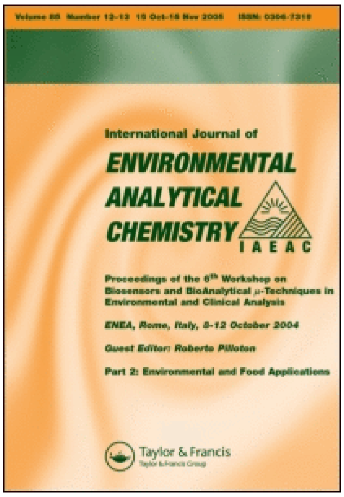

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A NEW METHOD FOR THE CHARACTERIZATION OF ORGANIC CARBON IN AQUATIC SYSTEMS

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Some problems in organic carbon characterization are briefly discussed. A new chromatographic multi-method for the direct characterization of organic matter in original waters with the simultaneous determination of UV-Vis, fluorescence, DOC, TIC, and organically bound nitrogen (DON) is described. Some applications with UV-Vis and DOC ("CODOC") detection are presented.

KEY WORDS: Organic carbon detector, gel permeation chromatography, UV-Vis, DOC, TOC, DON, CODOC.

INTRODUCTION

The parameters "DOC" (Dissolved Organic Carbon) or "TOC" (Total Organic Carbon) are among the most fundamental sum parameters for the characterization of organic matter of natural and human influenced aquatic systems. The DOC/TOC value is a mass value. It determines the amount of organic carbon present in a sample. As such it has to be seen in comparison with other "classical" sum parameters such as the "COD" (Chemical Oxygen Demand), the "BOD" (Biological Oxygen Demand) and spectral properties (light absorption, fluorescence). With exception of the DOC/TOC the parameters define and quantify certain properties of organic constituents, such as the chemical oxidizability (COD), the biological degradability (BOD), the presence of delocalized electrons (UV-Vis), and fluorescing properties (fluorescence).

It is widely accepted that there is a close relationship between these parameters in nature[e.g.1,2], as long as a homogeneous environment is studied. Therefore, UV-absorption has often been used as a reliable surrogate parameter for the quantification of the organic load of natural waters. Figure 1 shows as an example the correlation UV/DOC for organic matter isolated from different aquatic systems.

These relationships appear far more complex after chromatographic fractionation. In a pioneer paper[3], Gjessing showed that there are differences between COD, UV-Vis and

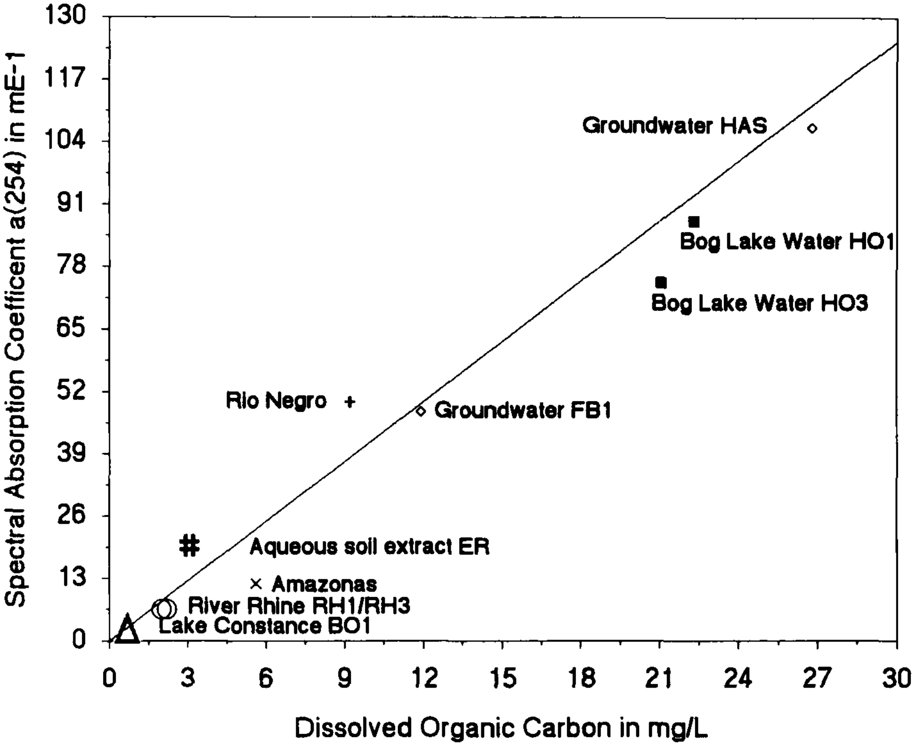

Figure 1 Correlation between UV absorbance and DOC for natural waters of different origin

organically bound nitrogen in different chromatographic fractions. Fuchs and Raue[4] found differences between UV-Vis and DOC, others found differences between UV-Vis and fluorescence[5], and between UV-Vis, fluorescence and DOC[6]. These few examples show that the mere determination of sum parameters has severe limitations as a method for the characterization of natural organic matter.

Some of the parameters can be directly determined in a continuous mode, thus they can be measured in connection with liquid chromatography. These are the optical properties (UV-Vis, fluorescence), and the mass of organic carbon (DOC). Combinations of two or more parameters lead to specific values which can be compared in natural samples of different origin.

The continuous determination of the DOC is still quite difficult. The first semi-continuous DOC determination was probably carried out by Axt[7] using the thermal combustion method. Later this method was optimized for liquid chromatography[8,9], but was eventually abandoned because of practical problems with accumulating buffer salts. UV-mediated wet combustion techniques for continuous and real time measuring of DOC and inorganic carbon (TIC) have—until recently—not been reported, but a commercially available flow injection system has been mentioned[10]. This system requires the elimination of TIC in the sample by prior acidification and thus restricts the applicability for liquid chromatography.

The sensitivity of these DOC-detection systems is in the range of a few milligrams per liter. Thus, for most aquatic samples, a preconcentration step is necessary before analysis. Preconcentration of natural organic matter is a very tedious task and may cause the formation of artifacts[11,12]. This and the fact that efficient chromatographic separation techniques are still missing may account for the present situation in which little is known about the associative behavior of natural organic matter in natural matrices.

A different reactor design[13] offers the possibility for the continuous and simultaneous determination of organic and inorganic carbon even in highly buffered salt solutions at very low concentrations[14]. In 1983, the apparatus was used for the direct determination of seawater-DOC on board of a vessel[15]. In recent years the detection limit of the detector was extended down to the low µg/l concentration range[16]. Thus, preconcentration of organic matter in natural samples can be made obsolete.

METHODS

In connection with liquid chromatography and further detection systems, a combined system can be used for a more detailed characterization of dissolved organic matter[17].

In Figure 2 the outline of the system is shown. A vertical thin-film reactor with a central low-pressure UV lamp is used for the oxidation and separation of organic and inorganic carbon. At the reactor inflow side, UV-Vis and fluorescence properties are measured. In the reactor outflow, oxidized reactions products can be further analyzed. In the present set-up, a further UV-Vis detector (set at 210nm) was installed. It is planned to determine with this

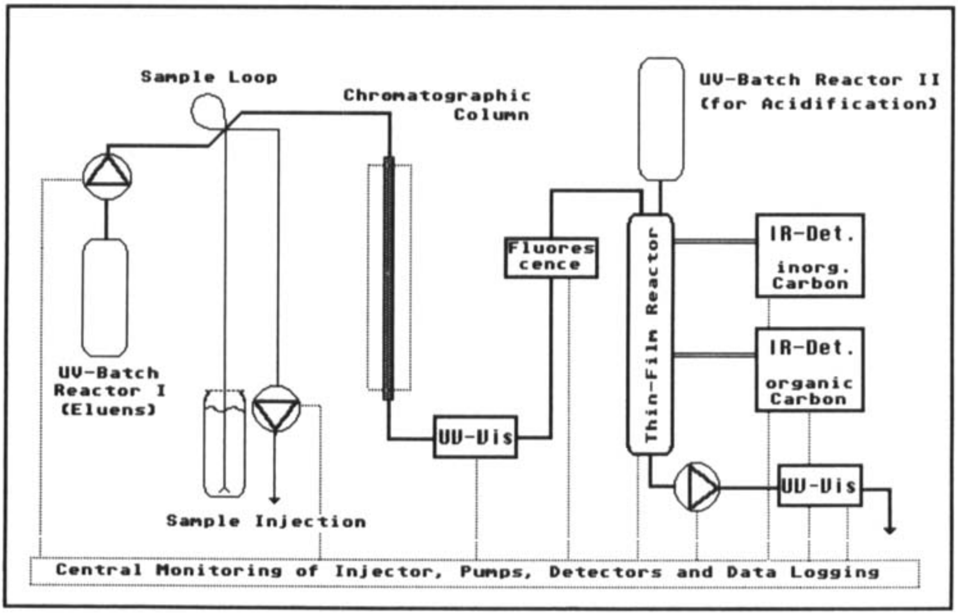

Figure 2 General outline of the analytical set-up for the direct characterization of natural organic matter

detector the organically bound nitrogen (DON) as secondary nitrite/nitrate. Primary nitrate present in the sample is retarded by a chromatographic size exclusion process (see Figure 3 below), whereas DON may be oxidized into nitrate which is a strongly UV-absorbing salt. Other heterocyclic elements like phosphorus and sulfur would be oxidized to non-absorbing phosphate and sulfate.

In Figure 3, a hardcopy of the computer screen with the signals for UV at the reactor inflow side, DOC, TIC, and for UV at the reactor outflow side (DON) is shown. The fluorescence detector was not used. The example shown is original River Rhine water separated on a size exclusion column (TSK HW 40 S). Owing to some dead volume in the tubing connections between the detectors, a slight time shift between the responses of the individual detectors had to be corrected by means of data processing (addition/substraction of "time").

Efficient chromatographic columns for the separation of natural organic matter are still not available. At present it seems that polymer based porous polyacrylate gels give the best results. However, since natural organic matter is composed of units with varying molecular weights and sizes, similar polarities and probably similar functional groups, baseline separation of different classes of compounds cannot be expected. This can be illustrated by the seemingly paradox observation in which a preparative chromatographic column with a number of theoretical plates of about 500 yields a similar resolution as an analytical HPLC column with about 10,000 theoretical plates[6]. In both cases a polymer-based size exclusion column has been used.

In the applications presented in this paper, size exclusion columns with porous polyacrylate gels (nominal upper separation limit of 4000 Daltons) have been used. According to theory, the high molecular weight organic matter eluted first. Calibration of the columns for natural organic polyelectrolytes with reference substances was not attempted because

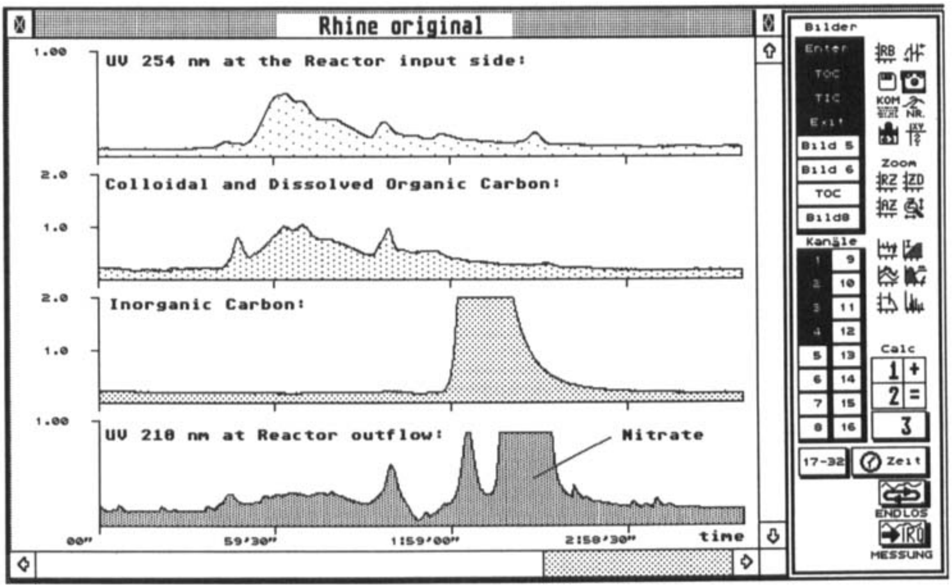

Figure 3 Screen hardcopy of the data acquisition system showing a gel permeation chromatogram of River Rhine water with the four signals obtained for UV inflow, CODOC, TIC, and UV outflow.

"good" reference substances are not yet known. Only the distinction between high molecular weight and low molecular weight organic matter was made after calibration with different polyethylene glycols.

The system is still in the experimental state and only a few measurements have been published. These include the characterization of surface and ground water[6], assessment of humification processes in waste waters[18], and a study on the impact of treatment steps on river bank water in a pilot plant[19]. In an unpublished study, a cationic flocculant in the low-ppb concentration range was directly determined[20]. Possible applications of the system in the field of environmentally related studies are the following:

— Characterization of natural organic matter
— Fingerprinting of aquatic systems
— Analysis of by-products in drinking water treatment
— Analysis of humification in waste water treatment
— Interaction of natural organic matter with pollutants

RESULTS

The applications of the system shown in this part should be regarded as case studies and only the signals obtained for UV-absorption (254nm) and DOC will be shown. All chromatograms were performed with low-pressure columns (length between 25 and 90 cm; diameter of 1.6 cm; Pharmacia, Uppsala, Sweden). The columns were packed with polyacrylate gel TSK HW 40 (S) (Merck, Germany) with an average particle size of 40 µm and pores in the 40 to 80 nm range. More data on the chromatographic conditions are given with the captions to the figures.

No pre-filtration of the samples has been carried out in order to minimize the risk of contamination. It must be stressed that for the chromatograms the term "DOC" can include the colloidal organic material in the range between 0.45 µm and 10 µm, since this material can also be chromatographed using low-pressure columns. This is one big advantage of LC over HPLC, as the DOC[21] comprises only a fraction of the more relevant TOC. Therefore it was suggested to introduce a new term to distinguish between filtered and unfiltered organic material[19]. The new term is called "CODOC", which is derived from **CO**lloidal and **D**issolved **O**rganic **C**arbon. The term implies that a dominant fraction of the colloidal fraction is included. CODOC is this part of the TOC which can be characterized by low-pressure liquid chromatography. CODOC can be determined by direct injection of a natural sample on the column. In the upper end of the column, a "net" with a nominal pore size of 10µm conducts an on-column filtration step. Therefore the "CODOC" instead of the "DOC" has been measured in the examples below.

Example 1:

In Figures 4 and 5 the UV-absorption and the CODOC of tap water from Karlsruhe on two different days (Jan 6 and 14 1991) are shown. The sample of Jan 14 (stippled lines)

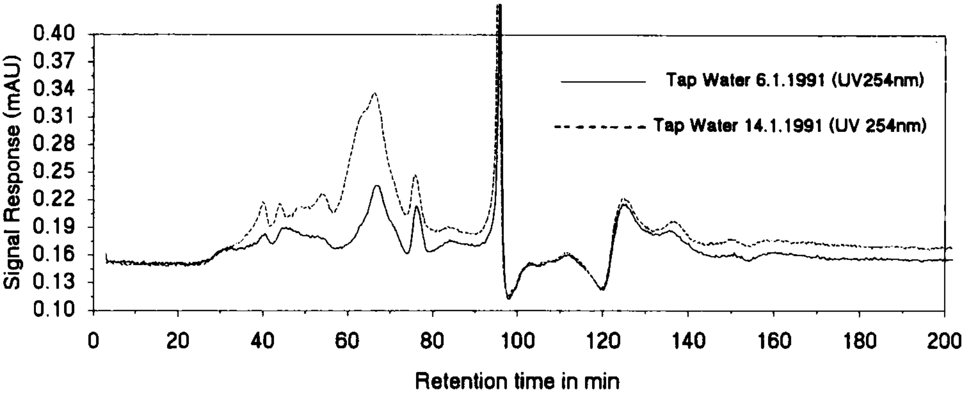

Figure 4 Gel permeation chromatogram of original tap water from Karlsruhe; fraction <10 μm (solid line: 6th of Jan 1991; stippled line: 14th of Jan 1991); Column: 90 cm length and 1,6 cm diameter; Packing: TSK HW 40(S); Eluent: UV-purified double-distilled-water with (purified) 28 mmol phosphate buffer, pH6.37; Flow rate 1ml/min; Sample volume 1.5 ml; UV-Detector: Linear Instruments 200, USA set at 254nm, 5 mAUFS; Counting rate 1/5s.

documents an unusual situation in which coloration of the tap water occurred due to the mobilization of ferric material in the water piping system.

Only within the area of high molecular weights (t_R=55min to about 70min) a relatively good correlation between UV and CODOC prevails. This fraction should be of humic origin as the retention times and the UV/DOC ratio resemble those of humic reference material.

The colored tap water sample (stippled line) has a much stronger impact on UV-absorption than on CODOC. Still, for CODOC a significant increase in the high molecular weight fraction can be observed. This new material is only in part of humic origin, as the fraction at t_R=70min did not contribute to UV.

The pronounced sharp peak at t_R=95min is low molecular weight organic matter which has a specific interaction behavior with the packing material. For UV, two deep "troughs" at t_R=98 min and t_R=120 min can be seen. These were presumably caused by matrix differences between the sample and the eluent: The sample was not buffered and therefore the two "missing" (weakly UV-active) buffer salts resulted in these two troughs. This

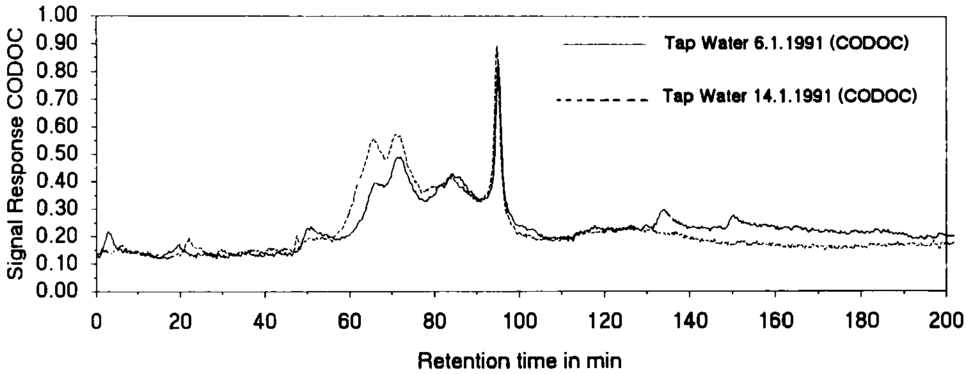

Figure 5 Same chromatogram as in Fig 4 but with the signals obtained for CODOC

conversely caused a salting-in-effect: Organic matter which otherwise would have eluted more slowly was transported through the column like a "bow wave" in front of the low ionic strength portion.

The anastomosing baseline signals for CODOC- (132min and 220min) may reflect long term instabilities, presumably caused by temperature changes in the laboratory.

Example 2:

Interstitial water from a brown water lake sediment (Lake Hohloh, Black Forest) before and after exposition to low-pressure UV-irradiation is shown in Figure 6. For both UV and CODOC, a complete reorganization of organic matter can be observed. In the original sample almost all material eluted in the high-molecular-weight fraction. After UV treatment, this fraction partly disappeared and new low-molecular-weight material was produced. No decrease in quantity of UV-active compounds can be found, but for CODOC an increase of about 25% was found. This shows that part of the particulate organic fraction (POC) was desintegrated and was made accessible for the column. A large part of the newly formed CODOC is UV-inactive. There are two attractive assumptions for this, (a) destruction of UV-active centers has taken place, (b) the new material originating from POC was UV-inactive. The chromatograms also show that the original material was disintegrated into higher structured sub-units with highly specific UV/CODOC ratios.

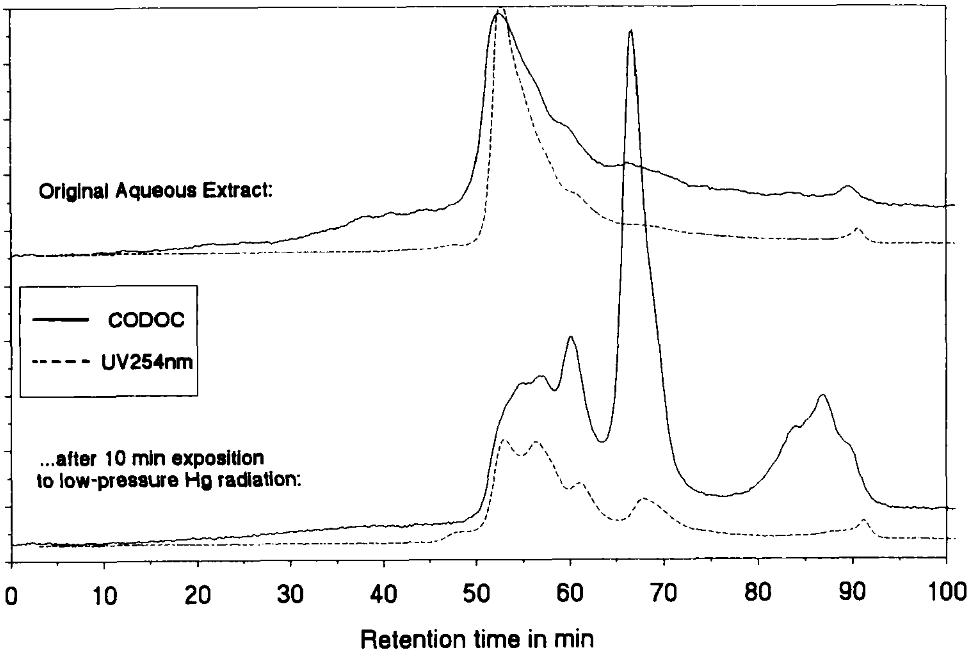

Figure 6 Gel permeation chromatogram of an aqueous filtrate of brown water sediment interstitial water, 1:10 diluted with eluent; Solid line: CODOC; Stippled line: UV 254nm. For chromatographic conditions, see Fig 4.

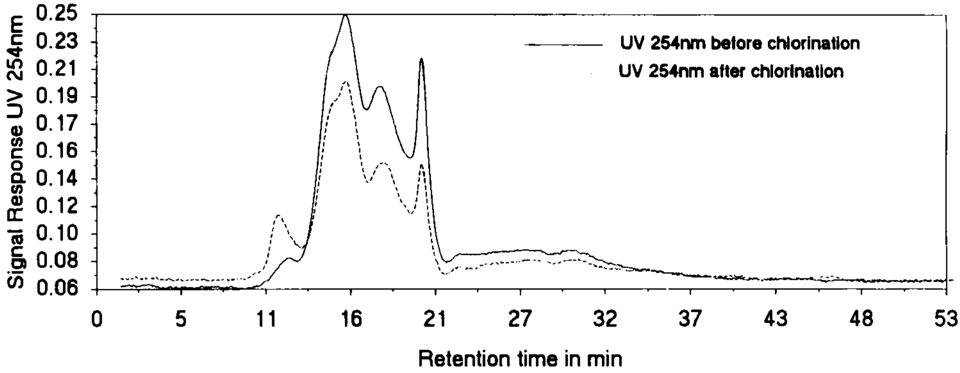

Figure 7 Gel permeation chromatogram of Lake Galilee surface water with UV detection (254nm). Solid line: original sample; Stippled line: chlorinated sample; Column: 25 cm length, 1.6 cm diameter. For chromatographic conditions, see Fig 4.

Example 3:

An example for chlorination of surface water (Lake Galilee, kind donation of Prof. M. Rebhun and Dr. Y. Manka, Technion City, Haifa, Israel) is shown in Figures 7 (UV) and 8 (CODOC). With exception of the first fraction (increase at t_R=12min), a general decrease of UV absorbance over the entire chromatogram can be observed. A more complex situation is found for the CODOC responses. A shoulder within the first eluting fraction was eliminated completely and in the low molecular weight fraction a new and quite dominant UV-inactive fraction was formed.

The results show that chlorination did not lead to a complete rearrangement of the organic matter but rather reduced non-specifically a certain percentage of high molecular weight material. This material was not mineralized but broken down into aliphatic structures of low molecular weight. The results differ fundamentally from the results found in the previous example for UV-irradiation.

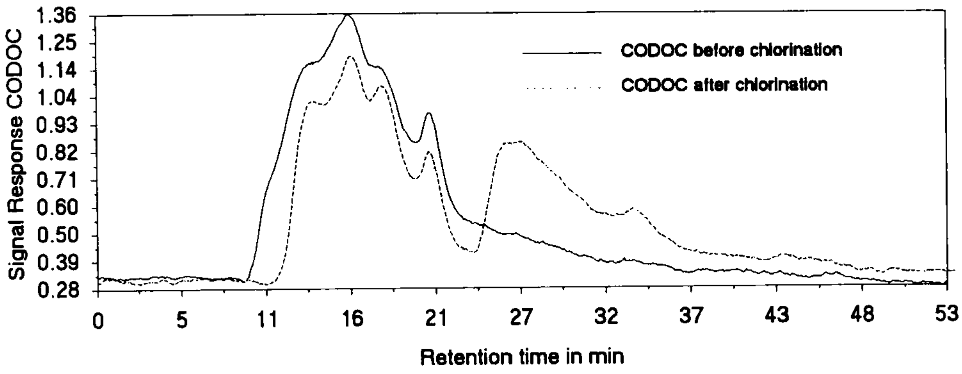

Figure 8 As Figure 7 but with CODOC detection.

CONCLUSIONS

The data presented here show that a new analytical system can be used for the direct characterization of organic matter in original water samples. Therefore, it is a powerful tool for the investigation of the occurrence and fate of non-volatile hydrophilic substances. The examples should be regarded as case studies to illustrate some possibilities for a new analytical setup.

Acknowledgements

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