Empirical formulae studies of chlorofluorocarbons using gas chromatography coupled to atomic emission detection

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Abstract

Empirical formulae determination on gas chromatographically resolved analytes, through specific element quantitation on eluted peaks, challenges experimental design and procedure in atomic emission spectral detection. Molecular structural dependence of elemental response factors is a factor which is element dependent, fluorine showing notable non-linear tendencies. This study of compound independent calibration for F, Cl, C, H for chlorofluorocarbon (CFC) molecules shows the necessity for reference compounds similar to the target analytes in element content, molecular structure, concentration and physical state. Best results were obtained in the nanomole range of analytes. The Cl/C and H/C ratios were found to be closer to the theoretical values than the F/C ratios, probably because fluorine strongly interacts with the silica discharge tube. The analysis of CFC mixtures gave valid empirical formulas and % (w/w) compositions. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Microwave-induced helium plasma (MIP) atomic emission detection (AED) provides both qualitative and quantitative information on eluates, in the presence of interfering background matrixes, by virtue of their elemental composition. Following the introduction of commercial gas chromatography (GC)–AED instrumentation in 1989 [1,2], the number of applications using this technique has grown considerably [3–6].

Ideally the high temperature of the plasma pro-
vides enough energy to decompose the entering molecules quantitatively into their constituent atoms and derived ions, which are excited by the plasma and subsequently emit radiation at wavelengths characteristic of the elements present [1,2].

Inconclusive results have however sometimes been obtained for compound independent elemental response and resultant empirical formula calculations [7–16]. It has been variously indicated that elemental response may also relate to molecular structure, concentration, nature of heteroelements and molecular mass [7–10].

Empirical formula studies of halogenated compounds showed as much as 20% differences between experimentally obtained carbon numbers and the

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theoretical values [10]. Determinations for halogenated compounds in environmental samples was found to be unsatisfactory due to dependence of elemental response on compound type and particularly poor chromatographic resolution and poor signal to background levels [17], but gas chromatography–mass spectroscopy (GC–MS) allowed enhanced data credibility. Compound independent chlorine elemental response was demonstrated for chlorophenols although carbon and oxygen responses showed molecular structure dependence and the presence of oxygen affected the carbon response [18].

In contrast, the presence of oxygen has little effect on the relative elemental responses of carbon and hydrogen in paraffin, olefin or aromatic hydrocarbons [19] and compound independent calibration curves for sulfur and oxygen were obtained for compounds in petrochemical fractions [11–13]. In the analysis of nitrogen-containing herbicides in water the deviations of elemental response for nitrogen, chlorine and sulfur were less than 6% [14]. Quantitation using both the traditional reference standard calibration and the compound-independent calibration based on elemental responses were found to be comparable [15]. The calibration curves for sulfur, oxygen, chlorine and carbon were linear irrespective of functionalities of the atoms in various compounds [16].

Hydrogen, fluorine, phosphorous and nitrogen may show larger discrepancies in elemental responses, the three former elements seeming to interact chemically with the discharge tube walls [20,22,23], yielding curved plots for response factor as a function of element amount injected. In one study the ratio of Cl/C for halocarbons was found to be compound independent within 2.5% relative standard deviation [20] but hydrogen responses were non-linearly dependent on the amount of hydrogen and also increased as the chlorine amount increased. The non-linear hydrogen response is suggested to be caused by a charge-transfer reaction between protons and oxygen according to one study [21].

The objective of this work was to investigate compound independent calibration for F, Cl, C, H in chlorofluorocarbons (CFCs) which comprise a versatile compound class with many applications but whose production and use has been curtailed due to environmental concerns [24]. GC–AED has been applied on a number of occasions to the study of fluorinated compounds [8,9,25–27] including the contamination of the pure CFC standards [7]. Although AED is less sensitive than electron-capture detection (ECD) for CFCs, it is important to establish if it responds uniformly to the content of each halogen irrespective of analyte molecular structure [28].

2. Experimental

2.1. Instrumentation

GC–AED was performed with a Model 5890 II Hewlett-Packard (HP) gas chromatograph equipped with a Model 5921A atomic emission detector and controlled by HP 35920A GC–AED software resident in a HP 300 computer (Hewlett-Packard, Little Falls, DE, USA).

2.2. Materials

The CFC standards were obtained from American Reclamation, Chicopee, MA, USA. All the standards were listed as more than 99% pure as confirmed chromatographically. Representative readily available freon standards were used viz. R-12 gas (CCl_2F_2), R-22 gas ($CHClF_2$), R-113 liquid ($C_2Cl_3F_3$), R-11 liquid (CCl_3F), and azeotropic gas mixtures R-500 and R-502. Standard gas mixtures R-500 and R-502 were treated as unknown samples for this experimental work. The R-500 gas has a composition of R-152a ($C_2H_4F_2$, 26.2%) plus R-12 (CCl_2F_2, 73.8%) % (w/w), whereas R-502 gas has a composition of R-115 (C_2ClF_5, 51.2%) plus R-22 ($CHClF_2$, 48.8%). The density parameters were obtained from Handbook of Chemistry and Physics [34]. Carbon tetrachloride and dichloromethane (certified A.C.S. spectranalyzed) were obtained from Fisher Scientific, NJ, USA and were chromatographically pure.

2.3. Experimental work

The gas samples were injected using gas-tight syringes, being withdrawn from the pressurized gas cylinders by inserting a needle into the septum

located at the outlet of the gas cylinder. The septum was held in place by a nut which was fitted on to the outlet of the gas cylinder.

Each sample was injected at least thrice and average peak area was used to calculate the elemental ratios using the relationship:

$$\frac{X}{C} = \frac{[(X-\text{area, unknown}) \cdot (C-\text{area, unknown}) \cdot (X-\text{moles, known})]}{[(C-\text{area, unknown}) \cdot (X-\text{area, known}) \cdot (C-\text{moles, known})]}$$

where, X is any element other than carbon "C", X−area is the chromatographic peak area from the X elemental chromatogram, X/C is the elemental ratio in a given compound.

The following formula based on the normalization method was used to calculate % composition of unknown sample mixture [19]

$$W_i \% = \frac{A_i M_i / C_i}{\sum A_i M_i / C_i} \times 100$$

where, W_i = % (w/w) of the compound determined; A_i = peak area of the compound determined for the specific element channel; M_i = molecular mass (calculated from empirical formula) of the compound determined; C_i = total atomic mass of the specific element in the compound determined.

The GC injection port and transfer line temperatures were maintained at 200°C and 150°C, respectively and block and AED cavity temperatures at 150°C and 250°C, respectively. A VOCOL column designed for highly volatile organic compounds (Supelco, Bellefonte, PA, USA) of 60 m×0.25 mm I.D., 1.50 μm film thickness was used. Injections were made through a split/splitless injector operated with a 1:130 split for all samples with helium carrier gas at a column head pressure of 29 p.s.i. (1 p.s.i.= 6894.76 Pa). For element signal measurements default recipes provided by the manufacturer were used at 495 nm for carbon (I), 486 nm for hydrogen (I), 479 nm for chlorine (II) and 690 nm for fluorine (II). Hydrogen and oxygen were used as AED plasma reagent gases. As the peaks were well resolved and well defined, the computer integration was feasible and considered to be fully reliable.

3. Results and discussion

R-12 (CCl_2F_2), R-22 ($CHClF_2$), R-113 ($C_2Cl_3F_3$), R-11 (CCl_3F), R-500 [a mixture of R-152a ($C_2H_4F_2$) and R-12 (CCl_2F_2)] and R-502 [a mixture of R-115 (C_2ClF_5) and R-22 ($CHClF_2$)] were used for this study along with chlorinated compounds CCl_4, CH_2Cl_2 and $C_2H_4Cl_2$. The aim was to observe how well the elemental ratios viz. C:Cl, C:F and C:H correlate with the theoretical values irrespective of the parent compound, and to observe the effect of concentration on these ratios. The elemental ratio information can be used as a qualitative analysis tool to identify an unknown halogenated peak in a given chromatogram. Potential for quantitative analysis was also explored by studying the compound independent elemental response in terms of nature of element, compound structure and concentration. Fig. 1 shows linear elemental calibration curves for chlorine, carbon and hydrogen also yielding similar linear calibration curves. Fig. 2 shows the fluorine elemental calibration curves which are of apparent second order paralleling other studies where fluorine, hydrogen and phosphorus elemental responses gave curved calibration plots [22]. However, in the present study hydrogen response gave a linear calibration curve. It does not appear that the analyte loading has exceeded the detector capacity as the carbon, chlorine and hydrogen calibration curves were straight with at least 0.995 R^2 values. Presumably, fluorine must be interacting with the walls of the silica discharge tube or undergoing chemical reactions in the helium plasma medium.

In principle, a single straight line calibration curve should be obtained for an element under consideration irrespective of the structure of the parent compound. Here, at higher elemental concentration, the calibration curves derived using different compounds did not overlap with one other. Samples differing in physical state at ambient temperature (gas vs. liquid) gave different responses (even after taking sample density into account). For CFCs having the same physical state, the elemental responses were compound independent in the nanomole concentration range (Table 1). Although the calibration curves do not precisely overlap each other, the range of the slope of a calibration line at the 95% confidence interval overlaps with corresponding slope ranges of other lines, defining the AED elemental response as compound independent.
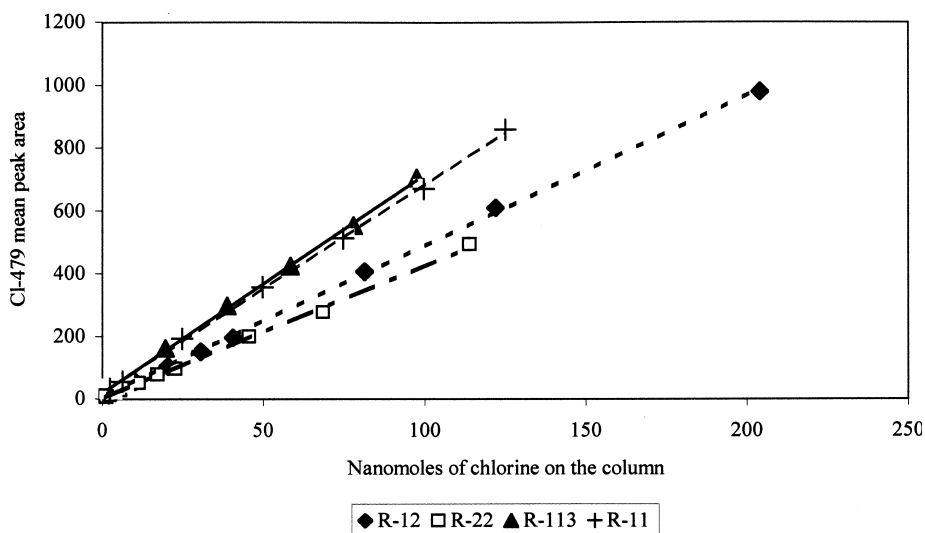
Fig. 1. Graph of chlorine peak area as a function of number of moles of chlorine on the column. Linear regression values for individual curves. R-113, $R^2 = 0.9994$; R-11, $R^2 = 0.9993$; R-12, $R^2 = 0.9995$; R-22, $R^2 = 0.9982$.

Quantitative analysis of unknown samples should be carried out in this concentration range. However above this narrow concentration range the elemental response is not compound independent.

The elemental response will be compound in-dependent if both the processes viz. molecular fragmentation and subsequent elemental excitation are quantitative and reproducible [29]. If there is a
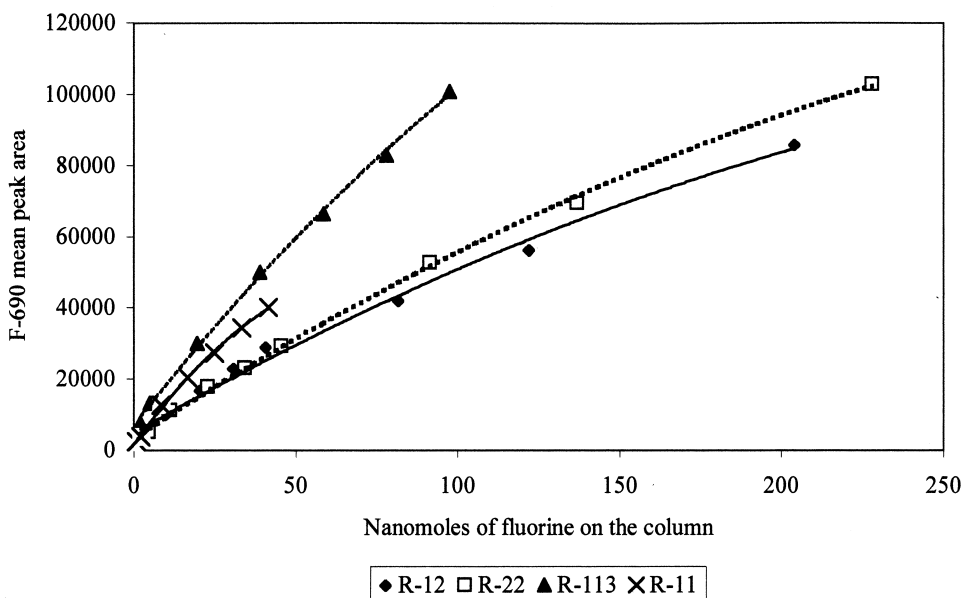

Fig. 2. Graph of fluorine peak area as a function of number of moles of fluorine on the column. Linear regression values for individual curves. R-113, $R^2 = 0.9986$; R-11, $R^2 = 0.9983$; R-12, $R^2 = 0.9919$; R-22, $R^2 = 0.9986$.

Table 1
Comparison of calibration curves and concentration ranges for compound independent chlorine elemental response

Compound type	Concentration range of chlorine on the column (nmol)	Slope of the calibration curve ($\cdot 10^{12}$)	Standard error of the slope ($\cdot 10^{11}$)	Range of the slope at 95% confidence interval ($\cdot 10^{12}$)
R-22 (CHClF$_2$) gas	1.14–5.71	4.66	1.40	4.33–4.99
R-12 (CCl$_2$F2) gas	2.04–4.09	4.96	3.31	4.04–5.88
R-11 (CCl$_3$F) liquid	2.49–49.9	6.91	1.50	6.57–7.24
R-113 (C$_2$Cl$_3$F$_3$) liquid	1.95–58.5	6.96	0.69	6.81–7.11
(CCl$_4$)	16.0–32.1	7.16	3.63	6.15–8.17
(C$_2$H$_4$Cl$_2$)	9.80–39.2	6.31	2.25	5.78–6.84

difference in the degree of fragmentation and/or the degree of elemental excitation either due to the structural differences among parent compounds or chemical reactions in the plasma, the elemental responses will not be compound independent. Both these processes are represented by the elemental calibration curve as a function of element concentration in the plasma. Hence it is difficult to obtain compound independent responses for some elements. The plot of elemental peak areas represents only the excitation phenomenon and the behavior of the elements which are freely present in the plasma subsequent to molecular fragmentation [29]. Thus even though the number of molecules fragmented may be different for different compounds, the area plot should be unaffected. A linear area plot indi-

cates that the excitation process for the elements under consideration is free of chemical or spectral interference. The peak area plots are related to the elemental ratios. Figs. 3 and 4 demonstrate that the peak area plots are linear except at a higher concentrations, the latter showing that the Cl/C elemental ratios can be correlated to the slopes of the linear plots obtained using different compounds. For R-22 (CHClF$_2$) the Cl/C ratio is 1:1 and the slope of the line is approximately 7 whereas the slope for the R-11 line is approximately 21, thus the ratio of Cl/C for R-11 should be 3:1 and in fact it correlates to the formula of R-11 (CCl$_3$F).

Tables 2, 3 and 4 show measured elemental ratio data for R-22 gas. To calculate the empirical formula, R-12, R-113 and dichloromethane were used
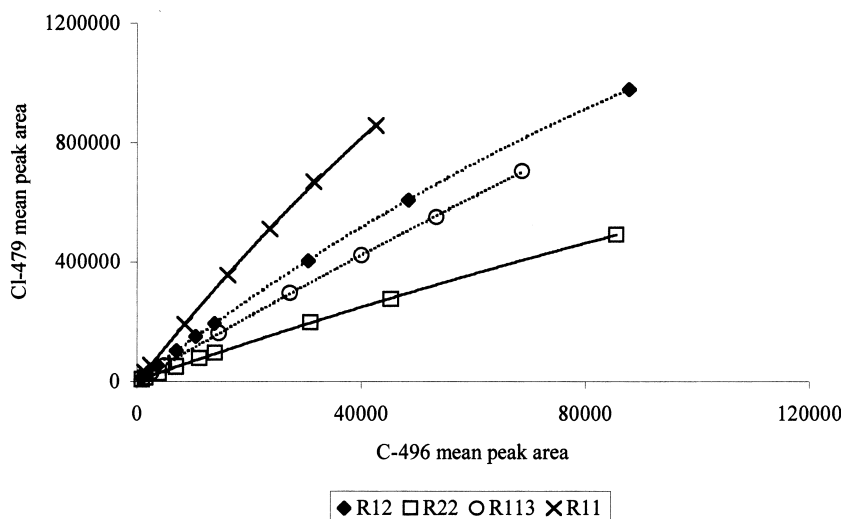

Fig. 3. Graph representing relation between chlorine and carbon peak areas. Linear regression values for individual curves. R-113, $R^2 = 0.9999$; R-11, $R^2 = 0.9999$; R-12, $R^2 = 1$; R-22, $R^2 = 0.9997$.
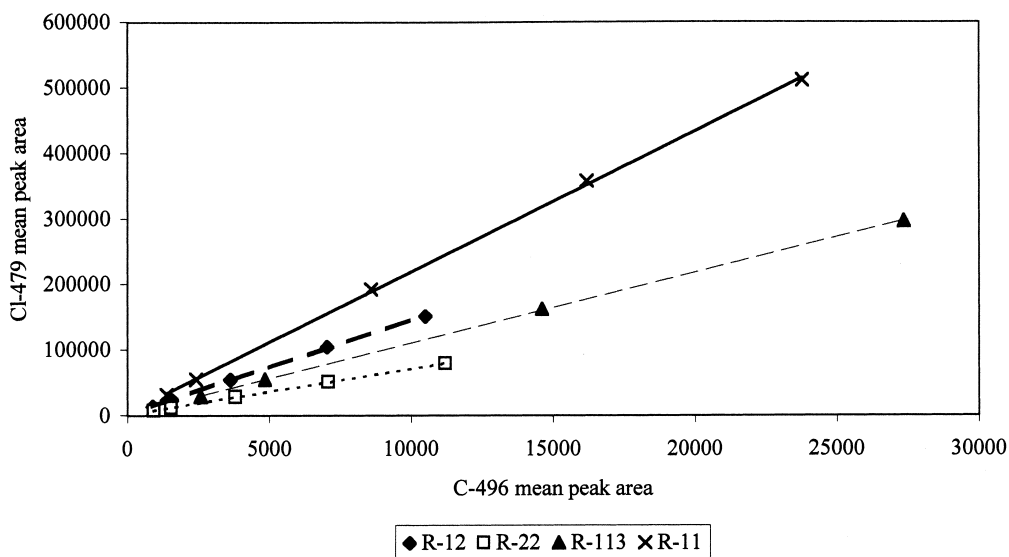
Fig. 4. Graph representing relation between chlorine and carbon peak areas at lower elemental concentration range. Linear regression values for individual curves. R-113, $R^2 = 0.9999$; R-11, $R^2 = 0.9996$; R-12, $R^2 = 0.9997$; R-22, $R^2 = 0.9997$.

independently as reference standards to investigate whether the type of reference affects the elemental ratio evaluation. The data in Tables 2 and 3 shows that Cl/C and F/C elemental ratios decrease with increase in analyte concentration from the formal Cl/C ratio of 1:1 and F/C ratio of 2:1, seen at low nanomolar analyte peak loading, irrespective of the standard used. This observation correlates to the graphs of peak area ratios in Fig. 3. Data in Table 4 however, for the dichloromethane standard, show the H/C ratio remains constant over the two-orders of

magnitude concentration range (1.14–114 nmol of both C and H) studied, in contrast with finding of other workers noted above, but is consistently lower than the formal 1:1 element ratio as is also seen in Fig. 5. Other CFC compounds viz. R-12, R-113 and R-11, investigated as ''unknowns'' as well as chlorinated compounds also showed similar behavior.

Tables 5 and 6 show Cl/C and H/C elemental ratio data respectively for dichloroethane ($C_2H_4Cl_2$), obtained over a restricted concentration range. It may be seen from Table 5 that the reference standard

Table 2

Cl/C elemental ratio data for R-22 ($CHClF_2$) gas

R-22 sample on the column (nmol)	Cl/C molar ratio of R-22, obtained using 10 µl (2.4 nmol on the column) of R-12 (CCl_2F_2) gas standard		Cl/C molar ratio of R-22, obtained using 0.2 µl (6.50 nmol on the column) of R-113 ($C_2Cl_3F_3$) liquid standard		Cl/C molar ratio of R-22, obtained using 0.2 µl (12.1 nmol on the column) of CH_2Cl_2 liquid standard	
	Mean	SD	Mean	SD	Mean	SD
1.14	0.99	0.09	1.01	0.06	1.12	0.07
2.28	0.99	0.08	1.01	0.04	1.12	0.04
5.71	0.98	0.10	1.00	0.05	1.10	0.09
11.4	0.96	0.07	0.97	0.02	1.08	0.03
17.1	0.93	0.17	0.95	0.11	1.05	0.18
22.8	0.92	0.07	0.94	0.02	1.04	0.03
45.6	0.85	0.09	0.87	0.06	0.96	0.08
68.5	0.81	0.08	0.83	0.05	0.91	0.07
114	0.77	0.07	0.79	0.03	0.87	0.04

Table 3
F/C elemental ratio data for R-22 (CHClF$_2$) gas sample

R-22 on the column (nmol)	F/C molar ratio of R-22 using, 10 μl (2.04 nmol on the column) of R-12 (CCl$_2$F$_2$) gas as a standard		F/C molar ratio of R-22 using, 0.2 μl (6.50 nmol on the column) of R-113 (C$_2$Cl$_3$F$_3$) liquid as standard	
	Mean	SD	Mean	SD
1.14	2.04	0.12	2.30	0.08
2.28	2.14	0.11	2.41	0.21
5.71	1.91	0.15	2.16	0.29
11.4	1.64	0.09	1.85	0.09
17.1	1.34	0.19	1.51	0.09
22.8	1.37	0.07	1.54	0.03
45.6	1.11	0.08	1.25	0.04
68.5	1.00	0.08	1.13	0.04
114	0.79	0.05	0.89	0.04

R-113 was used at almost half the concentration of the reference standard CH$_2$Cl$_2$ but the latter gives more accurate Cl/C elemental ratio for the dichloroethane sample. Although lower reference standard concentrations are advisable, concentration does not appear to be a critical factor within this range for measuring elemental ratios, but may be important for quantitative analysis. A similar finding for the H/C elemental ratio is indicated in Table 6. Rounding of these experimentally calculated elemental ratios gives correct empirical formulae.

As in the analysis of a CFC sample, the CFC standards gave more accurate elemental ratios than the chlorocarbon standard, so in the analysis of chlorocarbon samples one should use a chlorocarbon standard rather than a CFC. However even in these cases the working concentration range for viable ratio measurements is clearly very limited.

Thus the analyte and the reference standard should have similar structures and should contain the same elements. It was observed that, compared to CFCs, the chlorocarbons gave correct elemental ratio data at relatively higher concentrations. The data shows that Cl/C ratio can be more accurately determined than the F/C ratio. Fluorine response decreased more rapidly than chlorine response with increased concentrations, indicating fluorine to be more affected than chlorine. At higher concentrations the Cl/C and F/C ratios start decreasing, indicating that the emission signals from chlorine and fluorine ions are decreasing. Probable explanations are: (i) difficulty in quantitative excitation owing to lack to sufficient

Table 4
H/C elemental ratio data for R-22 (CHClF$_2$) gas sample

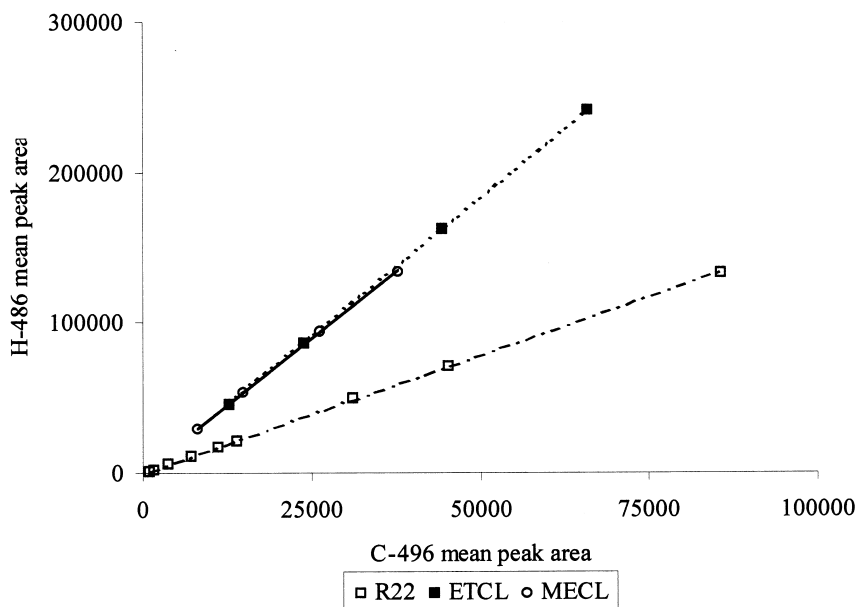| R-22 gas on the column (nmol)	H/C molar ratio of R-22 using 0.2 μl (12.1 nmol on the column) of CH$_2$Cl$_2$ liquid as a standard	
	Mean	SD
1.14	0.85	0.06
2.28	0.84	0.03
5.71	0.83	0.08
11.4	0.85	0.03
17.1	0.86	0.16
22.8	0.87	0.03
45.6	0.88	0.08
68.5	0.88	0.07
114	0.87	0.05

Fig. 5. Graph representing relation between hydrogen and carbon peak areas. Linear regression values for individual curves. R-22, $R^2 = 0.9961$; CH_2Cl_2, $R^2 = 0.9983$; CH_4Cl_2, $R^2 = 0.9999$.

Table 5
Cl/C elemental ratio data for 1,2-dichloroethane ($C_2H_4Cl_2$) liquid sample

$C_2H_4Cl_2$ on the column (nmol)	Cl/C molar ratio of $C_2H_4Cl_2$ using, 10 µl (2.28 nmol on the column) of R-22 ($CHClF_2$) gas as a standard		Cl/C molar ratio of $C_2H_4Cl_2$ using, 0.2 µl (6.50 nmol on the column) of R-113 ($C_2Cl_3F_3$) liquid as a standard		Cl/C molar ratio of $C_2H_4Cl_2$ using, 0.2 µl (12.1 nmol on the column) of CH_2Cl_2 liquid as a standard	
	Mean	SD	Mean	SD	Mean	SD
4.90	0.89	0.09	0.89	0.08	0.99	0.09
9.80	0.86	0.07	0.87	0.07	0.96	0.08
19.6	0.83	0.06	0.84	0.05	0.92	0.06
29.4	0.81	0.03	0.82	0.02	0.90	0.02

plasma energy and (ii) reactions with the plasma gases and/or chemical interactions with the walls of the discharge tube.

The ionic emission lines of halogens have higher excitation energies than their atomic emission lines. If chlorine and fluorine atoms were not fully ionized

Table 6
H/C elemental ratio data for 1,2-dichloroethane ($C_2H_4Cl_2$) liquid sample

$C_2H_4Cl_2$ on the column (nmol)	H/C molar ratio of $C_2H_4Cl_2$ using, 10 µl (2.28 nmol on the column) of R-22 ($CHClF_2$) gas as a standard		H/C molar ratio of $C_2H_4Cl_2$ using, 0.2 µl (12.1 nmol on the column) of CH_2Cl_2 liquid as a standard	
	Mean	SD	Mean	SD
4.90	2.38	0.21	1.99	0.18
9.80	2.41	0.18	2.02	0.15
19.6	2.42	0.17	2.04	0.14
29.4	2.42	0.07	2.04	0.05

in the plasma, leaving instead a mixture of ions and atoms, then the elemental responses detected for ionic emission would deviate from linearity [19]. Freeman and Hieftje showed that higher hydrocarbon concentration in the plasma contributes to this effect, reducing the fragmentation and excitation of halogenated compounds [31,32]. Atomic lines in the near-infrared region were used as these they require less excitation energy than ionic lines [32]. Here too the F/C elemental ratio was constant at lower sample concentrations, but at higher sample concentrations the relative intensity of fluorine emission decreased. For the aromatic fluorinated compound under consideration, F–C bond dissociation energy was lower than that of C–C and thus release of free F atoms should have been easier than the release of free C atoms. In fact the relative F intensity was found to be lower than the C intensity and thus elemental excitation rather than bond fragmentation appeared to be the critical step [32].

The loss of plasma energy was explained by two possible mechanisms when effects of addition of H_2 and CO_2 were investigated [33]. The dissociation of the CO_2 or H_2 or other molecular fragments could consume a significant portion of the available plasma energy, thereby weakening the discharge in its ability to promote the higher-energy transitions. However, the inability to measure optically such molecular fragments that may be formed in the discharge, limits the further investigation of this hypothesis [33]. A second explanation can be given in terms of the charge transfer theory for helium discharges [33]. According to this theory, the ability of the He discharge to populate the high-energy transitions is the result of a charge transfer between the He^+ species and the ionic transitions of non-metal species. This mechanism is viable for analyte excitation only if the energy defect (difference in the energy of the He^+ species and that of the excited state of the ion) is small. For the non-metals Cl, Br, I, S and P, this energy defect is less than 1 eV. If the He^+ population is adversely affected, due to addition of H_2, CO_2 or molecular fragments, the high-energy transitions will not be populated [33]. Charge transfer theory supports the loss of the more energetic ionic transitions, rather than the lesser energetic atomic transitions.

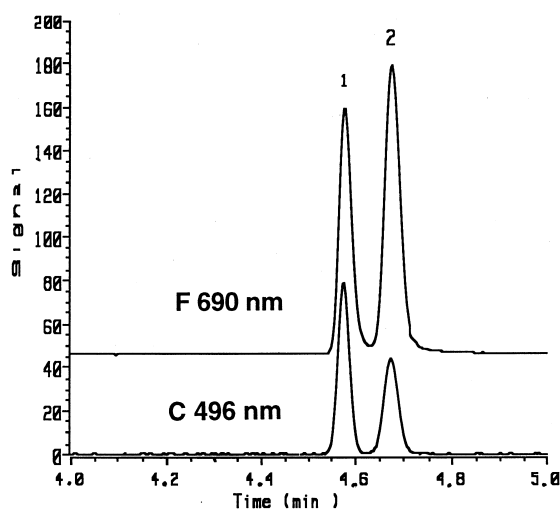The analysis of two reference CFC gas samples,

Fig. 6. GC–AED chromatogram of R-500 gas mixture. Fluorine and carbon chromatograms. Peak 1 = R-152a ($C_2H_4F_2$), peak 2 = R-12 (CCl_2F_2). GC conditions: isothermal at 35°C for 5 min, 5 ml injection. Split ratio = 1:130.

R-500 and R-502, as ''unknowns'' was undertaken at lower concentrations to obtain more accurate elemental ratios and quantitative results. Fig. 6 shows the GC–AED chromatogram (carbon and fluorine traces) for the R-500 gas mixture. Peak 1 corresponds to R-152a and peak 2 corresponds to R-12. Table 7 shows the results of elemental ratio calculations for R-500 gas samples, a valid estimation of elemental ratios being possible. For R-502 two chromatographic peaks were obtained. The component lacking hydrogen gave Cl/C and F/C rounded ratios of 0.5 and 2.5, respectively and hence the empirical formula C_2ClF_5. The molecular formula of this component is C_2ClF_5, R-502 being a mixture of R-115 (C_2ClF_5) and R-22 ($CHClF_2$). Although R-115 contains five F atoms per molecule, the F/C ratio of 2.50 was obtained accurately. The use of R-113 as a standard however gave a F/C ratio of 2.78. For the R-500 gas components, use of the R-113 standard gave slightly high F/C ratios.

Table 8 shows quantitative analysis of R-12, a component of R-500, in terms of absolute amounts, using standards R-12, R-22 and R-113. It can be seen that the liquid R-113 standard gave differing results whereas gas standards R-12 and R-22 gave similar lower results.

Table 9 represents percent compositional data for

Table 7
Empirical formula data for R-500 gas mixture

R-500 gas sample mixture	Standards used	Cl/C ratio		F/C ratio		H/C ratio	
		Mean	SD	Mean	SD	Mean	SD
R-152a	R-12	–	–	1.06	0.15	–	–
	R-22	–	–	1.00	0.14	1.87	0.32
	R-113	–	–	1.14	0.29	–	–
R-12	R-12	1.96	0.32	2.22	0.30	–	–
	R-22	1.99	0.32	2.09	0.29	–	–
	R-113	1.97	0.34	2.39	0.47	–	–

Table 8
Quantitative analysis of R-12 gas (CCl_2F_2) as a component of R-500 gas mixture

R-12 sample element (unknown)	Mean/SD (in terms of nmol)	R-12 (CCl_2F_2) gas standard	R-22 ($CHClF_2$) gas standard	R-113 ($C_2Cl_3F_3$) liquid standard
Carbon	Mean (nmol)	1.14	1.35	0.42
	SD	0.13	0.15	0.05
	Concentration range at 95% C.I. (nmol)	1.35 to 0.93	1.59 to 1.11	0.50 to 0.34
Chlorine	Mean (nmol)	2.24	2.68	0.82
	SD	0.25	0.30	0.10
	Concentration range at 95% C.I. (nmol)	2.64 to 1.84	3.16 to 2.20	9.78 to 6.62
Fluorine	Mean (nmol)	2.54	2.83	0.99
	SD	0.17	0.21	0.15
	Concentration range at 95% C.I. (nmol)	2.81 to 2.67	3.17 to 2.49	1.23 to 0.75

C.I.=Confidence interval.

the R-500 sample. The area normalization method was used to calculate compositions of gas mixtures R-500 and R-502 [19]. The results match well with the precertified values for R-500 of R-152a (26.2%) and R-12 (73.8%).

Table 9
Composition (%, w/w) of CFC sample mixture R-500

R-500 gas sample mixture	C-496 peak area based calculations, mean±SD	F-690 peak area based calculations, mean±SD
R-152a	27.5±3.9%	26.6±0.3%
R-12	72.5±9.9%	73.4±0.9%

4. Conclusions

The study of empirical formulae of chlorofluorocarbons has demonstrated that it is necessary to choose a reference compound which is similar to the unknown compounds in terms of the composition of elements, molecular structure, concentration and physical state. Qualitative and quantitative analysis should be done in the low nanomole range. Elemental ratios were reasonably accurate at lower concentration ranges and degraded at higher concentration. The Cl/C and H/C ratios were found to be closer to the theoretical values than F/C ratios. There is a decrease in elemental ratios Cl/C and F/C

as a function of the sample amount introduced into the plasma. Decrease in the F/C ratio appears to be more pronounced than the decrease in the Cl/C ratio probably because fluorine strongly interacts with the silica discharge tube. Another possible reason is the difficulty of excitation of fluorine in comparison to carbon and chlorine. H/C is linear over the entire range of concentration studied, contrary to other findings. The analysis of ''unknown'' gas mixtures R-500 and R-502 gave correct empirical formulas and % (w/w) compositions. Although absolute quantitative estimates for this class of compounds may be difficult, relative percent composition measurement of sample components is possible.

Acknowledgements

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