

## Abstract

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Colloids play an important role in the chemistry of natural water systems. Colloids are very small particles, which are small enough not to sediment out from the water, yet large enough to constitute a phase separate from the solvent (in this case water). In practical terms, colloids are said to be between 1 nm and 1  $\mu$ m in size. Trace metals associate with colloids together with other types of chemical species and are transported by the colloids through the water system.

In this work, two types of colloids have been of special interest, iron-based colloids and small humic-type organic colloids. These types of colloids have been characterised by size fractionation followed by elemental analysis and fluorescence excitation-emission matrix (EEM) spectrometry. The main focus, however, has been on the characterisation of fluorescent organic matter (FOM), which is a part of the organic colloids. FOM is produced both on land and in the water through degradation of dead plants and animals. Depending on the place of origin, the fluorescence properties will vary, thus acting as a virtual fingerprint.

FOM has been studied for a long time, although the use of EEM spectrometry, or total luminescence spectrometry has only recently become common. EEM spectrometry has the advantage over single-wavelength combination analysis that all fluorescence from within a certain range is measured, providing much more information about the FOM in the sample. An important interference in fluorescence spectrometry is the so-called inner-filter effect (IFE), or self-absorption, in which part of the excitation and emission light is absorbed by the sample. The result is that the fluorescence signal is diminished, and the correlation between fluorescence and concentration becomes non-linear. To reduce this effect, a mathematical correction based on the ubiquitous water Raman scatter was developed.

EEM data is usually interpreted by manual study of the fluorescence matrices, or EEMs, a procedure which quickly becomes very tedious, particularly for large datasets. In order to simplify the evaluation, it is becoming increasingly common to use chemometric methods, such as PCA, PLS and PARAFAC, to model the EEM data. The models consist of a number of components, each representing a recurring fluorophore (or, in the case of strong covariation, fluorophores). Although there are several variations of chemometric methods, the so-called multiway methods (e.g. PARAFAC) are most appropriate to model EEM data, as the theoretical bases are similar. EEM spectrometry followed by PARAFAC evaluation has been used to study such diverse areas as the Kalix River in northern Sweden and the Atlantic part of the Southern Ocean. The results show distinct differences, but similarities can also be found. In the Kalix River, a complete elemental analysis was performed, on the whole water as well as on the colloidal and truly dissolved size fractions respectively.

*KEYWORDS: fluorescent organic matter, multivariate, PARAFAC, colloids, natural waters*

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