PARAFAC TREATMENT IN 3D-FQ OF DOM-[M] COMPLEXATION

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Abstract
The DOM-Metal complexation propriety is accessible by fluorescence quenching (FQ). FQ spectrum can determine the fluorescent DOM composition by parallel factor analysis (PARAFAC) with excitation-emission matrix (EEM). [Cu^{2+}] titration onto a river water sample from Brésil: [C] =5mg/L, initial [Cu^{2+}]=1.68 nM , pH=4.5, [Cu^{2+}]=10^{-9}M~10^{-3}M is done with 50 Excitation and Emission Matrix (EEM) analyzed by PARAFAC, which has extracted 2 fluorescent components from all EEM: C1 (λex=235nm/λem=420-425nm) and C2 (λex=250-260nm and 345-355nm/λem=470-480nm) of which corresponding interatures were obtained by this new approach. It is confirmed that with PARAFAC FQ modification values fluorophores are better distinguished from the whole matrix.
Keywords: Organic Matter, Metals, Analytical Methods, Chemical Analysis, Surface Waters

Introduction

Dissolved Organic Matter (DOM) is a compled mixture existing everywhere in the environment. The studies of DOM in aquatic ecosystems enable us to obtain some information on its coming future and the importance of its role in the bio-geochemical processes. The fluorescence technique makes analyzes possible on the basis of the optical propriety of the DOM including its fluorophores composition and its complexation propriety face to face to certain metal[1]. Recently for luminescence spectrum it is possible to determine the fluorescent component composition by the statistical analysis of parallel factor analysis (PARAFAC) with excitation-emission matrix (EEM)[2].

Methodology

The complexation propriety between DOM and metals is accessible by measuring the fluorescence quenching (FQ) functional to the metal additions. The EEMs in the FQ experiments contain maximal information as a whole of fluorescent DOM (FDOM). This work presents a quenching experience brought from copper ions titration onto a river water sample from Brésil of 5mg/L carbon concentration and 1.68 nano-molaire initial copper ions concentration (pH=4.5). A titration of copper ions ($Cu(NO_3)_2$) has been applied in copper-ions concentration range from 10^{-9}M to 10^{-3}M. Fifty EEM were obtained and gathered in order to analyze the FQ by PARAFAC. This statistical treatment permits us to extract 2 fluorescent components from the whole EEM (Fig.1): C1 (λex=235nm/λem=420-425nm) and C2 (λex=250-260nm and 345-355nm/λem=470-480nm) corresponding to the peaks already described in the literature.

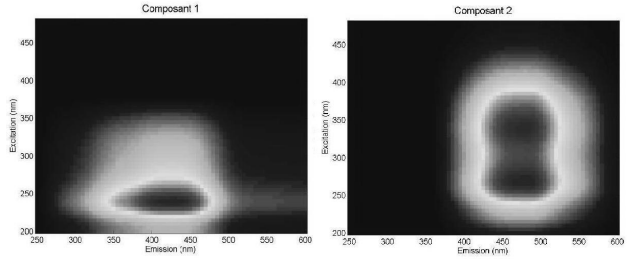

Fig. 1. Component 1 and Component 2 found by PARAFAC

Results and Discussion

Using the participation to the total fluorescence of these peaks, we have observed clearly that the fluorescence diminution was not uniform. The Fig.2 shows the relation between the Fluorescence Intensity Percentages (FI%)on function of logarithmic copper concentration (log[Cu]). The experimental points of Component 1 (C1, rhombus) show a stability near 100% at the begging of the copper ion titration just like those of Component 2 (C2, square) till to 10^{-7}mol/L. From this concentration, the C1 FI% continues decrease till to the end of titraton. But instead of decreation, the C2 FI% increases sharply from 90% to 170%, which dues probablly to the Inner Filter Effect[3] (While NOM concentrated in a sample, some of moleculars absorb the energy emitted by others, which shuts down the observed fluorescent light. This phenomenon is called "Inner Filter Effect", IFE)[3]. The current methods to correct IFE are unuseful in these continuous experimental measurements, although an other correcting idea is putting in the future trying. Anyway, C2 has shown its great fluorescent quenching characters by complexing with metal. The analysis of complexation propriety has found out two complexation compounds values: $K_1=10^{4.6}$; $L_1=10^{-7.8}$ et $K_2=10^{4.46}$; $L_2=10^{-9}$ all for the component C2 (Fig. 1). These results signifies at least 2 complexation compounds giving by a same EEM component. The utilisation of PARAFAC has confirmed the presence of just 2 fluorescence fluorophores but more than 3 complexing sites obeying to the treatment conditions given by Ryan and Weber[4]. Meanwhile, PARAFAC permits to better observe the FQ values' modifications by decomposition of fluorophores contribution from a whole matrix. That is why C2 contains 2 peaks identified: Peak C and Peak A[5]. No fluorophore no-affected by the copper titration has been detected.

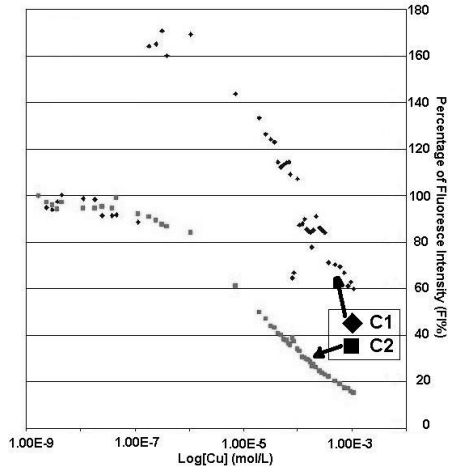

Fig. 2. Relation between fluorescence intensity and logarithmical copper ions concentration (FI%/log [Cu^{2+}])

This new coupled approach organizing the optical fluorescence measurements (FQ), the mathematical data analysis (PARAFAC) and informatical modeling method (PROCESE) permits us to observe a macro image on FNOM composition and to link it to its own micro complexation characters. Application of this approach to mditerranean samples will be in the coming work.

References

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