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Review

Fluorescence Excitation-Emission Matrix Spectroscopy and Parallel Factor Analysis in Drinking Water Treatment: A Review

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Abstract

Fluorescence excitation-emission matrix (EEM) spectroscopy coupled with parallel factor analysis (PARAFAC) is an established tool of organic matter fingerprinting in aqueous systems. Recently, EEM-PARAFAC has been successfully applied in drinking water treatment for simple, rapid, and sensitive evaluation of organic matter removal during different treatment processes. This review describes some recent applications of EEM-PARAFAC in the drinking water industry. It is divided into two sections according to field of application: characterization of organic matter and its removal in drinking water treatment, and determination of contaminants in drinking water.

Keywords: fluorescence spectroscopy, parallel factor analysis, drinking water treatment

Introduction

With the recent advances in spectroscopic techniques, fluorescence spectroscopy has received increased attention in a drinking water treatment industry. However, conventional fluorescence techniques relying on measurement of single emission or excitation spectrum are often insufficient in the analysis of complex water systems. In such cases, total luminescence spectroscopic technique may improve the analytical potential of fluorescence measurements. Total luminescence spectroscopy involves simultaneous collection of fluorescence data over a wide range of different excitation and emission wavelengths. The resulting excitation-emission data matrix (EEM) provides a total intensity profile of the sample over the range of excitation and emission wavelengths scanned. Thus, it is more informative in comparison to the traditional single-scan techniques [1-3].

Analysis of EEMs obtained for a number of samples is often coupled with the application of advanced statistical methods, with parallel factor analysis (PARAFAC) being the most popular [4]. To discuss the PARAFAC model, we consider the fluorescence data arranged in a three-way array $X(I\times J\times K)$ where I refers to the samples, J to the emission wavelengths, and K to the excitation wavelengths. PARAFAC decomposes three-way array $X(I\times J\times K)$ into three bi-dimensional matrices. Two of these matrices are related to the excitation (loading matrix B, $F\times K$) and emission (loading matrix C, $F\times J$) spectral profiles of the F components (fluorophores). The third matrix (scores matrix A, $F\times I$) is related to the variation of the concentration of the F components. This decomposition can be expressed for each element x_{ijk} of the three-way array $X(I\times J\times K)$:

$$x_{ijk} = \sum_{f=1}^{F} a_{if} b_{jf} c_{kf} + e_{ijk}$$

$$i = 1, ..., I;\ j = 1, ..., J;\ k = 1, ..., K$$

...where x_{ijk} is the intensity of the i^{th} sample at the j^{th} variable (emission mode) and at the k^{th} variable (excitation mode), F is the number of components (individual fluo-

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rophore moieties), a_{if} is the ith score for the f^{th} component and is related to the concentration of the f^{th} component in the ith sample, b_{if} and c_{kf} are estimates of the emission and excitation spectrum of the f^{th} component (defined as loadings), respectively, and e_{ijk} is the residual containing the variation not captured by the model [1-4].

Application of the PARAFAC model includes:
(1) initializing and/or constraining the algorithm
(2) establishing the number of components (fluorophores)
(3) identifying the fluorophores
(4) calibrating the model

It is expected that the spectra are non-negative and thus constraining to non-negativity is usually used. The number of components can be estimated by several methods (core consistency, split-half analysis), but for certain systems only experimental knowledge is useful. Identification of the fluorophore is based on a comparison of spectral profiles (loadings *b* and *c*) with the spectra of a standard of the analyte. Calibration model is obtained by least squares regression between the scores (*a*) related to the analyte and the reference concentration of the calibration samples [4, 5].

This review describes some recent applications of EEM-PARAFAC in the drinking water industry. It is divided into two sections according to the field of application: characterization of organic matter and its removal in drinking water treatment and determination of contaminants in drinking water.

Organic Matter and its Removal in Drinking Water Treatment

Drinking water treatment can consist of a raw water treatment by coagulation and flocculation, retention in water reservoir, rapid sand filtration, ozonation, biological activated carbon (BAC) filtration, chlorination, and slow sand filtration. Water samples can be collected from different points along the process. These samples can be used to characterize natural organic matter (NOM) and its temporal variation during drinking water treatment and/or to evaluate the performance of the treatment processes in terms of NOM removal [6].

The presence of NOM in all raw waters causes serious problems in the drinking water treatment – adverse color, taste, and odor; increased harmful disinfection byproduct (DBP) formation and biological growth; and increased levels of complexed heavy metals. The general conclusion is that NOM should be removed from drinking water. As both the quantity and composition of NOM affect the efficiency of its removal, a better characterization of NOM is necessary to optimize the water treatment process [3].

High performance size exclusion chromatography (HPSEC) coupled with an organic carbon detector (OCD), UV, or fluorescence detectors has been widely applied to fractionation and characterization of NOM [6-9]. For example, NOM samples were fractionated into six fractions: humic acids, hydrophobic acids, hydrophobic neutrals, hydrophilic acids, hydrophilic bases, and hydrophilic neutrals [8]. Chromatographic methods provide valuable insight into the nature of NOM, but they are often time consuming and may involve sample pretreatment. Thus, they are not well suited for monitoring NOM in drinking water treatment.

Fluorescence spectroscopy has received increased attention in the drinking water treatment, particularly due to its advantages such as rapid and sensitive characterization of NOM, no sample pretreatment, and the potential for on-line monitoring of NOM reactivity and treatability [3].

Various studies have demonstrated that EEM-PARAFAC may be a successful tool for characterization of drinking water sources/reservoirs or for investigating how the sources/ reservoirs and composition of dissolved organic matter (DOM) changes in both time and space [10-14]. Using asymmetrical flow field-flow fractionation (AF4) and EEM-PARAFAC analysis, physicochemical properties of DOM in the Beaver Lake Reservoir were stratified by depth (3-, 10-, and 18-m below the water surface). While humic-like fluorophores comprised the majority of the total fluorescence at each depth, a protein-like fluorophor was in the least abundance at the 10-m depth [13]. A few PARAFAC studies have been reported on changes in DOM during rain [15] and storm [16] events. For example, Hong et al. [16] observed a decrease in the protein-like component after storm events.

EEM-PARAFAC has been a valuable tool for studying the effect of the coagulation-filtration process on the DOM present in the raw water. The results of PARAFAC model allowed:
(1) determining the most amenable component to be removed in a specific treatment process
(2) establishing the order of preferred removal
(3) identifying recalcitrant components to be removed in a particular treatment stage.

Principal fluorophore groups (two humic-like and two with protein nature) present in the DOM of the raw, treated, and raw-treated combined water were identified through PARAFAC. Results of the EEM model indicated that the mostly removed component by coagulation (removal 50%) at full-scale operation is a humic-like fluorophore with predominance in the raw water, while removal of the protein-like components was about 30% [14]. The fluorescence EEMs, captured during the filtration runs and analyzed using a principal component analysis, allowed optimization fouling control strategies to be implemented for the effective maintenance and long-term application of filtration membranes in drinking water treatment [17].

Chlorination of both potable water and treated wastewater is widely used to effectively control most of the pathogens. The main drawback is that chlorine can react with NOM to generate various disinfection byproducts (DBPs). Humic acid and fulvic acid have been identified as the most important DBP precursors with different DBP formation potentials (DBPFPs) [18]. Trihalomethane (THM) and haloacetic acid (HAA) are two of most prevalent groups of DBPs, which are linked to increased cancer risk [19]. To predict DBP formation, specific ultraviolet absorbance (SUVA254) is routinely correlated with DBPs [20]. Many studies have illustrated that EEM fluorescence spectroscopy is a powerful tool for investigating the chem-

Table 1. Major fluorescence peaks for water samples.

Peak	Fluorescent component	Range of excitation (nm)	Range of emission (nm)
A	UVC humic-like	240-260	400-500
C	UVC humic-like and UVA humic-like	240-275 (330-360)	420-480
M	UVC humic-like and UVA marine humic-like	240-260 (290-320)	380-420
B	tyrosine-like, protein-like	225-237	310-320
T1 (T2)	tryptophan-like, protein-like	270-285 (220-235)	340-380

ical and physical characteristics of DOM and for interpreting the formation of DBPs [18,21-23]. EEM-PARAFAC analysis, AF4-UV254, and SUVA254 were applied to study DOM removal by enhanced coagulation and DBP formation during chlorination. PARAFAC analyses identified the three humic-like fluorophore groups and one protein-like fluorophore group in lake water. The humic-like PARAFAC component was more strongly correlated to chloroform formation potential compared to SUVA254 and was preferentially removed by alum coagulation. All methods showed that alum coagulation at pH 6 removed DOM more effectively than at pH 8 [22].

Variations in DOM spectroscopic properties and DBPFPs, and the correlations among these various parameters, were investigated in river water samples collected under two contrasting storm event conditions. EEMs-PARAFAC revealed that a combination of two humic-like components dominated the EEM data of the storm samples. Different trends of the formation potentials for THM and HAA acids suggest that the structures responsible for DBP precursors during storm events may not be the same for the two classes of DBPs [18].

EEMs together with validated regression models were used to determine the DBPFP of reclaimed water. A linear regression equation was developed to relate the formation potential of (THMFP) and the formation potential of haloacetic acid (HAAFP) to the humic acid and fulvic concentrations. Moreover, four linear regression equations were established to relate the measured peak fluorescence intensity to the THMFP or HAAFP of a water sample [23].

NOM in water samples from two drinking water treatment trains has been characterized using LC-OCD and EEM-PARAFAC (EEMs were measured separately) [7]. A five-component PARAFAC model was developed for the EEMs. Three of the components are humic-like, while two are protein-like. These PARAFAC components and the LC-OCD fractions represent effective tools for the performance of evaluation of the two water treatment plants in terms of the removal of NOM fractions.

Effect of Water Treatment Process on Fluorophores

Generally, two main fluorescence peaks are commonly observed in raw water samples. They include humic-like and protein-like fluorescence maxima, which can be further divided into three and two fluorescence centers, respectively (Table 1) [1, 2, 24].

Peak A, humic-like, occurring at the excitation/emission wavelengths of 240-260/400-500 nm, is relatively resistant to photodegradation. Peak C has a primary excitation peak similar to that of peak A. It also has a less intensive secondary excitation peak around 330-360 nm. Peak C is susceptible to UVA-induced photodegradation, its fluorescence intensity correlates with total organic carbon concentration [25], and emission wavelength correlates with the molecular weight, aromaticity, and the degree of hydrophobicity of the NOM [26]. Peak M also has a primary (240-260 nm) and secondary (290-320) excitation peak. It is less photodegraded by UVA light than peak C. Peak M consists of compounds that are less hydrophobic and smaller in molecular size compared to peak C [2, 27]. The intensity of fluorescence emitted at 330-370 nm after excitation at either 220-235 nm or 270-280 nm (protein-like fluorescence) has been demonstrated to relate to both algal and microbial-derived organic matter [28].

Peaks A and C are the most commonly observed fluorescence peaks in clean water. Literature concerning peak A in water treatment systems is infrequent. Baghoth et al. [7] investigated the effects of two different water treatment processes for the removal of NOM in surface and ground waters. These peaks were observed at the following excitation/emission wavelengths: peak A (240-260/420-470 nm), peak C (300-340/400-450 nm), and peak T (240-280/300-360 nm). Fluorescence of peak A was dominated in raw and treated waters. There was substantial reduction of all of the three fluorescence peaks across the two treatment process trains. For both plants, the percentage reduction of the three peaks (relative to that of raw water) were similar across the treatment processes: 55% after coagulation/flocculation, 85% after BAC filtration, and 86% after chlorination (final water). Gone et al. [29] evaluated the use of peaks A, C, and T fluorescence intensities to access the coagulation efficiency for removing dissolved organic carbon (DOC) in the raw water. A coagulation-flocculation was conducted with aluminium sulphate as coagulant and DOC residual and fluorescence intensities were acquired. The results indicate a strong linear relationship between DOC removal and fluorescence intensities. Furthermore, equal removal of peaks A and C was observed. The tryptophan-like (peak T) was found to be the least eliminated and thus, may be considered as an indicator of DOC residual after the coagulation-flocculation process.

Various treatment processes can reduce the fluorescence intensity of peak C: storage in a water reservoir, coagulation, ozonation, BAC filtration, membrane filtration, UV disinfection, and chlorination [2, 6, 29-32]. Photochemical or biological reactions can lead to reduction in peak C fluorescence during reservoir storage [10, 11, 13, 14]. Considering coagulation, Gone et al. [29] found equal removal of peaks A and C, and Baghoth et al. [6] found that coagulation significantly reduced fluorescence intensity of all humic-like components as well as of the tyrosine-like component, but not of the tryptophan-like component. Excitation-emission pairs, location, and intensity change of the peaks in the EEM before and after coagulation have been used to evaluate the performance of this process at different pH levels in a full-scale plant [33, 34] and at laboratory scale [29]. Results indicate that peak C is the most removed through coagulation (50%), followed by another humic-like component (peak M) whose fluorescence signal decreased approximately by 38%. Protein-like components were less removed with removal levels of 37% and 28% for tryptophan-like and tyrosine-like peak, respectively [14]. Baghoth et al. [6] found that the greatest reductions in peak C fluorescence intensity throughout two full-scale treatment trains resulted from ozonation and BAC filtration. Humic-like components were removed by BAC filtration just as effectively as protein-like components. Ozonation degraded humic-like components more than protein-like components. There was no significant difference between the rates of ozone-degradation of tyrosin-like and tryptophan-like components. It was found that the peak C was better rejected by reverse osmosis than peak T1, although typical rejection for both peaks was over 98%. Peak T1 rejection appeared to improve after each subsequent reverse osmosis stage, although the reason for this could not be determined [35]. UV disinfection also reduced peak C [36]. If chlorination preceded UV disinfection, peak C is reduced by chlorination, but it is relatively unaffected by UV light [31]. Moreover, peak C is positively correlated with disinfection byproduct (THM, HAA) formation upon chlorination [23, 25, 32] or extreme weather conditions (storm events) [18]. The composition of DOM in reservoirs used as drinking water sources may be substantially altered by storm events due to the rapid input of new terrestrial DOM sources from influent rivers [37]. Although peak C can be removed by various processes, it is the most commonly observed fluorescence peak in finished water [6, 31].

Various treatment processes can reduce the fluorescence intensity of peak M: coagulation, ozonation, BAC filtration, and ozonation. Peak M is relatively stable during storage in a water reservoir [6]. It is removed by coagulation, but less effectively than peak C [6, 32]. In two full-scale water treatment facilities, the greatest reductions in peak M (similar to peak C) resulted from BAC filtration and ozonation [6]. Considering UV disinfection and chlorination, ambiguous results were obtained. Murphy et al. [31] found that UV disinfection had variable effects on the fluorescence intensity of peak M. Seredynska-Sobecka et al. [36] suggests that peak M is more resistant to chlorination than peak C. Potential resistance to chlorination is confirmed by Murphy et al. [31] as peak M, in combination with peak C, commonly dominated finished water fluorescence. However, Baghoth et al. [7] found that chlorination had variable effects on the fluorescence intensity of peak M.

Several studies have demonstrated that EEM-PARAFAC can be used to decompose the total luminescence spectra of bulk organic matter into fluorescence spectra of individual PARAFAC components. However, it is still unclear whether PARAFAC components represent individual organic matter fractions or groups of fractions with similar fluorescence characteristics. The location and shape of similar components across studies are variable, in particular for component 3. The reason may be that a characteristic feature of fluorescence spectroscopy is dependence on environmental factors such as pH, ionic strength, dissolved oxygen, temperature, metal content, etc., which must be held constant when characterizing organic matters with EEM-PARAFAC. Unfortunately PARAFAC studies do not consider the effects of these water sample conditions on organic matter properties. In addition, PARAFAC studies do not recognize whether changes in component fluorescence are due to a chemical transformation, a physical transformation, or a change in the source of the organic matter. Research regarding the effects of water treatment processes on PARAFAC component fluorescence is minimal and additional work is needed to further establish relationships between treatment process and organic matter fluorescence [1]. It must also be determined whether these relationships are based on fluorescence quenching, organic matter removal, or a physical/chemical transformation of organic matter. Thus, fluorescence spectroscopy faces several challenges for future research with potential application in drinking water treatment monitoring.

Contaminants in Drinking Water

The review [38] has identified an urgent need for alternative monitoring techniques suited to distinguish recycled water from drinking water and to detect contamination of drinking water with low proportions of recycled water. Fluorescence spectroscopic techniques have considerable potential as monitoring tools over traditional methods, including UV spectroscopy, due to their greater sensitivity and selectivity. The review concludes that the sensitive detection of contamination events in recycled water systems may be achieved by monitoring peak T and/or peak C fluorescence [38]. Monitoring the fluorescence at peak C1 ($\lambda_{ex}/\lambda_{em}$ = 325/426 nm) was found to have a more significant role in distinguishing between recycled water from different treatment processes, such as between deep bed filtered and chlorinated samples, whereas peak T1 ($\lambda_{ex}/\lambda_{em}$ = 300/350 nm) was found to give a better separation between drinking and finished recycled water samples. It was determined that a 45% solution of recycled water in drinking water could be confidently identified (95% reliability). This was much more sensitive than conductivity that required a minimum of 70% recycled water in drinking water [39]. The results indicated that fluorescence is a promising tech-

nique for sensitive monitoring of reverse osmosis (RO) permeates from water recycling plants. Fluorescence intensity of peak C was found to be the most suitable for RO monitoring purposes [35]. Fluorescence measurements could be used as a more sensitive tool compared to conductivity profiling when assessing membrane installations [40].

The groundwater based drinking water systems, which consist of aeration and pre- and post sand filtration, and which are vulnerable to microbial contamination due to the lack of disinfectant treatment, can be easily monitored using on-line organic matter fluorescence (EEM-PARAFAC) as an early warning system. There was a strong linear relationship between the fluorescence of peak T and the amount of wastewater organic matter added. The fluorescence of peak T increased by 50% after laboratory additions of wastewater at levels <2% v/v [41]. This agrees well with results from surface waters [42] and recycled water systems [39] where tryptophan-like fluorescence has been found to be a good indicator of contamination.

Chemical compounds (contaminants) that could be potentially screened with fluorescence measurements can be classified as follows: compounds that are intrinsically fluorescent (polycyclic aromatic hydrocarbons, PAH, polychlorinated biphenyls, PCBs, phenols, some pesticides, dyes, lanthanides, and actinides), compounds that can form fluorescent derivatives (pesticides, amines, metals, and organic acids), and compounds that can modulate the fluorescence of another compound (petroleum hydrocarbons, nitroaromatics). Applications of EEM-PARAFAC to all three classes can be found in literature [43].

Room-temperature excitation-emission phosphorescence matrices combined with PARAFAC and partial least-squares with residual bilinearization (PLS/RBL) were applied to the determination of pyrene and benzo[*a*]pyrene in tap, ground, mineral, and river water samples [44-46]. While both PARAFAC and PLS/RBL allowed the successful determination of benzo[*a*]pyrene in water samples, the PLS/RBL prediction for the pyrene was better than that of PARAFAC [44].

The superiority of PLS/RBL to quantify benzo[*a*]pyrene and dibenzo[*a,h*]anthracene at concentrations below 10 $ng \cdot L^{-1}$ in the presence of the remaining fourteen PAHs at total concentrations ranging from 1,400 and 14,000 $ng \cdot L^{-1}$ in tap, underground, mineral, and river water samples was also demonstrated [45].

EEM-PARAFAC also was used to determine:

(1) a non-fluorescent pesticide methoxychlor based on interaction with Nile Red fluorescent dye
(2) three PAHs (naphthalene, fluorene, phenanthrene)
(3) two natively fluorescent pesticides (carbaryl and carbofuran).

Parts-per-billion detection limits were observed in waste and non-waste water samples [47].

A new analytical method has been proposed for determination of tributyltin based on the measurement of EEMs processed by PARAFAC and MCR/ALS (multivariate curve resolution/alternating least-squares). Fluorescence detection was based on the reaction between tributyltin and 3,5,7,2′,4′-pentahydroxyflavone (morin) in a Triton X-100 micellar medium, which yields a fluorescent complex. The proposed methodology was applied to tap, river, lagoon, and sea water spiked samples, obtaining satisfactory results at $ng \cdot L^{-1}$ levels after a pre-concentration step on a C18 membrane [48].

Recent works using EEM-PARAFAC revealed that different types of DOM components (e.g. humic-like and protein-like) were associated with metal binding [49-53]. For example, the binding characteristics of DOM, released by *S. acutus* during the exponential period of growth, with Cu, Cd, Pb, and Zn were studied using fluorescence quenching titrations combined with EEM and PARAFAC. Three fluorescent components (two humic-like: peak A+C and peak A+M; and one protein-like: peak T) were found in the exudates materials. Peak C was associated with microbial degradation of algogenic material, whereas peak M was associated with algal production. Negligible quenching effects for Cd, Pb, and Zn and strong quenching effects for Cu were observed. These results reveal that unlike Cd, Pb and Zn, Cu strongly binds to algogenic DOM. Significant differences in conditional stability constant values were found between humic-like PARAFAC components, indicating clear differences in the binding properties of humic-like components with Cu [50]. Knowledge on the function of individual components in DOM is essential for understanding the impact of DOM on occurrence and behavior of metal in water environments. Unfortunately, the function of the individual DOM constituent remains poorly defined owing to the complexity of DOM. Therefore, the role of individual DOM components needs to be further studied for a better understanding of their impact on the fate, mobility, and speciation of metals in the waters. Additionally, EEM-PARAFAC should be combined with other analytical methods to support that fluorescence quenching is really an indication of complex-forming reaction between a quencher and the DOM component [51-53].

A factor that limits wider application of EEM fluorescence to monitoring of the contaminants in drinking water is the lack of selectivity in fluorescence measurements. However, selectivity can be improved by using data sets obtained from kinetic experiments. The time profiles introduce a fourth dimension (*I*×*J*×*K*×*time*) that leads to increasing selectivity [54]. In some monitoring situations, however, high selectivity may not be necessary. In monitoring the extent of well established and characterized pollution (e.g. petroleum or sewage spill), non-specific measurements may be more important than detailed information on individual compounds. EEM fluorescence is promising but rarely used in the flow mode. Implementing reactions, dilution, separation, and EEM fluorescence measurement online could help improve monitoring capability.

Conclusions

As illustrated in this review, fluorescence EEMs combined with PARAFAC provide valuable information that can be used to characterize organic matters and its temporal variation during drinking water treatment and/or to evaluate the performance of organic matter removal processes, and to

determine various contaminants in drinking water. The advantages of fluorescence spectroscopy are rapidity, simplicity, sensitivity, and selectivity. A disadvantage is its dependence on environmental factors such as temperature, pH, ionic strength, etc.

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