Calculation of elemental ratios by on-column radiofrequency plasma atomic emission detection coupled with capillary gas chromatography

Tone Normann Asp[a,b,*], Stig Pedersen-Bjergaard[a], Tyge Greibrokk[a]

[a]Department of Chemistry, University of Oslo, P.O. Box 1033, Blindern, 0315 Oslo, Norway
[b]Department of Food Hygiene, Norwegian College of Veterinary Medicine, P.O. Box 8146–Dep, 0033 Oslo, Norway

Abstract

Atomic emission from a 350-kHz helium plasma was evaluated for the calculation of C/Cl and C/Br ratios in compounds separated by capillary gas chromatography. When the plasma was sustained inside the end of a 0.32 mm I.D. fused-silica GC column in 2 ml/min of GC carrier gas + 18 ml/min of make-up gas (helium), 94% of the elemental ratios obtained deviated by less than 20% from the theoretical values. These results with the on-column r.f. discharge were comparable to data obtained with a commercial GC–atomic emission detection system based on a microwave-induced plasma.

Keywords: Detection, GC; Atomic emission detection; Halogenated compounds

1. Introduction

Each of the traditional element-selective detection methods for capillary GC, such as the flame photometric detection (FPD), nitrogen–phosphorus detection (NPD), Hall electrolytic conductivity detection (ELCD), sulfur chemiluminescence detection (SCD) and oxygen flame ionization detection (O-FID), is typically capable of detecting only one or two different elements. Thus, several of these element-selective detection modes are necessary to cover the most important heteroatoms present in GC-amenable compounds. Alternatively, element-selective detection may be based on atomic emission spectrometric detection (AED), where emission is monitored from excited atoms formed by decomposition of the GC-separated compounds. Theoretically, every element in the Periodic Table may be monitored by a simple change of detection wavelength and, with a polychromator spectrometer, simultaneous multi-element detection is possible. Because GC–AED provides elemental responses largely independent of molecular structures, empirical formulae for the GC-separated analytes may be calculated [1–8]. This latter type of elemental information may be used to support effectively analyte identification based on mass spectrometry (GC–MS) and

* Corresponding author.

Fourier transform infrared spectrometry (GC–FTIR) [9–11].

In the period 1965–89, GC–AED research was carried out with laboratory-built systems owing to a lack of commercially available instrumentation. Microwave-induced plasmas (MIP) were preferred owing to their low gas consumption, and because the energy was coupled without direct contact between the discharge and the electrode system. In the first GC–MIP papers [12,13], results were reported with argon as the plasma gas. Especially for Cl, Br, F, N and O, the relatively low excitation potential of argon limited the sensitivity of these pioneering systems. However, after the introduction of the TM_{010} resonant cavity in 1976 [14], GC–MIP was carried out with a helium plasma sustained at atmospheric pressure. Owing to the high excitation potential of helium, the performance characteristics of GC–MIP were significantly improved. Although this improved cavity technology further increased the interest of GC–MIP, several minor technical problems remained. The MIP systems used required frequent tuning because the heat dissipated from the plasma changed the resonant frequency of the cavity, and the electric field in most microwave plasmas was strongest near the wall of the discharge tube. The high temperature frequently resulted in devitrification of the discharge tube, memory effects and nonspecificity problems. Therefore, alternative plasma sources were evaluated, including a 27.12-MHz stabilized capacitive He plasma [15], a 27.18-MHz capacitively coupled He plasma [16], a 60-Hz alternating current He plasma [17] and a 350-kHz radiofrequency He plasma [18–21], which all provided detection limits comparable to those obtained by GC–MIP.

In 1989, the first totally automated atomic emission detector for capillary GC became commercially available [22], consisting of an MIP for analyte excitation and a photodiode array for the optical measurements [23,24]. Unfortunately, in spite of high multi-element selectivity, sensitivity and versatility, the implementation of this system has been limited by a high initial cost. Thus, in order to make the advantages of GC–AED more available, inexpensive instrumentation has to be developed and commercialized.

Recently, a relatively inexpensive and simple atomic emission detector was presented [25], where a 350-kHz helium plasma was sustained inside the end of a 0.32 mm I.D. capillary GC column. Owing to the small volume of the detector cell, a high energy density was achieved within this new and miniaturized plasma. This resulted in improved detection limits [25–27] and in a reduced consumption of high-purity helium. Although these advantages have been discussed in detail, no information is at present available on the quantitative aspects of on-column AED. In this work, the 350-kHz on-column plasma was evaluated for the calculation of C/Cl and C/Br ratios for compounds present both in standard solutions and in complex environmental samples.

2. Experimental

2.1. Radiofrequency plasma equipment

The experiments with a 350-kHz radiofrequency plasma were carried out with a home-built r.f. plasma atomic emission detector coupled to a Model 4200 capillary gas chromatograph from Carlo Erba (Milan, Italy). The r.f. plasma was operated either "conventionally" inside a 1 mm I.D. discharge tube in 60 ml/min of helium [18–21], or "on-column" inside the end of the capillary GC column in 2–20 ml/min of helium [25–27]. In both cases, element-selective chromatograms for carbon (940.5 nm), chlorine (837.6 nm) and bromine (827.2 nm) were obtained from two independent channels and recorded with an SR6335 two-channel strip-chart recorder from Graphtec (Yokohama, Japan) or with an HP3395 A integrator from Hewlett-Packard (Avondale, PA, USA). With both plasma types, helium (99.9999%) (Hydro, Oslo, Norway) from 0 to 60 ml/min was utilized as the make-up gas, and oxygen (99.999%) (AGA, Oslo, Norway) was selected as the dopant gas. The GC system was equipped with a capillary split–splitless injection port, and with a 25 m × 0.32 mm I.D., 0.17 μm HP-5 (95% methyl–5% phenyl polysiloxane) fused-silica capillary column (Hewlett-Packard). Helium (99.9999%) (Hydro) at 2.5 ml/min was used as the GC carrier gas.

2.2. Microwave plasma equipment

The experiments with a 2450-MHz MIP were carried out with an HP 5921A atomic emission detector coupled to an HP 5890A capillary gas chromatograph from Hewlett-Packard. The element-selective chromatograms for carbon (second order of 247.9 nm), chlorine (479.5 nm), and bromine (478.6 nm) were obtained from three independent channels and recorded with an HP 35920A GC-AED ChemStation (Hewlett-Packard). Helium (99.9999%) (AGA) at 60 and 40 ml/min was utilized as the make-up and window purge gases respectively, and oxygen (99.999%) (AGA) was selected as the dopant gas for the plasma. The spectrometer was continuously purged with 2 l/min of nitrogen (99.996%) (AGA). The GC system was equipped with an HP7673 automatic sampler and a capillary split-splitless injection port with electronic pressure control (Hewlett-Packard). The gas chromatograph was equipped with a 60 m × 0.25 mm I.D., 0.10 μm HP-5 (95% methyl–5% phenyl polysiloxane) fused-silica capillary column (Hewlett-Packard). Helium (99.9999%) (AGA) at 2.5 ml/min was used as the GC carrier gas.

2.3. GC–MS equipment

GC–MS data with 70-eV electron impact ionization was recorded with a Fisons (Manchester, UK) VG ProSpec mass spectrometer interfaced to a Fisons GC-8065 gas chromatograph. The gas chromatograph was equipped with a capillary split–splitless injection port and a 25 m × 0.32 mm I.D., 0.17 μm HP-5 (95% methyl–5% phenyl polysiloxane) fused-silica capillary column (Hewlett-Packard). Helium (99.998%) (AGA) at 2.5 ml/min was used as the GC carrier gas.

2.4. Samples and reagents

The synthesis of the chlorinated thiophenes used in the test mixtures has been described elsewhere [28], whereas the other chlorinated and brominated compounds were commercially available and of analytical-reagent grade. Tables 1 and 2 show the test compounds used. The test

Table 1
Chlorinated model compounds used in the test mixtures

Symbol	Name	Formula
A	Hexachloroethane	C_2Cl_6
B	2-Chloropyridine	C_5H_4ClN
C	Chlorobenzene	C_6H_5Cl
D	1,2-Dichlorobenzene	$C_6H_4Cl_2$
E	1,3,5-Trichlorobenzene	$C_6H_3Cl_3$
F	2,6-Dichlorophenol	$C_6H_4Cl_2O$
G	2,3,6-Trichlorophenol	$C_6H_3Cl_3O$
H	2,3-Dichloro-4-acetylthiophene	$C_6H_4Cl_2SO$
I	2,3,5-Trichloro-4-formylthiophene	C_5HCl_3SO
J	2-Chlorobiphenyl	$C_{12}H_9Cl$
K	3-Chlorobiphenyl	$C_{12}H_9Cl$
L	4-Chlorobiphenyl	$C_{12}H_9Cl$
M	2,2'-Dichlorobiphenyl	$C_{12}H_8Cl_2$
N	4,4'-Dichlorobiphenyl	$C_{12}H_8Cl_2$
O	3,3',4,4'-Tetrachlorobiphenyl	$C_{12}H_6Cl_4$
P	1-Chloroanthracene	$C_{14}H_9Cl$
Q	9,10-Dichloroanthracene	$C_{14}H_8Cl_2$

mixtures were prepared at two concentration levels in such a way that the concentration of halogen was the same for each compound. Thus, the amount of bromine was adjusted to 7.6 and 38.0 ng/μl, whereas 10.0 and 30.0 ng/μl chlorine were used for the chlorinated compounds. Deposited sludge from a nickel refinery was prepared by Soxhlet extraction (24 h) with hexane.

2.5. Calculation of elemental ratios

Carbon-to-element ratios (C/E) for unknown compounds were obtained from the expression:

Table 2
Brominated model compounds used in test mixture

Symbol	Name	Formula
A	1,2-Dibromo-2-methylpropane	$C_4H_8Br_2$
B	2-Bromothiophene	C_4H_3BrS
C	2-Bromopyridine	C_5H_4BrN
D	3-Bromopyridine	C_5H_4BrN
E	Bromobenzene	C_6H_5Br
F	1,4-Dibromobenzene	$C_6H_4Br_2$
G	1,3,5-Tribromobenzene	$C_6H_3Br_3$
H	4-Bromophenol	C_6H_5BrO
I	2-Bromobiphenyl	$C_{12}H_9Br$
J	4-Bromodiphenyl ether	$C_{12}H_9BrO$
K	4,4'-Dibromodiphenyl ether	$C_{12}H_8Br_2O$

$$C/E = \frac{\text{C-response of unknown}}{\text{E-response of unknown}} \cdot RRF_{C/E}$$

where E is an element other than carbon (C) in the same molecule. The ratio response factor for C/E ($RRF_{C/E}$), which was based on analysis of a compound with known elemental composition, was defined as

$$RRF_{C/E} = \frac{\text{E-response of known}}{\text{C-response of known}} \cdot \frac{\text{C atoms in known}}{\text{E atoms in known}}$$

The peak heights were used as signal responses in the calculation of the RRFs, and the measurements for C and E were accomplished in the same chromatographic run.

3. Results and discussion

Recently, a simple and relatively inexpensive atomic emission detector was introduced for capillary GC [25], where a 350-kHz helium plasma was sustained inside the end of a 0.32 mm I.D. capillary GC column (on-column detection). Owing to the small internal volume of the plasma cell, a stable discharge of high energy density was obtained in only 2–20 ml/min of helium. Compared with preceding technology, where the 350-kHz discharge was maintained inside a 1 mm I.D. silica tube in 60 ml/min of helium [18–21], detection limits for most non-metallic elements were improved by a factor of 5–50 [25–27]. In addition, the operating costs were substantially reduced owing to the low consumption of high-purity gases.

From the literature, it is known that GC–MIP provides elemental responses almost independent of the original molecular structure [1–8]. Thus, by simultaneous multi-elemental detection, elemental ratios and empirical formulae may be determined. Because of their environmental importance, chlorinated and to a lesser extent brominated organic compounds have often been used in empirical formula calculations in GC–AED work. The estimated C/Cl and C/Br ratios reported are in most cases within an error of 20% of the correct value [2–8]. For the 350-kHz on-column plasma, however, no information is at present available on the calculation of elemental ratios. Therefore, the present work was focused on C/Cl and C/Br ratios obtained from on-column atomic emission data. In order to enhance the accuracy of elemental ratio calculations, the optical system of the on-column detector was expanded with a second channel to monitor two different channels simultaneously. The effects of plasma gas flow and analyte concentration were studied for compounds present in standard solutions, and the applicability was evaluated with a complex environmental sample. In addition, the results were compared with corresponding data obtained with a commercial GC–MIP-AED system.

3.1. Effect of plasma gas flow on the calculation of elemental ratios

In Fig. 1a, C/Cl ratios were calculated for seventeen different compounds with the on-column plasma sustained in only 2.5 ml/min of GC carrier gas. It was found that 53% of the C/Cl estimations deviated by more than 20% from theoretical values (R.S.D. 34.2%), which indicated that the elemental responses depended on the molecular structures. Especially the calculated C/Cl ratios for hexachloroethane (A) and chlorinated thiophenes (H and I), were too high. This indicated that both sulfur and very high levels of chlorine may elevate the responses for chlorine relative to carbon. However, although the detector sensitivity decreased by a factor of 3–4, the accuracies of the estimated C/Cl ratios were improved (R.S.D. 14.9%) when additionally 18 ml/min of helium was supplied to the discharge (Fig. 1b). This effect probably arose because recombinations of analyte constituents and interactions involving the wall of the plasma capillary were suppressed as the analyte residence time decreased. The latter results obtained with the on-column plasma were comparable to data obtained when the r.f. plasma was sustained conventionally inside a 1 mm I.D. discharge tube in 60 ml/min of helium (Fig. 1c). Thus the small internal diameter of the on-column plasma cell had no deleterious effects on the calculation of C/Cl ratios.
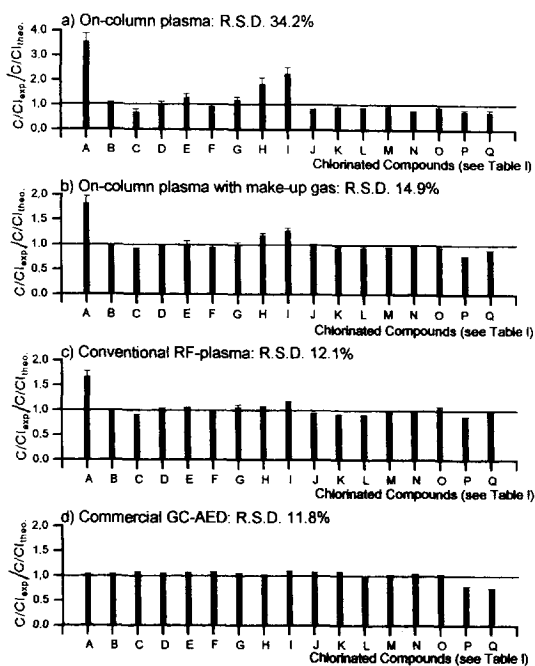
Fig. 1. C/Cl ratios obtained with (a) on-column r.f. plasma with no make-up gas, (b) on-column r.f. plasma with 18 ml/min make-up gas, (c) conventional r.f. plasma inside a 1 mm I.D. tube with 60 ml/min make-up gas and (d) commercial GC–AED with 60 ml/min make-up gas. The results were based on five repetitive injections, and calibration was performed with the mean ratio response factor ($RRF_{C/Cl}$) for all the compounds analysed. The chlorinated compounds used are listed in Table 1.

To evaluate further the on-column plasma, comparison with the commercial GC–AED system was carried out (Fig. 1b,d). Since the accuracies of C/Cl data obtained with the two systems were comparable, the emission characteristics of the 350-kHz on-column plasma apparently were close to those of the 2450-MHz MIP for quantitative applications. Furthermore, the simple optical concept of the on-column detector, where signals were recorded without spectral background correction, provided C/Cl ratios comparable to those with the commercial AED system, although the latter utilized an advanced scheme for multi-point background correction. This further supported the potential of atomic emission detectors based on simple and inexpensive optical systems [29].

Similar experiments of comparison were car-

ried out with eleven brominated compounds (Fig. 2). The results supported the trends discussed above for the C/Cl ratios. However, the C/Br ratios apparently deviated less from the theoretical values than reported for the C/Cl data. Thus, when the on-column plasma was operated with 18 ml/min of make-up gas, all of the results obtained deviated by less than 20% from the theoretical value (R.S.D. 8.5%).

3.2. Effect of analyte concentration on the calculation of elemental ratios

In a subsequent experiment, C/Cl ratios were calculated for seventeen different compounds present both at the 10 and 30 ng Cl/μl level (Fig. 3). Unfortunately, in most cases, the C/Cl ratios increased as the amount of analyte increased,
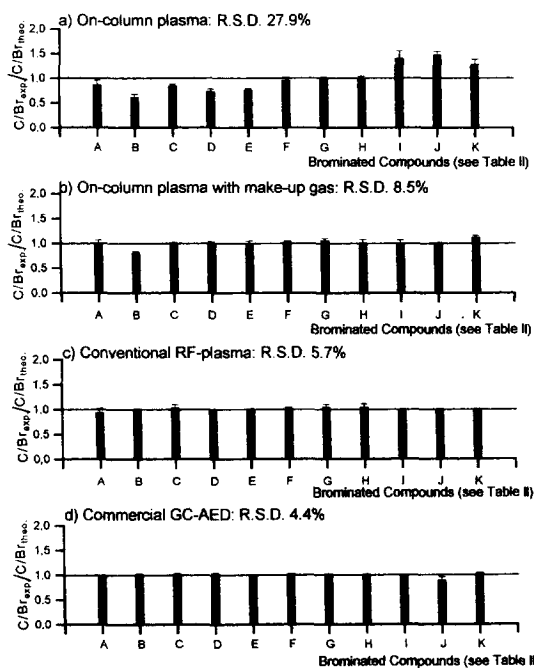

Fig. 2. C/Br ratios obtained with (a) on-column r.f. plasma with no make-up gas, (b) on-column r.f. plasma with 18 ml/min make-up gas, (c) conventional r.f. plasma inside a 1 mm I.D. tube with 60 ml/min make-up gas and (d) commercial GC–AED with 60 ml/min make-up gas. The results were based on five repetitive injections, and calibration was performed with the mean ratio response factor ($RRF_{C/Br}$) for all the compounds analysed. The brominated compounds used are listed in Table 2.
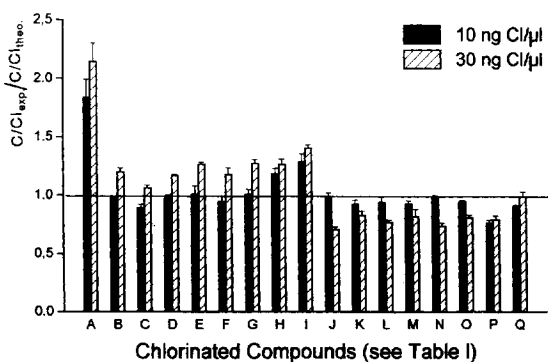
Fig. 3. C/Cl ratios obtained at 10 and 30 ng Cl/μl by on-column detection with 18 ml/min make-up gas. The results were based on five repetitive injections and calibration was performed with the mean ratio response factor (RRF$_{C/Cl}$) for all the compounds analysed. The chlorinated compounds used are listed in Table 1.

whereas for unknown reasons the reverse relationship was observed for some polychlorinated biphenyls. Similar trends were observed for eleven brominated compounds (Fig. 4), which supported the contention that the accuracy of elemental ratios obtained from on-column data was affected by the concentration of the analytes. When the 350-kHz plasma was sustained conventionally inside a 1 mm I.D. discharge tube in 60 ml/min of helium, a similar concentration effect
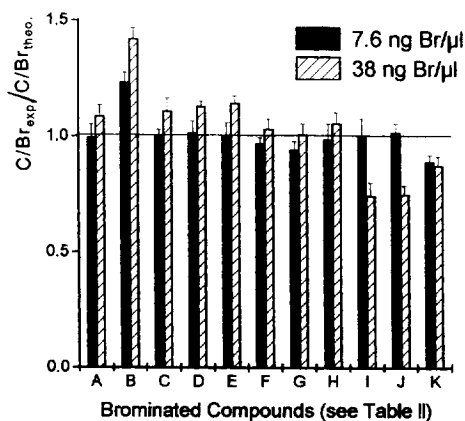

Fig. 4. C/Br ratios obtained at 7.6 and 38 ng Br/μl by on-column detection with 18 ml/min make-up gas. The results were based on five repetitive injections and calibration was performed with the mean ratio response factor (RRF$_{C/Br}$) for all the compounds analysed. The brominated compounds used are listed in Table 2.

was not observed. This suggested that the non-linearity problem was related to the small internal diameter of the on-column plasma cell. Although the energy density of the discharge increased, the sample capacity probably decreased as the size of the plasma was reduced. Thus, the concentration effect on the C/Cl ratios arose as a result of non-linearity of the elemental responses at the highest concentration level. Although the commercial AED system was found not to suffer from this problem, the limited sample capacity of the on-column plasma represented no major practical problem since highly concentrated samples may be diluted prior to injection.

3.3. Effect of optical resolution on the calculation of elemental ratios

With the two monochromators used in the present work, the effective bandpass improved from 3.2 to 0.8 nm as the slit width was reduced from 500 to 50 μm. Although this enhancement of the optical resolution resulted in decreased detector sensitivity, the halogen-to-carbon selectivities increased significantly, as discussed recently [29]. Because of this latter effect, C/Cl and C/Br ratios were calculated with different slit widths as reported below.

For both C/Cl and C/Br ratios, no major improvements were observed as the optical resolution of the system was enhanced. Thus, unless very high halogen-to-carbon selectivities ($>10^3$:1) were required, the on-column detector was operated with 500-μm slits to maximize the detector sensitivity. The experiments with different slit widths supported the trend observed above (Section 3.1) that calculations of elemental ratios were most sensitive to careful optimization of the plasma conditions, whereas the optical resolution of the spectrometer had a minor impact on the results.

3.4. Application of C/Cl and C/Br ratio calculations

In order to extend the study to real samples of high complexity, a hexane extract of sludge deposited from a nickel refinery was analysed

with the on-column plasma sustained in 18 ml/min of helium as make-up gas (Fig. 5). The extract consisted mainly of chlorinated and brominated alkylbenzenes as determined by GC–MS. The C/Cl and C/Br ratios were calculated for eleven of the identified compounds, based on external calibration with di- and trihalogenated benzenes. These values were combined with GC–MS information on the number of halogens, which allowed partial molecular formulae to be determined (Table 3). When the numbers of carbon atoms were rounded to whole

Table 3
Partial molecular formulae obtained by on-column detection for eleven halogenated compounds present in a deposited sludge from a nickel refinery

Peak	Experimental formula		Theoretical formula
	Halobenzenes as ref.	Peak 9 as ref.	
1	$C_{11.5}Cl_3$	$C_{10.7}Cl_3$	$C_9H_9Cl_3$
2	$C_{9.5}Cl_3$	$C_{8.8}Cl_3$	$C_9H_9Cl_3$
3	$C_{7.5}Cl_3$	$C_{7.0}Cl_3$	$C_9H_9Cl_3$
4	$C_{10.9}Cl_3$	$C_{10.2}Cl_3$	$C_{10}H_{11}Cl_3$
5	$C_{11.7}Cl_3$	$C_{10.9}Cl_3$	$C_9H_9Cl_3$
6	$C_{8.9}Cl_4$	$C_{8.3}Cl_4$	$C_9H_8Cl_4$
7	$C_{9.5}Cl_2/C_{9.x}Br$	$C_{8.8}Cl_2$	$C_9H_9Cl_2Br$
8	$C_{10.7}Cl_4$	$C_{10.0}Cl_4$	$C_{10}H_{10}Cl_4$
9	$C_{9.7}Cl_4$	ref.	$C_9H_8Cl_4$
10	$C_{10.9}Cl_5$	$C_{10.2}Cl_5$	$C_9H_7Cl_5$
11	$C_{9.8}Cl_5$	$C_{9.2}Cl_5$	$C_9H_7Cl_5$

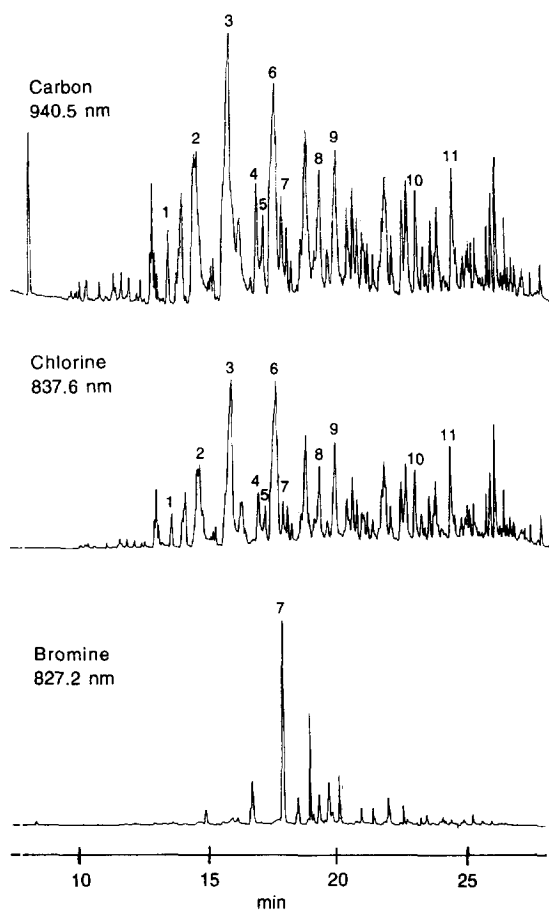Calibration was performed either with di- and trihalobenzenes (external) or with peak 9 (internal).

Fig. 5. C-, Cl- and Br-selective chromatograms of a nickel refinery deposited sludge detected on-column with 18 ml/min of additional make-up gas to the plasma. Conditions: 1 μl of extract was injected splitless at an injector temperature of 225°C. The oven was held at 50°C for 3 min and then programmed at 25°C/min to 100°C, 5°C/min to 220°C and finally at 25°C/min to 280°C.

numbers, a correct partial molecular formula was obtained only for a single compound (peak 6). However, for most of the peaks studied (73%), the calculated number of carbons deviated by no more than a single atom. All the calculated carbon numbers were within 30%. Because the concentration level of the calibration compounds was close to those of the unknowns, the experimental errors were principally attributed to variations of elemental responses and to incomplete chromatographic resolution. In order to suppress the contribution from the former, the partial molecular formulae were recalculated based on calibration with peak 9 in the sample. For eight of the peaks (80%), the accuracy was improved, and five (50%) of the partial molecular formulae agreed with the theoretical ones when the numbers of carbon atoms were rounded to whole numbers. Now the calculated carbon numbers were within 20%. Obviously, as reported also with the commercial GC–AED system [7], molecular formulae calculated from atomic emission data were in most cases not sufficiently accurate for analyte identification. However, the information on elemental content from the on-column plasma detector combined with other coupled techniques (GC–MS, GC–

FTIR) results in a strong analytical tool for qualitative applications.

4. Conclusions

The present work has demonstrated for the first time the calculation of C/Cl and C/Br ratios for GC-separated compounds based on atomic emission from a simple 350-kHz on-column helium plasma. In spite of instrumental simplicity, the C/Cl and C/Br ratios obtained with the on-column plasma were comparable to those reported in the literature [2–8]. This attractive quantitative aspect, in combination with high sensitivity and low costs, as reported recently [25–27], suggests that the 350-kHz on-column plasma is a very interesting alternative to microwave-induced discharges in GC–AED.

Acknowledgements

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