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Determination of Vacuum ultraviolet detector Response Factors by hyphenation with Two-dimensional Comprehensive Gas Chromatography with Flame ionization detection

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Abbreviations

FID – Flame ionization detector

GC×GC – Tridimensionnalite comprehensive gas chromatography

PIONA – Paraffin, isoparaffin, olefin, naphthene, aromatic

RC – Response coefficient

RRF – Relative response factor

RSD – Relative standard deviation

VUV – Vacuum ultraviolet spectroscopy

Key words: Vacuum ultraviolet spectroscopy, relative response factors, two-dimensional comprehensive gas chromatography, quantitative analysis

Abstract

GC×GC is an established technique, employed for the characterization of complex samples. Broad band vacuum ultraviolet absorption spectroscopy detector has recently attracted a lot of attention as it is a universal detection technique characterized by good selectivity but also ease of use and amenability to coupling with GC×GC. Vacuum ultraviolet spectroscopy is particularly interesting due to the possibility of performing spectral decomposition for species that coelute in GC analysis. This detector has quantitative capabilities, however not all species absorb vacuum ultraviolet radiation the same. Unfortunately, vacuum ultraviolet relative response factors for compounds are not always available. Methods to rapidly measure vacuum ultraviolet relative response factors and generate a large database that would allow calibration free quantitative analysis of complex mixtures are therefore of great interest. In this work, a universal methodology which permits rapid measurement of vacuum ultraviolet relative response factors is reported. It involves flow modulated GC×GC with dual vacuum ultraviolet and flame ionization detection. In this set-up, flame ionization detection is employed as a quantitative reference allowing to scale vacuum ultraviolet responses of investigated compounds. This approach was validated by flow measurements and by comparing relative response factors obtained for model compounds with literature data.

1. Introduction

Vacuum Ultraviolet (VUV) detector has recently attracted a lot of attention owing to its interesting properties. It offers qualitative information as almost all molecules absorb the vacuum ultraviolet radiation and have characteristic spectral signatures. Another interesting feature of VUV absorbance spectroscopy is the possibility of discrimination between isomers [1,2], small [3] and labile compounds [4] owing to their highly featured spectral signatures, while they traditionally pose a problem for MS detection. Spectral information can be ‘filtered’ to extract the response in the most informative spectral ranges and discern compounds, for example saturates and unsaturates [5]. In terms of quantification, vacuum ultraviolet detector follows Beer-Lambert law. As Beer-Lambert law is linear and additive, linear spectral mixture estimation algorithms can be used to investigate the composition of mixtures [6]. However, quantification by using VUV is not completely straightforward since different types of compounds exhibit different responses. For example, same mass of aromatic species absorbs almost three times more, depending on species, in the 125-240 nm range when compared to saturated compounds [6]. Hence, VUV responses need to be corrected by using appropriate VUV relative response factors (RRFs). VUV RRFs depend on absorption cross section of molecules and they are not dependent on system features, contrary to MS RRFs for example.

VUV RRFs have been already successfully used to perform PIONA analysis of gasoline samples [6]. In that study, a specific VUV response factor was attributed to each of the five PIONA (Paraffins, Isoparaffins, Olefins, Naphthenes, and Aromatics) classes. PIONA analysis was also performed for liquid hydrocarbon streams [7], demonstrating advantages of VUV in quantifying coeluting species when compared to conventional detailed hydrocarbon

analysis. Weber et al. [8] performed mass percent quantification of saturates, mono, di, and polyaromatics in diesel type samples. García-Cicourel and Janssen [9] developed a GC/VUV method for the measurement of the total level of aromatic hydrocarbons in purified mineral oils. VUV response factors in these studies were also class based. However, until today a universal methodology that would allow accessing individual VUV RRFs in more complex samples for which standards are not commercially available has not been reported. Being able to reliably measure VUV RRFs is of utmost importance for building a database for calibration-free quantitative analysis of complex mixtures and automated spectral decomposition algorithms.

Some efforts have been made to derive VUV absorbance spectra through theoretical computations by using a variety of methods [1,10–12]. Encouraging results have been obtained, however common consensus is that that improvements in computational methods are needed in order to obtain better agreement with experimental data.

For the analysis of complex volatile samples especially adapted is comprehensive two-dimensional gas chromatography (GC×GC) [13–26]. Introduction of GC×GC has enabled achieving higher sensitivity but also an order of magnitude higher peak capacity when compared to 1D GC. For GC×GC different modulation systems are available. Among them, flow modulation has numerous advantages, as it is not costly, it does not require cryogen and it allows modulation for a wide range of analytes with very different boiling points. Additional advantage of flow modulation is in the fact that it employs high 2D flows, which reduces the need for high pressures of make-up gas in the VUV instrument.

Vacuum ultraviolet broad band absorption spectroscopy has only recently been coupled with GC×GC for the first time [27–30]. Benefits of this hyphenation combine all the advantages of VUV with the high separation capabilities of GC×GC.

Owing to the properties of the VUV detector, the interest can be seen in devising a simple method which would allow accessing VUV RRFs for any kind of compound. This would allow straightforward and efficient building of large database which would in turn permit making the most of VUV capabilities for both qualitative and quantitative analysis. This is also important as the attribution of an identical response factor for a family of compounds applied in previous works does not consider the differences in absorption properties within families which can be significant. Thus, in this work, we describe a methodology to determine VUV RRFs thanks to a flow modulated GC×GC set-up involving simultaneous FID and VUV detection. This methodology can be applied to any compound of interest present in a sample, provided it is properly separated from the other compounds and correctly quantified by an FID detector, the latter being used as a quantitative reference allowing to scale VUV responses. As this hyphenation is reported for the first time in literature, possible discrimination effects have been thoroughly investigated, with the focus on 2D column flow splitting. Finally, the proposed universal methodology for deriving VUV RRFs has been evaluated on model compounds in order to demonstrate the validity of this approach.

2. Materials and methods

A mixture of normal alkanes containing: n-C₁₀ to n-C₂₈ (n-C₁₀, n-C₁₂, n-C₁₆, n-C₁₈, n-C₂₀, n-C₂₂, n-C₂₄, n-C₂₆, n-C₂₈) diluted in toluene was used for optimization and quantitative performance tests. Detailed composition of the test mix is provided in Supplementary material in Table S2. Mixture of assorted n-alkanes, i-alkanes, alkenes, cycloalkanes and

aromatic species diluted in toluene was prepared by weighing individual species and used for calculation of VUV RRFs and method validation. Detailed composition of the test mixture is provided in Supplementary material in Table S3. All chemicals were of 99% or greater purity and were purchased from Sigma-Aldrich (St. Louis, United States). Hydrogen (99.9999% purity) and nitrogen (99.999% purity) gases were purchased from Messer France SA (Asnières, France).

GC×GC experiments were run on a Agilent 7890A gas chromatograph with Agilent G4513A autosampler and a G3486A CFT forward fill/flush differential flow modulator (Agilent Technologies, Inc., Santa Clara, CA, United States). The selected column set consisted of a DB-1 ¹D column (100% dimethyl polysiloxane; 20 m, 0.1 mm ID, 0.4 µm; Agilent Technologies, Inc., Santa Clara, CA, United States) and a BPX-50 ²D column (50% Phenyl Polysilphenylene-siloxane, 3.2 m, 0.25 mm ID, 0.25 µm; SGE Analytical Science, Ringwood, Australia). Exact dimensions and shape of the modulator collection channel are not exactly known. However, according to literature, it was assumed that the volume of the collection channel is close to 35 µl and its length ~15 cm [31,32] with a circular shape. Carrier gas was hydrogen. For all samples, 1 µl injections with a split ratio of 150:1 were performed on a Agilent multi-mode inlet equipped with a single taper liner with glass wool. Injection port was heated to 300°C, then ramped to 330°C at 500°C/min, where it remained isothermal during 5 min. Initial inlet pressure was 26.86 psig (constant flow: 0.15 ml/min) and initial modulator pressure was 13.94 psig (constant flow: 25 ml/min, effective flow in the second dimension is actually lower as column outlet pressure is higher than 0 psig). Temperature program was 50 °C (3 min) – 325 °C (2.5 °C/min). Modulation period was set to 4.5 s, while different modulation injection times were tested. For simultaneous VUV and FID detection, GC effluent was fed into a SGE SilFlow™ GC three port splitter. Fused silica

restrictors' (Agilent Technologies, Inc.) were used to direct the flows from the splitter towards the two detectors. VGA-101 (VUV Analytics, Inc., Austin, TX, United States) detector was employed. VUV conditions were as follows: wavelength range 120–430 nm, acquisition frequency 50 Hz, flow cell and transfer line temperature 325 °C, make-up gas pressure 0.35 psig. FID conditions were as follows: 325 °C, air flow 400 ml/min, hydrogen 35 ml/min and make-up gas (nitrogen) 25 ml/min, frequency 100 Hz. All analyses were performed in three replicates, with method blanks used between each run. Flow measurements were performed by using Alicat WHISPER MW Flow meter.

Agilent ChemStation B.04.03-SP1 was used for GC method control and FID data acquisition. VUVision™ 3.0.1 software was used for VUV data acquisition. GC Image 2.7 software was employed for GC×GC chromatogram integration. Plug im! software [33] module dedicated to GC×GC/VUV data was employed for GC×GC data visualization, baseline and noise correction and spectra extraction. For fluid circuit modelling, all calculations were performed in Microsoft Excel.

3. Results and discussion

3.1. GC×GC-VUV/FID experimental set-up

The instrumental set-up used for this study is depicted in Figure 1. GC×GC separation was performed with a classical non-polar / medium-polar column set which enables separation of hydrocarbons according to increasing carbon number (1st dimension) and their polarity (2nd dimension) and generates highly ordered 2D chromatograms with good orthogonality. Regarding modulation, forward fill/flush differential flow modulation was employed.

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D column effluent was divided with the help of a three-way splitter towards FID and VUV detectors as shown in Figure 1. Such configuration allows to benefit from limited misalignment (retention time differences) between the two acquired signals and is more time efficient compared to two separate FID and VUV experiments. Restrictor lengths were chosen so as to direct the majority of the flow towards the VUV detector, since VUV detector is characterized by lower sensitivity when compared to the FID detector. Normally, low ppm LODs were reported for most compounds in the case of GC-VUV [34]. However, in the case of GC×GC/VUV, high levels of noise have been observed which significantly decreases method sensitivity (see Figure S2 in Supplementary material). Final restrictor dimensions resulted in about 75 % of the carrier gas flow from the 2D column going towards VUV and 25 % going to FID. Further increase of the portion of the flow going towards VUV will not bring significant benefits in terms of signal intensity, however significant signal loss can be incurred on the side of the FID as the portion of the analyte going towards FID is only one quarter of the total amount.

Forward fill/flush differential flow modulator involves a series of consecutive sampling and injection steps which are driven by the periodic switching of the three way solenoid valve receiving a supply of the carrier gas [31]. During the fill phase of the modulation, GC effluent coming from the ¹D column is entering into the modulator channel. In the next stage, this volume is quickly sent to the ²D column by applying a high-pressure pulse at the head of the modulator channel. In terms of parameters of the modulation process, ¹D flow (0.15 mL/min, H₂) was chosen to obtain 3-4 modulations per peak on the first dimension, ²D flow (25 mL/min, H₂) to minimize wraparound with maximal VUV response; and the modulation period of 4.5 s to maximize the space occupancy of the 2D chromatogram. Lower 2D carrier gas flow could be beneficial for VUV, as VUV is a concentration sensitive detector and its

response area is inversely proportional to the total flow in the flow cell. However, VUV features an addition of make-up gas whose purpose is to decrease the diffusion of analytes in the VUV flow cell. This make-up gas causes a dilution effect which decreases the analyte signal [35]. In the VGA 101 instrument, make-up gas mass flow is rather constant for a certain make-up pressure set point (Table 2). Thus, in the case of the decrease of 2D flow, the dilution effect of the make-up gas becomes more important. This make-up gas dilution effect counteracts the effect of the 2D flow decrease. Thus, it was found that 2D flow below 25 ml/min did not result in signal area enhancement in our case. This high carrier gas 2D flow contributes to preventing band broadening that could originate from imperfect connections with restrictors. In our case no significant change in peak widths was observed for the case of dual detection when compared to single detection mode without the splitter. In dual detection mode comparable modulated peak widths were obtained for both detectors (up to 500 ms at the baseline).

As reported in our previous work [36], efficient modulation process occurs when fill and flush distances of the modulation channel are at their optimal value. We have previously demonstrated that the sum of modulator fill and flush distance should be equal to the length of the modulator channel ± 2 cm (15 ± 2 cm); and that the ratio of flush and fill distances should not be less than 2.5. If these conditions are fulfilled, GC effluent in the modulator channel is sent in a tight band towards the ^2D column and unwanted effects of ^1D column effluent carry over are avoided. With a similar methodology to the one described in our previous study; volumetric flow calculations were performed for the GC \times GC-VUV/FID system (see details in Supplementary material in Section S2). Calculations have demonstrated that an injection time of 0.16 s should provide optimal fill and flush distances that ensure efficient modulation of each ^1D peak all along the oven temperature program. Table 1

summarizes calculated fill and flush distances for 0.12 s to 0.21 s modulator injection times. It can be seen that in the case of 0.16 s injection time sums of modulation fill and flush distances at both oven low and height temperatures are closest to the target value 15 ± 2 cm and flush/fill ratio is the highest.

Calculations of the optimal modulator injection time were validated by injecting a mixture of n-alkanes from n-C₁₀ to n-C₂₈ with injection times varying from 0.12 s to 0.21 s, and by monitoring the evolution of the peak shape and n-alkane response volume. When VUV was employed, peak shape was more difficult to evaluate owing to higher background specific to this detector when high acquisition frequencies are employed. Hence, FID responses of the analytes were investigated for assessing the modulation efficiency. To illustrate possible quantitative losses of analytes, a quantity named response coefficient (RC) was introduced. It represents the ratio of the detector response area per unit mass for compound “i” and the response area per unit mass of reference compound (in our case n-C₁₈ is chosen as a reference). In this way, n-C₁₈ response coefficient is equal to 1 by definition, while response coefficients lower than 1 indicate that analytes are subject to response loss. Normally of $1 \pm 10\%$ is taken as an acceptable range for RC.

Measured FID blob volumes and FID response coefficients for n-alkanes for all tested injection times are shown in Figure 2. Figure shows that the maximum response corresponds to 0.16 and 0.18 s injection times, the latter representing only 0.02 s deviation from the theoretical calculation findings mentioned in Table 1. Additionally, observation of chromatogram has demonstrated that the most optimal peak shape (in terms of tailing or fronting of peaks) along the entire n-alkane elution range was generated with these injection times. Good agreement between experimental results and calculations confirms that

theoretical estimations can help to estimate optimal modulation conditions and save time on the method optimization. However, it can be seen that even with the optimized modulation process, a loss of heavier analytes is perceived. This can be because with the chosen columns and system set up the best modulation performance with maximized responses still contains certain quantitative discrimination effects, but also due to inlet conditions or due to flow splitting between the two detectors. To further investigate other possible discrimination sources inlet discrimination was first investigated.

3.2. Study on inlet discrimination

To evaluate if inlet discrimination can be observed in our experimental conditions, splitter was plugged on the VUV side, and the entire GC flow was directed towards the FID detector. Inlet conditions were kept the same as for GC×GC experiments with VUV/FID dual detection. A weighed mixture of n-C₁₀ to n-C₂₈ standards diluted in toluene was injected and the observed response coefficients relative to n-C₁₈ were compared with theoretical FID response coefficients calculated according to ref [37] and normalized to n-C₁₈. Figure 3, in blue, shows average response coefficients calculated for three repeated measurements. For all n-alkanes, response coefficients were in the acceptable range of 1±10%. Even if a moderate inlet discrimination is perceived for the longest linear alkanes, this does not fully explain the bigger loss of heavier analytes observed in the previous Section for FID in the dual FID/VUV detection configuration.

3.3. Flow considerations at the splitter

As no significant quantitative discrimination was observed at the inlet, next possible discrimination source to investigate was column effluent splitter, which directed the flow towards the two detectors.

Weighed mixture of linear alkanes from n-C₁₀ to n-C₂₈ was injected in the GC×GC-VUV/FID set-up and was analysed for selected optimised modulation conditions. In this case both FID and VUV response coefficients for n-alkanes were calculated. Obtained response coefficients are plotted on Figure 4 for both detectors. For VUV the same trend was observed as for FID, with a loss of response toward heavier analytes.

Surprisingly, the response coefficients seem to be different for the two detectors which was confirmed by repeated measurements. Namely, according to theoretical calculations FID response coefficients for n-alkanes in the investigated range are expected to be almost equal. Regarding VUV response factors, it has been demonstrated that the excitation energy of n-alkanes progressively decreases with the increase of carbon number owing to destabilization of the carbon chain [38]. However, as in the case of the FID, not a significant response difference is expected in the range of n-C₁₀ to n-C₂₈ in case of the absence of discrimination sources. Thus, according to theory, there should be no difference in response coefficients of n-alkanes for both VUV and FID.

To explain the observed differences for the two detectors, gas flow measurements were performed at the exits of both detectors for several oven temperatures. Results are reported in Table 2. It was observed that, owing to VUV detector transfer line and flow cell being at constant high temperature during the entire run, gas flow at the splitter directed to VUV increases during the run owing to flow resistance of the VUV decreasing in proportion with

GC oven temperature increase. At the same time, the flow directed to FID progressively decreases with increasing GC oven temperature. The split ratio between FID and VUV changes from 26.1% of the total flow sent to FID for GC oven temperature equal to 50°C to only 20.8% at 325°C. Thus, due to the decrease of absolute mass going towards FID the response of analytes decreases. For VUV, the opposite would be expected but it has to be taken into the account that VUV is a concentration sensitive detector. Higher flows decrease the residence time of the same concentration of analyte in the VUV flow cell, thus causing decrease of the signal area. This counteracts the effect of the split change (theoretical considerations regarding analyte response area for the VUV detector are provided in the Supplementary material in Section S1). Based on the flow measurements, FID and VUV response coefficients that would be measured on this set-up for compounds having the same response on the detectors can be calculated. These are plotted in Figure 4 (see dotted lines).

The observed trends are in agreement with measured response coefficients for n-alkanes as the ratios between the VUV and FID response coefficients in two cases are the same (Figure 5). Different trend of the measured VUV and FID response coefficients when compared to the theoretical ones based on flow measurements (Figure 4) indicate that there are some discrimination effects present. These are primarily modulation effects (Figure 2B); however, all these effects (modulation, inlet, etc.) are identical for the two detectors, thus they ‘cancel out’ in the final calculation of VUV RRFs as it will be demonstrated in the following Section.

3.4.Determination of VUV relative response factors with GC×GC-FID/VUV

VUV relative response factor iii_{ii}^i is defined as the VUV mass relative response factor. It can be seen as a scalar if it comes from the measurement of the total absorbance in a given wavelength range but also as a reference VUV spectrum in the VUV range for a unitary mass

of compound i . It is a constant for a given compound i and it is directly linked to its absorption cross-section. Measuring VUV RRF (scalar) or spectral RRF (spectrum) is of utmost importance for building a database for calibration-free quantitative analysis of complex mixtures and automated spectral decomposition algorithms.

Determining VUV relative response factors using FID as a quantitative reference with the GC×GC-VUV/FID set-up used in this work requires a clear understanding of the splitter behaviour and knowing precisely the evolution of the splitting of the ^2D carrier gas flow between the two detectors during the run. It can be shown (see Supporting Information Section S1 for the detailed calculations) that VUV RRFs for any analysed compound i relative to a chosen reference compound obey the following equation:

$$\frac{Area_{FID}^X}{Area_{VUV}^X} = \frac{RRF_{FID}}{RRF_{VUV}} \cdot K \quad (1)$$

with $Area_{FID}^X$ and $Area_{VUV}^X$ representing the measured areas for the FID and VUV, respectively for compound i or the reference analyte, RRF_{FID} and RRF_{VUV} the relative response factors for the considered analyte and K a temperature dependent correction factor accounting for flow splitting changes which is defined as follows:

$$K = \frac{F_{VUV}}{F_{FID}} \cdot \frac{F_{VUV}}{F_{VUV}} \cdot \frac{F_{FID}}{F_{FID}} \quad (2)$$

where α^i and α represent the proportion of analyte i and the reference sent to FID at their elution temperature, Q is the total flow in the VUV cell at a given elution temperature.

The last two equations are fundamental on the way to obtain VUV RRFs for any compound with a GC×GC-VUV/FID set-up. Thanks to the FID detector, it is not necessary to know the exact amount of the analyte of interest in the injected sample in order to determine its VUV RRF, the FID response being used as a quantitative reference. It is also noteworthy to mention that discrimination before the entry of the splitter (for example inlet discrimination or unsatisfactory quantitative performances of the modulation process) has no influence on the VUV relative response factors determination since iii^i only depends on i values and on the total gas flow in the VUV flow cell. In other words, all discrimination effects common to both detectors cancel out, the only effect remaining being related to flow splitting changes between the two detectors. Thus, to measure VUV relative response factor for a compound i , the only prerequisite is to know the elution temperature dependent correction factor i and measure the areas of compound i and reference compound on both VUV and FID sides.

This correction factor was estimated from flow measurements and i calculations according to equation 2. The corresponding correction factors are plotted in red on Figure 5. Values are comprised between 0.9 and 1.1 demonstrating that such a correction is mandatory to obtain accurate VUV RRF estimations with a dual detection system.

But this approach has also some drawbacks, owing to tedious gas flow measurements and to the difficulties related to estimation of the actual flow reaching the flow cell from GC and make-up gas portion involved. An alternative methodology consists in evaluating this

correction factor through the measurement of FID and VUV areas for a mixture of n-alkanes and make the hypothesis in accordance with literature data that VUV and FID response factors for n-alkanes are constant. This approach was tested from ten replicates analyses of a mixture of n-alkanes. *iiii* values were determined as the ratio of VUV response coefficient and FID response coefficient for elution temperature from 110°C to up to 300°C with a good repeatability (see Figure 5). A linear fit was applied to estimate correction factors for any oven temperature leading to appropriate correction function and opening the way to VUV RRF measurements at any elution temperature and for any compound. Similar results were obtained with this approach compared to the flow measurement approach.

Finally, it is also interesting to note that this methodology can be successfully employed in the case of GC-VUV/FID measurements since similar discrimination effects between the two detectors should be observed.

3.5. Test mixture analysis

VUV RRFs measurement methodology was validated through the GC×GC-VUV/FID analysis of a weighed mixture containing n-alkanes, i-alkanes, alkenes, monoaromatics, diaromatics and triaromatics diluted in toluene. Figure 6 shows the obtained VUV chromatogram (125-240 nm Avg.).

VUV RRFs in 125-240 nm range were calculated according to the described approach based on the previous injection of a mixture of linear alkanes. Average values obtained from three repeated analysis along with determined RSDs are provided in Table 3. Very good repeatability is obtained and determined VUV RRFs values are in good accordance with the

ones already reported for PIONA type compounds [6]. However, response factors used in PIONA analysis are rather class based and they do not take into the account possible response differences between individual species of the same class. This can be neglected in the case of n-alkanes whose response is very similar (see Figure 7A). However, for other types of compounds larger variability can be expected within the same class of compounds. For example, if we look at the obtained spectra for various monoaromatic species in our test mixture (Figure 7B), we can clearly see that they can be very different. Thus, the interest can be seen in accessing the individual response factors for all these compounds for more accurate quantifications.

4. Conclusion

Being able to reliably and rapidly measure VUV RRFs is of utmost importance for building large database for calibration-free quantitative analysis of complex mixtures and automated spectral decomposition algorithms. This provides a universal methodology according which VUV RRFs can be obtained from complex samples. It involves using GC×GC with both FID and VUV detectors connected in split mode, where FID detector is used as a quantitative reference. A methodology based on either flow measurements or preferably the injection of linear alkanes to take into account changes in flow splitting with oven temperature as well as all other discrimination sources was proposed. This enabled to correct all discrimination effects of the experimental set-up and gave results in accordance with theoretical results. This easy and reliable approach for deriving VUV RRFs was validated on known compounds for which literature data were available. Compared to previous method based on identical family

response factors, a better quantification can be achieved. This methodology can be extended to any other compound or group of compounds for which VUV RRFs needs to be measured.

Data availability statement

Data available on request from the authors.

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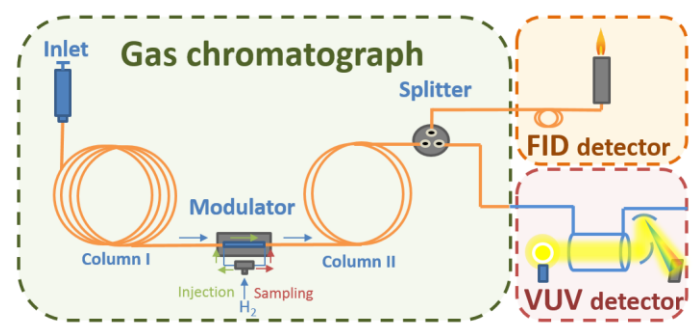


Figure 1. Illustration of the GC×GC-VUV/FID set-up. Modulation involves consecutive sampling and injection steps which are driven by the regular switching of the modulation valve.

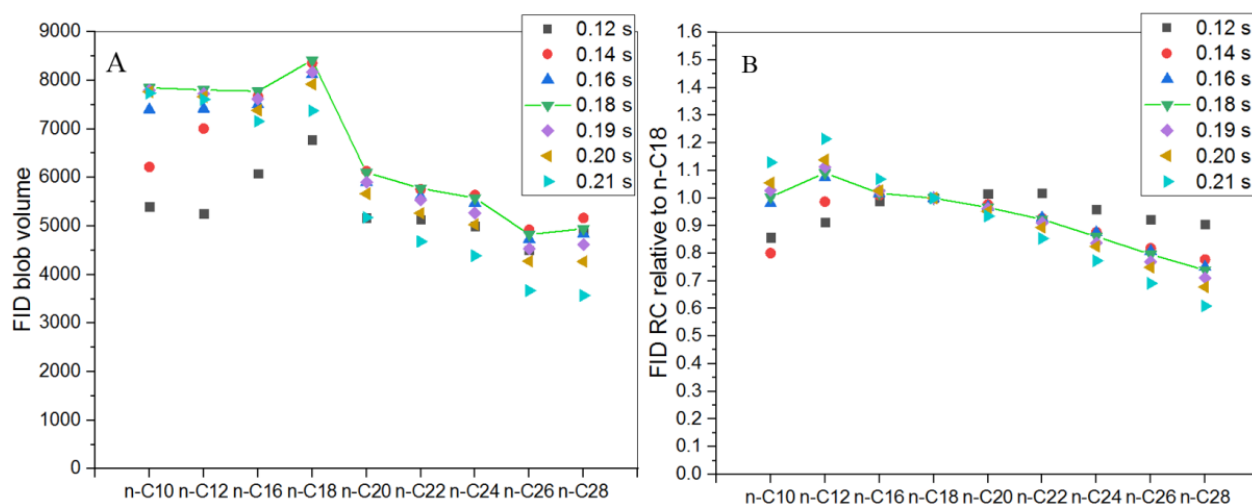


Figure 2. n-alkanes FID blob volumes for different modulator injection times (A) and corresponding FID response coefficients relative to n-C₁₈ (B).

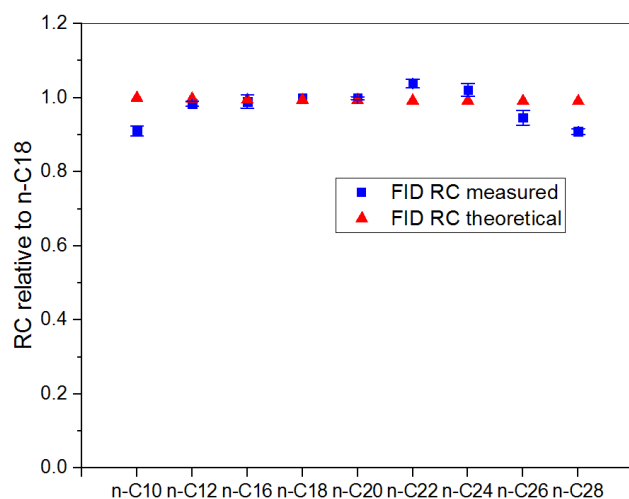


Figure 3. Response coefficients relative to n-C₁₈ for n-alkanes for GCxGC/FID analysis with a plugged splitter (blue) and theoretical FID response coefficients (in red).

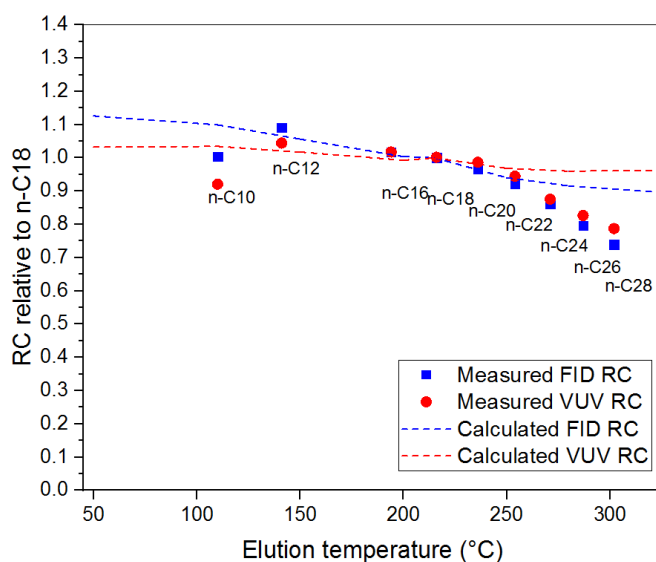


Figure 4. Response coefficients for n-alkanes for VUV (blue dots) and FID (red dots) obtained in the GC \times GC-VUV/FID analysis (modulator injection time = 0.18 s) and theoretical response coefficients from flow measurements (dotted lines).

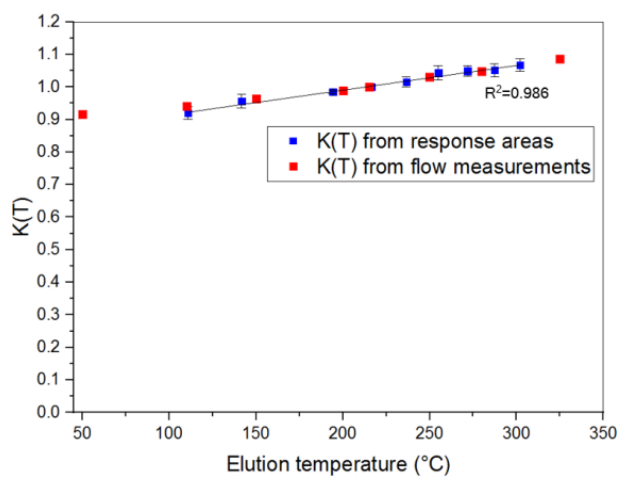


Figure 5. Correction function $K(T)$ calculated from the analysis of n-alkanes (blue) and from flow measurements (red). Error bars are calculated based on ten replicate analyses.

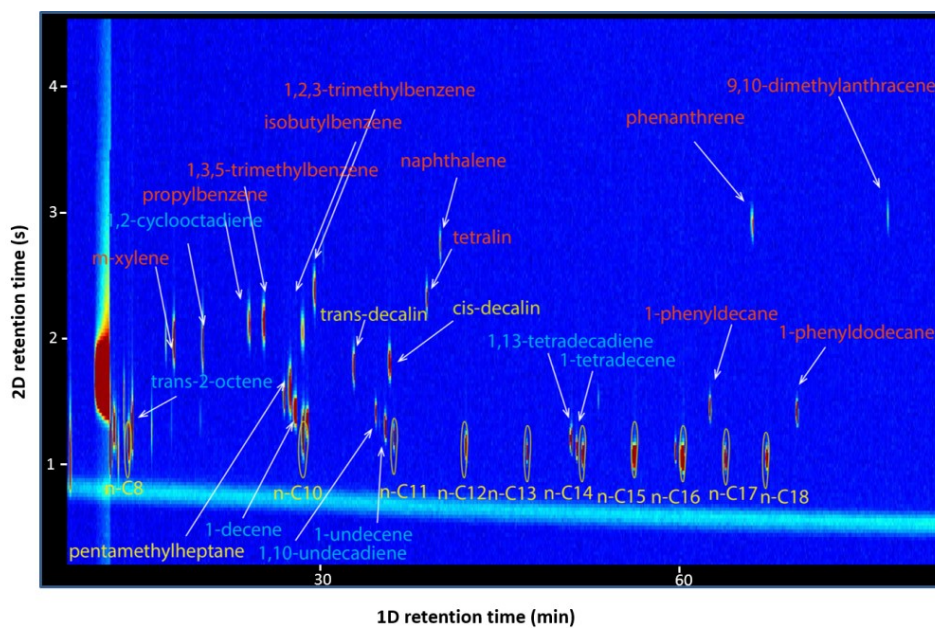


Figure 6. VUV chromatogram for a test mixture (Avg. Abs. 125-240 nm).

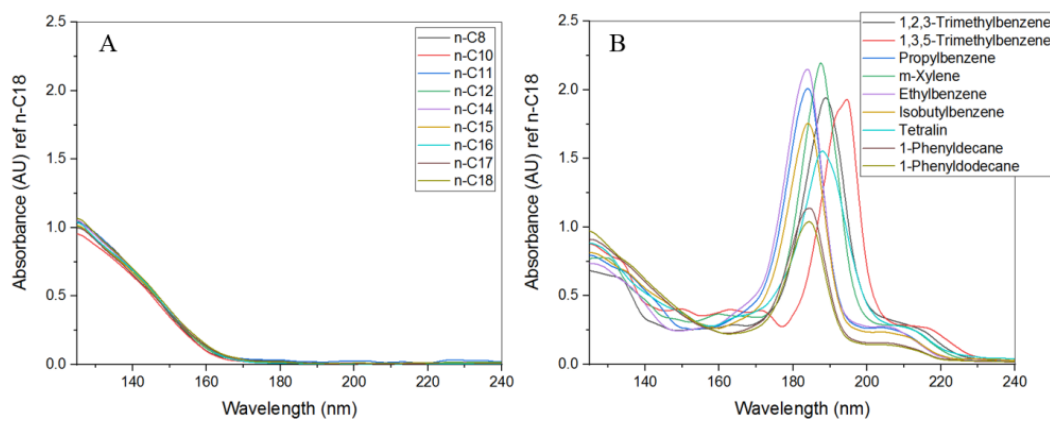


Figure 7. Determined spectral relative response factors for selected species.

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Table 1. Flow calculations for 0.12 to 0.21 s injection times for oven temperatures from 100 to 300°C. Temperatures around elution temperatures of n-C₁₀ and n-C₂₈ alkanes were taken as lowest and highest temperature values.

Table 2. Volumetric flows measured at the exit port of the VUV and FID at different oven temperatures; standard pressure 1 bar, standard temperature 25°C. For estimation of RC elution temperature of 215°C was taken as reference (elution temperature of n-C₁₈). **RC** —; $RC_{VUV} = \frac{m}{m_{ref}} \cdot \frac{F}{F_{ref}}$; m – mass%, F – VUV flow cell mass flow (ml/min).

Table 3. Calculated VUV RRFs relative to n-C₁₈ (125-240 nm). RSDs from three replicates.

Table 1. Flow calculations for 0.12 to 0.21 s injection times for oven temperatures from 100 to 300°C. Temperatures around elution temperatures of n-C₁₀ and n-C₂₈ alkanes were taken as lowest and highest temperature values.

Injection time (s)	Flush/Fill distance ratio				Fill+Flush distance (cm)			
	T (°C)				T (°C)			
	100	165	230	300	100	165	230	300
0.12	3.1	3.2	3.2	3.3	11.8	12.6	13.3	13.8
0.14	3.7	3.8	3.8	3.8	13.3	14.2	14.9	15.6
0.16	4.2	4.3	4.4	4.4	14.8	15.8	16.6	17.4
0.18	4.8	4.9	4.9	5.0	16.3	17.4	18.3	19.1
0.20	5.3	5.4	5.5	5.6	17.7	19.0	20.0	20.9
0.21	5.6	5.7	5.8	5.9	18.5	19.8	20.8	21.7

Table 2. Volumetric flows measured at the exit port of the VUV and FID at different oven temperatures; standard pressure 1 bar, standard temperature 25°C. For estimation of RC elution temperature of 215°C was taken as reference (elution temperature of n-C₁₈). —; — — ; m-mass%, F-VUV cell mass flow (ml/min).

T(°C)	Flow measurements (mL/min)			% of mass transferred		Flow estimated response coefficients (RC)	
	F _{VUV}	F _{VUV+make-up}	F _{FID}	to FID	to VUV	FID	VUV
				(α)	($1 - \alpha$)		
50	11.9	20.9	4.2	26.1	73.9	1.13	1.03
110	12	21	4.1	25.5	74.5	1.10	1.03
150	12.5	21.5	4.05	24.5	75.5	1.06	1.02
200	13.2	22.2	4	23.3	76.7	1.00	0.99
215	13.1	22.1	3.95	23.2	76.8	1.00	1.00
250	14	23	3.9	21.8	78.2	0.94	0.97
280	14.3	23.3	3.85	21.2	78.8	0.92	0.96
325	14.5	23.2	3.8	20.8	79.2	0.90	0.96

Table 3. Calculated VUV RRFs relative to n-C₁₈ (125-240 nm). RSD from three replicates.

Compound name	Molecular formula	VUV RRF	RSD	VUV RRF from literature [6]
n-C ₈	C8H18	0.96	3%	1
n-C ₁₀	C10H22	0.99	4%	
n-C ₁₁	C11H24	0.95	6%	
n-C ₁₂	C12H26	0.98	3%	
n-C ₁₃	C13H28	0.98	0%	

n-C ₁₄	C14H30	0.99	4%	
n-C ₁₅	C15H32	0.99	2%	
n-C ₁₆	C16H34	1.03	2%	
n-C ₁₇	C17H36	1.00	0%	
n-C ₁₈	C18H38	1.00	1%	
2,2,5-Trimethylhexane	C9H20	0.85	1%	1.02
2,2,4,6,6-Pentamethylheptane	C12H26	1.05	1%	
1,3,5-Trimethylcyclohexane	C9H18	0.80	0%	
Cycloheptane	C7H14	0.91	1%	
<i>tert</i> -Butylcyclohexane	C10H20	0.84	1%	1.02
<i>trans</i> -Decalin	C10H18	1.00	2%	
<i>cis</i> -Decalin	C10H18	1.14	0%	
<i>trans</i> -2-Octene	C8H16	0.72	1%	
1-Decene	C10H20	0.71	4%	
1-Undecene	C11H22	0.70	1%	
1-Tetradecene	C14H28	0.73	1%	
1-Hexadecene	C16H32	0.77	1%	0.6
1,7-Octadiene	C8H14	0.48	2%	
1,2-Cyclooctadiene	C8H12	0.55	1%	
1,9-Decadiene	C10H18	0.53	0%	
1,10-Undecadiene	C11H20	0.55	1%	
1,13-Tetradecadiene	C14H26	0.60	1%	
Ethylbenzene	C8H10	0.40	1%	0.38
<i>m</i> -Xylene	C8H10	0.41	1%	

Propylbenzene	C ₉ H ₁₂	0.44	1%
1,3,5-Trimethylbenzene	C ₉ H ₁₂	0.41	1%
Isobutylbenzene	C ₁₀ H ₁₄	0.45	6%
1,2,3-Trimethylbenzene	C ₉ H ₁₂	0.44	0%
Tetralin	C ₁₀ H ₁₂	0.47	1%
Naphthalene	C ₁₀ H ₈	0.32	0%
1-Phenyldecane	C ₁₆ H ₂₆	0.56	2%
Phenanthrene	C ₁₄ H ₁₀	0.38	1%
1-Phenyldodecane	C ₁₈ H ₃₀	0.59	1%
9,10-Dimethylantracene	C ₁₆ H ₁₄	0.41	2%