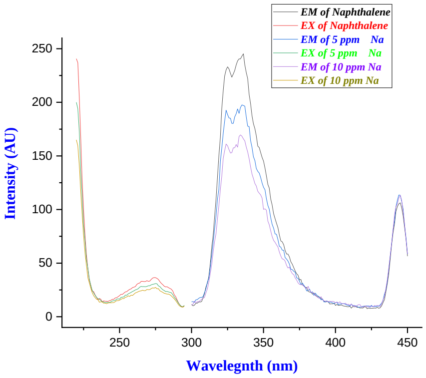

Figure (5) Ex-Em spectrum of Naphthaleneafter adding the sodium ions

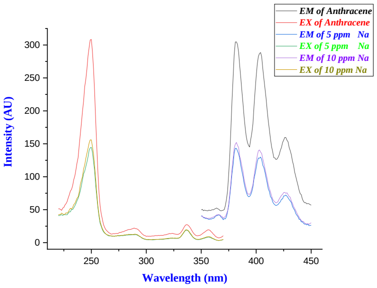

Figure (6) Ex-Em spectrum of Anthracene after adding the sodium ions

Table (2) show the signal values at maximum excitation wavelength for each compound using different ions and different concentrations

Name of compound	Maximum Excitation Intensity Value (AU)				
	No Natural ions	Calcium ions	Magnesium ions	Potassium ions	Sodium ions

		5mg	10mg	5mg	10mg	5mg	10mg	5mg	10mg
Naphthalene	242	210	205	195	183	197	187	200	167
Anthracene	307	227	209	228	201	147	133	156	144

For the AFOM, table 3 show the obtained values, and the results show that the AFOM values show no improvement for the detection of PAHs in aqueous solution, the reason is that the natural ions will reduce the fluorescence signal which cause higher values for LOD and LOQ, thus lower sensitivity.

Table (3) AFOM for PAHs in aqueous solution (with natural ions)

Name of compound	LOD μg/L	LOQ μg/L	R^2 —	RSD %	Ex-Em nm
Naphthalene	1.995	6.651	0.9959	2.1	220 – 336
Anthracene	0.0711	0.2371	0.994	1.3	249 – 382

Conclusion:

In conclusion, the Analytical figures of merits for analysis of Naphthalene and anthracene in aqueous solutions have been determined with and without presence of natural ions. The obtained results show that the values of LOD and LOQ were slightly higher in the presence of natural ions due to the fluorescence quenching ability of natural ions. future studies required to be designed to precisely assess the presence of naphthalene and anthracene in real water samples.

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