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Recent methods for the determination of volatile and non-volatile organic compounds in natural and purified drinking water

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ABSTRACT

Four analytical protocols for the extraction and preconcentration of organic residues in natural or purified drinking water were investigated and compared: closed loop stripping analysis; simultaneous extraction–distillation; purge and trap analysis; continuous liquid–liquid extraction. Organic extracts were submitted to a variety of separation and identification techniques. Volatiles were determined by conventional capillary column gas chromatography with tandem mass spectrometry, using triple-stage quadrupole instruments. Non-volatile and thermally labile molecules were investigated by several different techniques (high-temperature gas chromatography, capillary column supercritical fluid chromatography, pyrolysis gas chromatography–mass spectrometry, thermospray liquid chromatography with tandem mass spectrometry and conventional fast-atom bombardment with tandem mass spectrometry). Several samples recently examined in the laboratory provide examples of this multitechnique approach for a more complete knowledge of the organic carbon distribution in water-dissolved organic matter, taking into account organic substances with widely different volatilities, polarities and thermal stabilities.

INTRODUCTION

Although the number of known organic substances is estimated to be *ca.* $9 \cdot 10^6$ [1] only a few thousands, representing a few percent of the total organic carbon content, have been identified in natural and in purified water.

Since the first report of trihalomethanes (THMs) in chlorinated water [2], dissolved organic compounds in water have become a subject of increasing concern. Some of them are presumed toxic, either directly, or after chemical reactions with oxidizing additives and detergents, whose increasing domestic use appears to be inevitable. Specific trace volatile substances affect water quality, degrading its organoleptic parameters, whereas some other classes of compounds are responsible for bacterial regrowth in water distribution systems. Consequently, accurate

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and sensitive analytical methods that determine levels of trace constituents are being developed or improved. They are required for routine quality monitoring and for validating new water purification procedures.

More generally, water-soluble organic matter poses a wide variety of analytical problems, depending on such physicochemical factors as polarity, volatility, thermal stability, etc., and their determination requires a careful choice between different extraction, concentration, chromatographic separation and mass spectrometric identification procedures.

Among the organics suspected to be present in drinking water (Table I), many are ignored by conventional accepted methods, especially non-volatile and polar volatile substances. The latter are particularly responsible for bad tastes and odours that affect water quality. Non-volatile matter amounts to *ca.* 90% of the total organic carbon content of water-soluble organic substances. This major fraction is largely responsible for chemical interferences during water chlorination processes and is the main source of THMs.

TABLE I

CLASSIFICATION OF ORGANIC COMPOUNDS PRESENT IN WATER

	Volatile	Semi-volatile	Non-volatile
Polar	Alcohols Ketones Fatty acids	Alcohols Ketones Fatty acids Phenols	Polyelectroytes Carbohydrates Fulvic acids
Semi-polar	Ethers Esters Aldehydes	Ethers Esters Aldehydes Epoxides Heterocyclic compounds	Proteins Carbohydrates Humic acids
Non-polar	Aliphatic HCs[a] Aromatic HCs	Aliphatic HCs Alicyclic HCs Arenes Aromatic HCs	Non-ionic polymers Lignins Hymatomelanic acids
	———— Increasing molecular mass ————→		

[a] HCs = Hydrocarbons.

Several modern analytical methods have been recently investigated in the research laboratory of the Société Lyonnaise des Eaux. This paper discusses their potential for the determination of various classes of organic substances, with widely differing physicochemical parameters, in natural and in purified water.

EXPERIMENTAL

Four extraction and preconcentration methods that could be applied to volatile and semi-volatile compounds were tested and compared: closed loop stripping analysis (CLSA); simultaneous distillation extraction (SDE); "purge and trap"; and continuous liquid–liquid extraction (CLLE). The experimental details of these methods have been reported elsewhere [3]. Non-volatile molecules were separated by size-exclusion chromatography on Sephadex gels, or capillary column supercritical fluid chromatography (CSFC). Identification was achieved by gas chromatography (GC)–mass spectrometry (MS), whenever possible, and by thermospray liquid chromatography–MS and direct-probe fast-atom bombardment (FAB) MS. Various commercial models of GC and high-performance liquid chromatographic (HPLC) instruments available in the laboratory were used; the CSFC instrument was from Carlo Erba; GC–MS was performed with a Finnigan ITD; FAB-MS, GC–MS, LC–MS and MS–MS experiments were conducted on either a Nermag R-30-10 or a Finnigan TSQ70 multiquadrupole machine. Experimental conditions for chromatographic separations are described in the figure legends.

RESULTS AND DISCUSSION

Extraction and preconcentration methods

Volatile solvents by "purge and trap". The classical "purge and trap" method of Bellar and Lichtenberg [4] is the method of choice for determining non-polar solvent residues (*e.g.* aromatic and chlorinated solvents) in drinking and in waste water. Capillary column GC combined with one or more of the available detection systems (flame ionization, electron capture, photoionization, mass spectrometry, etc.) provides sensitivity levels in the range 0.1–200 μg/l. EPA-approved methods (*e.g.* standard methods 502.1, 503.1, 524, 601, 602, 624) mainly address non-polar volatile compounds. However, the "purge and trap" method can also be applied to more polar solvents, *e.g.* oxygenated solvents. For example, using this extraction and preconcentration method followed by conventional GC, samples from a drinking water reservoir with a newly installed vinyl coating revealed contamination by methyl ethyl ketone and ethyl acetate, which were used in the vinyl coating material (Fig. 1).

Polar volatile and semi-volatile substances by CLSA and SDE. Despite their abundance at the low ppb level, volatile and semi-volatile soluble matter are of utmost importance for water organoleptic quality. The CLSA method of Grob and Zürcher [5] remains unsurpassed for target compound determination of well-known pungent contaminants, *e.g.* geosmine and methylisoborneol, and they can be accurately quantitated at the ng/l level [6] (*e.g.* 10 ng/l for geosmine). However, CLSA is limited to easily stripped substances that can then be absorbed on activated carbon; other substances are better extracted by SDE.

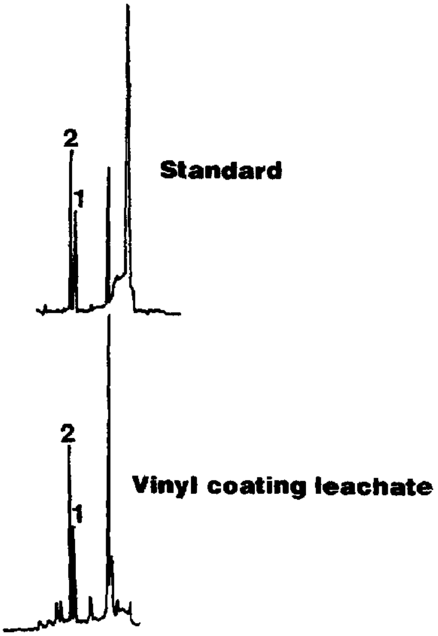

Fig. 1. Analysis of semi-polar volatile solvents by purge and trap GC–flame ionization detection. Lower trace: volatile solvents from a purge and trap extract of a reservoir water with a newly installed vinyl coating. Upper trace: reference volatile solvents used in the vinyl plastic coating material. Isothermal GC at 30°C, J&W capillary column (15 m × 0.53 mm I.D. coated with DB624-30M, d_f = 3 μm (J&W, Chromoptic, Montpellier, France). Peaks: 1 = Methyl ethyl ketone; 2 = ethyl acetate.

Comparison studies using CLSA and SDE for volatile and semi-volatile constituents of the soluble organic matter from an underground water sample revealed that, although the total extract is four times less abundant with SDE, classes of more polar substances, *e.g.* alcohols, ethers, pyridines, ketones, carboxylic acids, amines, and heavier non-polar alkanes were better extracted (Fig. 2 and Table II). For favourable substances, *e.g.* *n*-alkanes, a limit of detection of 20 ng/l can be reached, using SDE. On the other hand, CLSA is a better extraction and preconcentration method for other classes of pollutants, *e.g.* aliphatic aldehydes, terpenes, iodo-THMs, alkylnaphthalenes, etc. Consequently, the two methods appear to be complementary rather than concurrent.

Semi-volatile compounds by CLLE. Size-exclusion chromatography through XAD-type macroporous resins has been used since 1974 for the selective extraction and characterization of semi-volatile and humic substances from large-volume water samples [7]. However, the resin requires tedious and lengthy cleaning and activation protocols, and careful blank experiments to avoid background interferences. In addition, extraction yield varies with sample load, making the

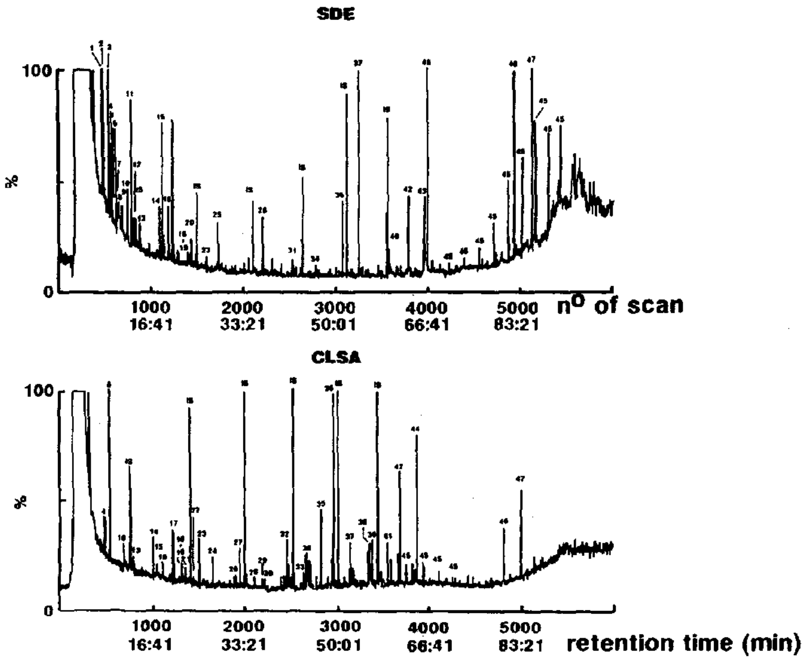

Fig. 2. Comparison between SDE and CLSA techniques applied to a ground water sample for the investigation of volatile and semi-volatile compounds. ITD GC–MS, 50 m × 0.32 mm I.D., OV 1701 capillary column, d_f = 0.2 μm (Chrompack, Les Ulis, France); temperature programme: 5 min at 25°C, then to 280°C at 3°C/min, and 10 min at 280°C. For compound identification, see Table II.

method poorly quantitative. Continuous liquid–liquid extraction avoids these two problems and is recommended for use whenever possible [3].

Comparison between baregraph reconstructed GC chromatograms from a raw Seine river sample, using CLLE and SDE, clearly demonstrates the increased extraction power of CLLE (Fig. 3).

Non-volatile pollutants by high-temperature GC and CSFC. Conventional capillary column GC is limited to volatile molecules with masses up to 500–700 Da. Heavier substances, up to 1000–3000 Da depending on the chemical structure, can be handled using either high-temperature GC (HTGC) or CSFC. The better chromatographic efficiency of HTGC makes the former method more attractive for thermally stable substances, *e.g.* triglycerides [8]. Because there is a growing need for the determination of this group of lipids in waste water, the feasibility of HTGC was tested on model mixtures, with satisfactory results (Fig. 4).

On the other hand, heat-sensitive molecules are better tackled by CSFC [9]. The analysis of a river water assumed to be polluted with poly(ethylene glycol) oligomers (PEG) by an accidental spillage was the occasion to test the possible application of CSFC to non-volatile contaminants (Fig. 5). The comparison between the chromatograms of a river extract and of an authentic PEG mixture

TABLE II

ORGANIC COMPOUNDS IDENTIFIED IN AN UNDERGROUND WATER

Compound	SDE	CLSA	Compound	SDE	CLSA
1 Alcohol or ether	+	−	25 2-Propenylidenecyclobutene	+	−
2 Alcohol or ether	+	−	26 Naphthalene	−	+
3 Alcohol or ether	+	−	27 Decanal	−	+
4 Toluene	+	+	28 Benzothiazole	+	+
5 Acetic acid	+	−	29 Aliphatic alcohol	−	+
6 Tetrachloroethylene	+	+	30 Methylnaphthalene	−	+
7 Pyridine	+	−	31 Amine	+	−
8 1,1-Diethoxypropane	+	−	32 Aliphatic alcohol	−	+
9 Chloroketone	+	−	33 2,6-Di-*tert.*-butylquinone	−	+
10 Dibromochloromethane	+	+	34 Aliphatic alcohol	+	+
11 Methylpentenone	+	−	35 1,5-Di-*tert.*-butylmethylbicyclohexanone	−	+
12 Chloroketone	+	−			
13 Xylene	+	+	36 Trimethylpentanediol, diisobutyrate	+	+
14 Bromoform	+	+	37 Diethylphthalate	+	+
15 Alcohol or ether	+	+	38 Fatty acid ester	−	+
16 2-Butoxyethanol	+	+	39 Methanoazulenol, octahydrotetramethyl acetate	−	+
17 $C_{10}H_{16}$ terpene	−	+			
18 Dichlorobenzene	+	+	40 Tetradecanoic acid	+	−
19 Benzaldehyde	+	+	41 Aliphatic alcohol	−	+
20 Alcohol or ether	+	−	42 Diisobutylphthalate	+	+
21 Octanal	−	+	43 Hexadecanoic acid	+	−
22 Dibromoiodomethane	−	+	44 Dibutylphthalate	+	+
23 Aliphatic alcohol	+	+	45 Alkane	+	+
24 Nonanal	−	+	46 Dioctylphtalate	+	+
			47 Not determined	+	+

indicates that CSFC could be used to monitor the pollution level, provided that some on-line identification method is added at the column end.

Heterobiopolymers by pyrolysis GC–MS. Humic substances are the major constituent of water-soluble organic matter and arise from chemical and bacterial

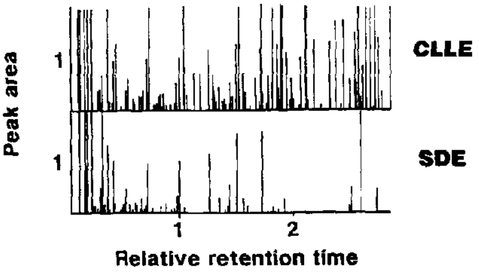

Fig. 3. Idealized baregraph reconstructed chromatograms from the GC analysis of a Seine river (before ozonation) sample extracted by CLLE and SDE techniques.

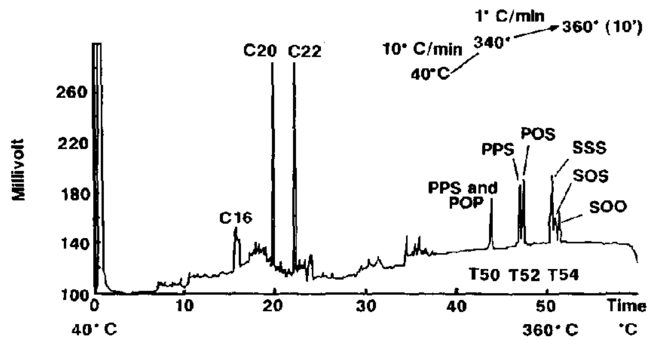

Fig. 4. High-temperature GC separation of a natural triglyceride mixture (P = palmityl, O = oleyl, S = stearyl). Rescom "golden capillary column" (25 m × 0.25 mm I.D.) coated with OV-1, d_f = 0.1 μm (Rescom, purchased from Delsi, Argenteuil, France).

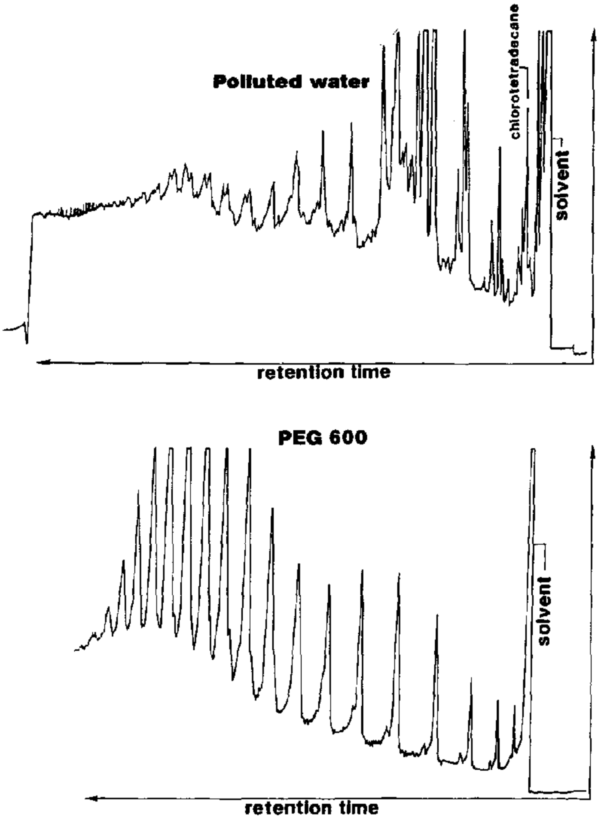

Fig. 5. Upper trace: capillary SFC separation of the organic content of a river water presumably contaminated with poly(ethylene glycol) oligomers. Lower trace: separation of a synthetic PEG 600 mixture, using same temperature and pressure conditions. J&W capillary column (10 m × 0.050 mm I.D.) coated with DB 5, d_f = 0.4 μm (column purchased from Erba Sciences, Massy, France); temperature, 140°C; pressure, 12 min at 15 MPa, then from 15 to 35 MPa at 0.3 MPa/min.

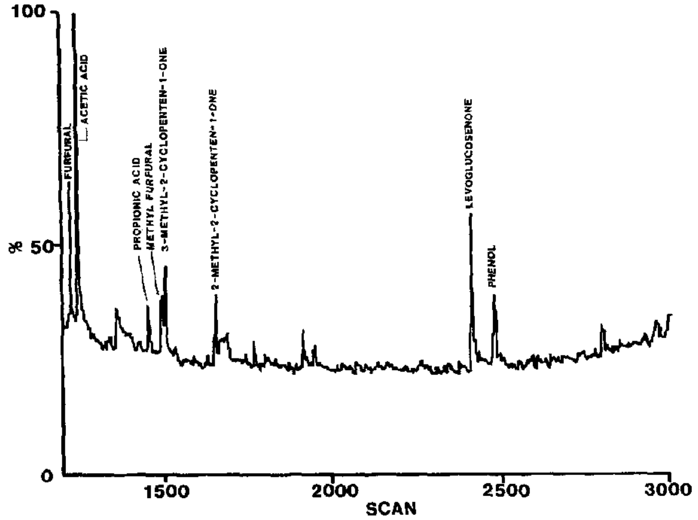

Fig. 6. Pyrolysis GC–MS determination of the substances with masses > 5000 Da from the Sephadex separation of a raw ground water concentrate (Le Pecq-Medium, France). ITD GC–MS, DB-WAX-30W capillary column (J&W) (30 m × 0.32 mm I.D.); temperature, 5 min at 30°C, then to 220°C at 3°C/min and 10 min at 220°C.

degradation, followed by polycondensation, of plant and animal organic constituents. They accumulate in water either directly after burial of dead organisms, or indirectly, after soil leaching. Classical analytical methods include size-exclusion chromatography through XAD resins followed by more or less extensive chemical degradation, then derivatization to make suitable volatile derivatives for GC and GC–MS investigations. Polysaccharide and peptide subunits of the humic matrix are excluded by this protocol, and it could be the reason for the probably excessive success of the polyhydroxyaromatic model suggested for fulvic acids [10].

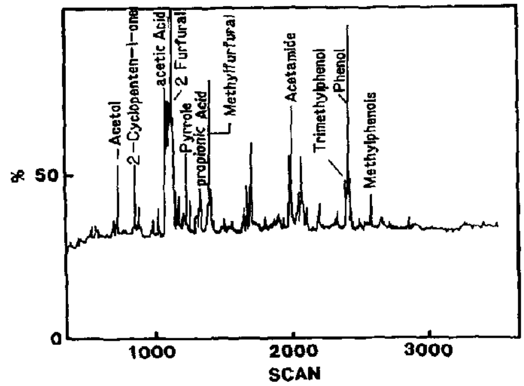

Fig. 7. Pyrolysis GC–MS determination of the substances with masses > 5000 Da from the Sephadex separation of a prechlorinated water from a dam reservoir (Cholet, France). Conditions as in Fig. 6.

Sephadex type size-exclusion chromatography followed by pyrolysis GC–MS does not discriminate very polar molecules and is a better approach for the characterization of humic matter, since it may take into account all organic classes contributing to the total water organic content.

For example, two Sephadex extracts corresponding to mixtures of substances with masses greater than 5000 Da, from a raw ground water (Le Pecq Medium, France, Fig. 6), and a prechlorinated water from a dam reservoir (Cholet, France, Fig. 7), respectively, were submitted to pyrolysis GC–MS investigation. Furane derivatives (furfural, methylfurfural), anhydro-sugars (levoglucosenone) and cyclic ketones (cyclopentenone) arise from pyrolytic dissociation of sugar substructures; pyrrole arises from proteins and peptides; acetamide is from amino-sugars; phenols and cresols arise from polyhydroxyaromatic fragments. The method provides clear evidence of chemical differences between humic substances from water samples of different origins. The investigation of a large number of natural water samples has revealed the greater importance of polysaccharides, amino-sugars and protein constituents, compared with polyphenolic compounds that often appear to be much less abundant [11].

Modern MS identification methods

Thermospray MS–MS. The potential of HPLC for the separation of polar non-volatile molecules is very high. However, detection in general, and in particular on-line MS monitoring, is much more complex compared with GC–MS or CSFC–MS. The thermospray interface for LC–MS offers some interesting features and is a possible method for the investigation of water pollutants, as demonstrated by the separation of selected model pesticides (Fig. 8), which are thermally labile and therefore difficult to analyse by GC (except for linuron and alachlor).

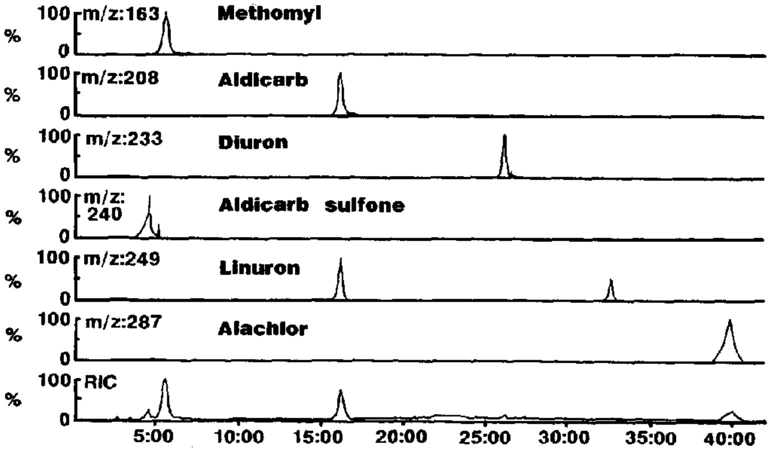

Fig. 8. LC–thermospray-MS separation of a synthetic mixture of six pesticides. Nucleosil C_{18} reversed-phase column (25 cm × 4.6 mm I.D.) (SFCC, Neuilly Plaisance, France), MeOH–0.1 *M* NH_4OAc (50:50) at 1.0 ml/min; interface control T_1 = 100°C, T_2 = 220°C, T_4 = 250°C.

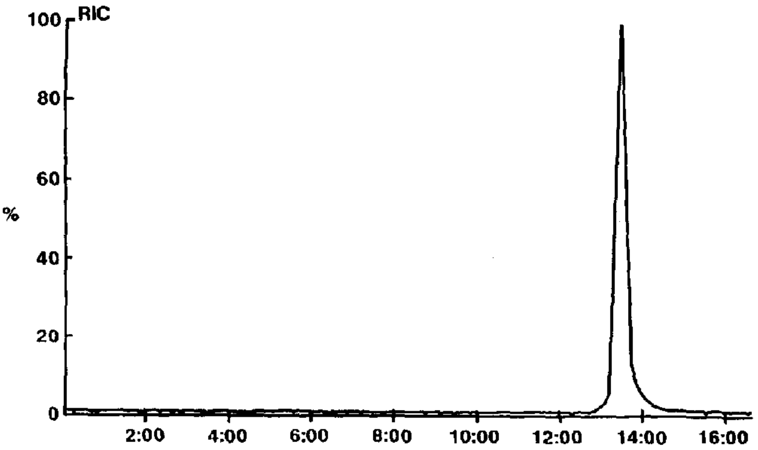

Fig. 9. LC–thermospray-MS–MS determination of a polluted water extract spiked with 100 pg/μl aldicarb. Cell collision energy, 20 eV.

For water samples containing high contaminant levels, a daughter ion scan during an MS–MS investigation excluded matrix interferences and significantly lowers the minimum detection limit. For instance, a polluted water extract was spiked with aldicarb at a concentration of 100 pg/μl, corresponding to the European maximum contaminant level of 100 ng/l, assuming an enrichment factor of 1000 after initial extraction and preconcentration of the water extract. Thermospray MS–MS was found to meet the sensitivity requirements for rapid quantitative determination of aldicarb in the spiked sample (Fig. 9). The result con-

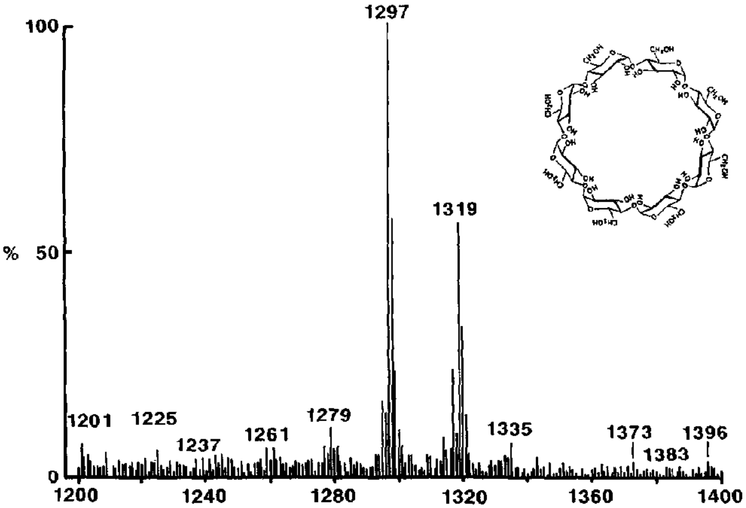

Fig. 10. Partial mass spectrum in the molecular mass region, from the FAB-MS analysis of a γ-cyclodextrin standard in a glycerol matrix, obtained with a quadrupole instrument.

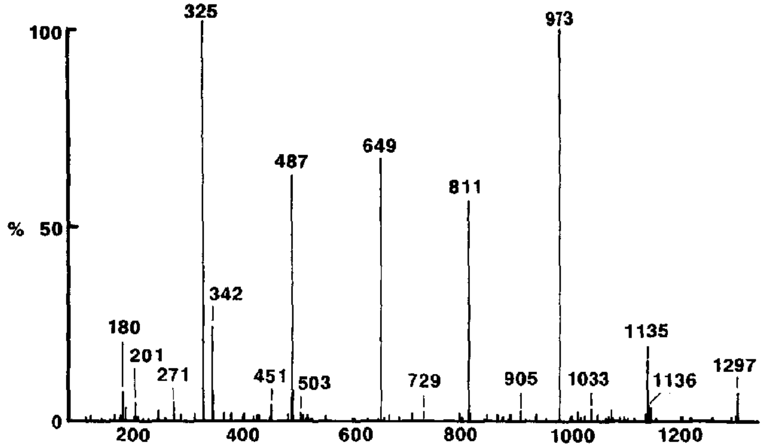

Fig. 11. FAB-MS–MS spectrum of γ-cyclodextrin by collision-induced dissociation of the MH^+ ion; cell collision energy, 10 eV.

firms the high potential of thermospray for quantitative determination of middle-sized polar molecules, already noted by another group [13].

FAB-MS–MS. Fast-atom bombardment is an effective ionizing method for high-mass non-volatile samples. In particular, the method appears to be feasible for the determination of cyclodextrins in water extracts. Cyclodextrin analogues with various ring sizes can be used as additives in water for masking volatile molecules responsible for bad tastes or odours through the formation of insertion complexes. As a preliminary study, with a view to future determination in the laboratory, γ-cyclodextrin, an eight-residue cyclic sugar of formulae $C_{48}H_{80}O_{40}$ and a nominal mass of 1296.4 Da, was investigated by FAB-MS and FAB-MS–MS.

Abundant intact molecule-derived ions (MH^+ and MNa^+) are produced on FAB ionization (Fig. 10), making possible target compound analysis. Collision-induced dissociation of the MH^+ precursor ions at a collision energy of 10 eV produces successive losses of glucopyranose units (Fig. 11) and can be used for structure elucidation of modified residues.

The same FAB-MS–MS method is expected to be succesfully applied to other classes of water additives and pollutants, especially tensio-active molecules that until now lacked specific determination methods [14].

CONCLUSIONS

The analytical investigation of organic matter in water is a rapidly changing field of research. Chromatographic couplings to MS using capillary column separation have made possible the identification of thousands of low-molecular-mass compounds (< 500 Da). The paradox is that instrumental efforts have been mostly devoted to the determination of trace water constituents, and thus the total percentage of known total organic carbon present in dissolved water constituents has remained practically constant over recent years. Methods described here are not intended to be exhaustive and definitive, but we consider them to be a coherent array of experimental methods that can be used routinely in the laboratory for odour and taste-quality controls, and for the determination of macromolecules of biological origin that may have a significant bearing on the efficiency of water purification processes.

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