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The gas-chromatographic and gas-chromatographic–mass-spectrometric identification of halogen-containing organic compounds

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ABSTRACT. The problem of identifying halogen-containing organic compounds in their gas-chromatographic and gas-chromatographic–mass-spectrometric (GC-MS) determination in different materials has been examined. Particular attention has been paid not to the complete characterisation of methods for carrying out this analysis but to the most important problem of increasing the selectivity at the stages of sampling, separation, and interpretation of the gas-chromatographic and GC-MS information.

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I. Introduction

The examination of the gas-chromatographic and mass-spectrometric analysis of halogen-containing organic compounds (HOC) is important, since these compounds are widely used in industry, agriculture, medicine, and everyday life. Since only a few compounds of this class are found in natural materials, and most are manufactured by man, the analysis of materials of this kind often requires their selective determination in much larger quantities of a large number of compounds of other classes. Thus the problems of selective sampling, separation, detection, and the reliable interpretation of the data are extremely important for halogen derivatives.

Published data on methods for analysing halogen-containing compounds in various materials, developed up to the early nineteen-eighties, have been summarised in various reviews[1–3] and monographs.[4–6] Special sections in handbooks[7,8] have been devoted to the determination of traces of HOC in the air of industrial plants and in the atmosphere.

Several hundred studies of different aspects of the analysis of HOC are now published every year, and these data require systematisation. In addition to an increase in the range of substances determined, there is a tendency towards a more rigorous characterisation of procedures in order to increase the accuracy and selectivity of analysis and to simplify methods of sampling. A number of topics, in particular the selection of sorbents for concentrating traces of substances to be analysed and the conditions for their gas-chromatographic separation, to which particular attention was paid in earlier reviews,[1–7] do not now require examination, since the corresponding procedures have been systematised and standardised.[9] Thus in the present review particular attention is paid not to a detailed description of specific procedures for analysing HOC in different materials but to the presentation of the general principles of their gas-chromatographic and mass-spectrometric identification, quantitative analysis, and methods for increasing the selectivity of the determination by using special methods of detection.

In recent years, more accurate data have been obtained on the high toxicity of various halogen-containing compounds.[10–12] Mutagenic activity has been noted for 40 substances of this type used in industry.[13] Thus it is necessary to develop reliable highly sensitive procedures for determining HOC in the atmosphere, water and effluents, soils, biological materials, foodstuffs, and other substances.

The large number of HOC produced on the industrial scale can be classified in two groups, according to their physicochemical properties. The first group consists of volatile polyhalogenocarbons, Freons, halogen-containing monomers, and solvents. The second group consists of high-boiling polychlorinated hydrocarbons, pesticides, the starting materials for their synthesis, and metabolism products. The particular danger of the contamination of the environment by materials of the first group (in particular the simplest polychlorofluorocarbons) is now considered to be the possible destruction of the ozone layer in the atmosphere as a result of photochemical reactions involving Hal' radicals, first noted in 1974 [14,15] (these questions have been discussed in detail[8]). Until recently it was considered that these compounds are produced exclusively by man, but in 1985, chloro- and chlorofluoromethanes were detected in volcanic gases.[16,17] Previously, only the natural production of CH_3Cl,[16] CH_3Br, and, possibly, CF_4,[18] had been noted. The existence of natural sources of HOC may lead to a re-examination of estimates of the potential danger of these substances for the ozone layer of the atmosphere.

Polychlorinated aromatic hydrocarbons, chlorine-containing pesticides, and other compounds of this kind are not highly volatile, so that they are concentrated in condensed media.[19–21] Nevertheless, they are detected at considerable distances from their sites of use (as far as the Arctic regions).[22–26] The global contamination of the biosphere by chlorine-containing compounds makes it important to control their concentration in compounds of food chains[27] and biological materials.[28]

The most toxic representatives of this group of HOC are polychlorinated dibenzo-*p*-dioxins, dibenzofurans, diphenyl ethers, and similar substances having a teratogenic action. The intensive study of methods for detecting and identifying these compounds began after the chemical plant disaster in Seveso (Italy) in 1976, which led to the sudden release of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin, long-term contamination of the environment, and cases of acute poisoning.[29] Polychlorodibenzodioxins and -furans may be formed by the oxidation of polychlorobiphenyls (added to pesticides)[30] or by the oxidative chlorination of aromatic compounds by HCl in air,[31] but most of these compounds released into the atmosphere are produced by the thermal treatment of chlorine-containing polymers, including the combustion of household refuse.[32–35] The chlorination of drinking water leads to the appearance in it of traces of polychloro-aromatic hydrocarbons and phenols,[36,37] whose concentration also requires effective control.

II. Basic principles of the separation, selective detection, and gas-chromatographic identification of halogen-containing substances

One of the most important tasks in the gas-chromatographic analysis of HOC is to achieve the maximum selectivity with respect to compounds of this type, in order to eliminate the influence of interfering components and to increase the reliability of identification and quantitative analysis. The possibilities for achieving this are different at the stages of sampling and preparing specimens for analysis, chromatographic separation, and detection of the substances being determined.

1. Sampling and preparation of specimens for analysis

The reactivity and specific chemical properties of halogen-containing compounds generally do not differ significantly from those of their analogues not containing halogens. For this reason, the selective extraction of HOC from specimens being analysed at the stages of sampling and specimen preparation is usually impossible. Only isolated examples of this selectivity are known, based on specific reactions of the substances being analysed. Thus a method for determining hexachloroacetone in air[38] is based on its absorption by anhydrous methanol, which is accompanied by the quantitative reaction:

$$(CCl_3)_2CO + CH_3OH \rightarrow CCl_3CO_2CH_3 + CHCl_3.$$

Both reaction products are determined in the subsequent gas-chromatographic analysis of the solution obtained. The detection limit using an electron capture detector is 3 $\mu g\ m^{-3}$.

The same principle (trapping in liquid absorbers which react with specific substances) is used successfully in the analysis of free halogens and hydrogen halides in air.[1,39–42]

The anlaysis of traces of organic halogen-containing compounds in gases at the level of several p. p. t. (parts per trillion by volume) is carried out by the direct introduction of large gas specimens using highly sensitive selective detectors,[43,44] or cryogenic concentration in special traps or preliminary columns not selective with respect to substances of other classes,[18,45,46] or trapping on solid sorbents. The subsequent desorption of the substances being determined is carried out thermally, directly in the analytical column, or by treating the sorbent with organic solvents and analysis of the eluate.[47] The desorption of halogen-containing compounds from active carbon by water vapour is possible in principle.[48] To trap the most volatile compounds, including perfluoroalkanes, Freons, etc., active carbons with a specific surface of up to 1000 $m^2\ g^{-1}$ [47,49-52] or graphitised carbon black (Carbopack B type) with a specific surface of about 100 $m^2\ g^{-1}$ [53] are used. The thermally stable polymeric sorbent Tenax (poly-*p*-2,6-diphenylphenylene oxide) is effective not only for concentrating low-boiling halogenoalkanes and chlorinated aromatic hydrocarbons[54–57] but also chlorine-containing pesticides.[58] The carbon sorbent Ambersorb XE-340 is used for the same purposes.[59]

In thermal desorption from carbon sorbents and even the chemically most inert Tenax, however, it is necessary to take account of the possible thermal decomposition of primarily high-boiling halogen-containing compounds as a result of their dehydrohalogenation. Thus the recovery of various pesticides in desorption from 0.11 g of Tenax at temperatures of 250–325 °C and a carrier-gas (helium) velocity of 11.2 ml min^{-1} has the following values (% of the original quantity)[58]:

α-$C_6H_6Cl_6$	97±8	*pp'*-DDT	60±2
Heptachlor	26±5	*pp'*-DDT	20±1
Dieldrin	120±3	perylene (for comparison)	82±2 .

Another factor responsible for the loss of compounds being analysed and distortion of the results of a quantitative analysis may be incomplete trapping in the cryogenic trap, particularly for low-boiling compounds.[60]

When working with polymeric sorbents, it is necessary to take account of the presence of traces of halogen-containing substances in the background emanation of the polymer itself.[61,62] To prevent the incomplete trapping of low-boiling compounds, polymeric sorbents with a specific surface of up to several hundred $m^2\ g^{-1}$ are used (Chromosorbs 101, 103, 107, Porapaks M, Q, T, Cekachrom 2, 3, CE-1, CE-2, etc.).[63–65] The basic characteristics of all solid sorbents are the specific retention volumes of each of the substances being determined at the sampling temperature (V_g, litre g^{-1}) and the maximum sample gas volumes, related to V_g by the simple expression $V_g^{max} \simeq V_g(1 - 2/\sqrt{N})$,[7] where N is the efficiency of the sorption tube in theoretical plates. These data have been published for the simplest HOC.[63,64]

In the study of the concentration of volatile halogen-containing compounds in liquid specimens (including aqueous solutions), the best method is apparently vapour-phase analysis (VPA),[66] which is based on information on the composition of the condensed phases obtained by analysing the gaseous media present in contact with them. The possibilities provided by the method are determined by the distribution coefficients of the substances being analysed between the liquid and gas phases. In some cases the differences in these coefficients for different substances make it possible to increase the selectivity. In general, the term vapour-phase analysis includes both the analysis of the equilibrium or non-equilibrium gas phase above the specimen[66] and the complete sweeping of the components being determined from solutions by a stream of carrier gas followed by their sorption.[55,67] The detection limit of the method can be varied by changing the temperature of the analysis and by adding salting-out agents. For example, the addition of sodium sulphate (20 g) to an aqueous solution (50 ml) when capillary columns and an electron capture detector are used lowers the detectable concentrations of CH_3Cl from 1.6 p. p. m. to 1.3 p. p. m., $CHCl_3$ from 2.4 p. p. m. to 0.9 p. p. m., and C_6H_5Cl from 1.5 p. p. m. to 0.4 p. p. m.[68]

Vapour-phase analysis is effective in the determination of a wide range of chlorine and bromine derivatives of methane and ethane in drinking water,[69–73] traces of chloroform in blood plasma,[74]

monomer residues in polymeric materials (for example vinyl chloride in polyvinyl chloride[75,76]), solvents in foodstuffs,[77] traces of volatile halogen-containing substances in organic electrolytes,[78,79] etc. Of particular interest is the vapour-phase analysis of specimens which cannot be introduced into a chromatographic column because of their thermal instability, reaction with a phase, etc. This method has been used to determine traces of polychlorinated C_1-C_3 hydrocarbons in $SiCl_4$, $POCl_3$, $GeCl_4$, BBr_3, and BCl_3.[80]

The extraction of solid or liquid specimens by organic solvents (usually with boiling points not higher than 100 °C) is most frequently used in the analysis of less volatile halogen-containing organic compounds: herbicides,[81] chlorobenzenes, chlorotoluenes, hexachlorobutadiene, and polychlorobiphenyls,[82,83] chlorostyrenes,[84] and polychlorodibenzo-*p*-dioxins.[85,86] After concentration of the extract, it is possible to achieve a degree of enrichment of up to $(1-3) \times 10^3$ with a degree of extraction of 50–98%. Light halogenomethanes can be analysed in this way only by electron capture detectors and solvents with respect to which their sensitivity is low.[81,87] Concentration in this case becomes impossible, and direct VPA of the original specimens is preferable.

The large number of preliminary stages in the analysis of traces of HOC in dilute solution (gas or liquid extraction, concentration on solid sorbents) leads to a slight regular decrease in the accuracy of quantitative determinations as a result of the accumulation of both random and systematic errors. Thus in a number of cases the direct introduction of the specimens being analysed into packed or capillary columns with grafted stationary phases is more appropriate. For example, when this method is used to analyse aqueous solutions, it is possible to achieve detection limits of 2 p. p. b. for CH_2Cl_2, 0.1 p. p. b. for CH_3CCl_3, 0.15 p. p. b. for $CCl_2=CHCl$, and 0.1 p. p. b. for C_2Cl_4.[88] A similar method has been used not only for aqueous solutions but also for dilute solutions in organic solvents.[89,90]

A particular case of the special treatment of specimens of non-volatile or thermally unstable compounds for analysis involves the preparation of derivatives suitable for gas-chromatographic analysis.[91] If these derivatives contain halogen atoms, the problem of increasing the selectivity of detection is solved simultaneously (see above). For compounds containing active hydrogen atoms (NH, OH, SH groups), the derivatives are most frequently heptafluorobenzoates, trifluoroacetates, pentafluoropropionates, and heptafluorobutanoates. This method is used to analyse amino-acids,[92–94] dipeptides,[95] mono-, di-, and oligosaccharides,[96–99] aromatic amines,[100,101] β-arylamines, their metabolites, and aliphatic diamines,[102–104] ethylene glycol in blood serum,[105] the oxidation products of coal[106] (in the last case, use is made of peroxotrifluoroacetic acid, which acts simultaneously as oxidant and as reagent for derivative formation), etc. The analysis of organic acids as their hexafluoroisopropyl esters after treatment with $(CF_3)_2CHOH$ has been recommended.[107]

Various halogen-containing compounds (the halides of silicon, boron, etc.) are highly reactive and unstable under the conditions of gas-chromatographic analysis. Special methods for dealing with compounds of this kind have been described.[108]

2. The gas-chromatographic separation of halogen-containing compounds

The conditions for the optimum gas-chromatographic separation are different for volatile halogen derivatives and high-boiling polychlorinated aromatic compounds. The analysis of substances of the first group is usually carried out on packed columns with a high concentration of the stationary phases[69,81] or on polymeric or inorganic sorbents modified by various additives. Thus a column containing Carbopack B treated with 0.5% SP-1000 (3 m) is effective for separating halogen derivatives with boiling points from –24 °C (CH_3Cl) to 121 °C (C_2Cl_4).[109] A packing with similar characteristics consisting of 0.2% of polar Carbowax 1500 on Carbopack C (specific surface about 10 $m^2\ g^{-1}$) is effective for the temperature-programmed separation of a mixture of substances with boiling points from 40 °C (CH_2Cl_2) to 132 °C (chlorobenzene), that is practically all aliphatic C_1 and C_2 chlorine derivatives.[110] Combined colums with polar and non-polar stationary phases,[69] molecular sieves,[109] or silica gels[52] are sometimes used.

Gas-adsorption capillary columns with a coating of aluminium oxide or silica gel are effective for separating low-boiling halogen-containing compounds.[18,111]

Compounds of the second group are usually analysed on glass or quartz capillary columns containing high-temperature silicone stationary phases with low or medium polarity,[30,43,46,83,85,112–120] or on packed columns with a low concentration (not more than 5%) of similar phases.[81,110,121] Since polychlorinated biphenyls, dibenzo-*p*-dioxins, dibenzofurans, and other representatives of this group of compounds are specific materials distinguished by the simultaneous presence of a large number of similar substances, including isomers (polychlorobiphenyls, for example, form a "group" of 209 theoretically possible compounds), in a number of cases special optimisation of the temperature conditions of the analysis is appropriate, to increase the efficiency of their separation.[122] This analysis requires high temperatures (150–300 °C), at which it is necessary to take account of the possible decomposition of various substances in the chromatographic column. Thus dehydrochlorination of chlorine-containing pesticides has been observed on glass columns with surfaces modified by $BaCO_3$.[123]

An increase in the selectivity of the determination of halogen-containing compounds at the separation stage is possible by using reaction gas chromatography,[1] including the removal of interfering components in preliminary or subsequent columns. This method is effective for determining traces of CH_3Cl, CH_3Br, and C_2H_5Cl in CH_3OH using a capillary column. The solvent is trapped selectively at the column outlet in a trap containing activated Al_2O_3 at 30 °C, which is heated to 200 °C when the analysis is complete.[124] For chlorine-containing pesticides, polychloroaromatic compounds, etc., a useful version of reaction chromatography involves their catalytic hydrogenation to hydrocarbons with preservation of the carbon framework of the molecules (the so-called "carbon skeleton chromatography"),[1,125] carried out in a preliminary column reactor by means of the hydrogen used as carrier gas. This method makes it possible to lower the temperature and time of the analysis, and does not require the use of selective detectors.

Other effective methods for separating mixtures of polychloroaromatic compounds are liquid[126,127] and "fluid"[128,129] chromatography (in a stream of non-ideal eluants at pressures and temperatures in the column exceeding the critical parameters of the eluant).

3. Methods for detecting halogen derivatives

The maximum selectivity in the analysis of halogen-containing compounds is achieved at the stage of their detection using selective gas-chromatographic detectors or mass spectrometers. The widely used electron capture detectors (ECD) solve this problem effectively, but increasing use is being made of mass spectrometers, which provide much greater possibilities and a controllable selectivity of detection.

Chromatographic detectors based on the general principle of the change in the electronic conductivity of the gaseous medium in the presence of halogen-containing substances (electron capture and constant recombination) are fairly simple to use, and have been employed in a large number of studies of the analysis of varied halogen-containing compounds, for example free iodine,[130] volatile halogenocarbons in water and in air,[38,47,57,81,88,131,132] 1-bromo-1-chloro-2,2,2-trifluoroethane (Halothane) in air,[133] chlorobenzenes,[82] polychlorophenols,[134] halogen-containing pesticides,[81,89,135] etc. Signals from three detectors have been recorded simultaneously to increase the selectivity of the determination of halogen-containing substances in air.[136]

Important features of electron capture detectors are the comparatively short linear range (about two orders of magnitude),[137] which makes it difficult to carry out quantitative analysis, and the marked dependence of the relative response of the detector on the nature, number, and even the position of the halogen atoms in the molecule. The use of these detectors therefore requires the constant application of specially prepared calibration mixtures of the compounds being analysed.[138–140] The dependence of the relative response of ECD on the number of chlorine atoms in a series of chlorobenzenes is illustrated by the results of a study[141] given in Table 1. Since the relative sensitivity coefficients depend on the operating conditions of the detector and differ considerably even for isomers, in quantitative analysis it is necessary to have standard specimens of all the substances being determined. A practical consequence of this is a difference in the detection limits for chlorobenzenes using ECD. For example, when aqueous solutions are extracted with pentane, about 0.01 ng litre^{-1} penta- and hexachlorobenzenes can be determined, whereas the corresponding value for the mono-substituted compound is only 500 ng litre^{-1}.[82] It is not yet possible to calculate the relative sensitivity coefficients for ECD. These parameters of halogen derivatives can be calculated by an additive scheme only for thermal conductivity detectors.[142]

Table 1. Relative response of the electron capture detector for chlorobenzenes.[141]

Degree of substitution	Relative response	Degree of substitution	Relative response
Monochlorobenzene	1	Tetrachlorobenzenes	
Dichlorobenzenes		1,2,3,4-	$12\cdot10^3$
1,2-	550	1,2,3,5-	$10\cdot10^3$
1,3-	610	1,2,4,5-	$5.8\cdot10^3$
1,4-	280	Pentachlorobenzene	$23\cdot10^3$
Trichlorobenzenes		Hexachlorobenzene	$30\cdot10^3$
1,2,3-	$7.2\cdot10^3$		
1,2,4-	$4.0\cdot10^3$		
1,3,5-	$4.5\cdot10^3$		

The low sensitivity of ECD to compounds containing one fluorine or chlorine atom explains the observed[1] difficulty of determining vinyl chloride. Thus for substances of this kind, it is preferable to use flame ionisation[76] or photo-ionisation[143,144] detectors. It has been reported,[145] however, that the sensitivity of ECD to vinyl chloride increases by a factor of about 10^3 (from 1 ng to 1.4 pg) when N_2O (10–50 p.p.m.) is added to the gas (nitrogen) passing into it. The observed effect is due to the appearance in the gas phase of O^- ions, formed by the reaction of N_2O with thermal electrons. A chromatograph with a detector modified in this way, when 1 cm^3 of air is introduced directly, can determine vinyl chloride at a concentration of about 0.5 p.p.m. (1.4 mg m^{-3}), which, however, is higher than the level officially established in the USSR for the limiting permissible concentrations of this substance (0.1 mg m^{-3} for a working area, and 0.005 mg m^{-3} for atmospheric air).

The mass spectrometer, used as a chromatographic detector under total ion current recording conditions or under the conditions of mass fragmentography (detection of the signals of ions with previously specified mass numbers), has a longer linear range than ECD.[146] An additional advantage of the mass spectrometer is that it is possible to carry out a quantitative analysis not only by absolute calibration but also by isotopic dilution. Thus in the determination of the isomers of hexachlorocyclohexane, known quantities of its completely deuteriated analogue $C_6D_6Cl_6$ were added to the specimens.[146] Analysis by absolute calibration or mass-spectrometric detection is complicated by the difficulty of determining the ionisation cross-sections of different substances, but according to recent data, they can be calculated by additive schemes to within about 5%.[147]

Gas chromatographic–mass-spectrometric (GC-MS) analysis is widely used in the selective determination of poly-chlorinated aromatic hydrocarbons and their derivatives in complex mixtures with ionisation by electron impact[148–151] and with chemical ionisation.[152,153] The method involving the detection of the negative ions formed in chemical ionisation is particularly important for determining traces of the most toxic chlorinated dibenzo-*p*-dioxins, dibenzofurans, etc., since it has the lowest detection limit (down to 10^{-18} g according to some estimates).[154–161] The method involving ionisation at atmospheric pressure has similar advantages.[162,163]

Because of the importance of the selective detection of HOC, detectors of other types are used for their determination. It has been shown possible to identify halogens in organic compounds and to determine their mass fractions to within 3–6 rel. % with a detection limit down to 1 pg s^{-1} using detection in a corona discharge [a helium plasma with an electronic temperature of $(5-7)\times10^3$ K] from the wavelengths and intensities of the lines of the atomic emission of free halogen atoms in both the microwave[164,165] and near infrared[166] ranges. These plasma detectors are fitted with monochromators (usually diffraction gratings) and a set of recording assemblies, making it possible to determine several elements simultaneously (C, H, N, O, F, Cl, Br, I, S) [165,166] and to establish the empirical formulae of the compounds being analysed. The construction of detectors of this kind designed for capillary columns has been described.[167,168]

The possibilities provided by molecular emission spectroscopy have made it possible to produce another type of selective gas-chromatographic detector having a long linear range and a low noise level. The halogen-containing compounds leaving the packed column react with metallic indium in a hydrogen flame, after which the molecular emission signals of the indium halides are recorded at 360 nm (chloride), 376 m, (bromide), or 410 nm (indium iodide).[169] An infrared detector with Fourier transformation has been used for the chromatographic determination of polychlorodibenzo-*p*-dioxins. New electrical conductivity detectors can be used even with capillary columns.[170,171] The construction of selective detectors based on the Hall effect has been proposed.[172,173]

In the analysis of traces of polychlorinated aromatic compounds, extensive use is made of mass spectrometers with several mass analysers, effective for the analysis of complex mixtures (MS-MS). In this case, the chromatographic separation need not be so efficient,[173–175] and this stage may even be eliminated completely.[175] The direct analysis of mixtures for individual components by MS-MS using comparatively simple instruments makes it possible to develop the most rapid methods for their determination.[176–178]

The possibilities provided by the use of resonance two-photon ionisation for the detection of halogen-containing compounds have been studied.[179]

When ionisation is carried out by electron impact, the most widely used method of selective detection is mass fragmentography, which is effective both for volatile halogen-containing compounds[180–182] and for polychlorinated aromatic hydrocarbons[183,184] and pesticides.[115] The mass numbers of the principal peaks in the spectra of each component (m/z), some of which are given in Table 2, are usually chosen for diagnostic purposes.

Table 2. Mass numbers of the principal peaks of the mass spectra for the detection of various halogen-containing compounds under mass-fragmentographic conditions.[180–182]

Compound	m/z	Compound	m/z
Methyl chloride	50	1,2-Dichloroethylene	61
Dichloromethane	49, 84	1,2-Dichloropropane	63
Trichloromethane	83	2,3-Dichloroprop-1-ene	75
Tetrachloromethane	117	1,3-Dichloroprop-1-ene	75
Freon 13	69	Dichlorobromomethane	83
Freon 12	85	Chlorodibromomethane	129
Freon 11	101	Tribromomethane	171
Freon 22	67	1,2-Dibromoethane	107, 108
Freon 114	85	Chlorobenzene	112
Freon 113	101	Chlorotoluenes	91
1,1,1-Trichloroethane	97	Dichlorobenzenes	146
Trichloroethylene	95	Dichlorotoluenes	125
Tetrachloroethylene	129, 166	Trichlorobenzenes	180
1,1-Dichloroethane	63	Fluorobenzene	96
1,2-Dichloroethane	62	Difluorobenzenes	95
1,1,2-Trichloroethane	97	Pentafluorobenzenes	168
1,1,2,2-Tetrachloroethane	129	Fluorobromobenzenes	95
1,1-Dichloroethylene	61	Lindane	181

If this method of detection is used with chemical ionisation, the signals of the protonated molecular ions $[M + H]^+$ are usually recorded.

In mass fragmentography, instruments with a low resolution $[(1-1.5) \times 10^3]$, calibrated from integral mass numbers, are most frequently used. Comparatively recently (1981), an improvement of this method, namely high-resolution mass fragmentography, was proposed for instruments with a resolving power of not less than 2.5–3 thousand.[185] The extremely high selectivity of this method of detection has proved useful in the analysis of halogen-containing substances.[109,186] This selectivity is based on the specific values of the mass "defects" (ΔM) for the halogens [the differences between the exact masses of the atoms and their integral (by definition) mass numbers], which distinguish them from other elements found in organic compounds:

Element	ΔM	Element	ΔM	Element	ΔM
^{19}F	−0.0015	^{12}C	0	^{28}Si	−0.0231
^{35}Cl	−0.0311	^{1}H	0.0067	^{32}S	−0.0279
^{79}Br	−0.0183	^{14}N	0.0031	^{31}P	−0.0262
^{127}I	−0.0553	^{16}O	−0.0051		

In this case the mass fragmentograms are recorded from the exact values of the masses of the characteristic ion detected, given in Table 3.

Table 3. Exact masses of halogen-containing ions for the detection of various compounds under the conditions of high-resolution mass fragmentography.[109]

Compound	Ions detected	Masses of the ions (a.m.u.)	Compound	Ions detected	Masses of the ions (a.m.u.)
CHF_2Cl	$CHF^{35}Cl$	66.975	$CFCl_3$	$CF^{35}Cl_2$	100.936
	$CHF^{37}Cl$	68.972		$CF^{37}Cl^{35}Cl$	102.933
CF_2Cl_2	$CF_2{}^{35}Cl$	84.967	$C_2F_3Cl_3$	$CF^{35}Cl_2$	100.936
	$CF_2{}^{37}Cl$	86.964		$CF^{35}Cl^{37}Cl$	102.933
$CHFCl_2$	$CHF^{35}Cl$	66.975	CH_3CCl_3	$C_2H_3{}^{35}Cl_2$	96.961
	$CHF^{37}Cl$	68.972		$C^{35}Cl_3$	116 906
CH_2Cl_2	$CH_2{}^{35}Cl_2$	83.953	CCl_4	$C^{35}Cl_3$	116.907
	$CH_2{}^{37}Cl^{35}Cl$	85.950	C_2HCl_3	$C_2H^{35}Cl_2$	94.945
$C_2F_4Cl_2$	$CF_2{}^{35}Cl$	84.967			
	$CF_2{}^{37}Cl$	86.964			

4. The gas-chromatographic identification of halogen-containing substances

The gas-chromatographic identification of organic compounds is based on the accurate measurement of the retention parameters, of which the most reproducible forms are interpolation relative quantities, called retention indices.[187] Under isothermal analysis conditions, Kovac's retention indices are generally used:

$$I = 100n + 100\,(\lg t'_x - \lg t'_n)/(\lg t'_{n+1} - \lg t'_n),$$

where t'_x, t'_n, and t'_{n+1} are the corrected retention times of the substance being determined and the nearest reference components (n-alkanes) containing n and $n + 1$ carbon atoms, and $t' = t - t_0$, where t_0 is the retention time of the non-sorbed gas.

There is as yet no single generally accepted system of retention indices for temperature-programmed conditions. Among different methods for calculating them, mention may be made of a recently proposed system of linear–logarithmic indices,[188] in which the uncertainties in their calculation are smaller than those for other methods.

When non-selective chromatographic detectors are used, the reliability of identification only from the indices is low. Any additional information increased considerably the reliability of the assignment. Detailed catalogues of retention indices[189,190] have now been produced, but successful identification from these data requires the maximum possible additional characterisation of compounds of different classes. This explains the appearance of a large number of special publications giving the results of the determination of the retention indices of series of compounds with similar structures, including homologues, on different stationary phases. Among halogen derivatives, data of this kind have been obtained for alkyl chlorides,[191] the alkyl esters of chloroacetic acids,[192] chloromethyl esters,[193,194] chloroethanols,[195] the corresponding carboxylates,[196] chloroalkyl acetates,[197] chloropropanoates and chlorobutanoates,[198,199] chloroalkyl chloroacetates,[200] methyl chloro-

propanoates,[226] and the products of the halogenation and hydrohalogenation of alkyl acrylates.[201] The following aromatic compounds have been characterised: alkyl chlorobenzoates,[202] chloroalkyl benzoates and nitrobenzoates,[203,204] halogen-substituted benzenes, toluenes, and anisoles,[205,206] chlorinated 4-hydroxybenzaldehydes,[207] isomeric chlorophenols,[208] and pentafluorobenzoates.[209] The relationship between the structure of chlorophenoxyalkanecarboxylic acids and their retention indices has been discussed.[210] The relative retention times of 39 polychlorodibenzo-*p*-dioxins on weakly polar polydimethylsiloxane stationary phases have been determined.[30,211] Among the isomeric tetrachlorodibenzo-*p*-dioxins, the shortest relative retention time is shown by the isomer with the chlorine atoms in positions 1, 3, 6, and 8 (0.55), and the maximum by the 1,2,8,9-isomer.[1,21] The retention time of the most toxic 2,3,7,8-tetrachloro-derivative is usually taken as unity.[30] The retention indices of these dioxins can be calculated using additive schemes.[212–214] The difficulty of the gas-chromatographic identification of the compounds of these groups, however, makes it necessary to develop more complex methods based on pattern recognition techniques.[215,216]

Data on the retention indices of a number of toxic substances, including halogen derivatives, were published only in 1985.[217] More than 600 compounds, including chlorine-containing pesticides, have been characterised by their so-called effective retention temperature.[218]

The low sensitivity of selective gas-chromatographic detectors towards reference n-alkanes makes it necessary to use other reference homologues. As compounds of this kind for use with ECD, the esters of trichloroacetic acid CCl_3CO_2R, where R = n-C_nH_{2n+1}, have been recommended; the esters are given standard values of $100n$.[219] The method of identification based on this system for calculating the indices has been used in the determination of chlorine-containing pesticides and polychlorobiphenyls.[219,220] This set of reference components cannot be used to analyse low-boiling polyhalogenomethanes and -ethanes, however, since the first member of the series of trichloroacetates in the n-alkane system has an index of about 900 on non-polar silicone phases, so that lower values of the indices cannot be determined. For this reason, n-alkyl bromides[222] and n-alkyl iodides[223] have also been recommended as reference halogen-containing compounds.

Thermospray detectors are suitable for the analysis of both halogen-containing compounds and N- and P-containing substances, so that the homologous series of tri-n-alkylamines can be used as reference components.[223] The proposed[224,225] "universal" reference homologous series of bis(trifluoromethyl)thiophosphonates $(CF_3)_2P(S)OC_nH_{2n+1}$ can be used with practically all types of chromatographic detector, since the molecules contain halogen, sulphur, and phosphorus atoms simultaneously.

III. The mass-spectrometric characterisation and identification of halogen derivatives

According to present-day ideas, the fragmentation of halogen-containing organic compounds on electron impact shows no specific patterns. The most general direction of the decomposition of the molecular ions of all compounds of this type is the formation of $[M - Hal]^+$ ions and, less frequently, $[M - HHal]^{\cdot +}$. The probability that Hal$^{\cdot}$ radicals are removed increases in the order F < Cl < Br < I (with decrease in the electronegativity of the halogen).[226] The presence of other functional groups in the molecule may suppress considerably the fragmentation with rupture of C–Hal bonds, particularly for fluorides and chlorides. This is related to the relatively high ionisation energies (IE) of the non-bonding molecular orbitals localised on the halogen atoms, and the high probability of removal of an electron from other orbitals. This can be illustrated by the ranges of the IE of aliphatic halides, 10.7 ± 0.2 eV. (chloroalkanes), 10.1 ± 0.2 eV (bromoalkanes), and 9.2 ± 0.2 eV (iodoalkanes), compared with –9.2 ± 0.4 eV for alkanes, –9.3 ± 0.2 eV for ethers, –8.4 ± 0.1 eV for sulphides, etc.[227] The ionisation potentials of fluorine-containing compounds with different structures are generally greater than 10 eV. The fragmentation shows specific regularities only for polyhalogeno-derivatives, in particular perfluorinated derivatives.

The mass-spectrometric study of halogen-containing compounds is complicated by the low intensities of the peaks of the molecular ions, which correlate with the electronegativities of the halogen atoms and decrease in the order I > Br > Cl > F. The greatest difficulties are encountered in the detection of the mono-isotopic iodine and fluorine in organic compounds. Iodo-derivatives with sufficiently intense molecular ion peaks (not less than 1% of the total ion current) can be recognised from the large negative values of the homologous increments in the intensities of the [M + 1] isotopic peaks,[227] whereas the analysis of the spectra of fluoro-derivatives, which rarely give signals of this kind, is one of the most complex problems in mass-spectrometric identification. A general structural requirement for the production of the signals of the molecular ions of all halogen derivatives is the presence in the molecule of a p-π conjugated system for example $\rangle C=C-Hal$.[227]

The most important characteristic of polychloro- and polybromo-compounds is the presence of specific multiplets of the isotopic peaks in the mass spectra.[226,227] Their appearance makes it possible to achieve selectivity in the detection of halogen deriatives during GC-MS analysis by another period. A specially developed computer program makes it possible to detect these multiplets and to obtain information on the number of chlorine atoms in an unknown compound.[228,229] In this case the selective detector is a "mass spectrometer + computer" combination.

The difficulty of interpreting the mass spectra of fluorine-containing compounds makes it important to develop algorithms based on new principles. These include a method which requires a two-stage analysis of the data.[227] In the first stage (group identification or classification), an unknown compound can be assigned to a definite homologous series or group of homologues according to the numbers of homologous groups of principal peaks in the mass spectrum or (and) the statistically treated spectra of ion series. The subsequent refinement of the structure of the substance in the second stage is carried out with allowance for the known regularities of the fragmentation of the given series, together with the gas-chromatographic retention parameters.

Algorithms for group identification based on the statistically treated spectra of ion series have been characterised in detail, and the data for 20 series of halogen-containing substances have been given.[227] The further extension of the data base is extremely important, primarily to decrease the number of errors in second-order identification (the assignment of unknown substances to one of the series already characterised).[227] Table 4 gives the spectra of the ion series for several groups of fluorine-containing compounds. This method makes it possible to describe series in which the compositions of the members differ not by a CH_2 group but by another homologous difference, for example CF_2 (mass number 50).

In this case, compounds belonging to different homologous groups are obtained in a single series $y_M \equiv M \pmod{14}$, and the spectra of the ion series have a slightly lower reproducibility, which does not prevent the practical utilisation of these data.

Table 4. Mass spectra of the ion series of various groups of organofluorine compounds.[227]

Class of compound	Homologous group y_M	I_y in order of increasing y from 0 to 13*
n-Alkyl fluorides	6	$25_4\ 30_8\ 1_1\ 3_1\ 2_1\ 6_2\ 0\ 0\ 0\ 0\ 0\ 4_2\ 2_1\ 27_7$
s- and t-Alkyl fluorides	6	$4_4\ 4_3\ 1_1\ 4_1\ 8_5\ 57_8\ 3_2\ 0\ 0\ 0\ 0\ 2_2\ 1_1\ 12_4$
gem-Difluoroalkanes	10	$0\ 2_2\ 1_1\ 8_2\ 2_2\ 16_9\ 1_1\ 0\ 3_2\ 62_{10}\ 2_2\ 0\ 1_1\ 2_2$
Aryl fluorides	12	$1_1\ 3_2\ 0\ 1_1\ 1_1\ 4_1\ 2_1\ 3_1\ 3_1\ 4_1\ 2_1\ 46_9\ 23_9\ 7_2$
Perfluoroalkanes	**	$0\text{-}4_4\ 4_3\ 4_1\ 0\ 4_1\ 0\ 13_8\ 3_2\ 1_1\ 0\ 1_1\ 0\ 66_7$
Perfluoroalkenes	**	$2_2\ 5_4\ 5_4\ 6_4\ 3_3\ 9_7\ 2_2\ 6_4\ 2_1\ 4_2\ 2_2\ 2_2\ 1_1\ 51_{13}$
Perfluorocarboxylic acids and their esters	**	$1_1\ 9_4\ 5_2\ 40_4\ 1_1\ 3_3\ 0\ 4_4\ 3_2\ 5_5\ 1_1\ 4_3\ 0\ 24_6$

* I_y represents the total intensities of the signals of the homologous group y as a percentage of the total ion current ($\Sigma I_y = 100\%$); the subscripts give the standard deviations characterising the scatter in these quantities for different compounds of the given group.
** The mass numbers of the homologues are compared with respect to the modulus 50 (homologous difference CF_2) and not 14 (CH_2 group), so that they relate to different homologous groups $y_M = M \pmod{14}$.

An increase in the reliability of mass-spectrometric identification requires the elimination of the principal sources of inter-laboratory uncertainties in the mass spectra and the observation of various critria proposed for estimating the "quality" of mass spectra.[230] The simplest method of verifying the operating conditions of an instrument involves recording the spectra of standard compounds and comparing the peaks with tabulated values. Recommended reference substances are phenylbis(pentafluorophenyl)phosphine and *p*-bromofluorobenzene,[182,231,232] the data for which are given in Table 5.

The mass-spectrometric characterisation of halogen-containing compounds which have not been studied before covers an extremely wide range of materials. Because of the objective characteristics of the dissociative ionisation of substances of this class, however, the specific characteristics of their fragmentation often are not related to the presence of the halogen atoms in the molecule, but are determined completely by other functional groups. The fundamental facts include a new skeletal rearrangement in the molecular ions of dichloro- and difluorosilanes, associated with the elimination of dichloro- and difluorosilenes respectively:

$$[RR'SiHal_2]^{+\cdot} \rightarrow [RR']^{+\cdot} + SiHal_2.$$

The structural requirement for this process is the presence of multiple bonds or heteroatoms in the groups R and R'.[233] General rearrangements take place in the molecular ions of the trimethylsilyl and t-butyldimethylsilyl ethers of chlorine-containing alcohols, accompanied by the migration of a Cl atom to silicon and leading to the appearance in the spectra of peaks due to the ions $[(CH_3)_2SiCl]^+$ with *m/z* of 93 and 95.[234,235]

Polychlorinated compounds have been studied in detail not only in the solution of special analytical problems[236–239] but also frequently in the development of methods of detection and the interpretation of the mass spectra of these substances in the determination of pesticides and insecticides,[240–242] toxic polychloro-aromatic compounds,[148–151,243–245] etc. An independent direction of mass-spectrometric studies involves the investigation of potential metabolites of halogen-containing drugs.[246] A large number of papers have been devoted to the analysis of the regularities of the fragmentation of halogen-containing cyclo- and polyphosphazenes $(-PR_2=N-)_{3-n}$, a new promising class of monomers for the preparation of polymeric materials.[247–255] The mass spectra of the adducts of unsaturated compounds with 5,5-dimethoxytetrachloro-cyclopentadiene, which is a specific reagent for GC-MS analysis, have been characterised to establish not only the positions of the double bonds in unknown compounds but also, in the opinion of the authors cited,[256] their configuration.

Table 5. Standard mass spectra of phenylbis(pentafluorophenyl)-phosphine and *p*-bromofluorobenzene for standardising mass spectrometers.[182,231,232]

$C_6H_5P(C_6F_5)_2$		BrC_6H_4F	
m/z	I_{rel}, %	*m/z*	I_{rel}, %
51	30—60	50	15—40
68	$<0.02\ I^*_{69}$	75	30—70
69	not estimated (impurity)	95	100
		96	5—9
70	$<0.02\ I^*_{69}$	173	<1
127	40—60	174 M	>50
197	<1	175	2.5—4.5
198	100	176 M	$>50;\ 1.01\ I^*_{174}$
199	5—9		
275	10—30	177	2.5—4.5
365	~1		
441	<8		
442 M	>40		
443	>8		
444	7—9		

*Relative to the intensities of the signals with the mass numbers indicated.

Chemical ionisation is most frequently used in mass fragmentography for detecting polyhalogeno-aromatic compounds.[152,153] Halogen-containing compounds are promising reagent gases for the selective detection of compounds of different chemical character. For example, the use of chlorobenzene (IE 9.04 eV) for this purpose in the analysis of mixtures of petroleum hydrocarbons makes it possible to record only the aromatic hydrocarbons (IE range 8.5 ± 0.3 eV), whereas alkanes (10.4 ± 0.5 eV) and cycloalkanes (10.1 ± 0.3 eV) are not detected.[257] The use of CH_3I leads to the formation in the gas phase of dimethyliodonium cations $[(CH_3)_2I]^+$, capable of effectively methylating the compound being analysed.[258] The characteristics of the production and reactivity of $[CCl_3]^+$ and $[CCl_3]^-$ ions under chemical-ionisation conditions have been discussed.[259,260]

The high electron affinity of halogen-containing compounds, compared with other organic compounds, is responsible for the large negative ion formation cross-section,[261] and makes negative ion mass spectrometry a promising method for detecting and identifying compounds of this type. In practice, anions are most frequently generated under chemical-ionisation conditions, when thermal electrons are present in the ion source. Under these conditions, aromatic compounds give intense signals due to the molecular radical-anions $M^{\cdot-}$ at a low fragmentation depth, and signals of the ions $[M - H]^-$ are typical of compounds not containing conjugated systems. Chemical ionisation with detection of negatively charged ions does not impose fundamental restrictions on the nature of the reagent gases (methane is usually employed), but in some cases, mixtures with halogen-containing substances, for example CH_3OH and $CHCl_3$ [262] or CH_4 and CH_2Cl_2,[263] are used. This method leads to the preferential formation of $[M + Cl]^-$ anions.

The mass spectra and optimum detection conditions for these ionisation conditions have been studied for a series of pentafluorophenyl compounds C_6F_5R (R = F, CH_3, NH_2, OH, SH, OCH_3, $OCOCH_3$, CHO, NO_2, and CN),[264] pentafluorobenzoyl derivatives of aminoacids,[92] chloro- and fluorochloroethylenes,[265,266] the pentafluoropropionates of hydroxylamine derivatives,[267] chloroglucuronides,[268] trifluoroacetyl derivatives of polyols (in particular myoinositol[269]), derivatives of α,β-difluorocinammic acids,[270] halogen-containing derivatives of dipeptides and their metabolites,[271] etc. The method is highly sensitive, since the efficiency of ionisation is high (close to 100%), and the spectra of the negative ions of the halogen-containing compounds in a number of cases have a high structural specificity, making it possible to distinguish isomers, which have similar positive-ion spectra. Only this method makes it possible to differentiate perfluorobuta-1,3-diene and the isomeric perfluorobut-2-yne and perfluorocyclobutene.[272] The high sensitivity of the method has led to its extensive application in the analysis of toxic polychlorinated aromatic compounds by GC-MS analysis.[154–161,273–277]

The detection of negative ions is also possible in so-called thermospray ionisation in liquid chromatograph–mass spectrometers used in the analysis of non-volatile or thermally unstable compounds, including pesticides.[278–280] The process of anion formation can be controlled by adding special halogen-containing additives to the eluant. For example, the addition of only 0.1–1% chloroacetonitrile increases considerably the sensitivity of the detection of phenols, as a result of the formation of $[M + Cl]^-$ ions.

Mass-spectrometric studies of one of the most important types of non-volatile compound, namely organic salts, including the large group of salts of hydrogen halides, have been reviewed.[281] The special methods of ionisation used to record the mass spectra of substances of this kind and high-boiling halogen derivatives include the field desorption of pesticides,[282] which may be combined with separation of the mixtures on a liquid chromatograph.[283] The mass spectra have been obtained under photo-ionisation conditions and analysed for halogenomethanes,[284] 1,1-difluoroethane,[285] 1,1-dichlorodifluoroethylene,[286] fluoroethylenes,[287] and 5-fluorouracil derivatives.[288] One of the promising methods of secondary ion emission with ionisation on solid supports, so-called fast atom bombardment (FAB), has been used to study fluoroalkyl sulphonates,[289] metabolites of 2-chloro-N-isopropylacetanilide,[290] iodoxamic acid and its dimethyl ester,[291] and the halides of various elements of Group IV of the periodic system.[292]

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The variety of existing methods and the constant development of new methods for the chromatographic and mass-spectrometric identification and quantitative determination of halogen-containing organic compounds is related to the need to solve a number of fundamental urgent problems. One of these is the contamination of the environment by substances which are produced almost exclusively by man. There are no effective natural decomposition mechanisms for these substances, which accumulate in different materials and have a cumulative effect. The influence of the emission of volatile fluorochlorohydrocarbons into the atmosphere on the stability of the ozone layer is now a controversial topic. The reliable control of the concentration of aromatic polychlorinated organic compounds in foodstuffs, soils, natural waters, effluents, etc. is undoubtedly important.

The effective solution of these problems makes special demands on analytical methods for determining halogen derivatives. These requirements include ensuring the minimum detection limit, decreasing the systematic and random errors of the analysis, and achieving the maximum selectivity, discussed in the present review, of the determination of HOC against a background of predominant quantities of interfering components of different chemical character. In addition a completely unique type of problem involves increasing the efficiency of methods for interpreting the results of gas-chromatographic and GC-MS analyses to establish the composition and structure of unknown components in complex mixtures. The greatest difficulties are encountered in the structural analysis and identification of fluorine-containing compounds, and the improvement of the appropriate algorithms is an extremely urgent task.

The variety of methods and techniques for carrying out all stages of the gas-chromatographic and GC-MS analysis and identification of HOC in different materials, reflected in the present review, provides an objective prerequisite for the selection of the best methods for solving specific problems. This characterisation of the determination of HOC by means of the single most important criterion, namely the maximum selectivity, should not however be considered in isolation from other parameters of analytical procedures, in particular the reliability of the identification of these compounds.

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