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Compound retention dependence of the response in a gas chromatography–atomic emission detection system

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Abstract

The relationship between the response of a laboratory-made GC–microwave-induced helium plasma atomic emission detection (MIP) system prototype and compound nature was studied by monitoring the carbon 247.9 nm atomic emission line. The test samples for this study were solutions of alkanes, arenes and haloarenes prepared at two concentration levels; varied plasma generation conditions (microwave input powers and helium support plasma gas flows) were evaluated. The statistical examination of the data pointed to a dependence between MIP signal and compound retention – less retained compounds tend to show reduced MIP signals. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Microwave-induced helium plasma atomic emission detection; Detection, GC; Retention–detection response relationships; Alkanes; Arenes; Haloarenes

1. Introduction

Two of the most interesting features of microwave-induced helium plasma atomic emission detection for gas chromatography (GC–MIP) are the possibility of identification of unknown eluates through the determination of their minimum formulae and the potential use of compound-independent calibration curves. The first feature can be carried out by simultaneous monitoring of atomic emission intensities at different wavelengths using poly- or multichannel GC–MIP systems, which allows the calculation of interelemental stoichiometric relations of the eluates, and in sequence, their minimum formulae [1]. The compound-independent calibration curves allow one to quantify any analyte with the same calibration curve no matter what substance was used in the standard calibration solutions, if the same atomic emission line was used to generate the chromatograms of the standards and samples.

Both applications are based on the assumption that ideally, when monitoring an elemental atomic emission line, the GC–MIP response does not depend on the nature of the substance being eluted, but only on the mass of the monitored element contained in the eluted analyte. However, there is controversy in the literature about this topic. Some authors noticed a dependence between the GC–MIP signal and the compound structure, which makes the above-mentioned analytical applications impossible [2–4]. Studying the determination of minimum formulae of polycyclic aromatic hydrocarbons (PAHs) and halogenated aliphatic hydrocarbons, Huang et al. [5] observed signal-to-structure dependencies for these compounds. Errors in the determination of C/H and C/N ratios for diverse compounds were attributed both to signal-to-structure and signal-to-eluate concentration dependencies [6]. Another possible source of deviations in the calculation of interelemental

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ratios is the well-known non-linearity of the GC–MIP signal when monitoring the hydrogen atomic emission line [7], which demands a more sophisticated mathematical treatment of the data. On the other side, in a considerable number of reports independence between signal and compound structure had been demonstrated [8,9]. Perpall et al. [10] identified 26 out of 39 unknown compounds generated in the pyrolysis of polyethylene, using GC–MIP-generated C/H ratios. Combining minimum formulae calculated from GC–MIP data and MS data, Hooker and DeZwann [11] identified 23 compounds of varied chemical structures.

Therefore, a significant amount of the research on development of GC–MIP systems has been devoted to the determination of the relationship between signal and structure and the operational conditions where this independence occurs. In this work, the signal characteristics of a laboratory-assembled GC–MIP system were evaluated. The atomic emission line monitored was the 247.9 nm carbon line and the tests were conducted with solutions containing 11 different alkanes, arenes and haloarenes at two concentration levels. Normalized response ratios of these compounds were measured for various MIP operating conditions of helium plasma flow and of microwave input power. Although no evidence of signal-to-structure dependence was found, there were indications of correlation between the response and the chromatographic retention of the test compounds.

2. Experimental

2.1. Instrumental

The monochannel GC–MIP system evaluated here was assembled in our laboratory and consisted of the following modules:

(a) Plasma generation. Composed of a microwave generator GMW 24-303DR (AHF Analysentechnik, Tübingen, Germany), connected through a coaxial cable to a enhanced Beenaker TM_{010} resonant cavity (AHF) and with quartz tubes (3 mm O.D.×1 mm I.D.) as detection cells fitted to the resonant cavity with an brass adapter.

(b) Helium supply line and GC–MIP interface. 99.997% purity helium (Air Products and Chemicals, Allentown, PA, USA) was supplied to the plasma generation module through a gas line fitted with Drierite, 4A and 13X molecular sieve and active charcoal traps for additional gas purification; this line allowed controlled helium flows from 10 ml min^{-1} to 2000 ml min^{-1}. The interface between the HP-5890A gas chromatograph (Hewlett-Packard, Avondale, PA, USA) and the plasma generation module was provided by an insulated 1/4 in. copper tube, directly heated by the GC oven (1 in.=2.54 cm).

(c) Optical module. Emission from the plasma was focused through a f=150 mm fused-silica lens (Oriel, Stratford, CT, USA) in the entrance slit of a 125 mm optical path Multispec monochromator (Oriel), equipped with a 1200 lines mm^{-1} holographic diffraction grating and a 77344 (Oriel) photomultiplier tubing.

(d) Signal acquisition and conditioning. The signal from the photomultiplier tubing was sequentially amplified by a 7070 Photometer Readout (Oriel) – which also supplied the high voltage to the photomultiplier – and by a laboratory-made amplifier device based on an OP-07 op-amp (RS Components, Corby, UK). The amplified signal was digitized by a 12 bits DT-2801A A/D board (Data Translation, Marlboro, MA, USA) connected to a 486 DLC-40 IBM-compatible personal microcomputer (FreeStyle, São Paulo, Brazil). The software for A/D board control and for chromatographic data acquisition and treatment were written using Turbo Pascal 5.5 compiler (Borland, Scotts Valley, CA, USA).

The schematic of the GC–MIP system is shown in Fig. 1.

2.2. Materials

Two sets of solutions were used in the tests: set A contained alkanes and arenes: benzene, toluene, ethylbenzene, *o*-xylene, *n*-nonane and *n*-decane; and set B contained halorenes and alkanes: fluorobenzene, chlorobenzene, bromobenzene, *p*-chlorotoluene, *o*-dichlorobenzene, *n*-nonane and *n*-decane. All solutions were made with analytical grade reagents (Aldrich, Milwaukee, WI, USA) and with isooctane as solvent. The solutions of both sets were prepared at two different concentrations: in the less concentrated solution, the equivalent carbon mass

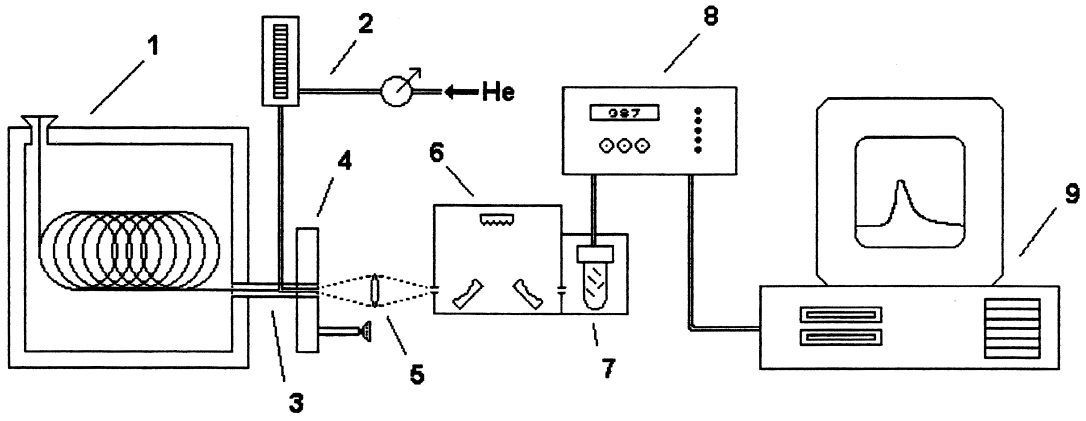

Fig. 1. Schematic of GC–MIP system: 1=HP-5890A gas chromatograph; 2=helium supply line; 3=interface GC–plasma; 4=enhanced Beenaker TM_{010} resonant cavity; 5=fused-silica lens; 6=Multispec monochromator; 7=photomultiplier; 8=7070 Photometer readout; 9=DLC-40 microcomputer. Not shown: GMW 24-303DR microwave generator.

reaching the detector for each analyte was 14 ng, and in the most concentrated, 45 ng.

2.3. Operational conditions

(a) Chromatographic conditions. A SE-30 capillary column of 30 m×0.25 mm I.D. and d_f=0.25 μm (Alltech, Deerfield, IL, USA) was used. The carrier gas was helium at 0.8 ml min^{-1}. Sample injection conditions: injection temperature 240°C; split ratio 1:60 and injection volume 0.2 μl. Column oven temperature program: 60°C at 10°C min^{-1} to 120°C (set A) or 60°C at 7.5°C min^{-1} to 112°C (set B).

(b) Plasma generation module. Microwave input powers (P) of 60 W, 80 W and 100 W were studied. Helium plasma flow (F_P) ranged from 35 ml min^{-1} to 146 ml min^{-1} (for compound set A tests) and from 33 ml min^{-1} to 150 ml min^{-1} (for compound set B tests).

(c) Optical and signal conditioning modules. Monitored wavelength was 247.9 nm (carbon atomic emission line). Monochromator entrance and exit slits: 0.1 mm. Photomultiplier operation voltage: 900 V. Signal amplification ranged from $5\cdot10^{-7}$ A/V to $5\cdot10^{-9}$ A/V. Digitized data collection rate: 20 points s^{-1}.

Triplicate injections of set A and set B test solutions were made under the varied microwave input powers and helium plasma flows listed above (Figs. 2 and 3 show typical chromatograms obtained for the less concentrated set A and set B solutions). For each compound, solution concentration, microwave input power and helium plasma flow the response factor, R, was calculated as:

$$R = \frac{A}{m_C} \quad (1)$$

where A is the chromatographic peak area and m_C is the carbon mass contained in the eluate.

The R values were normalized to the response

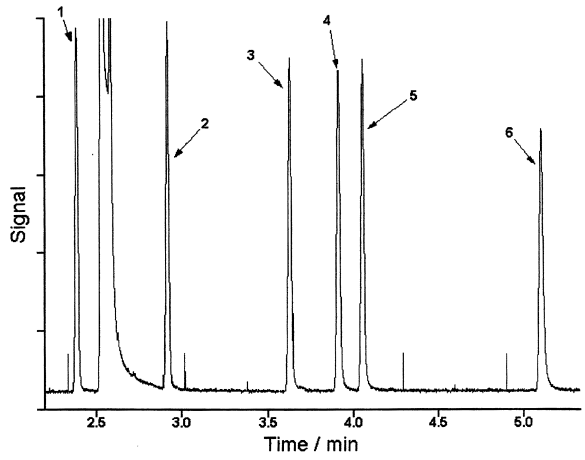

Fig. 2. Chromatogram of set A (P=80 W, F_p=95 ml min^{-1}). Peak identification: 1=benzene; 2=toluene; 3=ethylbenzene; 4=*o*-xylene; 5=*n*-nonane; and 6=*n*-decane. Solvent (not numbered)=isooctane.

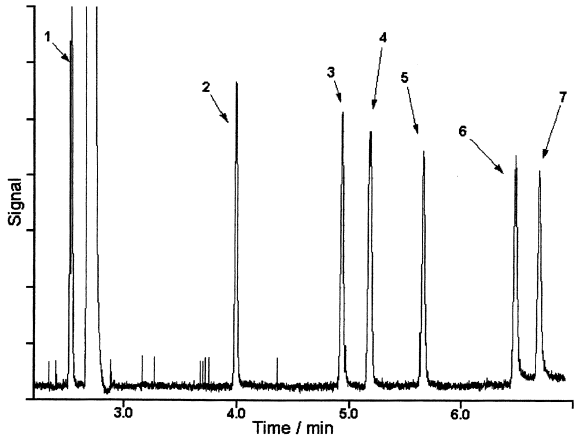

Fig. 3. Chromatogram of set B ($P=80$ W, $F_P=96$ ml min^{-1}). Peak identification: 1=fluorobenzene; 2=chlorobenzene; 3=*n*-nonane; 4=bromobenzene; 5=*p*-chlorotoluene; 6=*o*-dichlorobenzene; and 7=*n*-decane. Solvent (not numbered)=isooctane.

factor of *n*-nonane obtained with the same operational conditions, resulting in the normalized response factors, R_N :

$$R = \frac{R_X}{R_{Ref}} \quad (2)$$

where R_X is the response factor of any X compound and R_{Ref} is the response factor of *n*-nonane, adopted here as reference compound. For each compound and plasma operational condition, the average and estimated standard deviation of the R_N values obtained in triplicate were calculated.

3. Results and discussion

The average values of R_N are expected to be exactly equal to 1 for a pure elemental response; the existence of a dependence between response and eluate structure or some other operational parameter would result in R_N values different from 1. The occurrence of statistically significant deviations of the average R_N values from unity for each compound and plasma generation condition were checked using the standard Student *t*-test at the 95% confidence level [12,13]. The results are shown in Tables 1 and 2. In these tables, each cell represents the result of the Student *t*-test for a compound, carbon mass, helium plasma flow and microwave input power. The cells marked with ''<'' symbols correspond to average R_N values statistically lower than 1 and the cells marked with ''>'' symbols to average R_N statistically higher than 1. The cells marked with ''='' symbols correspond to average R_N values statistically equal to 1. In the first row of each table the compounds are ordered according to their crescent elution order. The use, in these tables, of the results of Student test instead of the R_N values themselves was intended to make them more readable and simplify the interpretation of data.

Several general remarks can be made from the evaluation of these tables:

(i) There is a tendency of the R_N measured with higher carbon masses reaching the detector being different than unity, when compared with the data for minor carbon masses: for $m_C=45$ ng 81 of the 150 R_N (54%) are different from 1, when only 12 out of 150 R_N (8%) for $m_C=14$ ng depart from unity.

(ii) For both sets, the R_N values tend to be lower than 1 for the less retained compounds (benzene, toluene and fluorobenzene), especially when $m_C=45$ ng: $R_N<1$ in 40 out of 45 listed values. The opposite happens for the most retained compounds (*o*-xylene, *o*-dichlorobenzene and *n*-decane): 31 $R_N>1$ out of 60 values for $m_C=45$ ng.

It can be concluded that when the analyte mass increases and the chromatographic retention decreases the GC–MIP system fails to a show compound-independent signal. These observations indicate that the concentration of analyte inside the detection cell could affect the GC–MIP response. Increasing the amount of material entering the detection cell during a fixed space of time will increase the concentration of the analyte present in the plasma spot at the time of the detection process. In an analogous fashion, if similar quantities of an analyte pass through detection cell in different spaces of time, there will be different concentrations of material inside the plasma zone – if the same mass of material takes a smaller space of time to pass through the cell, the concentration of eluate inside the plasma zone during the process will increase.

The difference between the results corresponding to the less concentrated solutions and the similar for the most concentrated solutions can be attributed to an increase in the analyte concentration inside the

Table 1
Results[a] of Student *t*-test for set A, as a function of the microwave input power (P) and plasma helium flow (F_P, ml min^{-1})

P	F_P	m_C = 14 ng					m_C = 45 ng				
		PhH[b]	PhMe	PhEt	$PhMe_2$	n-C_{10}	PhH	PhMe	PhEt	$PhMe_2$	n-C_{10}
60 W	35	<	<	=	=	=	<	<	=	>	>
	65	<	<	=	=	=	<	=	=	=	>
	95	<	=	<	=	=	<	<	>	=	>
	125	<	=	=	=	=	<	<	=	=	>
	146	=	=	=	=	=	<	<	>	=	>
80 W	35	=	=	=	=	=	<	<	>	>	>
	65	=	=	=	=	=	<	<	=	>	>
	95	=	=	=	=	=	<	<	=	=	>
	125	=	=	=	=	=	<	<	=	=	=
	146	=	=	=	=	=	=	=	=	=	=
100 W	35	=	=	=	=	=	<	<	=	>	>
	65	=	=	=	=	=	<	<	=	=	>
	95	<	=	=	=	=	<	<	=	=	>
	125	=	=	=	=	=	<	<	=	=	>
	146	=	=	=	=	=	<	=	>	=	>

[a] Cells marked with ">" correspond to average R_N significantly higher than 1, with "<" to average R_N significantly lower than 1 and with "=" to average R_N statistically equal to 1.
[b] PhH = Benzene, PhMe = toluene, PhEt = ethylbenzene, $PhMe_2$ = oxylene, n-C_{10} = n-decane, PhF = fluorobenzene, PhCl = chlorobenzene, PhBr = bromobenzene, PhMeCl = *p*-chlorotoluene and $PhCl_2$ = *o*-dichlorobenzene.

detection cell caused by an increase of analyte mass. The tendency of $R_N < 1$ for less retained compounds, can be also attributed to an augmentation in the analyte concentration inside the detection cell, but produced by differences in the chromatographic retention of the compounds. From the basic theory of

Table 2
Results[a] of Student *t*-test for set B, as a function of the microwave input power (P) and plasma helium flow (F_P, ml min^{-1})

P	F_P	m_C = 14 ng						m_C = 45 ng					
		PhF[b]	PhCl	PhBr	PhMeCl	$PhCl_2$	n-C_{10}	PhF	PhCl	PhBr	PhMeCl	$PhCl_2$	n-C_{10}
60 W	33	=	=	=	=	=	=	<	=	>	=	>	>
	66	=	=	=	=	=	<	<	=	=	=	>	=
	96	=	=	=	=	=	=	<	=	=	=	>	=
	123	=	=	=	=	=	=	<	=	=	>	>	=
	150	=	=	>	=	=	=	=	=	=	>	>	=
80 W	33	=	=	=	=	=	=	<	<	=	=	>	=
	66	=	=	=	<	=	=	<	=	=	>	>	=
	96	=	=	=	=	=	=	<	=	=	=	>	>
	123	=	=	=	=	=	=	<	=	=	>	>	=
	150	=	=	=	=	>	=	<	=	=	=	=	=
100 W	33	=	=	=	=	=	=	<	=	=	=	>	=
	66	=	=	=	=	=	=	<	=	=	=	>	=
	96	=	=	=	=	=	=	<	=	=	=	=	=
	123	=	=	=	=	=	=	<	=	=	=	=	=
	150	=	=	=	=	=	=	<	=	=	>	=	>

[a,b] Footnotes as in Table 1.

chromatography [14], the chromatographic bandwidth can be related, among other factors, to the retention time of the eluate – ideally, an increase of the retention of an analyte usually imparts a broadening of the chromatographic band. Therefore, the analyte concentration inside the detection cell is also a function of peak width: comparable masses of differently retained analytes will take different amounts of time to pass through the detector, since their chromatographic bandwidth tends to increase with the retention time.

The presented data do not allow one to associate the absence of a compound-independent signal in some situations to the existence of dependence between the chemical structure of the eluates and the MIP response; for example, the behavior of benzene and *o*-xylene – analytes with very similar structures – are completely different. For $m_C = 45$ ng, 14 in 15 measured benzene R_N are statistically lower than 1 and the remaining are equal to 1; for *o*-xylene 13 in 16 R_N are higher than 1, with three values equal to 1. Additional evidence of the effect of retention can be seen in Fig. 4 which depict the peaks obtained for benzene and *o*-xylene at $P = 60$ W and $F_P = 35$ ml min^{-1}:

(iii) For benzene the peak for $m_C = 14$ ng is well shaped while for $m_C = 45$ ng there is a clear suppression of the signal in the region of the peak maximum, which corresponds to the point where the concentration of eluate inside the detection cell is maximized.

(iv) For *o*-xylene the peaks for $m_C = 14$ ng and $m_C = 45$ ng do not present the distortion in the region of their maxima.

o-Xylene is more retained than benzene, and its chromatographic peak is broader; there is no suppression of MIP signal in the center of the chromatographic band. A different behavior is shown by the less retained benzene: for $m_C = 45$ ng, the deformation of the peak top indicates that the response is quenched in the center of chromatographic band, which is the point of the chromatographic band where the concentration of eluate is maximum.

A deeper investigation of the mechanisms responsible for the above-discussed effects is beyond the scope of this work. However, some conjectures can be made. The molecular fragmentation and subsequent electronic excitation and ionization of the formed fragments, responsible by the GC–MIP signal, are caused by collisions between the eluate molecules and metastable species as He^m, He_2^m and He_2^{+m} [15] continuously formed in the plasma. After such collisions, the metastable species lost energy to the eluate and/or to its fragments, returning to their fundamental states. If the helium metastable species are consumed in the fragmentation–excitation reactions at a rate faster than they are produced, part of the eluate introduced in the plasma will not generate a signal. This situation would occur when a large amount of analyte is introduced the plasma as a narrow band – the amount of molecules entering the media during a determined space of time is greater than the production of metastable helium species, resulting in an apparent quenching of the signal. Considering the complex nature of the chemical phenomena occurring inside a plasma [16], this is certainly a simplified picture of the phenomena.

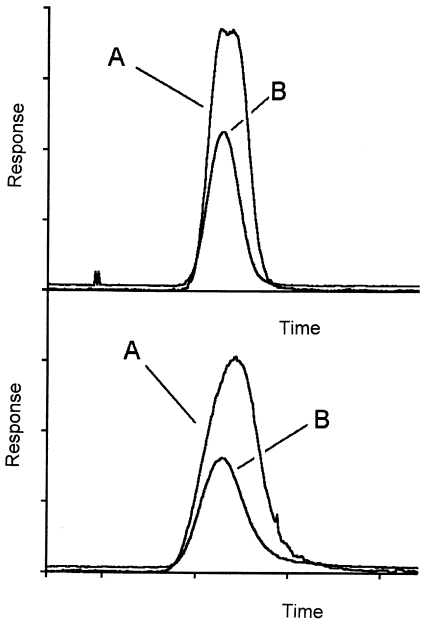

Fig. 4. Benzene (upper section) and *o*-xylene (lower section) peaks for $P = 60$ W and $F_P = 35$ ml, corresponding to $m_C = 45$ ng (A) and $m_C = 14$ ng (B). Retention times: benzene 2.40 min and *o*-xylene 3.92 min.

4. Conclusions

From the above discussion, it can be concluded that changes in the chromatographic retention of a compound can change its GC–MIP response, since it causes variations in the chromatographic bandwidth of the eluate. There is no clear indication, in the present data, of dependence between MIP signal and compound structure. However, the possibility of the presence of dependence between GC–MIP signal and compound retention here detected has some important implications in the use of these devices. The comparison of signals generated by differently retained compounds may lead to a misinterpretation of results (e.g., attribution of different responses in a MIP to the signal to compound structure dependence).

It is also likely that for GC–MIP applications such as the compound-independent calibration or the determination of empirical formulae, the choice of standards should be carefully made to take in account their retention in the chromatographic system used – chromatographic standards and analytes should have similar chromatographic behaviour.

Acknowledgements

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