

MONITORING NATURAL ORGANIC MATTER IN SURFACE WATER BY UV SPECTROSCOPY: EFFECTS OF CALCIUM, MAGNESIUM AND PH VALUE

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ABSTRACT

The aim of this study was to evaluate the effects of dissolved magnesium and calcium ions on the determination of humic substances in water by spectrophotometry at 254 nm. Quantifications were carried out for different pH values, both with and without filtration of the samples. The smallest effects were observed for unfiltered samples and neutral pH values.

KEY WORDS

Natural organic matter, fresh water; pH; magnesium, calcium, spectrophotometry

1. Introduction

Natural organic matter is largely allochthonous and originating from terrestrial sources. It represents a complex mixture with great variance in composition due to the different origins such as plant and microbial residues, and the numerous degrees of transformation by microbiological, chemical and photochemical processes [1]. NOM may be classified in two main categories: non-humic and humic substances (HSs). About 75% of the dissolved organic carbon (DOC) in rivers consists of HSs [2]. The presence of HSs in water treatment plants is undesirable because they increase coagulant and disinfectant demands, and in the presence of chlorine may provoke the formation of dangerous disinfection by-products (DBPs) such as the carcinogenic trihalomethanes (THMs). Because of their role of DBP-precursor, the HS content of the raw water is an important analytical parameter in water treatment processes [3].

HSs such as fulvic acids (FAs) and humic acids (HAs) are polydisperse mixtures of natural organic polyelectrolytes. Among the main chemical groups they contain carboxylic, phenolic-OH, amino and quinone containing aromatic nuclei with low degrees of condensation due to the presence of non-aromatic components. In general, the number of carboxylic and phenolic-OH groups is largely dominating. HSs play an important role in the behavior

and fate of metal ions in the natural environment [4]. The intramolecular and intermolecular interactions of these ions with HSs may change their physical properties. Those interactions depend on pH, ion strength, and type of ions in solution [5].

HSs are usually classified into three fractions as a function of their solubility. Humins are the fraction of HSs that is not soluble in water at any pH value, fulvic acids are soluble in water under all pH conditions and humic acids (HAs) are the fraction soluble at high pH but insoluble under acid conditions [6]. HAs are complex aggregates of brown to dark color, amorphous and typically characterized by high molecular weight. They are able to create soluble and insoluble complexes and chelates with metal ions [7]. In the complexation reactions an electron pair is shared between the metal ions and the HAs, while in the chelation reactions the formation of a ring structure between the ligands and the metal ions takes place [8]. Tan [8] suggest that complex formation in humic substances occurs mostly at low pH conditions, whereas chelation reaction is more dominant at elevated pH values. Factors affecting the solubility of HA complexes and chelates with metal ions are the origin of humic substance, the dissociation of functional groups, the saturation of binding sites and the types of metal ions. For instance, the monovalent alkali metal ions (e. g. sodium, potassium) generate complexes and chelates soluble in water, while the multivalent metal ions (e. g. calcium, magnesium, iron) lead to formation of insoluble complexes and chelates [6].

The concentration of HAs in water is not directly accessible to common analytical methods due to their heterogeneous chemical structure [9, 10]. Instead, total organic carbon (TOC) and spectrophotometric absorbance of ultraviolet light at 254 nm (UV_{254}) are used as surrogates to represent the concentration of HSs in water [11, 12].

The capacity of aqueous HSs to absorb ultraviolet light of 254 nm increases with their content of aromatic rings, their ratio of carbon in aromatic nuclei to carbon in aliphatic or alicyclic side chains, the total carbon content

in the water, and the molecular weights of the HSs [9]. As long as the absorption characteristics are stable, the UV light absorbance of HSs at a specific wavelength is proportional to their concentration according to Beer's law [13].

The aim of this study was to quantify the effects of magnesium and calcium ion concentration, pH-value, and sample filtration on spectrophotometric measurements of HS.

2. Materials and methods

Stock solution

A commercial humic acid (Sigma Aldrich, 53680 Humic acid) with a carbon mass fraction of 48.95 % was used to simulate NOM in surface waters. A concentrated stock solution was prepared by dissolving 204.3 mg of humic acid in 1 L of an aqueous solution of 4 g/L NaOH. The solution was stored in the dark at 4 °C. Ultrapure water was used in the preparation of all solutions.

UV absorbance of humic acid in the presence of divalent ions

A series of solutions containing different ion concentrations and 20.43 mg/L of humic acid, were prepared by dissolving a weighed amount of $MgSO_4 \cdot 7H_2O$ or $CaCl_2 \cdot 2H_2O$ (Sigma Aldrich, p.a.) in a ten-fold dilution of the humic stock solution. Designated samples were filtered through a 0.45 μm filter (514-4156 Membrane disc filters Supor, VWR). UV absorbance of the samples was measured at 254 nm with a single beam Shimadzu UV-160A spectrophotometer (Düsseldorf, Kent, Germany) using a 1 cm quartz cell.

Experiments were performed at three different pH values: 4.0, 7.0 and 9.5. The pH was adjusted using either 73.0 g/L of HCl or 80.0 g/L of NaOH.

Absorbencies of magnesium and calcium solutions without humic material were also measured.

Statistical analyses

A *t*-test was used where specific means were being compared. Acceptance or rejection of the null hypothesis was based on an α -level of 0.05 in all cases.

3. Results and discussion

In order to quantify the effects of dissolved magnesium, calcium and pH on the results of the spectrophotometric determination of humic acids, the following metal ion concentrations in mg/L were used:

- Magnesium 0.0, 4.9, 7.3, 7.4, 9.9, 17.0, 24.3 and 34.5
- Calcium 0.0, 10.0, 19.5, 38.2, 79.1 and 136.3

For all twelve concentrations samples were prepared and adjusted in triplicate to pH values of 4.0, 7.0 and 9.5 respectively, yielding a total of 108 samples. UV₂₅₄ absorbance of these samples was determined before and after filtration, the results are depicted in Figures 1 and 2.

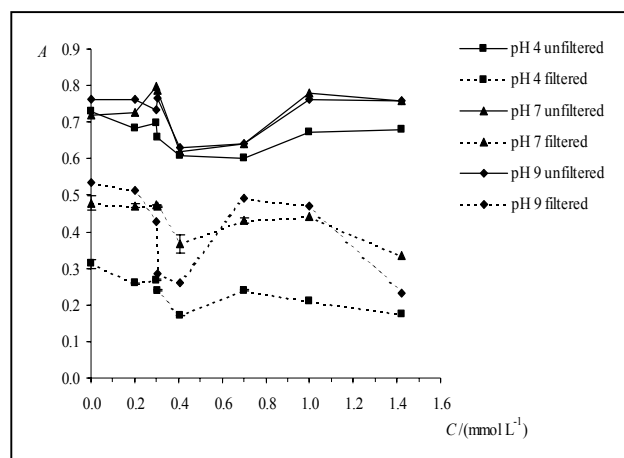


Figure 1: Humic material absorbance versus magnesium ion concentrations

Blank measurements carried out with pure solutions of magnesium sulphate and calcium chloride at the concentrations in question never yielded absorbance values above 0.06, so that direct influence of these substances on the absorbance was considered negligible.

In all cases unfiltered samples presented considerably higher absorbance values than filtered ones, independently of magnesium or calcium concentration and pH values. Obviously, with increasing metal ion concentrations a considerable portion of the absorbing molecules was removed in the filtration process.

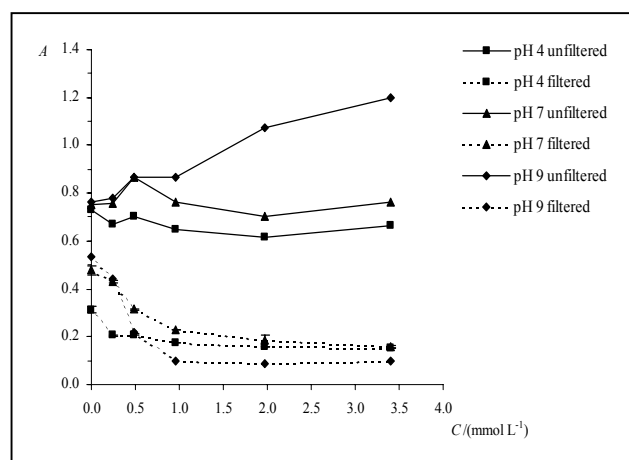


Figure 2: Humic material absorbance versus calcium ion concentrations

For the strong removal of absorbing molecules in the filtration process there are two hypotheses. The first is based on molecular interactions between metals and humic substances. According to Tan [8] a complexation of these substances may occur at low pH and a chelation at higher pH, both effects increasing with higher metal ion

concentrations. In both reactions, complexation and chelation, metal ions may link humic acid molecules with each other, thus provoking the growth of molecular aggregations which are easier removed by the filtration than individual HA molecules that prevail in the absence of metal ions.

The second hypothesis is based on the adsorption of humic acid molecules onto the filtration membrane. Since each sample was filtered with a fresh filter, the latter always had its full adsorption capacity. Several authors [14, 15, 16] reported experiments in which dissolved humic acids were adsorbed by filtration membranes. In all of these experiments the adsorption of HA increased with the metal ion concentration, which shielded the electrostatic repulsion among humic acid molecules and thus facilitated their deposition on the membrane surface.

Unfiltered samples with high calcium concentrations and elevated pH-values appeared to have a significant increase in UV₂₅₄ absorbance. Under these conditions, however, the formation of insoluble CaCO₃ must be taken into account, which creates mineral precipitates and thus leads to an increased turbidity of the sample. In this case no true specific absorption at 254 nm occurs, but the light reflected and scattered by the precipitates dissipates from the system and thus provokes a falsely increased UV₂₅₄ absorbance reading.

Except for this specific case, samples with low pH-values, both filtrated and unfiltered, always presented a significantly lower UV₂₅₄ absorbance than neutral or basic ones. A possible explanation might be the lower solubility of HAs at acidic pH [17].

4. Conclusion

From this work's results can be concluded that humic acid monitoring by spectrophotometric absorbance must be conducted with care due to possible interferences from pH-values and metal ions, which may vary with the local conditions. Further research will be necessary in order to better understand and quantify these interferences.

Acknowledgments

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