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ORIGINAL PAPER

Spectrofluorimetric Determination of 3-hidroxy-2-naphthoic Acid by Use of Its Ternary Complex with Zirconium (IV) and Beta-Cyclodextrin: Application to Determination in River Water

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Abstract A spectrofluorimetric method has been developed for the determination of 3-hydroxy-2-naphthoic acid (3H2NA) by formation of a ternary complex with zirconium (IV) and β-cyclodextrin (β-CD). It has been observed that the fluorescence intensity of 3H2NA is greatly enhanced when the ternary complex is formed and is accompanied with shifts in the excitation and emission wavelengths. The conditions for the formation of the ternary complex have been optimized and the stoichiometry has been calculated, resulting a 1:2:1 complex (3H2NA:Zr: β-CD). The linear range was 20–2000 ng mL^{-1} and the detection and quantification limits calculated were 17 and 58 ng mL^{-1}, respectively. The proposed method was applied to the determination of 3H2NA in river water. To eliminate interferences an off-line solid phase extraction (SPE) procedure using C18 cartridges was used. The extraction procedure was optimized and good recoveries were obtained (around 100%) with relative standard deviations (RSDs) of less than 5%.

Keywords 3-Hydroxy-2-naphthoic acid · β-Cyclodextrin · Zirconium · Ternary complex

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental pollutants. Due to their carcinogenic/mutagenic properties, these molecules are considered priority pollutants by the Environmental Protection Agency (EPA) and the European Union. For example, a list of 16 PAHs designated as priority pollutants has been published by the EPA. The PAH benzo[a]anthracene, is one of the most toxic compounds of this list. The bacterial degradation of benzo[a]anthracene by Sphingomonas or Pseudomonas produces several metabolites, the principal of which is 3-hydroxy-2-naphthoic acid (3H2NA) [1, 2]. It is noted that this compound is a skin irritant, can cause serious damage to the eye, is a skin sensitizer and there are indications of a teratogenic potential [3].

PAHs can be found in the atmosphere, aqueous media, soil, etc. These compounds are emitted during combustion processes as a result of incomplete combustion and originate from both natural and anthropogenic sources (wood burning, forest fire, fossil fuel, coke oven). These compounds are very persistent in the environment and they can cause ecological damage by entering the food chain [4].

No references have been found for the determination of 3H2NA by HPLC or GC. Only a separation method by capillary zone electrophoresis (CZE) has been proposed for monitoring the impurities of the production of 3H2NA in the industry [5], because 3H2NA is used as precursor for the synthesis of dyestuffs and drugs.

The compound 3H2NA [6–8] has been widely used for the determination of metal ions. For instance, beryllium has been determined by flow-injection analysis after preconcentration on a silica gel micro-column by fluorimetry [6]. This method has also been applied to bronze samples and foundry dust. For the determination of copper (II) in urban atmospheric aerosols, a catalytic spectrophotometry method was developed by Casassas et al. [7]. The sample was first treated with H_2O_2 and 3H2NA in ammonium media. The mixture was heated, then cooled and diluted and after 15 min the absorbance was measured at 425 nm. The determination of scandium has been performed fluorimetrically with 3H2NA [8].

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Others metal ions such as vanadium [9], nickel [10], lanthanoids [11], aluminium [12] or scandium [13] have been determined by the use of 3H2NA derivatives. A factor analysis plus target factor analysis approach was used by Casassas et al. [14] to determine the protonation constants in dioxin/water mixtures.

In general, most of the methods found in the literature have used 3H2NA for the determination of metal ions. Only, an extraction-spectrophotometric method has been proposed by Shi et al. [15] for the determination of 3H2NA in a dye. The dye is dissolved in nitrobenzene and it is mixed with aqueous sodium carbonate. The aqueous phase was treated with DMF and $FeCl_3$ and anhydrous ethanol. The absorbance was measured at 585 nm.

With regard to the analyses zirconium, this metal has been used as an analytical reagent in fluorescence for the formation of complexes with several fluorophores. Thus, different complexes such as Zr-Alizarin Red S-EDTA [16], Zr-Oxalate-Alizarin Red S [17], Sulphate-Calcein-Zr [18], Zr-Morin [19] have been studied. Different surfactants such as hexadecyltrimethylammonium bromide [16], cetylpyridinium chloride [17], Triton X-100 [20] have also been used to enhance the fluorescence of these complexes.

It is well known that cyclodextrins complex a wide variety of analytes into their hydrophobic interior [21, 22]. The most likely mode of binding consists of inclusion of the less polar portion of the guest within the cavity while the polar o hydrophilic part of the guest remains exposed to the solvent. This inclusion often leads in to fluorescence enhancement.

In previous studies, the interaction of 3H2NA with β-cyclodextrin (β-CD) has been reported [23]. The same authors have determined the formation constants of the complex 3H2NA:β-CD in the presence and absence of different buffer systems [24, 25]. In our research group, the interaction between Zr(IV) and 3H2NA was studied, resulting a report of enhanced fluorescence in the presence of 0.1 M of glycine/HCl (pH 2.5) [26]. In both cases, only a theoretical evaluation was performed and no application was developed.

Another study [27] in which the effect of the position of the substituents on the formation of metal complexes with substituted naphthalenes has also been reported. In this study, the complexes formed between 3H2NA and 1-hydroxy-2-naphthoic acid (1H2NA) (positional isomers) with Zr(IV) were reported. While 1H2NA is quenched in the presence of Zr(IV), 3H2NA provided an enhancement. The stoichiometry of the complexes was studied at several pH values.

In the basis of the previous studies reported above, the luminescence characteristics of the inclusion complex of 3H2NA: β-CD in the presence of Zr(IV) has been further investigated. The enhancement of the fluorescence intensity, due to the formation of a ternary complex, has been used to develop a rapid and sensitive spectrofluorimetric method for the determination of 3H2NA in river water.

Experimental

Apparatus

Fluorescence measurements were performed using a Fluorescence Spectrophotometer Varian Model Cary Eclipse, equipped with a Xenon flash lamp. Respective excitation and emission bandwidths of 5 and 10 nm were used in these studies. Intensity was measured at 468 nm (excitation at 368 nm), which is the emission maximum of the 3H2NA:Zr:β-CD ternary complex. All measurements were performed in 10 mm quartz cells at 20°C by use of a thermostatically controlled cell holder and a Selecta Model 382 thermostatically controlled water-bath. A Crison MicropH 501 meter was used for pH measurements.

Reagents and materials

All chemical and solvents used in this study were of analytical grade. Ultra pure water was provided by use of a Millipore Milli-Q system (Millipore, Bedford, MA, USA). 3-hydroxy-2-haphthoic acid, $ZrCl_4$ and β-cyclodextrin were obtained from Sigma.

The standard stock solution of 3H2NA (5.2×10^{-4} M) was prepared in methanol. The 1×10^{-2} M β-CD and 1×10^{-2} M Zr(IV) stock solutions were prepared in the ultra pure water. Diluted solutions were prepared by appropriate dilution of the stock standard solutions. Sep-Pak Plus C18 SPE cartridges filled with 360 mg of packing were purchased from Waters (Milford).

General procedure for fluorescence measurements

An aliquot of 3H2NA solution was placed in a 5-mL volumetric flask and Zr(IV) and β-CD standard solutions were added to give a final respective concentrations of 4×10^{-4} M and 4×10^{-3} M. Then, the solution was diluted with ultra pure water to the mark and the fluorescence was measured at 468 nm (excitation at 368 nm).

Water samples treatment

Two types of water were analyzed: pure water and river water. The river water was collected from the Guadiana River close to Badajoz (Spain); it was filtered before use. An aliquot (50 or 100 mL, $n = 3$), was spiked with the 3H2NA standard. The spiked samples were homogenized by shaking and then passed through a SPE cartridge to extract the analyte. Recovery of 3H2NA standards was determined at four concentration levels (C1–C4). Sample solution C1 contained 2 μg mL^{-1} of 3H2NA. Solutions C2, C3 and C4 were 2, 5, 10 times diluted C1, respectively.

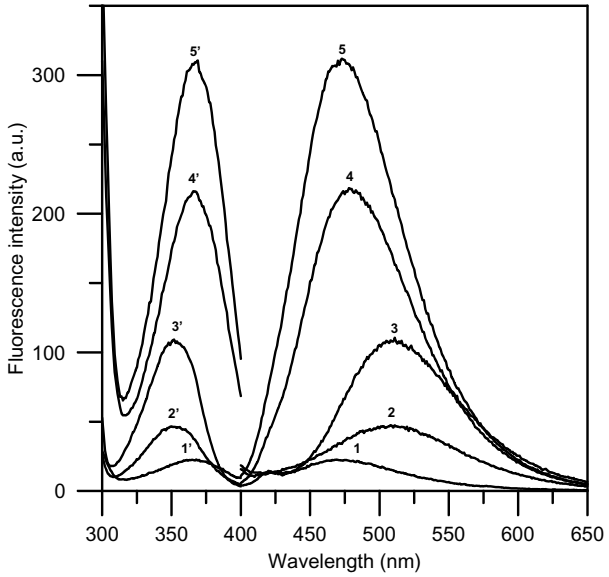

Fig. 1 Excitation (1′...5′) and emission (1...5) spectra for several fluorescence systems: (1′ and 1) Zr:β-CD; (2′ and 2) 3H2NA; (3′ and 3) 3H2NA:β-CD; (4′ and 4) 3H2NA:Zr; (5′ and 5) 3H2NA:Zr:β-CD. [3H2NA] = 500 ng mL^{-1}; [β-CD] = 4×10^{-3} M; [Zr] = 4×10^{-4} M

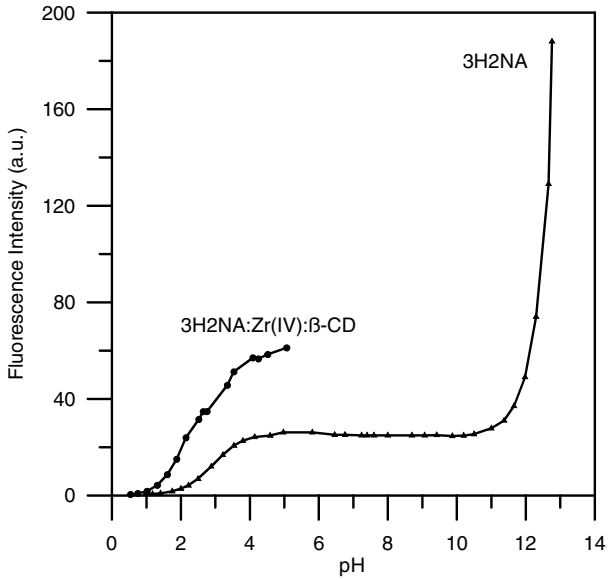

Fig. 2 Effect of pH on the fluorescence intensity of 3H2NA (1) and 3H2NA:Zr:β-CD (2). [3H2NA] = 500 ng mL^{-1}; [β-CD] = 4×10^{-3} M; [Zr] = 4×10^{-4} M

The SPE C18 cartridges were equilibrated with 5 mL of methanol and 5 mL of pure water. Then, the aqueous samples, adjusted to pH 2, were passed through the cartridges. Sample loading was followed by flushing 3 mL of ultra pure water. After that, the cartridges were dried. Finally, the analyte was eluted with 3 mL of methanol and 100 μL of the final extracts were treated as described in the previous section.

Results and discussion

Fluorescence spectra

The emission and excitation spectra of the various fluorescence systems are shown in Fig. 1. It is noted that the fluorescence of 3H2NA (2 and 2′) is weak with emission and excitation maxima located at 350 and 515 nm, respectively. When β-CD is added to the solution of 3H2NA, the fluorescence increases (3 and 3′) and no significant differences in the wavelengths of excitation and emission are observed. However, when Zr(IV) is added to the 3H2NA solution (4 and 4′) the fluorescence increases and a shift of the wavelengths is observed. Thus, while the excitation wavelength has a blue shift of 18 nm, the emission has a red shift of 37 nm.

The highest increase of the fluorescence intensity is observed when the ternary complex is formed (5 and 5′). In this case the wavelengths are the same as for the 3H2NA:Zr complex, i.e. 368 and 478 nm for excitation and emission, respectively.

Effect of surfactants

A survey of the literature shows that surfactants can enhance the fluorescence intensity of the complexes with Zr(IV) [15, 16, 19]. On this basis, a study was performed for addition of different solutions of anionic (SDS), cationic (CTAC, CPC, HTAB) and non-ionic (TX-100) surfactants to the 3H2NA:Zr:β-CD complex, with fixed concentrations of Zr(IV) 1×10^{-3} M, β-CD 2×10^{-3} M and 3H2NA 1 μg mL^{-1}. All surfactants were tested below and above their critical micelle concentration (cmc). When the anionic surfactant was used, it was observed that the solution became turbid. In contrast, a decrease in intensity was observed for the non-ionic (TX-100) surfactant and for several of the cationic surfactants (HTAB, CPC). The intensity remained constant only for CTAC. Thus, the use of surfactants was not considered for additional experiments.

Effect of pH

The effect of the pH on the fluorescence intensity of 3H2NA and 3H2NA:Zr:β-CD is shown in Fig. 2. It is noted that for the analyte the fluorescence intensity increases with the pH until pH 4, then remains constant in the range comprises between pH 4 and 10.5 and afterwards increases again. In the case of the ternary complex 3H2NA:Zr:β-CD the fluorescence increases with pH until pH 4.5. The highest pH values could not be studied due to the appearance of a white precipitate probably from $Zr(OH)_4$.

The changes in the fluorescence intensity with pH allowed the calculation of pK_a values of 3H2NA and the ternary

complex by use of the Strenström and Goldsmith method [28] adapted to fluorescence measurements [29]. Values of 2.7 and 12.6 were obtained for 3H2NA, which are in agreement with the values reported previously by Kovi et al. (2.6 and 13.0) [30]. For the 3H2NA-Zr-β-CD complex, a pK_a of 2.8 was obtained. The values of the pK_a found in the absence and presence of Zr + β-CD are not significantly different. This indicates that in the inclusion complex of the carboxylic group is likely located outside the cavity.

In order to obtain the maximum fluorescence intensity a pH of 4.5 was chosen for further analysis and the effect of different buffers, such as acetic acid-sodium acetate, phosphate buffer, formate acid-sodium hydroxide, sodium tartrate-chloride acid and sodium oxalate-chloride acid were tested. With all buffers used, the fluorescence intensity decreases when the buffer concentration increased. This is in agreement with the studies performed by Johnson and Bernard [31] that reported that some buffers dramatically influence the magnitude of cyclodextrin inclusion of transition metal complexes. In addition, Yi et al. [25] suggested that buffers should not be used in aqueous solutions of cyclodextrins. Finally, a lower pH (3.0) was chosen trying to avoid the formation of a precipitate and this was fixed by adding HCl 0.1 M.

Influence of the zirconium and β-CD concentrations

The effects of the zirconium and β-CD concentration on the fluorescence intensity for solutions containing 5×10^{-6} M of 3H2NA were studied. The fluorescence intensity increases when β-CD concentration increases up to 2×10^{-3} M and then remained at a constant maximum. Thus, a 4×10^{-3} M β-CD concentration was chosen. Using this fixed value, the influence of the concentration of Zr(IV) was examined. Maximum fluorescence intensity was achieved at 1×10^{-4} M of Zr(IV), and then remained constant up to 5×10^{-4} M, decreasing at the highest values. A 4×10^{-4} M of Zr (IV) was selected for further experiments.

Effect of order of addition, temperature and stability of the complex

When the order of addition was studied, no variation in the fluorescence intensity was observed. In all cases, the complex was formed immediately. Nevertheless, for all experiments the order of addition chosen was: 3H2NA, Zr(IV) and β-CD.

The effect of temperature was studied between 5 and 60°C. The fluorescence intensity remained constant up to 30°C and decreased gradually thereafter. Therefore, a temperature of 20°C was used throughout the remainder of these studies. The stability of the complex was studied for several hours and it was concluded that the complex is stable for at least 1 h after the reagents have been mixed.

Stoichiometry and stability constant of the ternary complex

The stoichiometry and stability constants of the ternary complex were studied spectrofluorimetrically under the established conditions by use of the Benesi-Hildebrand [32] method. Firstly, assuming that 3H2NA:β-CD and 3H2NA:Zr(IV) form a 1:1 complexes, the following Eq. (1) is applicable:

$$\frac{1}{(F - F_0)} = \frac{1}{(F_\infty - F_0)K_1[\beta\text{-CD}]_0} + \frac{1}{(F_\infty - F_0)} \qquad (1)$$

When a graph of $1/(F - F_0)$ versus $1/[\beta\text{-CD}]_0$, is plotted, a straight line is obtained, which is indicative of a 1:1 stoichiometry and this is in agreement to the value found by Yi et al. [25], in the absence of Zr(IV). The K value obtained from the ratio of the intercept to slope was 857 L mol^{-1}. With regard to the Zr(IV):3H2NA stoichiometry, in the presence of 4×10^{-3} M of β-CD, when a plot of $1/(F - F_0)$ versus $1/[\text{Zr(IV)}]_0$ is constructed, a downward concave curvature is obtained. In the case where a 2:1 stoichiometry is predominant, the applicable equation is (2):

$$\frac{1}{(F - F_0)} = \frac{1}{(F_\infty - F_0)K_1[\text{Zr(IV)}]_0^2} + \frac{1}{(F_\infty - F_0)} \qquad (2)$$

If a plot of $1/(F - F_0)$ versus $1/[\text{Zr(IV)}]_0^2$ is carried out, a straight line is obtained providing evidence that the stoichiometry of 3H2NA:Zr(IV), in the presence of β-CD, is 1:2, the same as in the absence of β-CD [26]. It was concluded that the composition of the ternary complex was 1:2:1, 3H2NA: 2 Zr:β-CD.

Effect of foreign substances

Several foreign substances were tested as interferences in the determination of 500 ng mL^{-1} of 3H2NA. An interference to analyte ratio of 1000 (M/M) was tested, and if interference occurred, the ratio was gradually reduced until the interference ceased. The results given in Table 1 show the majority of substances which produced interferences. The criterion for interference was fixed at a $\pm$ 5% variation of the average fluorescence intensity calculated for the established level of 3H2NA.

Analytical parameters

Under optimum experimental conditions, there was a linear relationship between the fluorescence intensity and the concentration of 3H2NA in the range of 20–2000 ng mL^{-1} with a correlation coefficient of 0.9971, the linear regression equation was $I_F = 0.437C(\text{ng mL}^{-1}) + 20.18$. The detection and quantification limits, as defined by IUPAC [33, 34] are 17

Table 1 Maximum tolerated concentrations of foreign substance. Conditions: [3H2NA] = 2.6×10^{-6} M; [Zr(IV)] = 2×10^{-3} M; [β-CD] = 4×10^{-3} M

Tolerated concentration* (mol L^{-1}) (3H2NA:interferente) (M:M)	Foreign substance
2.6×10^{-3} (1:1000)	K^+, Cl^-
	NH_4^+, Cl^-
5.2×10^{-3} (1:500)	Al^{3+}, Cl^-
	Ca^{2+}, Cl^-
	Ba^{2+}, Cl
4×0^{-4} (1:150)	Al^{3+}, NO_3^-
	Na^+, CO_3^{2-}
6×10^{-5} (1:25)	Mg^{2+}, SO_4^{2-}
4×10^{-5} (1:15)	Mn^{2+}, SO_4^{2-}
	Fe^{2+}, SO_4^{2-}
1×10^{-5} (1:5)	Fe^{3+}, NO_3^-
2.6×10^{-6} (1:1)	1H2NA
	2,3DHNA
	1,2DHNA

*5% as limit of error

and 58 ng mL^{-1}, respectively. For a series of ten measurements of a solution containing 500 ng mL^{-1} of 3H2NA, the relative standard deviation was ± 3.20 and the relative error was 2.03% (95% confidence level).

Analytical application

The optimized spectrofluorimetric method was applied to the determination of 3H2NA in river water from the Guadiana River. In Fig. 3, the emission spectra corresponding to river water spiked with 3H2NA (500 ng mL^{-1}) (1) and ultra pure water spiked with the same concentration of 3H2NA (2) are

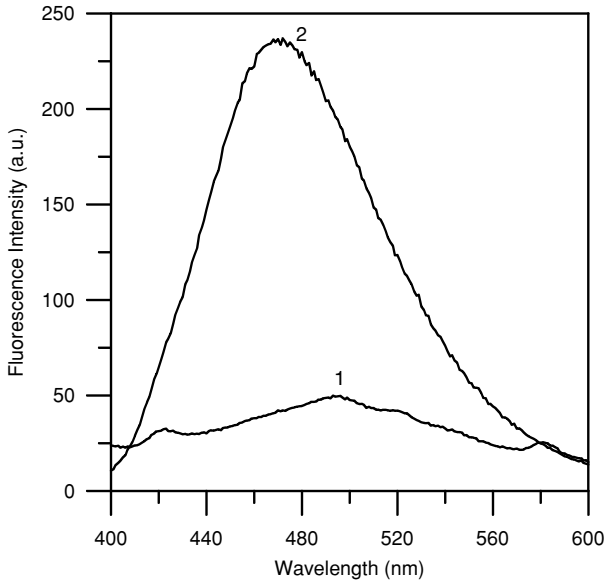

Fig. 3 Emission spectra of river water sample (1) and pure water sample (2) spiked with 3H2NA. [3H2NA] = 500 ng mL^{-1}. λ_{ex} = 368 nm

Table 2 Recoveries obtained for spiked samples at different concentration levels

Sample	Concentration level (μg mL^{-1})	Pure water % R* ± RSD	River water % R* ± RSD
C1	2.0	105.0 ± 2.0	91.5 ± 2.5
C2	1.0	104.5 ± 1.5	99.2 ± 0.3
C3	0.4	107.4 ± 4.0	102.0 ± 1.0
C4	0.2	103.7 ± 3.2	97.3 ± 1.5

*Mean value for three individual samples

shown. As seen, there is a strong matrix effect, and therefore, the determination of the analyte is not possible. Due to this problem and the lower concentration at which PAHs are found in water, an SPE method is necessary to concentrate the analyte and also to eliminate interferences. The optimized method has also been applied to determine the analyte in ultra pure water, in order to compare the recoveries found after SPE procedure for both forms of water and for checking the elimination of interferences.

Four different concentrations levels (C1–C4) were tested. In all cases, 50 mL of water sample were spiked with the analyte of interest and then the SPE procedure (see details in experimental section) was applied. After that, optimum concentration of Zr(IV) and β-CD were added. The spectra were registered and the concentrations were calculated by use of an external standard. In Table 2, the recoveries found for both forms of water are summarized. As can be seen, recoveries are around 100% for the concentration ranges tested. This leads to the conclusion that the applied SPE method eliminates the interferences.

It is worth noting that a study of the retention of 3H2NA was performed at several pH values and pH 2 was chosen to prepare the sample before it was passed through the cartridges because at higher pH values, the analyte was less retained in the cartridges, and recoveries around 80% were obtained.

Moreover, another study was achieved with the aim of testing if the volume of water passed through the cartridges had any influence on final recoveries. For this purpose, three different volumes of river water, 50, 100 and 250 mL, respectively, were spiked with the same volume of 3H2NA, leading to final concentrations of 600, 300 and 120 ng mL^{-1}. The recoveries found were, 101, 97.3 and 105% and the RSDs 1.0, 1.5 and 0.5, respectively.

Conclusions

In this manuscript, a new fluorimetric method for the determination of 3H2NA has been reported. The formation of a ternary complex, among 3H2NA, Zr(IV) and β-CD with stoichiometry of 1:2:1, resulted in enhanced fluorescence. The method was applied to the determination of 3H2NA in

river water. For that procedure, a clean-up of the sample was necessary to remove interferences using SPE. The recoveries were around 100%.

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