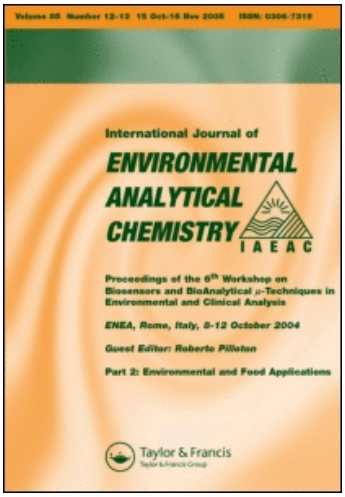

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The Detection and Identification of Unknown Halogenated Compounds in Environmental Samples†

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A new method is described in which the mass spectrometer is an element specific detector for a gas chromatograph. The elements investigated in this study are F, Cl, Br, J, S and N, but the method might be applied to other elements as well. The molecules coming from the gas chromatograph are atomized in a microwave induced discharge, located in the interface between the gaschromatograph and the mass spectrometer. Unknown compounds containing specific elements can be detected and their retention times can be determined. The method is applied to samples of surface water, fat of a grebe and human adipose tissue for halogenated compounds. Unknown halogenated compounds were found. A number of them were identified in samples of surface water.

KEY WORDS: Halogenated compounds, gas chromatography, mass spectrometry, surface water, biological tissue, element analysis

INTRODUCTION

Among the numerous micropollutants found in surface water, the halogenated organic compounds form a special group. Many of them have a lipophilic character and are degraded only slowly. These features suggest that they might accumulate in food chains. The identification of these halogenated compounds in environmental samples is therefore of interest. Part of the identification procedure is the gas chromatographic separation of the complex sample. The next step is the detection of the still unknown halogenated compound in the gas chromatographic eluate. An element

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specific detection in the eluate of the gas chromatograph would be the solution to this problem. In the literature many detectors for certain elements are described For the halogens the choice is small. The electron capture detector can be used to some extent for halogens. However, this detector will respond to any molecule with a large electron attachment cross-section. Therefore it may respond also to other substances than halogenated compounds. The sensitivity of this detector is high for molecules containing many halogen atoms, but low when the number is small.

The emission spectroscopy detector is a multi-element detector, and is probably the best element specific detector, commercially available, today (for the halogenated compounds).[1,2]

With such a detector mounted on the gas chromatograph, unknown compounds containing specific elements can be detected and their retention time can be determined. A subsequent identification has to be done on a gas chromatograph-mass spectrometer system. To achieve this, the gas chromatographic column has to be transferred from the emission spectroscopic system to the mass spectrometric system. After this procedure the retention time (or relative retention time) of the unknown compound might have changed, making an identification impossible.

A solution would be the combination of a mass spectrometric system with an emission spectroscopic detector and a gas chromatograph. With the commercially available systems this is not easy to realize.

In this paper a new method will be described in which the mass spectrometer is used as an element specific detector as well as a "normal" mass spectrometer used for the identification of unknown compounds.

It is a multi-element method. However, in this investigation the halogens are studied in particular; the subsequent mass spectrometric identification of the halogenated molecules can be done without changing the gas chromatographic conditions.

THE MASS SPECTROMETRIC ELEMENT ANALYSIS

When a gas chromatographic column is coupled directly to a mass spectrometer, the connection usually consists of a heated tubing. When the tubing is made out of quartz glass, it is possible to create a microwave induced discharge inside the tubing (Figure 1). In this way it is possible to atomize organic molecules coming from the gas chromatograph. This is comparable to the situation as encountered in the emission spectroscopic methods.[1,2] The mass spectrometer is then used as a detector for the atomized eluate of the gas chromatograph. The mass spectrometer is an element specific detector for the gas chromatograph when it is tuned to the m/e value characteristic for a particular element. When the mass

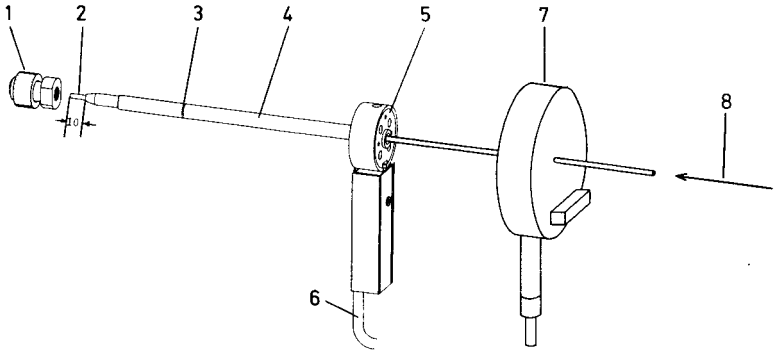

FIGURE 1 Schematic representation of the interface between the gas chromatograph and the mass spectrometer with the microwave induced discharge.

1) entrance vacuum lock;
2) quartz tubing;
3) mark for vacuum lock on line of sight;
4) line of sight;
5) hinge on line of sight;
6) electrical connections of line of sight;
7) microwave cavity; 8) eluate from gas chromatographic column.

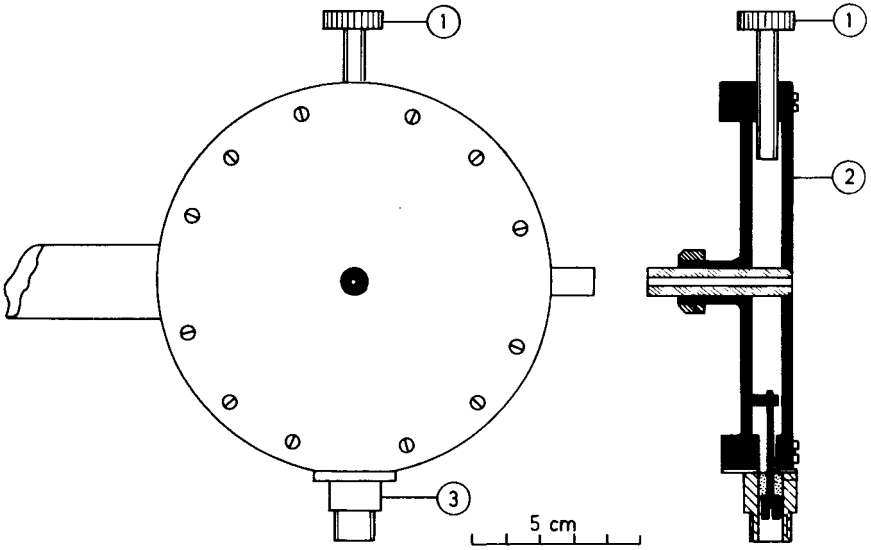

FIGURE 2 Cavity used to produce the discharge in the quartz tubing of the interface between the gas chromatograph and the mass spectrometer.

1) tuning stub;
2) cavity;
3) electrical connection microwave power.

spectrometer is used in this mode of operation, molecules containing specific elements can be detected in the gas chromatogram. Then in a second gas chromatographic run, with the microwave discharge off, identifications can be made under normal glc-ms conditions.

The microwave discharge is created inside a microwave cavity. This cavity is given in Figure 2 and a rather similar one has been described in the literature.[3] The power is obtained from a microwave generator of Electro Medical Supplies type Microton 200, Mark III. The discharge can be ignited with a Tesla coil, if necessary. The usual operation conditions were 40 Watt incident power, and a few Watts reflected power.

The optimal dimensions of the discharge tube have to be obtained empirically. The processes in the discharge itself and in the region between the discharge and the ionization chamber of the mass spectrometer are controlled by parameters as pressure, gas, flow etc. These parameters again are controlled by the dimensions of the discharge tube.

Since we were using capillary columns with a carrier gas flow of Helium of 4 ml per min, the discharge tube was optimized on this flow. The discharge tube had a total length of 62 cm, O.D. of 3 mm and I.D. of 0.9 mm. At the end of the discharge tube at the side of the capillary chromatography column is a quartz glass restriction with a length of 30 cm. This restriction should be made such that there is a pressure drop from 1 atmosphere to around a few Torr at a Helium gas flow of 4 ml/min.

The restriction and the capillary gas chromatographic column are connected with Teflon shrinkable tubing. At this connecting point the pressure should be 1 atmosphere or even somewhat higher. Without the restriction the pressure would be lower and there would be a gas leak from outside, particularly at elevated temperatures in the gas chromatograph. This gas leak will disturb the discharge.

The discharge tube is partly-mounted in the line of sight, a mass spectrometric inlet system (Figure 1), with a swagelok coupling of $\frac{1}{8}$ in. The mass spectrometers were a Varian Mat CH5 and a Varian Mat 731 mass spectrometer.

PROCESSES IN THE DISCHARGE AND BETWEEN THE DISCHARGE AND THE IONIZATION CHAMBER OF THE MASS SPECTROMETER

When molecules, coming from the gas chromatograph, enter the microwave discharge region, they will be atomized. When a chlorinated compound enters this region the chlorine atom will be freed. This does not mean that the chlorine atom as such will reach the ionization

chamber of the mass spectrometer. It reacts rapidly with hydrogen atoms present in the discharge area and in the area between the discharge and the ionization chamber of the mass spectrometer.

Characteristic m/e-values for a number of elements were obtained from mass spectra. They are given in Table I.

TABLE I

Characteristic m/e-values used in the mass spectrometric element analysis for several elements

Element	m/e-value	Elemental composition
^{19}F	20	$H^{19}F$
^{35}Cl	36	$H^{35}Cl$
^{37}Cl	38	$H^{37}Cl$
^{79}Br	80	$H^{79}Br$
^{81}Br	82	$H^{81}Br$
^{127}J	128	$H^{127}J$
^{14}N	30	$^{14}N^{16}O$
^{16}O	30	$^{14}N^{16}O$
^{32}S	64	$^{32}S^{16}O_2$

Fluorine

When a molecule contains the element fluorine it will effectively be removed from the molecule in the discharge region. Thereafter it will react with a hydrogen atom, forming HF. This is a fast reaction. Even when one does not admit substances containing hydrogen atoms the fluor atoms will find them. Probably they originate from impurities in the helium used as the carrier gas. (The helium had a stated purity of 99.995%, Hoek Loos). Experiments were carried out to find out whether these traces of hydrocarbons or water vapor came from the carrier gas. An extremely pure helium has been used for this purpose. (Helium 99.9999%, Matheson.) In this case a shortage of hydrogen was observed indeed. Mixing the helium with traces of propane or water vapor brought the reaction of fluorine and hydrogen back to the original level.

Chlorine

The behavior of chlorine is similar to that of fluorine, except that the reaction with hydrogen is somewhat slower.

Bromine

The reaction of bromine with hydrogen is again slower than for fluorine or chlorine. The amount of hydrogen present in the impurities in the

carrier gas helium (purity 99.995%) is not sufficient any more. One has to add some hydrogen to the helium carrier gas. The addition of some hydrogen gas (H_2) does not work out properly. An organic molecule as propane was being used. This gave enough hydrogen atoms, but after some time the discharge tube was covered with carbon also. The use of water vapor resulted in enough hydrogen to form HBr. At the same time the formation of carbon in the discharge tube was suppressed too. Maybe the oxygen of the water vapor reacts with the carbon to form CO and CO_2. These gases again are then carried away to the mass spectrometer.

Iodine

The behavior of Iodine is similar to that of Bromine. Additional hydrogen has to be supplied.

Sulfur

The element sulfur is best detected at SO_2. The oxygen has to be supplied by a molecule that contains oxygen. Acetone is an adequate additive. The use of water generates also enough oxygen; the advantage of water vapor is again that it prevents carbon formation in the discharge area.

Nitrogen

The element nitrogen can be detected as NO. The discharge conditions are similar to those of sulfur.

THE INFLUENCE OF THE SOLVENT ON THE DISCHARGE

When the solvent peak of the gas chromatographic run passes the discharge area, a carbon deposit on the quartz tube will be the result. With such a carbon deposit the properties of the discharge are not reliable any more. Therefore the discharge has to be extinguished as long as the solvent peak has a high concentration.

Another method to circumvent this problem is to adapt the injection part of the gas chromatograph. We used a "solvent-free' injection of the type already described elsewhere.[4]

THE QUANTITATIVE DETERMINATION OF AN ELEMENT

When the destruction of the organic molecules in the microwave discharge is complete, a quantitative determination of an element should be possible. Of course, it will not depend on the destruction only but also on the quantitative reaction of the element after the atomization process.

For the element chlorine this was investigated. Different molecules containing chlorine were compared in a quantitative way. In Table II the results are given for the reproducibility of the method. Furthermore a comparison between molecules with different structures is made. From these results it appears that the relative standard deviations are small and the number of ions per nanogram chlorine are almost independent of the structure of the molecule, and therefore one may assume that the atomization process is complete. In the literature similar results were obtained for comparable microwave discharges.[5]

TABLE II

Relative standard deviations for quantitative mass spectrometric element determinations for hexachlorobenzene (HCB), DDE and hexachlorocyclohexane (HCH) β-isomer.

The first two series of measurements were carried out on one day, the last two on a different day.

Sample	Number of measurements	Ions/ng Cl	S.D. (%)
1.98 ng HCB	10	654,435	3.87
0.994 ng β-HCH	3	643,365	3.27
1.98 ng HCB	4	571,929	1.67
9.94 ng DDE	5	593,188	1.03

INTERFERENCES

When the mass spectrometer is focussed on an element with a certain m/e-value, one might get a response from another element also appearing on the same m/e-value. In this case a false positive is recorded, and an interference exists at that particular m/e-value.

In order to describe this phenomenon, in the plasma emission spectroscopy selectivity has been introduced.[6] It is defined as: the ratio between the molar concentration of carbon and the molar concentration of the element, which would give the same signal at the analysis wavelength. Selectivity is determined with hexane as reference compound. The interference of carbon with the element which is analyzed is considered here. The ratio is in the range of a few hundred, depending on the element. Of course interferences with other elements are possible too.

For the mass spectrometrical element analysis the interferences were investigated. However, in this study the interferences were determined not just with carbon, but with other elements as well.

Large amounts (micrograms) of parathion (containing the elements C, H, O, P and S) were introduced in the gas chromatograph. Responses on

the element specific m/e-values for the halogens were checked. No interference was observed for Chlorine, Bromine and Iodine. For Fluorine an interference could be observed. The interfering ion was identified as $(C_3H_4)^{++}$ (Figure 3). The interference already appears when hydrocarbons are passing the discharge. This interference can be removed by increasing the resolution of the mass spectrometer to 3,000 (10% valley definition).

A background on m/e = 36 was found for the chlorine response. It is the background caused by the ^{36}Ar occurring naturally in the air leaking into the mass spectrometer. The detection limit of chlorine depends on the level of ^{36}Ar in the ionization chamber of the mass spectrometer. The detection limit for chlorine is about 1 picogram for the total gas chromatic peak. (Or a few tenths of a picogram per second.) The sensitivity of chlorine in the emission spectroscopy is around 1 ng/second.[7]

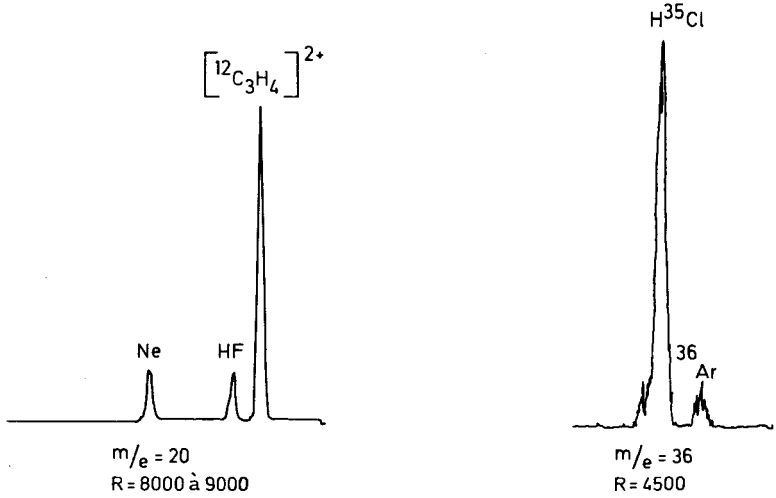

FIGURE 3 Medium and high resolution mass spectra at m/e = 20 and m/e = 36. Notice the interfering ion $(C_3H_4)^{++}$ at m/e = 20. At m/e = 36 there is some background from ^{36}Ar.

RESULTS, ELEMENTAL ANALYSIS

When the mass spectrometer is focussed on one particular mass, it can serve as a specific detector for the gas chromatograph. In fact it is mass fragmentography with an element specific detector. When the mass spectrometer is focussed on m/e = 36, the molecule HCl, we call the fragmentogram a chlorogram. When the mass spectrometer is focussed on m/e = 80, a bromogram is obtained.

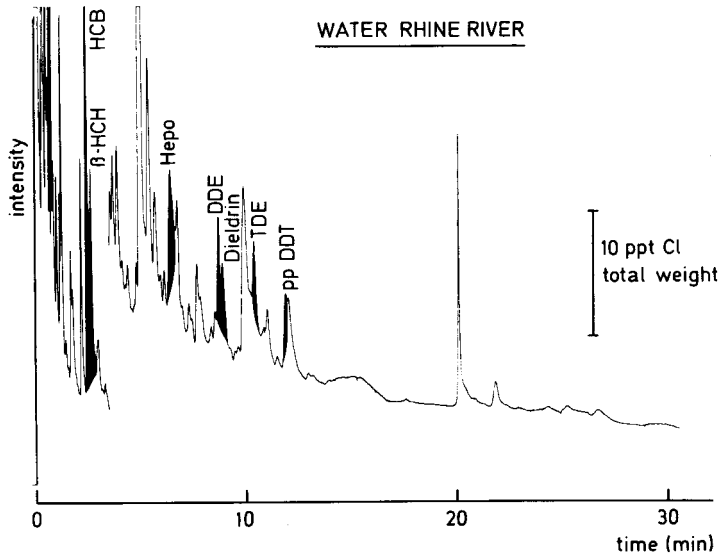

FIGURE 4 Chlorogram of a sample of Rhine River water.

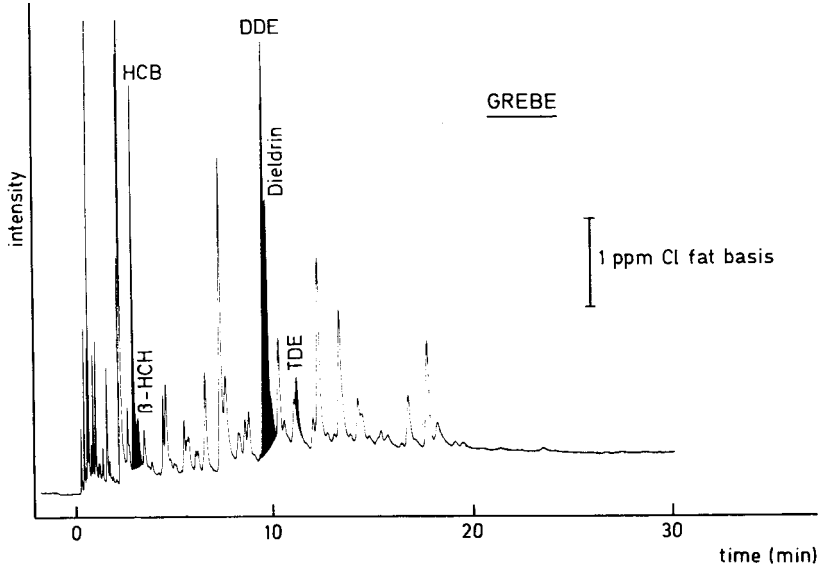

FIGURE 5 Chlorogram of the fat of a great crested grebe, a fish-eating bird. The common chlorinated pesticides are indicated in the chlorogram.

In Figures 4, 5 and 6 chlorograms are given for surface water of the Rhine River, the fat of a great crested grebe (a fish-eating bird) and for human adipose tissue. The positions of the common chlorinated pesticides are indicated in the chlorograms. Most of the chlorinated substances detected in this way are still unknown. The next step is identification of the unknown substances.

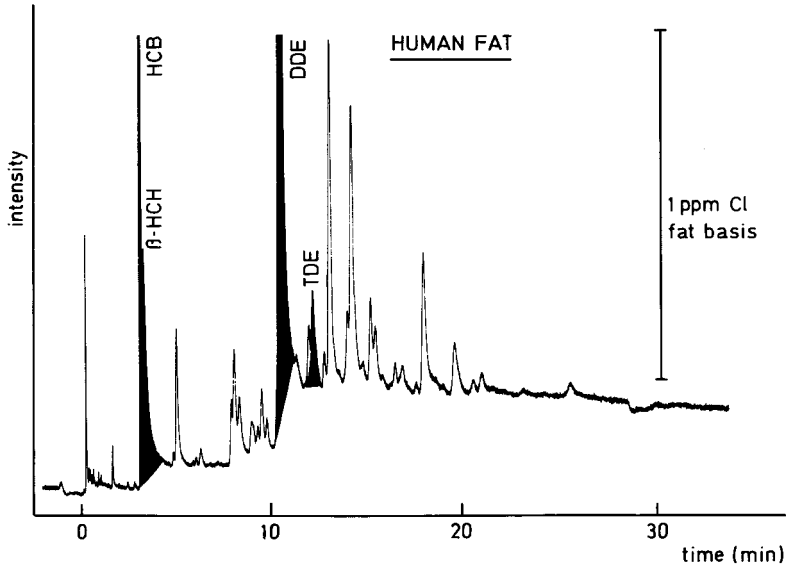

FIGURE 6 Chlorogram of human adipose tissue. The common chlorinated pesticides are indicated in the chlorogram.

IDENTIFICATION

A normal gas chromatograph-mass spectrometer system exists when the microwave discharge is off. Once the retention times of unknown compounds are determined with the discharge on, normal mass spectra can be taken with the discharge off at the exact retention times.

In order to be able to find the mass defect halogenated ions high resolution mass spectra were taken on photographic plates at the retention times determined before. The mass spectrometer was a Mattauch–Herzog mass spectrometer (Varian Mat 731). From these spectra the mass positions of interest were obtained. Subsequently a more accurate mass determination was obtained with peak match procedures as described in a previous paper.[8]

In this way part of the unknown substances were identified in Rhine River water. The results are represented in Table III.

TABLE III

Substances identified (and confirmed) in Rhine River water

tetrachloroethylene	4-chloroanaline
tetrachlorobutadiene	dichloroanaline
pentachlorobutadiene	trichloroanaline
hexachlorobutadiene	tetrachloroanaline
pentachlorobutene	dichlorotoluidine
hexachlorocyclohexane (α, β, γ)	2-chlorophenol
dichlorobenzene	3-chlorophenol
trichlorobenzene	4-chlorophenol
tetrachlorobenzene	2,4-dichlorophenol
pentachlorobenzene	2,5-dichlorophenol
hexachlorobenzene	2,6-dichlorophenol
dichloromethylbenzene	3,4-dichlorophenol
trichloromethylbenzene	3,5-dichlorophenol
tetrachloromethylbenzene	2,3,5-trichlorophenol
pentachloromethylbenzene	2,3,6-trichlorophenol
chlorobiphenyl	2,4,5-trichlorophenol
dichlorobiphenyl	2,4,6-trichlorophenol
trichlorobiphenyl	2,3,4,6-tetrachlorophenol
tetrachlorobiphenyl	2,3,5,6-tetrachlorophenol
dichlorotoluene	2,3,4,5,6-pentachlorophenol
heptachlorostyrene	4-chloro-o-cresol
octachlorostyrene	4-chloro-m-cresol
dichloronitrobenzene	6-chloro-o-cresol
trichloronitrobenzene	4,6-dichloro-o-cresol
chloronitromethylbenzene	trichlorocresol
bis-(chloroisopropyl)ether	hexachloroethane
dichloromethoxybenzene	pentachlorobiphenyl
trichloromethoxybenzene	tributylphosphate
tetrachloromethoxybenzene	dipropylphtalate
pentachloromethoxybenzene	dibutylphtalate
2-chloroanaline	di-2-ethylhexylphtalate
3-chloroanaline	methylstearate

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