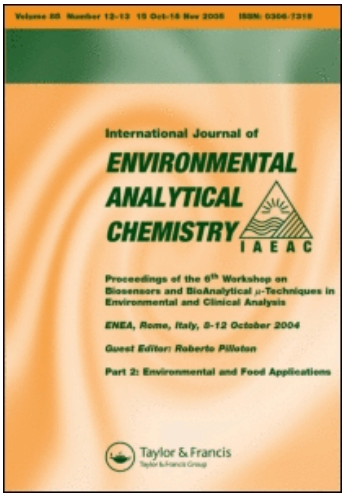

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Subra, P. , Hennion, M. C. , Foucault, A. and Rosset, R.(1987) 'Analysis of Organic Matter in Water of Low TO C (Total Organic Carbon) Content by Chromatographic Techniques', International Journal of Environmental Analytical Chemistry, 31: 2, 197 — 217
To link to this Article: DOI: 10.1080/03067318708077141
URL: http://dx.doi.org/10.1080/03067318708077141

Intern. J. Environ. Anal. Chem., Vol. 31, pp. 197–217
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Printed in Great Britain

Analysis of Organic Matter in Water of Low TOC (Total Organic Carbon) Content by Chromatographic Techniques

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Dedicated to Professor W. Haerdi on the occasion of his 60th birthday

(*Received 7 April 1987; in final form 10 May 1987*)

The problems encountered when analyzing organic pollutants in drinking water stem from the large number of unknown compounds at very low concentration.

The concentration of the organics is carried out on *n*-alkyl silica, after a rigorous cleaning, or by liquid–liquid extraction. The complexity of these extracts renders a direct analysis by gas chromatography coupled with mass spectrometry impossible; hence, a pre-separation step is required.

Reversed and normal phase chromatography have been investigated with these extracts. The former leads to informative fingerprints but subsequent identification is difficult.

Normal phase liquid chromatography is more suitable and a separation by chemical classes of increasing polarity is applied to water extracts. The eluent is fractionated, each fraction is then gently evaporated and subsequently analyzed by GC. Identification is then possible by coupling with mass spectrometry.

These procedures are used to follow the change in organic matter during the two last steps of the drinking water treatment: ozonation and filtration on active charcoal.

Another application is the analysis of humic extracts.

KEY WORDS: Organics in water, drinking water, trace enrichment, HPLC, humic acids.

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INTRODUCTION

The analysis of organic matter dissolved in waters which are characterized by low total organic carbon content (TOC), varying from 1 to 3 $mg\,l^{-1}$, is complicated by the fact that there is a large number of unknown compounds, each at a very low concentration in the ppt range. The complexity of these samples requires a high resolutive chromatographic system including a necessary trace enrichment or preconcentration step.

Many applications deal with the analysis of water organic matter but most of them concern industrial or river waters with high TOC content. Publications about drinking waters or low TOC waters are much less numerous. The organic matter in such waters is a complex mixture with both synthetic and natural origins. Among them, we find compounds of low solubility but with a sufficient volatility for easy concentration by closed loop stripping techniques for instance and further separation and quantification by GC/MS.[1-4]

It has been estimated that volatile organics are for only 10% of the total organic material[5] in drinking water and 90% of them are easily identified and quantified. The non volatile organics are much more difficult to characterize because of their wide range of polarity.

A part of the organic carbon is also in the form of high molecular weight compounds, known as humic substances, which form micelles and solubilize smaller molecules;[6] they are hard to characterize and may be a trouble for the analysis of simpler substances.

In a recent ultrafiltration study,[7] it has been shown that, in a drinking water having a TOC of 1.5 $mg\,l^{-1}$, the part of TOC represented by solutes of molecular weight between 5000 and 1000 daltons is 40%, between 1000 and 300 daltons is 30%, and below 300 daltons is also 30%.

Some general analysis of organic matter contained in drinking water have been reported,[5,8-11] with identification of various solutes as aromatic hydrocarbons, phthalate esters, benzofuran, or chlorophenols.

Walton *et al.*[6] have shown that the fraction containing the non polar compounds of water effluents was the most toxic one. Tabor *et al.*[5] recently concentrated the organic material from 12001 of drinking water and fractionation of the residue indicated the mutagens to be among the mid polar and the non polar fractions. Another

study[12] proposed the first priority compounds for isolation should be lipid soluble, in the < 500 molecular range.

So there is evidence for studying and identifying the bulk water organics and specially the mid and the non polar fractions at the ppb level or below. These compounds are concentrated by extraction or by adsorption on non polar adsorbents such as C_{18} bonded silicas or carbonaceous adsorbents or divinylbenzene copolymers.

The on-line enrichment has been largely studied. Organic traces are preconcentrated on a small precolumn[13-15] (no larger than 1×0.2 cm i.d.), in order to avoid band broadening upon the subsequent analysis. High selectivity toward some compounds can be achieved by the preconcentration column or the analytical column, and by the detection mode, including chemical derivatization.[16,17] For example, polar anilines are detected at a 10 ppb level from 10 ml of industrial waters[18] and 30 ppt of metoxuron can be detected from 10 ml of surface waters.[19] Nevertheless, this method requires the knowledge of what is looked for to exhaust the selectivity of the chromatographic system at one point; it is very useful for the EPA pollutant research and for "trace hunt" in complex matrices.[20]

When a more general analysis is emphasized, off-line method is more suitable, even if it presents risks of contamination and degradation upon evaporation to dryness. The first risk is avoided if care is taken and the second one can be largely limited by operating at ambient temperature. The compounds lost during this step are the volatile ones which can be analyzed by other techniques. From a study of literature,[21] it appears that a direct analysis of the extract by GC/MS is impossible because of interfering compounds. It is then necessary to fractionate the extract prior GC/MS analysis. Reversed phase chromatography is a suitable method to separate solutes according to their polarity and chiefly their size. Adsorption chromatography is more convenient to separate extracts in chemical classes of increasing polarity.[21,22] This is why fractionation is more interesting with adsorption separation. We can expect solutes of same chemical group to be in the same fraction and then a further GC/MS analysis is more efficient.

In this study, we present analysis of low TOC water extracts both by reversed phase and by adsorption chromatography. Fractionation of the eluent during adsorption separation is carried out for a coupling with GC analysis. These procedures are used to monitor

the changes in organic matter during the two last steps of the drinking water treatment: ozonation and filtration on active charcoal.

Another application is the analysis of humic water extract.

EXPERIMENTAL

Concentration of samples

a) By adsorption on reversed phase material Samples up to 4 l of filtered water were passed through a 30×1 cm i.d. column packed with C_{18} bonded silica, Lichroprep RP18, mean particle size 40–63 μm (Merck, Darmstadt, FRG) via a preparative Analprep EC93 pump (Touzart and Matignon, Vitry-sur-Seine, France) at a flow rate of 10 ml min^{-1}.

The column was rinsed with 20 ml of distilled water in order to remove mineral salts and then eluted by 50 ml of methanol and 50 ml of methylene chloride, which were gently evaporated at 35°C under a light stream of nitrogen gas until dryness. Before each preconcentration, column was washed by successively 250 ml of methanol, 250 ml of methylene chloride, and 250 ml of methanol.

b) By liquid extraction Water sample (1 l) was extracted twice by 40 ml of chloroform stabilized with amylene and a third time after acidification by high purity hydrochloric acid, at pH 2.

The extract was then gently evaporated until dryness at 35°C.

Liquid chromatography

Reversed phase separation was performed on a 15×0.48 cm i.d. column, home-packed with octadecyl silica Nucleosil 5 C_{18}, mean particle size 5 μm (Macherey Nagel, FRG), using a SP 8000 chromatograph (Spectra Physics, Santa Clara, CA, USA), coupled to a spectrophotometer SPD-2A (Shimadzu, Kyoto, Japan) and a spectrofluorimeter FS 970 (Schoeffel, Ramsey, NJ, USA).

Adsorption separations were performed on a 20×0.48 cm i.d. column packed with silica Spherosil XOA 600, mean particle size 5 μm (Prolabo, Paris, France), using a 5060 pump (Varian, Palo Alto, CA, USA).

Injections were done through a variable volume sample loop with a conventional injection valve.

Gas chromatography

Analysis was carried out using a 3400 chromatograph (Varian) equipped with a flame ionization detector, an on-column injector, and a 25 m × 0.32 mm i.d. fused silica CP Sil 5 CB capillary column (Chrompack, Les Ulis, France), temperature programmed from 100 to 300 °C.

Carrier gas was helium at a flow rate of 3 ml min^{-1}.

Some fractions were esterified by heating with a 14% BF_3 in methanol (2 ml, 50 °C) for 20 min. Alkanes, alcohols and fatty acid methyl esters were identified by comparison of their retention time with authentic standards and quantified by internal or external method.

Chemicals

Most of chemicals were purchased from Merck and Prolabo.

Humic acids were from Fluka (Buchs, Switzerland).

Demineralized water, treated in Milli-Q ultrafiltration system (Millipore, Bedford, MA, USA), or quartz distilled (Quartex, Paris, France) was used for blanks.

All solvents were HPLC grade from SDS (Valdonne, France), or from Rathburn (Walkerburn, Scotland).

Water samples were obtained from "Compagnie Générale des eaux", (Paris, France), and were originated from the Choisy-le-Roi and Méry-sur-Oise water treatment plants.

RESULTS AND DISCUSSION

Concentration step by adsorption on C_{18} material

As we are looking for a screening and a possible identification of numerous compounds of various polarity at a very low concentration level, a trace enrichment step is necessary from a large sample volume.

The concentration of polar and weakly polar solutes is more difficult than the concentration of non polar compounds and is related to the choice of the dimensions of the preconcentration column and of the sample volume.

Dimension of the precolumn If neglecting the band broadening in a first approximation, there is a relation between the length L, the section S, the packing porosity ε, and the percolated volume V_p, which is:

$$V_p = \varepsilon LS(1 + k'_{\text{lim}}) \tag{1}$$

where k'_{lim} is the capacity factor, the breakthrough volume of which corresponds to V_p. If the capacity factor of a solute in pure water, k'_{H_2O}, is larger than k'_{lim}, the breakthrough volume is larger than V_p and, if assuming a complete desorption, a recovery of 100% is reached.

If k'_{H_2O} is smaller than k'_{lim}, the maximum recovery will be:

$$\text{Ri}(\%) = \frac{1 + k'_{H_2O}}{1 + k'_{\text{lim}}} \times 100.$$

So it is necessary to know k'_{H_2O} or to be able to predict it in order to choose both the precolumn dimensions and the sample volume.

Prediction of k'_{H_2O} It has been shown[23] that k'_{H_2O} can be extrapolated from k' measurements in water-methanol mixtures, assuming the curves $\log k'$ *versus* the water content are linear. It is then necessary to measure k' of each solute for two different water–methanol compositions at least; but these extrapolations are not accurate as the linearity for rich water mixtures is not always observed.

A small column (10×0.46 cm i.d.) was packed with the same C_{18} silica as the preconcentration column in order to shorten the elution volumes with pure water as eluent. It was experimentally verified that the retention volume of a solute on the preconcentration column was derived from k'_{H_2O} measurement on the small column, knowing the masses of bonded silica in each column.

In Figure 1, it is shown that $\log k'_{H_2O}$ is linearly related to the water–octanol partition coefficient which can be readily calculated from Rekker fragmental constants.[24]

From the measurements of two or three retention volumes in water, k'_{H_2O} can be predicted for any solute. With a 30 cm × 1 cm i.d. column and a sample volume of 41 k'_{lim} is equal to 210 assuming a porosity of the stationary phase of 0.8. For solutes such as *o*-nitroaniline or *p*-chlorophenol the recovery is ~50%.

Blank problem Blanks of preconcentration made with pure water ("Millipore" or "Quartex" grade) are satisfactory when the subsequent analysis is carried out by reversed phase or adsorption chromatography coupled to UV spectrophotometric or fluorimetric detector.

When further analysis is performed by GC/FID, some impurities coming from the bonded silica are revealed and trace level analysis becomes impossible; this was already mentioned for adsorption on polystyrene–divinylbenzene copolymers.[25,26] A drastic cleaning of bonded silica is necessary before using for preconcentration at the ppb trace level determination. This cleaning step is on study.

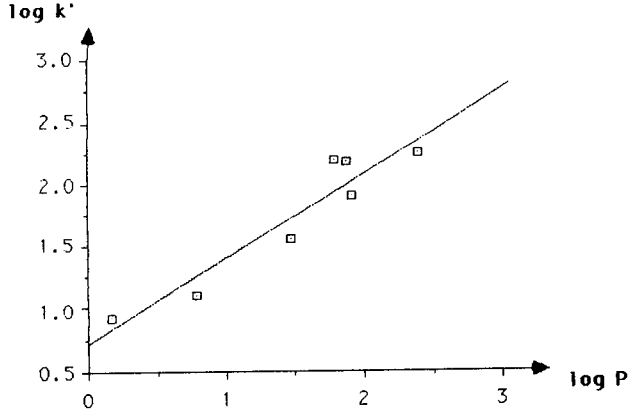

Figure 1 Variation of the capacity factor logarithm of various solutes eluted by pure water *versus* the logarithm of their water–octanol partition coefficient. Solutes: amino-3-phenol, resorcinol, phenol, *p*-cresol, nitrobenzene, nitroaniline, *p*-chlorophenol.

Concentration step by liquid extraction

When subsequent analysis is made by GC/FID, the concentration step was carried out by liquid extraction. Though it is really time consuming and any contamination from the laboratory surroundings has to be eliminated, this concentration technique leads to good quality blank, allowing a detection of compounds at the 8×10^{-12} attenuation range of the FID detector.

The organic matter extracted by chloroform is, by definition, the lipidic fraction and contains also various organic compounds as alkanes, aromatic hydrocarbons, phthalate esters, pesticides, phenolic and organophosphorous compounds.

The composition of the lipidic extract seems to be similar to the extract obtained by adsorption on C_{18} material. But with this method the prediction of recoveries is impossible, those being difficult to measure for the simple reason that it is impossible to spike correctly water with low soluble solutes.

Extracts were generally saponified before analysis.

Reversed phase chromatography

The total extract of 41 samples was dissolved in 500 μl of methanol; the enrichment factor is then 8000 for solutes having a capacity factor k'_{H_2O} higher than 200. A part of the dissolved extract (100 μl) is injected on a reversed phase analytical column eluted by a water–methanol gradient.

Some solutes were analyzed in these conditions and Table 1 re-assembles their retention time and their detectability at 210 and 254 nm and by fluorescence. It can be observed that the elution order is much more related with the solute size than with its chemical class: phthalate esters or aromatic hydrocarbons are found all along the gradient.

Nevertheless, we can expect a fingerprint indicating the size and polarity of the extract; this was applied to water at different points of the treatment plant for drinking purposes. In modern plants, river water is successively purified by clarification (filtration or floculation), filtration on sand, ozonation, filtration on granular active charcoal, and finally a light chloration for bactericide purposes before distribution.

Table 1 Retention time and detectability for some test compounds

Solutes	t_R *(min)*	*UV 210 nm*	*UV 254 nm*	*Fluorescence*
Resorcinol	6	+ +	+	no
Benzylic alcohol	17	+ +	+	no
Cafeine	27	+	+	no
o-Nitroaniline	35	+	+	no
Acetophenone	35	+ +	+ +	weak
Phenylpropanol	37	+ +	+	no
Dimethylphthalate	40	+ +	+	no
Benzene	41	+ +	+	no
Diethylphthalate	48	+ +	+	no
Naphthol	49	+ +	+	yes
Toluene	52	+ +	+	no
Anthraquinone	53	+	+ +	no
Benzophenone	55	+	+ +	no
Naphthalene	55	+ +	+	no
Dibuthylphthalate	58	+ +	+	no
Biphenyl	58.5	+	+ +	no
Fluorene	59.4	+ +	+	yes
Phenanthrene				
Anthracene	61	+ +	+	yes
Fluoranthrene	62.8	+	+ +	yes
Pyrene	63.2	+	+ +	yes
Chrysene	64.4	+	+ +	yes

After sand filtration, the TOC of the water is not higher than 2 to 3 $mg\,l^{-1}$, the tap water TOC being 1 to 2 $mg\,l^{-1}$. So, TOC values do not indicate a great variation of the organic content during the ozonation and active charcoal filtration steps.

As it can be seen in Figure 2 there is a real difference between the reversed phase fingerprints of water extracts after filtration (2a), ozonation (2b), and active charcoal filtration (2c). Three detection modes (UV 210, UV 254, fluorescence ($\lambda_{ex}=254$)) are represented. The water extract after sand filtration is rich of organic matter, much more visible at 210 nm than at 254 nm and non fluorescent. The ozonation step eliminates most of the less polar compounds and fluorescent ones appear. Active charcoal filtration eliminates most of the matter, the residual one being however visible at 210 nm, 254 nm and by fluorescence.

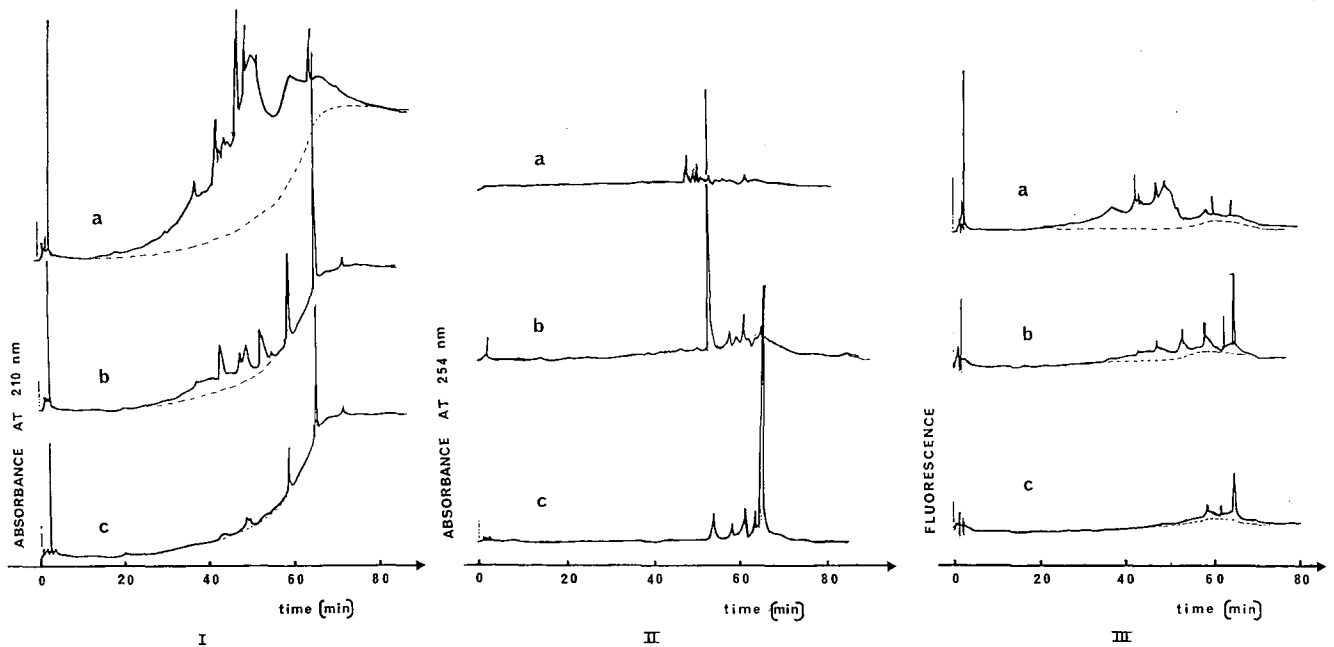

Figure 2 Fingerprints obtained by reversed-phase chromatography of water extracts at different steps of the drinking water treatment: (a) after sand filtration; (b) after ozonation; (c) after active charcoal filtration. Column: Nucleosil C_{18}, 5 μm, 15 × 0.48 cm i.d. Mobile phase: Water-methanol gradient (step at 10% of methanol from 0 to 5 min, increasing to 100% of methanol from 5 to 60 min, step at 100% of methanol). Flow rate: 1.5 ml min^{-1}. Detection: (I) UV at 210 nm; sensitivity, 0.16 a.u. (II) UV at 254 nm; sensitivity, 0.64 a.u. (III) Fluorescence, $\lambda_{ex} = 300$ nm, $\lambda_{em} > 340$ nm; sensitivity, 1 μA.

These fingerprints are much more informative than TOC measurements to follow the efficiency of the treatment steps. We see also on these chromatograms that an identification is impossible, maybe except for 4 or 5 compounds with a diode array detector.

If we want to identify what is affected by the different treatment steps, a fractionation of the eluent before a subsequent GC/MS analysis is necessary to reduce interference among components.

Coupling fractionation with reversed phase chromatography is not adapted for such a purpose because solutes having nearly the same size and different functionalities are not separated. A separation by chemical group is more suitable.

Adsorption chromatography

The fractionation was studied with various known solutes. The chosen eluting gradient is a mixture of isopropanol and isooctane in order to detect solutes at 210 nm. It is represented in Figure 3.

In adsorption chromatography, the condition for reproducible analysis is to use isohydric eluents.[27] In our experiments, this is achieved by using dry isooctane and isopropanol containing 0.7% of water. When starting the gradient by 0.5% of isopropanol, the water content coming from isopropanol is enough for settling the isoactivity all through the gradient, and equilibrium time of 10 min between two successive injections allow reproducible retention times. This could not be achieved by starting with pure isooctane and a strict control of the water content should be necessary.

Table 2 reports the retention times of the tested solutes. It can be seen, by comparison with Table 1, that adsorption chromatography is much more suitable for re-assembling solutes according to their chemical function, independently of their size.

The resolution between groups is fairly good except for fraction I which contains together alkanes, HAP, phthalate esters and ketones. Separation between these groups can be easily achieved by a subsequent separation on another silica column with an elution by dry hexane.

Fraction II contains solutes as *n*-fatty acids and phenolic compounds.

In fraction III we find some more polar compounds as *n*-alcohols, whereas most polar compounds are in the last fraction.

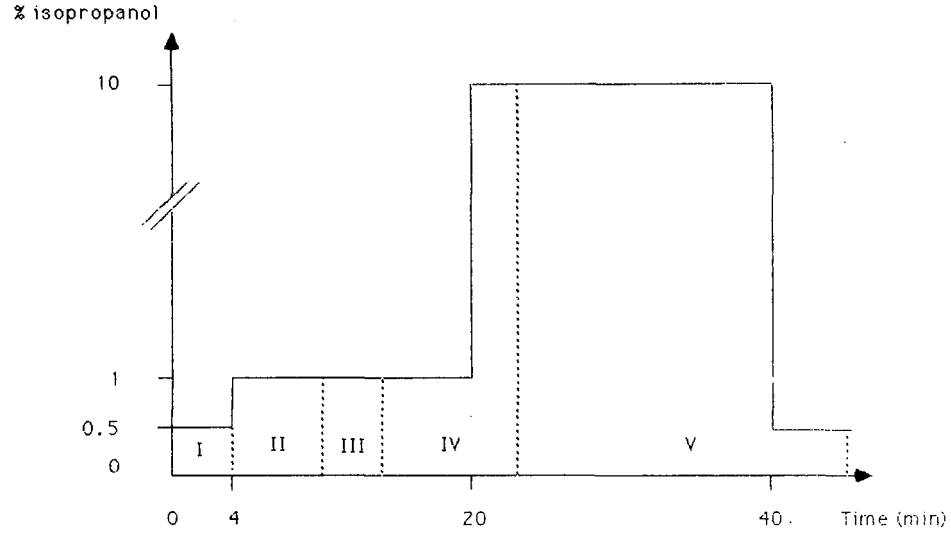

Figure 3 Gradient used in adsorption chromatography and fractionation according to chemical classes. Column: Spherosil XOA 600, 5 μm, 20 × 0.48 cm i.d. Flow rate: 2 ml min^{-1}.

This fractionation was applied to water extracts of the plant. Figure 4 shows two fingerprints before (a) and after (b) ozonation. As for reversed phase chromatography, these fingerprints show the apparition of mid polar and polar compounds during the ozonation step, but no subsequent identification can be carried out.

Each fraction was collected and gently evaporated and analyzed by GC.

Figure 5 shows the gas chromatogram of an extract (after ozonation step) before fractionation, and Figure 6 the gas chromatograms, for the same extract, of the various fraction collected through gradient elution in adsorption chromatography. It is visible that the fractionation has reduced the interference among compounds. The organic matter is well separated in polarity groups and a coupling with mass spectrometry is possible.

Quantitative analysis is also possible by external standardization or, which is more accurate, internal standards introduced in water before concentration step, as we can expect the losses during the

Table 2 Retention times (min) of various solutes with isopropanol–isooctane gradient elution

n-alkanes ($n > C_{12}$)	1.3–2	Chlorophenols	
HAP	1.3–3	2,4,6-trichlorophenol	6.1
Phthalates		2,4,5-trichlorophenol	10.1
dimethyl phthalate	6.4	*n*-alcohols	
dihexyl phthalate	2.6	docosanol (C_{22})	13
didecyl phthalate	2.2	dodecanol (C_{12})	14
Aldehydes and ketones		Phenol	14.1
octanal	2	Sterols	
decanal	2.8	cholesterol	14.6
benzoic aldehyde	3	campesterol	14.4
benzophenone	2.5	stigmasterol	14.4
n-fatty acids		lanosterol	9.4
$C_{28:0}$	4	Nitrophenols	
$C_{10:0}$	10	*p*-nitrophenol	18.1
Methyl phenols		*m*-nitrophenol	24.4
2,4-dimethyl phenol	6.3	Hydroxy-fatty acids	>23
2,6-dimethyl phenol	7.2		
2,5-dimethyl phenol	10.9		
3,5-dimethyl phenol	13.1		

different steps of the procedure to be the same for the standards and for the other compounds.

In fraction I, an alkane distribution is identified with a maximum value between C_{32} and C_{36}. The same distribution is found in natural waters. External standardization indicates a concentration of $1\ ng\ l^{-1}$ for these alkanes, and this concentration was found at every step of the drinking treatment.

Another application is an analysis of humic acid water extract, in order to determine the part of the humic material analyzable by our method in drinking water. Humic substances are known to constitute the major part of the organic matter in lake or river water, and they are still present in drinking water.[28–31]

Literature values for molecular weight range from a few hundreds to a few hundred thousands. Most of the heavy substances are eliminated by the floculation and the sand filtration steps, but we can expect the fraction of molecular weight above 500 which

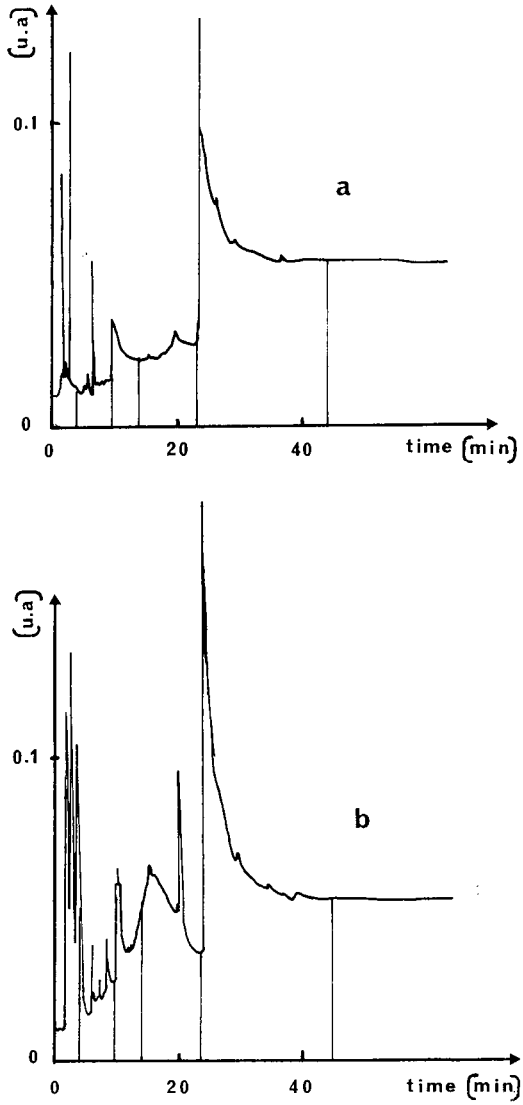

Figure 4 Fingerprints obtained by adsorption chromatography of water extracts at different steps of the drinking water treatment: (a) after sand filtration (analysis of an extract from 1.3 l) and (b) after ozonation (analysis of an extract from 4 l). Same operating conditions as Figure 3.

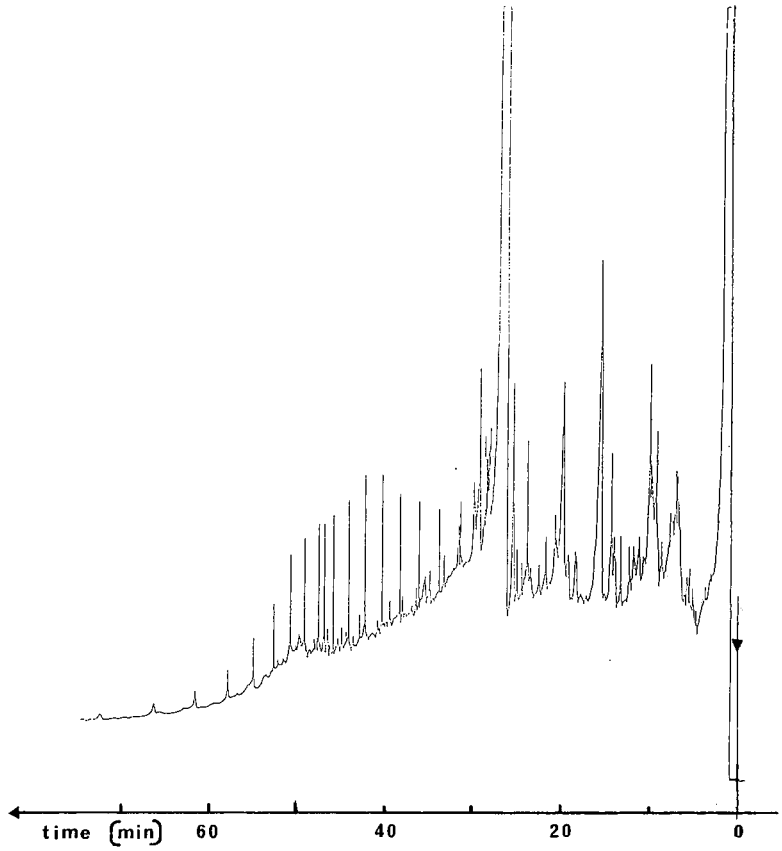

Figure 5 Gas chromatogram of the total extract from 8 l of water after the ozonation step. Column: CP Sil 5 CB 25 m × 0.32 mm i.d. Temperature programmation, 100 °C to 300 °C at 4 °C min^{-1}. "On column" injector: temperature programmation, 50 °C to 300 °C at 100 °C min^{-1}; injection of 1 μl of the extract (dissolved in a total volume of 500 μl of isooctane–isopropanol (90/10 v/v)). FID detector: $T = 300$ °C; sensitivity, 8×10^{-12}.

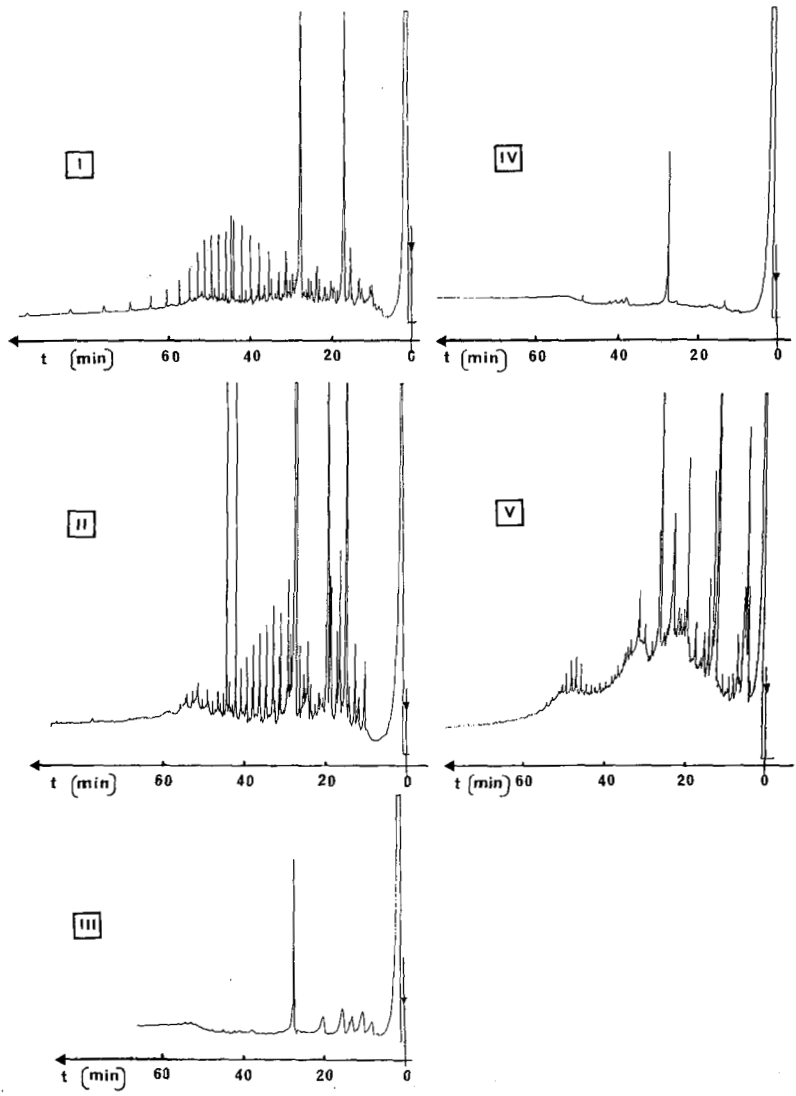

Figure 6 Gas chromatograms of the different fractions obtained during the analysis by adsorption chromatography of an extract from 41 of water after the ozonation step. See Figure 3 for the fractionation and Figure 5 for the operating conditions. Injection of 1 μl (each fraction has been evaporated and the dry extract dissolved in 100 μl of isooctane–isoporpanol (90/10 v/v)).

represents about 50% of the TOC, to be constituted of humic substances.

Humic substances are poorly known. They are extracted (generally from soil) at pH 13 to 14, and by definition the fraction which precipitates at pH 2 constitutes the humic acids, the soluble one being the fulvic acids. The chemical nature of aquatic humic substances is a subject of great interest to environmental scientists, and most of the water soluble substances are polymeric complex organic acids.

Our aim is not an identification of the humic substances in drinking water, but rather to know the behavior of these substances when analyzed by the adsorption chromatography with fractionation procedure.

XAD resins have been shown to be effective adsorbents for removal of humic substances from natural waters;[30] Aiken *et al.*[31] used XAD-7 and XAD-8 acrylic ester resins to concentrate fulvic acids and obtained complete recovery by desorption with 0.1 N NaOH.

We thus can expect a part of the humic substances to be concentrated by adsorption on C_{18} material or by liquid extraction, even if the recovery is not of 100%.

We chose, for a first investigation, humic acids of low molecular range from 600 to 1000. It is possible to dissolve a maximum of $36\,mg\,l^{-1}$ of the sample in "quartex" grade water, and three liquid extractions (the last one performed at pH 2) yield to a quantity of dry extract of $4.4\,mg\,l^{-1}$. This represents the lipidic extract of humic acids dissolved in water. Internal standardization was made with 11 μg of eicosane and 11 μg of *n*-octadecanol.

After saponification, only 0.8 mg is obtained, and the corresponding GC chromatogram shows a complex mixture of compounds (Figure 7). The chromatograms after adsorption fractionation are shown in Figure 8, and here again coupling with MS can be achieved. In fraction I we find an alkane distribution. Many compounds are found in fraction III, where is also the internal standard *n*-octadecanol. Many polar or high molecular weight compounds are in fraction V.

More information could certainly be derived from the chromatograms obtained by methylation of the fractions. Nevertheless, by comparing Figure 6 and Figure 8, we can say that humic acids of low

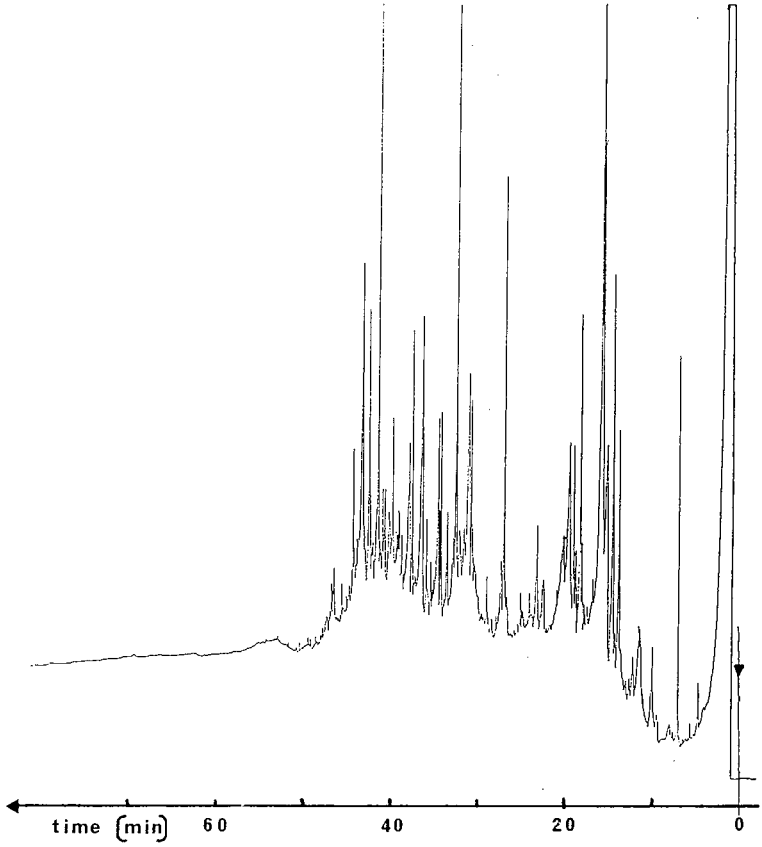

Figure 7 Gas chromatograms of the extract from 1 l of water saturated by humic acids. Injection of 1 μl (the dry extract has been dissolved after saponification in 500 μl of isooctane–isopropanol (90/10 v/v)). Same operating conditions as Figure 5.

molecular range may be analyzed by this method, and information about them can certainly be drawn by coupling with MS.

CONCLUSION

This study has shown that analysis of a highly complex mixture as

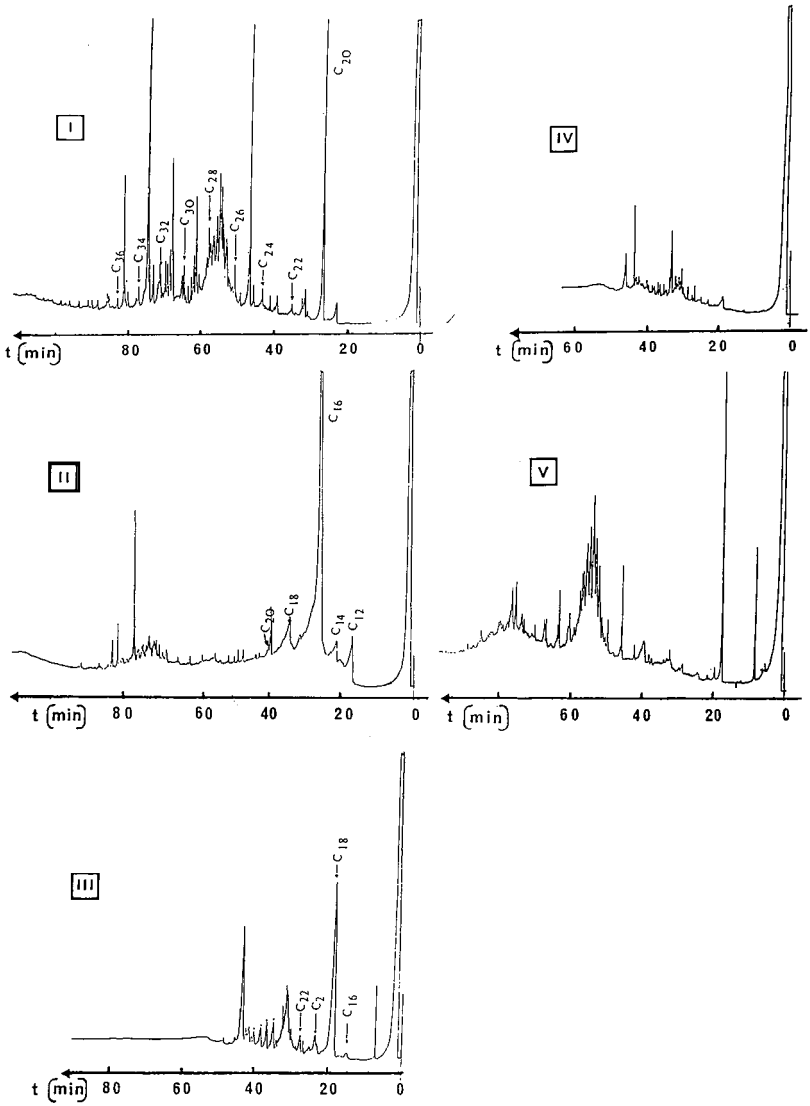

Figure 8 Gas chromatograms of the different fractions obtained during the analysis by adsorption chromatography of the humic acid water extract. Same operating conditions as Figures 5 and 6. (*n*-Alkanes, *n*-fatty acids and *n*-alcohols have been identified in fractions I, II and III.)

organic matter in drinking water, when looking for many components, each at a very low concentration, is difficult, but can be partly resolved by adsorption chromatography, fractionation of the eluent, and subsequent analysis by GC.

Coupling with MS cannot be realized for the GC analysis of the total extract, but the fractionation by chemical groups of increasing polarity allows the MS coupling.

Though this method is time consuming and requires some precautions, it is performant in analyzing water with low TOC content as in the case of drinking waters.

On the other hand, short analysis, coupling preconcentration on C_{18} bonded silica and gradient elution, allows to follow the efficiency of the various steps in water treatment plants.

Acknowledgements

Compagnie générale des eaux, and the Syndicat des eaux de l'Ile-de-France are thanked for having supported a great part of this work.

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