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A fast vacuum ultraviolet absorption array spectrometer as a fast and selective detector for comprehensive two-dimensional gas chromatography: Concept and first results

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ABSTRACT: Fast and selective detectors are very interesting for comprehensive two-dimensional gas chromatography (GC×GC). This is particularly true if the detector system can provide additional spectroscopic information on the compound structure and/or functionality. Other than mass spectrometry (MS), only optical spectroscopic detectors are able to provide selective spectral information. However, until present the application of optical spectroscopy technologies as universal detectors for GC×GC has been restricted mainly due to physical limitations such as insufficient acquisition speed or high detection limits. A recently developed simultaneous-detection spectrometer working in the vacuum ultraviolet (VUV) region of 125 to 240 nm overcomes these limitations and meets all the criteria of a universal detector for GC×GC. Peak shape and chromatographic resolution is preserved and unique spectral information, complementary to mass spectrometry data, is gained. The power of this detector is quickly recognized as it has the ability to discriminate between isomeric compounds or difficult to separate structurally related isobaric species, thus, it provides additional selectivity. A further promising feature of this detector is the data analysis concept of spectral filtering, which is accomplished by targeting special electronic transitions that allows for a fast screening of GC×GC chromatograms for designated compound classes.

INTRODUCTION:

Comprehensive two-dimensional gas chromatography (GC×GC) is a powerful instrumental analytical technology for the separation of compounds from highly complex samples containing hundreds or thousands of vaporizable compounds.[1] The first applied detection systems for GC×GC was the non-selective flame ionization detector (FID) for the detection of organic compounds.[2-4] Although an FID is an excellent detector for quantitative studies, qualitative analysis of highly complex samples by means of retention time matching is challenging. However, other more selective but non-spectroscopic GC detection methods such as thermionic detection, electron capture or chemiluminescence may suffer either in sensitivity and/or acquisition speed; nonetheless, they have been successfully applied in combination with GCxGC.[4] It is known that for some applications the high chromatographic separation power of GC×GC reduces the need for selective detection systems, but the analysis of extremely complex samples such as petrochemical fractions[5-7], ambient aerosols [8-10], forensic[11-13] or metabolic samples [14-17] remains challenging, even with the high separation power of GC×GC. This is in particular true regarding the identification of unknown compounds in non-targeted analytical approaches if the differentiation of isomeric compounds or compounds with similar separation and mass spectrometric properties (e.g. cycloalkanes and alkenes) has to be addressed. For this reason almost all of the commonly used detectors for one dimensional gas chromatography (GC) have been adapted and tested for their applicability as a GC×GC detector to gather as much selective information as possible about the separated compounds. However, there are important requirements for GC×GC detectors; these detectors need to have a large dynamic range, a high acquisition frequency, as well as exhibit sensitivity and selectivity.[18] Currently, the only detectors which meet all of the abovementioned criteria in a sufficient manner, are fast mass spectrometric detection sys-

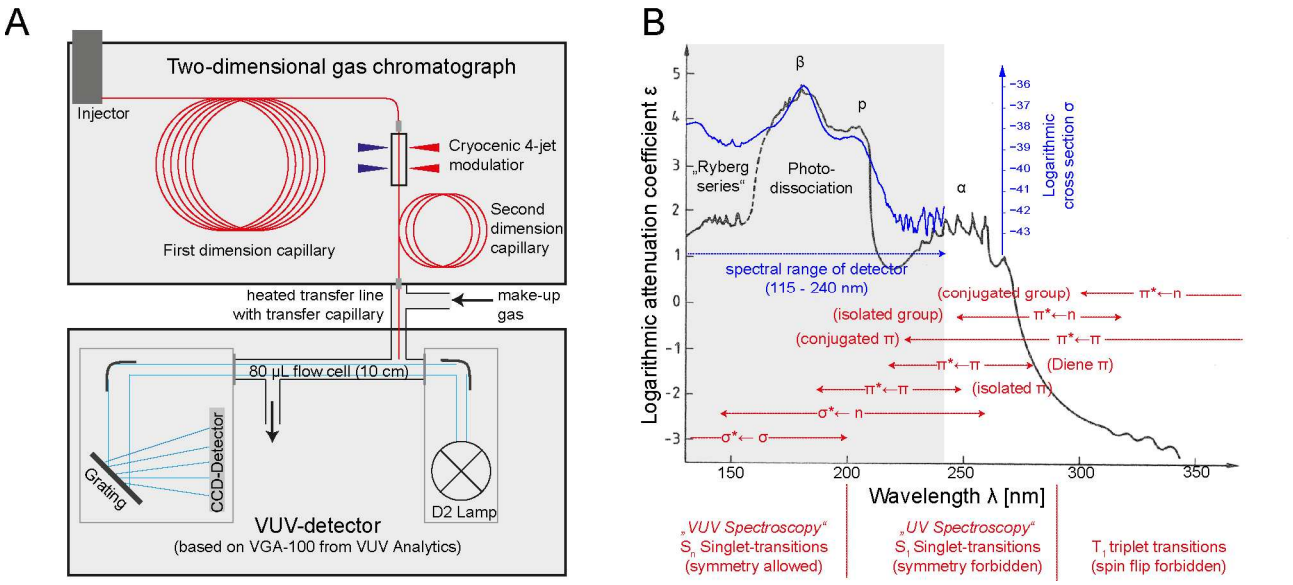

Figure 1 (A) Instrumental setup of the comprehensive two-dimensional gas chromatography-VUV-absorption spectrometer (GC×GC-VUV). (B) VUV-absorption spectrum of benzene (gas phase) with assignment of electronic transitions. Blue: spectra acquired with VUV-spectrometer; Black: reference from literature[19] (with kind permission of Springer). In the VUV-region (~170 nm) the absorption cross section is between two and three orders of magnitude larger than in the classical UV absorption range (up to 250 nm).

tems like time-of-flight mass spectrometer (TOFMS) or latest generation quadrupole mass spectrometer (QMS)[20]. Even though these MS detectors has been already established as standard selective detectors for GC×GC, there has been a noticeable amount of development for the aforementioned MS-technologies over the last decades mainly regarding mass accuracy and mass resolution[21-23] as well as different ionization techniques[24-26], all of which have demonstrated their benefits. Having said this, restrictions concerning the analysis of isomeric, isobaric, small and very fragile compounds still remain. As GC×GC is quickly gaining importance in fields of complex sample analysis[27] there is an increasing interest in alternative detection systems for GC×GC.

A further class of interesting GC and GC×GC detectors are spectroscopic detectors, using light absorption or emission processes for fast and highly selective detection. Infrared (IR) spectroscopy[28] and atomic emission spectrometry[29] have been successfully applied in conjunction with GC or GC×GC. These spectroscopic methods provide very specific and complementary information to MS which includes the distinguishability between structural isomers or elemental compositions. A critical point in combination with GC×GC is the demanded high acquisition frequency. For spectroscopic detectors this criterion will be only sufficiently fulfilled if the spectra are collected simultaneously. This is technically realized by either a detection based on light separation (dispersion or diffraction and array detector) or Fourier transform (FT) analysis (e.g. FTIR). Unfortunately the application of IR based systems is restricted due to insufficiently low sensitivity caused by small molecular absorption cross sections in the infrared range. For the same reason gas phase ultraviolet (UV) spectroscopy has rarely been applied as a GC detector[30,31] and has also not been extensively established as a GC×GC detector. However, the molecular absorption cross section in the vacuum ultraviolet region (VUV) is generally by orders of magnitude larger than it is in the IR or UV. Therefore, the use of the VUV-absorption region for spectroscopic detection is very promising as it will result in orders of magnitude higher sensitivities than that of classical UV detection; although, the fingerprint selectivity in the gas phase UV spectroscopy is often higher.[32,33] The higher sensitivity in the VUV-range allows fast and sensitive spectroscopic detection and it is also possible to draw structural and isomer-selective information from the VUV-absorption spectra[34]. These alluring factors motivate the use of VUV-absorption techniques for complex matrices. The first VUV-absorption detection systems applied for GC were limited to a narrow band of Vacuum-UV radiation, or even only to single wavelengths, which resulted in no qualitative information[35,36]. Consequently, a simultaneous VUV-absorption spectrometer was introduced by Lagesson et al.[37,38] in 1998 providing quantitative and qualitative analysis with good detection, classification and identification limits in the wavelengths range between 168 to 330 nm.

Recently, a matured simultaneous vacuum ultraviolet absorption spectroscopy system was introduced which provides full absorption spectra in the accessible wavelengths-region down to 125 nm within milliseconds.[39] In the aforementioned spectral range, all organic chemical compounds absorb VUV-radiation strongly resulting in very rich and selective spectrometric information. This VUV-detector is considered the first ultraviolet absorption based detector that complies with the requirements for GC×GC and operates with promising analytical performance characteristics to an MS regarding the speciation of compounds. In this work a VUV-absorption spectroscopy based detector was hyphenated to a GC×GC system in order to demonstrate and explore the gain in qualitative information due to the integration of VUV spectral information to GC×GC, which hasn't been reported in literature before.

EXPERIMENTAL SECTION:

VUV absorption detector:

The working principle of the VUV-spectrometer VGA-100 (VUV Analytics, Inc., Austin, TX, USA) has been described elsewhere.[39] Briefly, the eluent from the gas chromatographic column is directly fed into a 10 cm long absorption flow cell and the broad band light emission from a high power deuterium lamp is diffracted by means of a holographic grating

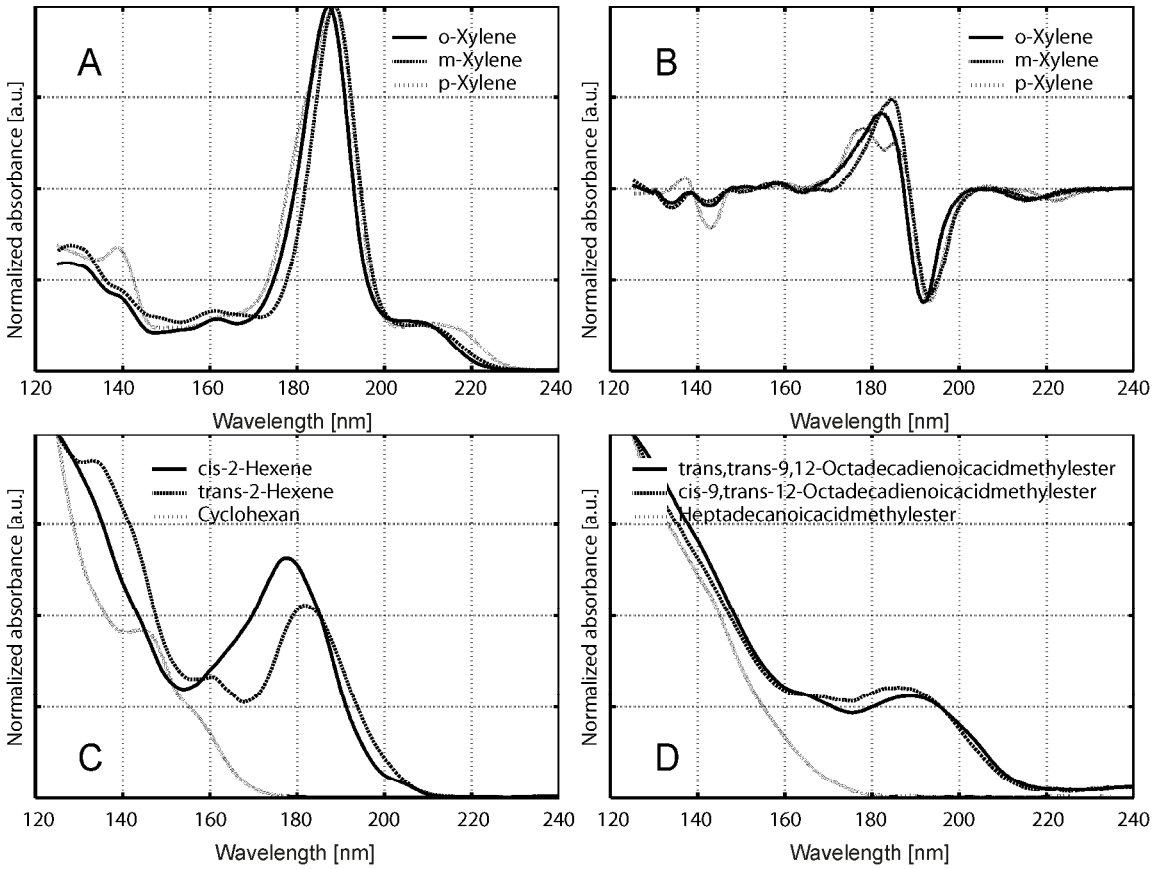

Figure 2 VUV Spectra and first derivation of VUV spectra for different types of isomers. (A) VUV spectra of xylene position isomers. Spectra are dominated by $\pi^* \leftarrow \pi$ transition between 170 – 200nm. Distinct features will allow a differentiation. (B) First derivative of VUV Spectra of Xylene. O- and m-xylene show similar shapes. Derivative of p-xylene indicate a shoulder in $\pi^* \leftarrow \pi$ region and a second local maximum in the $\sigma^* \leftarrow \sigma$ region. (C) Common separation problem in GC×GC-MS: Differentiation of compounds which have similar retention characteristics (GC×GC) as well as similar 70eV fragmentation pattern (MS). VUV Spectroscopy allows an explicit differentiation of these compounds. (D) VUV spectra for selected higher boilers in middle distillates. Also larger isomeric compounds show distinct spectral features.

after passing through the flow cell in the same direction as the eluent. Wavelengths in the range of 125 – 240 nm are focused onto a back-thinned charge-coupled device (CCD) – array detector. For GC×GC setup A a prototype and for GC×GC setup B a further developed commercial available detector was applied. The system used for GC×GC setup B had an advanced flow path with reduced void volume.

GC×GC Setups:

The hyphenation between the GC×GC and the VUV-detector were accomplished by means of directly coupling to the second dimension capillary column (Figure 1A). Two different GCxGC setups were applied.

Setup A: For the first experiments comprising the one-dimensional GC measurements as well as the two-dimensional analysis of the diesel and syncrude, a VGA-100 detector (VUV Analytics, Austin, TX, USA) was directly coupled to an Agilent 6890 gas chromatograph from a LECO GC×GC-FID (LECO, St. Joseph, MI, USA). The samples were directly injected at 250°C with a split ratio of 1:50 using helium as carrier gas. The GC oven was programmed with a constant column flow of 1.2 ml/min starting at a temperature of 60°C which was held for 2 min, ramped up to 320°C and held for 10 min. The temperature of the transfer line to the VUV-spectrometer was set to 250°C. Chromatographic separation in the first GC dimension was carried out on a 60 m x 0.25 mm i.d. x 0.25 µm BPX5 capillary column (SGE Analytical Science, Ringwood, Australia). For GC×GC-VUV-analysis a 2 m x 0.25 mm i.d. x 0.25µm BPX50 capillary column (SGE Analytical Science, Ringwood, Australia) was chosen for the second dimension and directly connected to a 0.25 mm i.d. transfer capillary. The makeup gas (pure nitrogen >5.0) was set to 0.4 psi to control the residence time of the compounds within the flow cell of the VGA-100. According to the given peak width an acquisition frequency of 50 Hz was chosen for two-dimensional gas chromatography and 5 Hz for one-dimensional application. (Variable parameters are listed in supporting information table S1).

Setup B: For quantitative measurements and comparison to GC×GC-TOFMS a further developed VGA-100 detector was connected to an Agilent 7890A equipped with a ZOEX ZX1 modulator. A HTOF (TOFWerk, Thun, Switzerland) was taken as reference. For the analysis the following column combination was applied: 30 m x 0.25 x 1µm 007-FFAP (Quadrex, Woodbridge, USA) + 3 m x 0.1 007-1701 mm x 0.5 µm and a makeup gas of pressure of 1.5 psi.

Sample material:

A common diesel fuel with up to 7% bio diesel constituent (fatty acid methyl ester, FAME) and two Fischer Tropsch (FT) syncrudes (high and low temperature iron catalyzed FT processes) were analyzed using GC and/or GC×GC-VUV. The diesel fuel is a standard German B7 diesel fuel from a petro station according to DIN EN 590. Information about

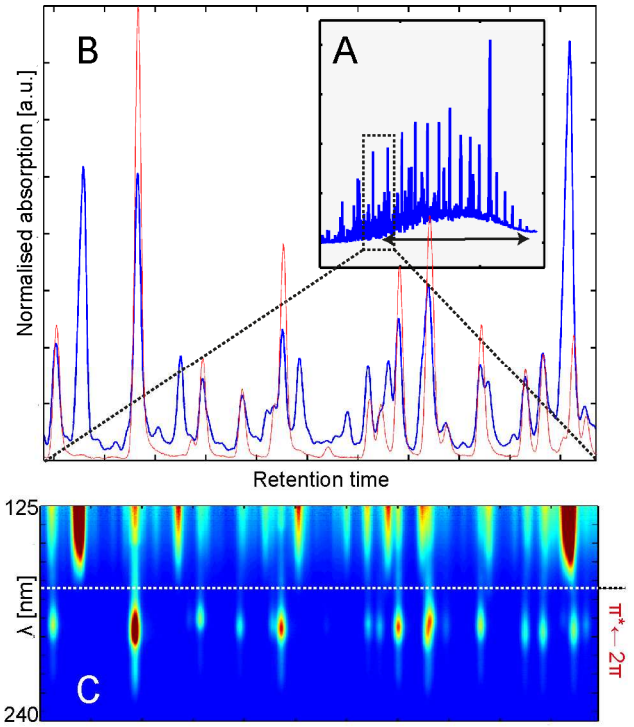

Figure 3 One-dimensional chromatographic separation of B7 Diesel fuel with VUV-detection. (A) Total absorption signal. Vertical arrow indicate chromatographically not sufficiently resolved region. (B) Enhancement of partial chromatographically resolved region. Blue: Total absorption signal; Red: summed absorption signal within spectral range of filter (170 – 200 nm) for selection of compounds with π*← π chromophores. (C) Corresponding two dimensional representation of (B).

similar diesel fuel compositions based on the GC×GC-TOFMS data have already been published.[7] The FT syncrudes were generated in a laboratory fixed bed FT-bench reactor by means of an iron based polymeric catalyst reaction at the University of Rostock. The FT reactor was operated at 250°C (low temperature FT sample) and at 350°C (high temperature FT sample). Complementary GC×GC-TOFMS were recorded as well.

Data handling:

The chromatographic data were recorded as a one dimensional data string composed of the subsequently but simultaneous acquired VUV-absorption spectra. The data acquisition of the VUV-system is designed for a maximum duty cycle leading to non-uniformly spaced time vectors while spectral data were stored uniformly from 125 to 240 nm with 0.05 nm increments. Time resolved predefined summed wavelength domains (125 – 240 nm, 140 – 165 nm and 170 – 200 nm) and full spectral data were exported separately in an ASCII format. For matrix operations, and two-dimensional visualization, the data were interpolated to a 20 ms uniformly spaced time vector and reshaped to build up a two- (summed wavelength domains) or three- (spectral data) dimensional data array. The size of the array was defined as following: first dimension = number of modulation cycles ("retention time first dimension"), second dimension = modulation time × acquisition frequency ("retention time second dimension"), third dimension (if applicable): spectral range with an increment of 0.05 nm. Two dimensional plots as well as volume plots were generated with MatLab (R 2013b).

RESULTS AND DISCUSSION

Chromatography and peak shape:

Both generations of the applied VGA-100 detector were designed for the hyphenation with one-dimensional gas chromatography (1DGC) and peak shape as well as peak width are influenced by the applied make up gas flow. When a typical makeup gas pressure for 1DGC of 0.05 psi was utilized, a peak width of 2 seconds (FWHM) was obtained. This, however, is too long for GC×GC applications and therefore, the makeup gas pressure was increased stepwise to 0.4 psi for setup A and 1.5 psi for setup B. For both setups this resulted in a reduced peak width of approximately 300 milliseconds FWHM (Table 1) and an almost Gaussian peak shape. A further increase of the makeup gas pressure led to a substantial decrease in peak height. The observed peak bordering compared to GC×GC-TOFMS (Table 1) was referred on the one hand to different flow conditions (vacuum outlet for TOFMS and slightly elevated ambient pressure for VUV) and on the other hand to the residence time within the flow cell (1 mm; i.d. and 80uL) of the VGA-100 prototype. Smaller inner diameter[40] flow cells are currently under investigation but were not available for the experiments. Table 1 also list the received detection limits for the compounds. The sensitivity of the system would gain from a smaller inner diameter of the flow cell due to a higher absorbance and smaller make-up gas flows. The special design of the applied VUV detector would also recommend the use of a flow modulator since high flow rates in the second dimension are compatible with the detector.

		GC×GC-TOFMS	GC×GC-VUV
Peak width [ms]	Benzene	170	300
	n-Hexane	100	300
Limit of detection [ng]	Benzen	0.1	16
	n-Hexane	0.07	7

Table 1 Comparison between GC×GC -TOFMS and GC×GC -VUV for selected compounds

Spectroscopy:

The obtained VUV-absorption spectra reflect mainly the interaction of electrons of the higher occupied molecular orbitals of the gas phase molecules with VUV-photons.[19] Unlike scanning instrumentation, where individual transitions are excited mainly independently, the molecules are exposed to a continuous broadband VUV-emission from a strong deuterium light source. The shorter-wavelength photons also exceed the ionization- and dissociation energies of most organic compounds, leading to the presence of some ionized or photolyzed species in the measuring volume.[41] Also secondary chemical reactions such as chemical ionization by proton transfer may occur.[42] Although, the relative concentration of photo-radicals and ions is supposedly relatively low, the absorption of photochemical products might explain the observed differences in the appearance of VUV-spectra obtained with scanning or simultaneous VUV-spectrometers. The spectral acquisition range of the detector is restricted to 125 – 240 nm due to the low end cut-off of the MgF_2 windows. The used early stage of the system did not correct for higher order reflection, therefore the spectral range over 240 nm is not shown. In the accessible range low lying σ*← σ, σ*← n, π*← π and π*← n transitions can be excited and are responsible for the VUV-light adsorption.

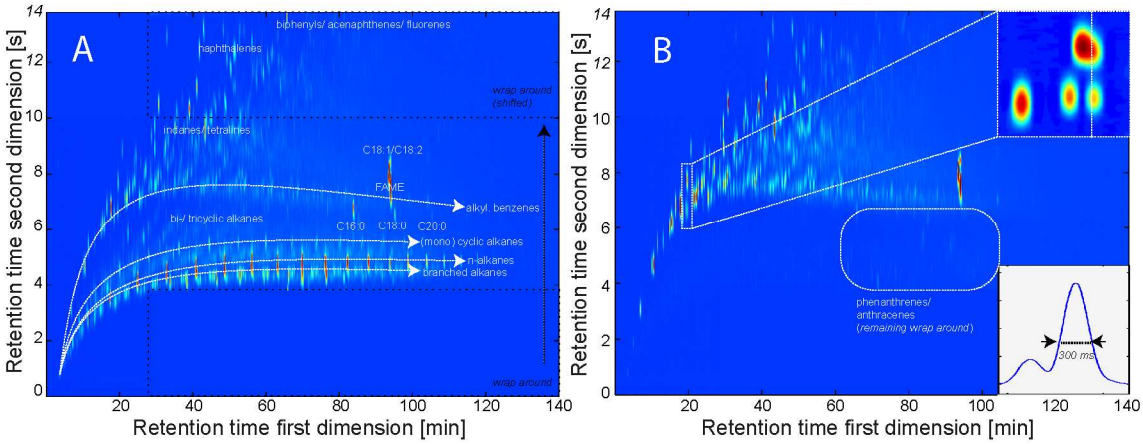

Figure 4 Application of spectral filters for different petrochemical matrices. (Highlighted regions are described in results and discussion, all chromatograms show some degree of wrap around.) (A) GC×GC-VUV-chromatogram of B7 diesel fuel (total VUV-absorption 125 – 240 nm). (B) Application of 170 - 200nm filter to (A) for the discrimination of π*← π chromophores. Compounds with solely σ*← σ chromophores will disappear.

Figure 1B shows the VUV-spectrum of benzene acquired with the VUV-spectrometer as well as a reference spectrum from the literature.[19] The intense and characteristic p - band as well as β – band of the electronically allowed and the forbidden π*← π singlet transitions qualitatively corresponds with the reference spectrum. The information content of MS as well VUV spectroscopy is mainly dependent on the spectral resolution of the system and nowadays state-of-the-art high resolution and accurate mass time-of-flight technology allows the calculation of elemental composition and decomposition of the isotopic pattern. This could be thought as a fingerprint of the compound.[21] The resolutions of both spectra shown in Figure 1B are not sufficient to make a distinct assignment of vibronic transitions. In particular the rotational and vibrational fine structure is not or only in a limited manner accessible. Therefore, filtering or scripting approaches may not address the selectivity of such very discrete transitions. Moreover, they rely on target selective discriminating characteristics of the shape of the absorption bands. Mathematically, distinct features like extrema, saddle points or shoulders could be found by the first or higher derivative of the spectra (Figure 2). Nevertheless, the spectral information allows also differentiation of closely related structural isomers and the coincidence of very high attenuaion coefficients with the emission maxima of common deuterium lamps lead to low achievable detection limits.

Investigation of diesel fuel with one-dimensional gas chromatography VUV absorption spectroscopy and concept for spectroscopic filtering:

The investigated diesel matrix is a blend of petrochemical derived diesel with a defined mixture of fatty acid methyl esters (FAME, "bio diesel" constituent). Due to the refinery and upgrading process the petroleum matrix is as mixture of saturated alkanes (linear, branched and cyclic), aromatic hydrocarbons and their condensation and alkylation products. Unsaturated aliphatic molecular structures as well as carboxylic structures are only introduced by the FAME mixture. Other organic compounds bearing heteroatoms, such as benzofurans or benzothiophenes are present only at low trace levels and are not considered. The σ*← σ chromophoric contribution of the absorption spectra is mainly caused by the C-C and C-H bonds. These transitions are only excited in the far VUV-range below 190 nm and could be detected very sensitively due to their very high ε. Consequently, common GC-UV systems working only up to the near VUV-range could not address compounds which exclusively exhibit σ*← σ chromophores, even if they are predominant ingredients of the matrix (e.g. alkanes in petrochemical matrices, examples shown in Figure 2). Since isolated double bonds do not occur in fully processed and standardized middle distillate diesel (without FAME), the π*← π contribution could be exclusively assigned to conjugated double bonds of aromatic structures. Therefore, the wavelengths region of (170-200 nm) can be used to selectively detect (i.e. "filter out") compounds with aromatic π*← π chromophores for the given matrix. In mass spectrometry unique (mass) spectral features are already used for the assignment to substance classes and very complex algorithm can be applied to e.g. 70 eV EI fragmentation spectra, which is known as scripting.[43,44] Figure 3 shows the adaption of this filter concept to GC-VUV-data. However, while σ*← σ transitions are not very class specific, the π*← π transition is a unique feature for the presence of aromatic or unsaturated structures. For a defined matrix without alkenes like Diesel this absorption can be exclusively attributed to aromatic compounds. The first part of the 1DGC chromatogram (Figure 3) is dominated by a limited number of alkyl substituted benzenes[7] which could be visualized even within a very complex matrix of alkane isomers. Differentiation of individual peaks is well possible and even deconvolution of peaks based on VUV-spectra has already been demonstrated for a xylene isomers[39] and gasoline. However, gasoline has a simpler composition due to its relatively limited carbon number distribution and lower boiling point. Diesel fuel in contrast exhibits a much higher complexity and only the early eluting compounds can be sufficiently separated by 1DGC. For later eluting fractions, more selective chromatographic separation approaches are required. For such cases, the achieved peak widths and shapes allow the application of the detector for comprehensive two-dimensional gas chromatography.

Investigation of diesel fuel with comprehensive two-dimensional gas chromatography VUV absorption spectroscopy:

The VUV-spectral data could be assumed to be widely orthogonal to GC-separation whereas some mass spectrometric information is highly related to the retention times of the molecules. Especially the molecular mass, one of the most

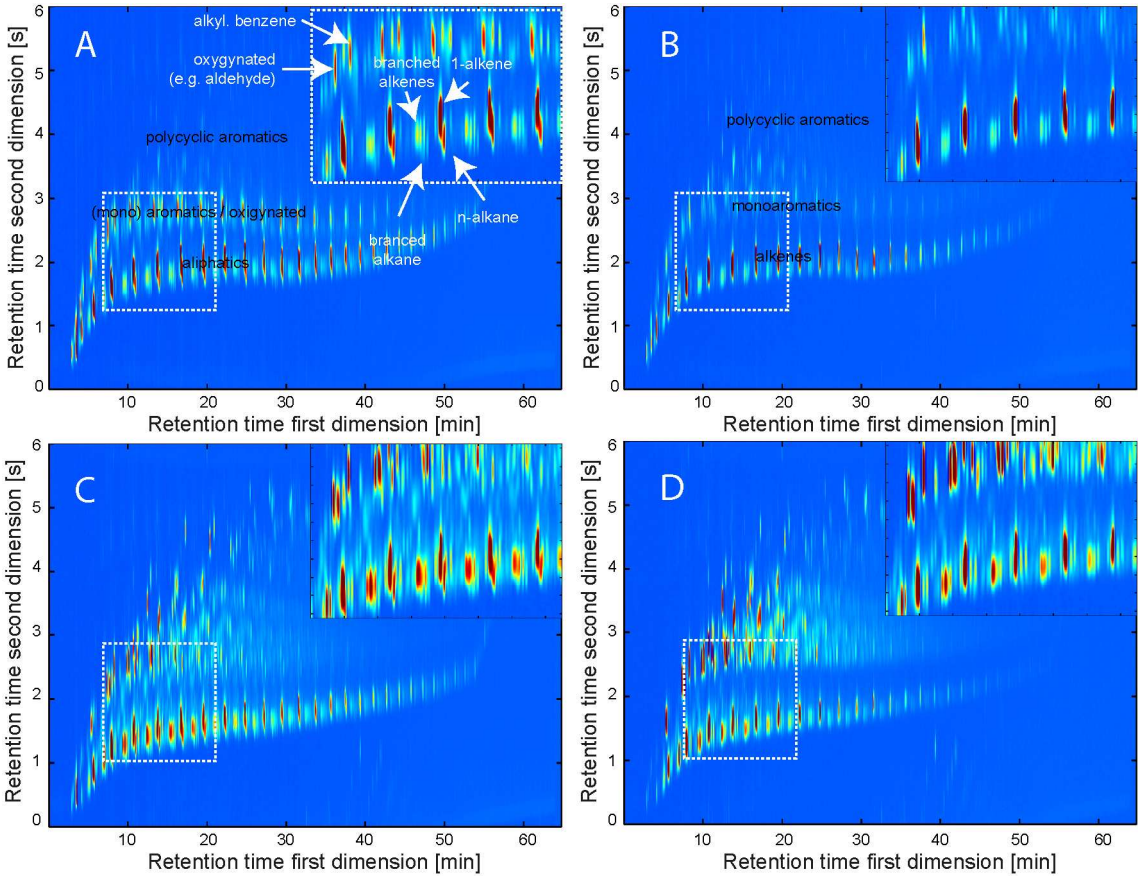

Figure 5 (A) GC×GC-VUV-chromatogram of low temperature Fischer-Tropsch (LTFT) syncrude (total VUV-absorption 125 – 240 nm). (B) Application of 170- 200 nm filter to for the discrimination of π*← π chromophores. The filter also allows for some discrimination of oxygenated compounds. (C) GC×GC-VUV-chromatogram of high temperature Fischer-Tropsch (HTFT) syncrude(total VUV-absorption 125 – 240 nm). (D) Application of 170 - 200nm filter to for the discrimination of π*← πchromophores. The filter also allows some discrimination for oxygenated compounds.

selective information in GC×GC-MS, is highly related (non-orthogonal) to the elution order of the corresponding com pound and becomes obvious for soft ionization techniques like photoionization.[24] Figure 4A shows the typical structured pattern of GC×GC separation for middle distillates. Z-intensities reflect the summed VUV-absorption (125-240 nm) and could be compared to total ion current in mass spectrometry. Saturated and branched alkanes are the dominant peaks caused by both their high relative concentrations and also very high absorption cross sections or ε. While cyclic alkanes are clearly extracted from the bulk of linear and branched compounds, a co-elution with alkenes could not be excluded based on GC×GC separation.[45] The presence of reactive compounds like alkenes would affect the storage stability of the fuel in a negative manner. Also additional mass spectrometric information often fails to differentiate the compounds. However, VUV-spectral data clearly indicate the absence of π*← π chromophores in the corresponding chromatographic elution region for alkenes (Figure 4B). The application of the 170 – 200 nm π*← π filter also confirms the locations of the aromatic compounds. Due to their high absorption polyaromatic compounds are also evident despite of the fact that their spectral maxima are outside the spectral range of the filter and only the tails of the absorption peaks contribute. According to the elution pattern of aromatic compounds for the given chromatographic system, the row of substituted benzenes are eluting first from the second dimension followed by condensed aromatic – cyclic compounds and poly aromatic hydrocarbons. Unlike aromatics, FAME's are only partially discriminated by the filter. Fully saturated FAME's have their main absorption almost exclusively below 170 nm while the π*← π chromophores in unsaturated FAME'S will also absorb very strongly within the range of the filter. A comparison of the filtered and unfiltered chromatograms qualitatively indicates the high amount of not fully saturated FAME's. While the C16 fraction is dominated by C16:0, the C18 fraction is dominated by C18:1 and higher unsaturated FAME's.[7] Therefore, C16 FAME's are not shown in the filtered chromatogram while C18:1 and C18:2 are still dominating co-eluting peaks due to their high concentrations.

Investigation of Fischer-Tropsch syncrude with comprehensive two-dimensional gas chromatography VUV absorption spectroscopy:

Fischer-Tropsch (FT) syncrude is an intermediate product in fuel production from fossil as well bigenic sources. At this stage it is not refined or upgraded like diesel. Due to a defined syngas composition and pretreatment of the syngas the compounds within syncrude will be composed almost exclusively by C, H and O (like B7 diesel). Trace impurities like metals and gasification artifacts, e.g. pyrolysis liquids, are not considered. Main differences are the high abundance of unsaturated and oxygenated compounds. Alkenes are quantitatively dominating (>> 10%), followed by different species of oxygenated and aromatic compounds. The exact composition of the syncrude is also affected by the reactor parameters like

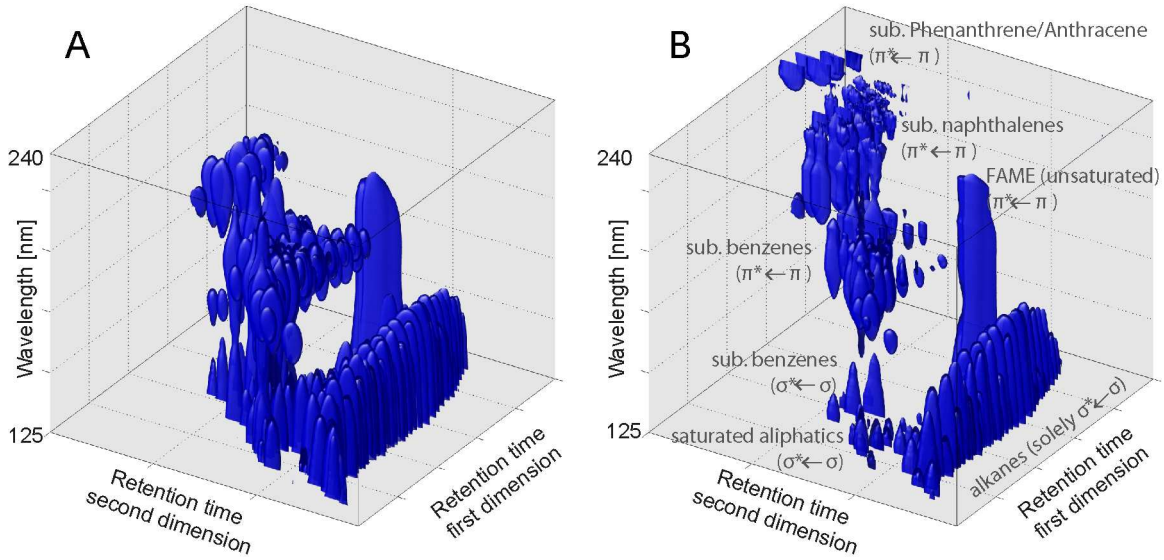

Figure 6 Three-dimensional illustration of B7 Fuel analyzed with GC×GC-VUV. (A) Raw VUV-spectra are arranged along the Z axis. Only the highest absorption regions are depicted. For details see text. (B) Same matrix as (A) but each VUV-spectrum was normalized to 1. The normalization makes also compounds with lower concentrations visible (here the condensed ring aromatics)

temperature and the catalyst which is used. Typical parameters which are associated with a shift towards higher temperatures are an increase of the degree of unsaturation (aromatics and alkenes) associated with a higher degree of branching. Figure 5 show two examples for a low and high temperature Fischer-Tropsch syncrude analyzed by GC×GC-VUV. For these experiments, GC×GC was operated under "screening" conditions, applying a fast heating rate of 5°K/min (Table S1). The total run time will decrease while the elution temperature of the compounds will increase compared to lower ramping rates. Therefore, retention times on the first and second dimension will be reduced with the drawback of a reduced separation power. Saturated and unsaturated compounds will overlap to a greater extent and for the given example e.g. alkanes are only shifted slightly from the dominating alkenes. In addition also a well know separation problem for GC×GC-TOFMS, namely the separation of cyclic alkanes and alkenes[45] in petrochemical matrices will aggravate but could be addressed by the application of VUV-spectroscopy. The already mentioned spectral filter 170-200 nm clearly discriminates between unsaturated and saturated aliphatics even in cases of partial overlap. For the given example the row of normal alkanes vanishes in the spectral filtered chromatograms. The HTFT syncrude also indicates a relatively higher constituent of branched alkenes. The spectra of oxygenated species are more complex. While they have usually very strong absorbance in the region below 170 nm they could have also some absorption within the region of the applied spectral filter 170 – 200 nm. In particular, very small oxygenated compounds (< 3 C atoms) show very distinct absorption spectra with isolated high absorption bands above 170 nm. Oxygenated with longer (linear) alkyl chains have only weak and broad bands above 170 nm. Therefore, a fading or complete disappearing of peaks in the region of benzenes could indicate the presence of oxygenated compounds. In the case of LTFT especially the linear oxygenated compounds are present and discriminated by the applied filter. The remaining peak in this region of the chromatogram could be identified as benzenes which are much more dominant in HTFT. The results presented are consistent with the expected composition of HTFT and LTFT syncrude and have been confirmed by GC×GC-HRT (not shown).

Visualization of GC×GC-VUV Data for data interpretation:

The two dimensional GC×GC-retention time data can be also combined directly with the VUV-spectroscopic data to produce a three-dimensional representation. Figures 6 shows the three-dimensional visualizations of the B7 diesel fuel matrix GCxGC-VUV-measurement (see Table S1 for different GC×GC parameter). The x- and y-axes represent the two dimensional GC×GC retention time plane while the z-axis comprises the VUV-spectroscopic information. For Figure 6a the spectroscopic raw signal was incorporated and the volume plot was performed with a cut off level of 0.2 absorbance unit. For better visualization the spectroscopic resolution was reduced to 1 nm during post processing. The size of the volumes is significantly influenced by the concentration of the individual compounds and their ε, hence, compounds in low abundance are suppressed due to the applied cut off level. Therefore, compounds in high concentration and/or those possessing strongly absorbing chromophores dominate the plot. The visual appearance of the different compounds shows some similarities to GC×GC-SPITOFMS where the z-axis would reflect the mass spectrometric information.[24]

Characteristic features of the VUV-spectra can also be visualized through normalization of the spectra. In Figure 6B each spectra is normalized to 1. The normalization will emphasize the position of the absorption maxima within the spectral range, which is a basic target for filtering approaches. The analogue classifier approach for mass spectrometry is known as "domain knowledge based rules"[46]. Due to the selected column combination saturated hydrocarbons elute at very early second dimension retention times and their spectra are dominated by high absorption tails tending towards the high energetic end of the spectral range of the detector. (The actual absorption maxima for the σ*← σ transition of alkanes is

outside the spectral range of the detector, around 80 nm). On a first glance, the bands of the alkanes look very similar and the cross section of the alkanes in the volatility range of the diesel matrix is increasing only moderately. More specific information is gained from a closer inspection of the shape of the tail, which will allow some within-group discrimination for e.g. isomeric structures (Figure 2). For the given defined matrix a combination of the regional information from GC×GC with this spectral characteristics will give a sufficient classifier for alkanes but it can't be used as a bijective global criterion for this compound class, since virtually all organic compounds will have $\sigma^* \leftarrow \sigma$ transitions. More class selective are the regions for the $\pi^* \leftarrow \pi$ transitions. With a higher number of condensed aromatic systems the maxima are shifted substantially to the red while within-group variations are only moderate and e.g. the already mentioned filter of 170-200 nm will discriminate pure saturated aliphatic compounds from aromatic structures in a defined GC×GC region for the given matrix.

CONCLUSION:

The introduced fast VUV-absorption detector shows great potential to become a complementary selective and universal detector for GC×GC next to mass spectrometry. Extension of the spectral range toward the higher energetic VUV-region substantially enhances the sensitivity and selectivity of the measured spectral information. In combination with the regional information of GC×GC, overall group specific spectral information allows a discrimination of compound classes by filtering or scripting. At the same time small differences in the absorption characteristics of homologous and isobaric compounds will also facilitate a discrimination of these compounds and will give complementary information to mass spectrometric information. The application of these features to different petrochemical matrices could also demonstrate the adaptability to important applications in the field of very complex matrices.

ASSOCIATED CONTENT

Supporting Information

Table S1: GC- and VUV-parameters for shown data

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Author Contributions

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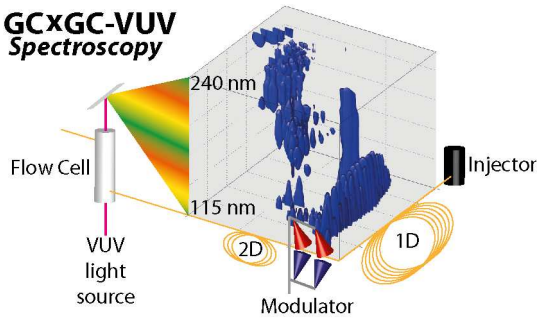
GCxGC-VUV
Spectroscopy
240 nm
115 nm
Flow Cell
VUV
light
source
2D
1D
Injector
Modulator

TOC graphic

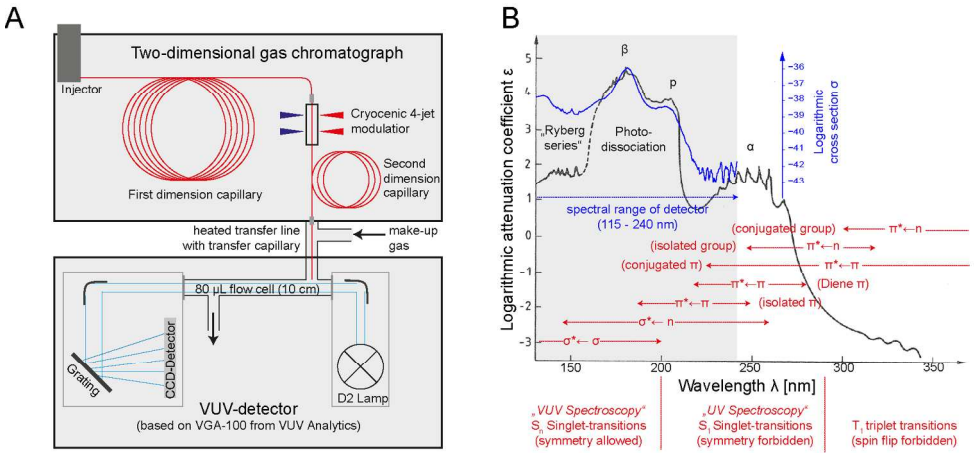

Figure 1 (A) Instrumental setup of the comprehensive two-dimensional gas chromatography-VUV-absorption spectrometer (GC×GC-VUV). (B) VUV-absorption spectrum of benzene (gas phase) with assignment of electronic transitions. Blue: spectra acquired with VUV-spectrometer; Black: reference from literature[19] (with kind permission of Springer). In the VUV-region (~170 nm) the absorption cross section is between two and three orders of magnitude larger than in the classical UV absorption range (up to 250 nm).
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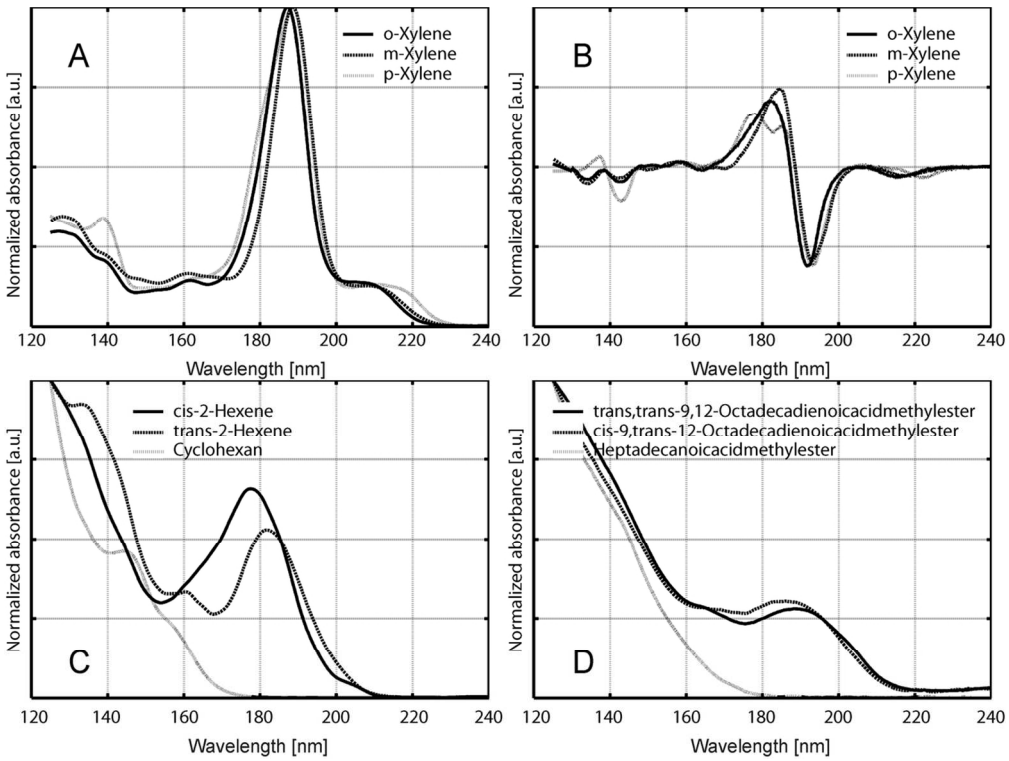
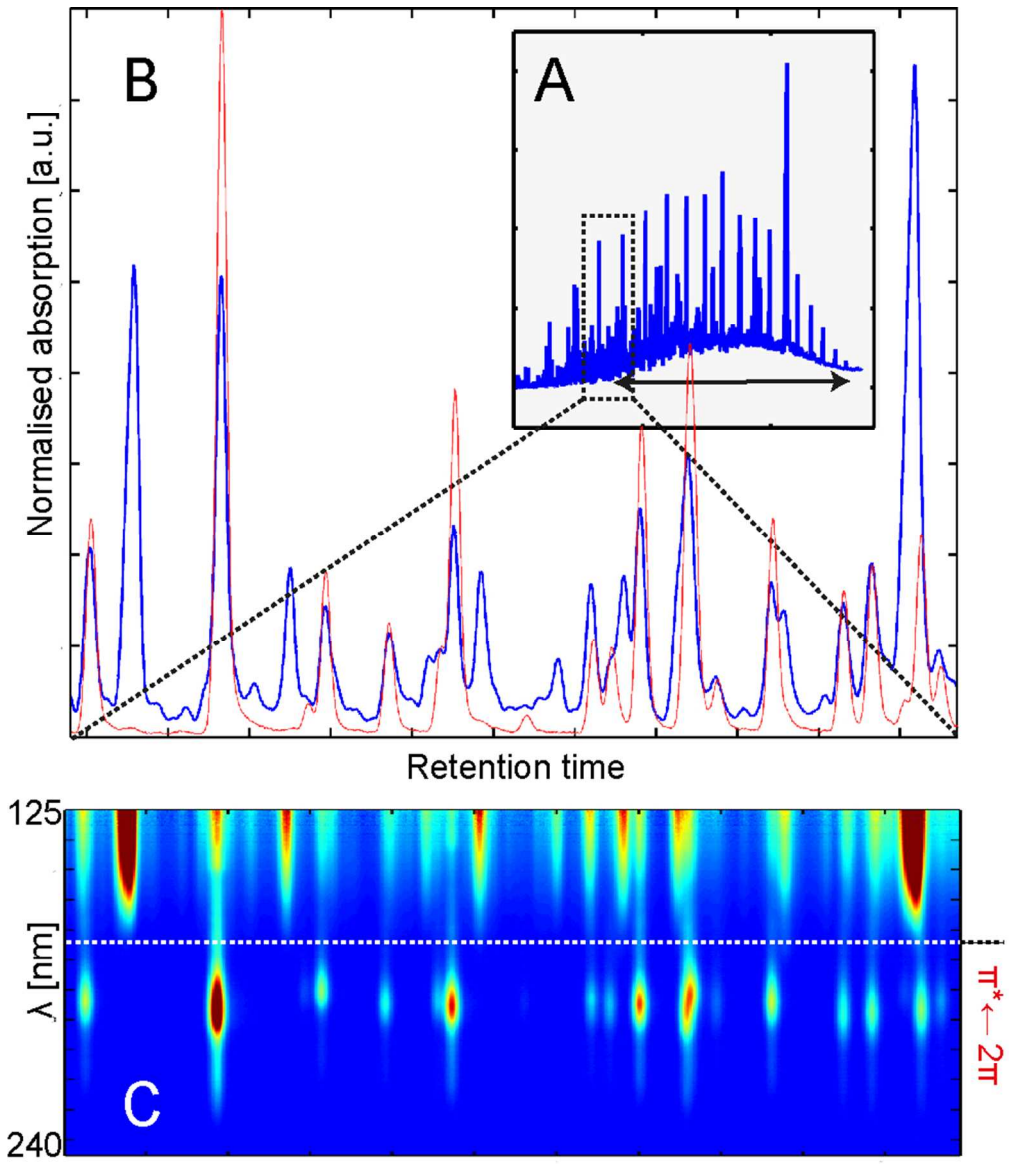
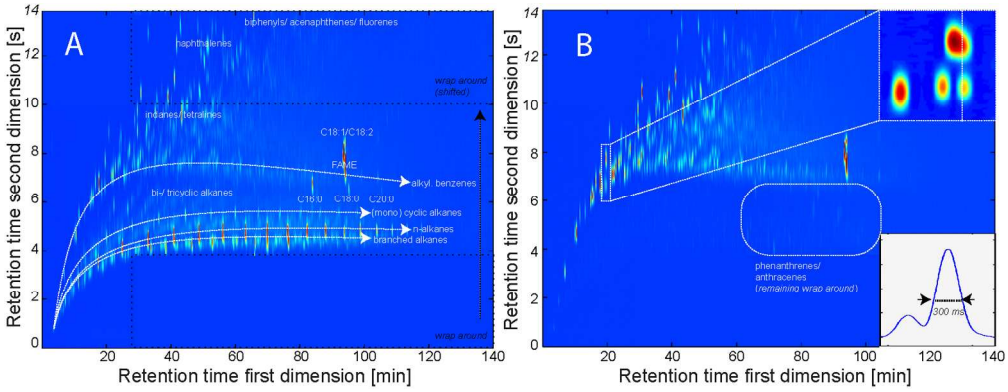


VUV Spectra and first derivation of VUV spectra for different types of isomers. (A) VUV spectra of xylene position isomers. Spectra are dominated by π*← π transition between 170 – 200nm. Distinct features will allow a differentiation. (B) First derivative of VUV Spectra of Xylene. O- and m-xylene show similar shapes. Derivative of p-xylene indicate a shoulder in π*← π region and a second local maximum in the σ*← σ region. (C) Common separation problem in GC×GC-MS: Differentiation of compounds which have similar retention characteristics (GC×GC) as well as similar 70eV fragmentation pattern (MS). VUV Spectroscopy allows an explicit differentiation of these compounds. (D) VUV spectra for selected higher boilers in middle distillates. Also larger isomeric compounds show distinct spectral features.
113x85mm (300 x 300 DPI)



One-dimensional chromatographic separation of B7 Diesel fuel with VUV-detection. (A) Total absorption signal. Vertical arrow indicate chromatographically not sufficiently re-solved region. (B) Enhancement of partial chromatographically resolved region. Blue: Total absorption signal; Red: summed absorption signal within spectral range of filter (170 – 200 nm) for selection of compounds with π*← π chromophores. (C) Cor-responding two dimensional representation of (B).
82x95mm (300 x 300 DPI)



Application of spectral filters for different petrochemical matrices. (Highlighted regions are described in results and discussion, all chromatograms show some degree of wrap around.) (A) GC×GC-VUV-chromatogram of B7 diesel fuel (total VUV-absorption 125 – 240 nm). (B) Application of 170 - 200nm filter to (A) for the discrimination of π*← π chromophores. Compounds with solely σ*← σ chromophores will disappear.
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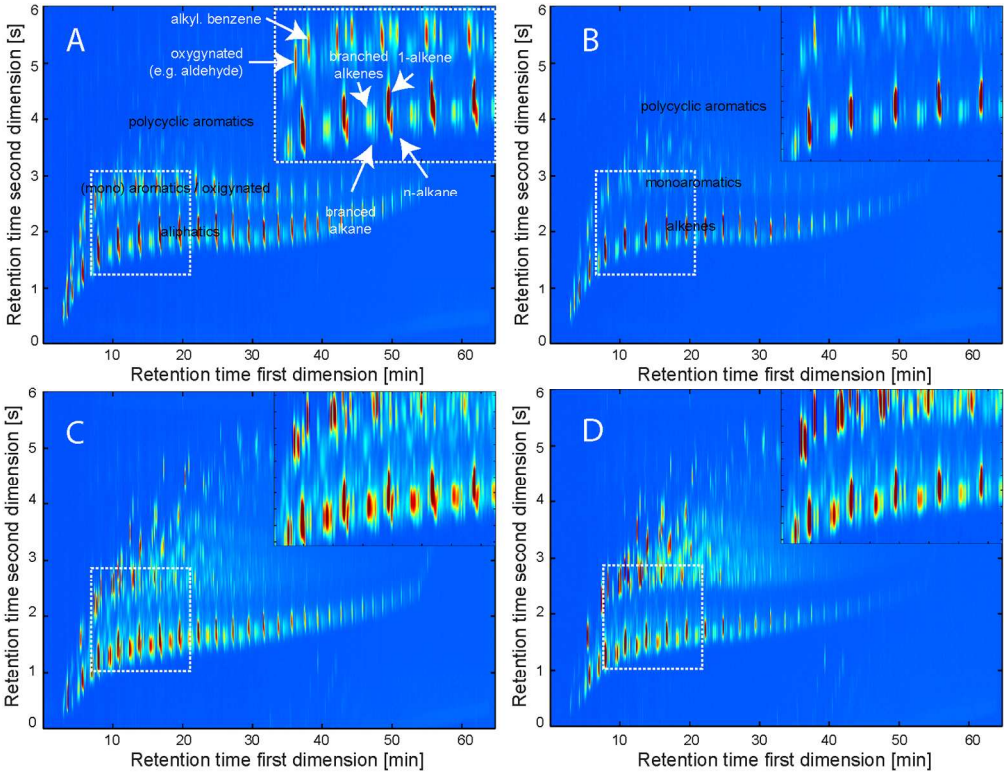

(A) GC×GC-VUV-chromatogram of low temperature Fischer-Tropsch (LTFT) syncrude (total VUV-absorption 125 – 240 nm). (B) Application of 170- 200 nm filter to for the discrimination of π*← π chromophores. The filter also allows for some discrimination of oxy-genated compounds. (C) GC×GC-VUV-chromatogram of high temperature Fischer-Tropsch (HTFT) syncrude(total VUV-absorption 125 – 240 nm). (D) Application of 170 - 200nm filter to for the discrimination of π*← πchromophores. The filter also allows some discrimination for oxygenated compounds.
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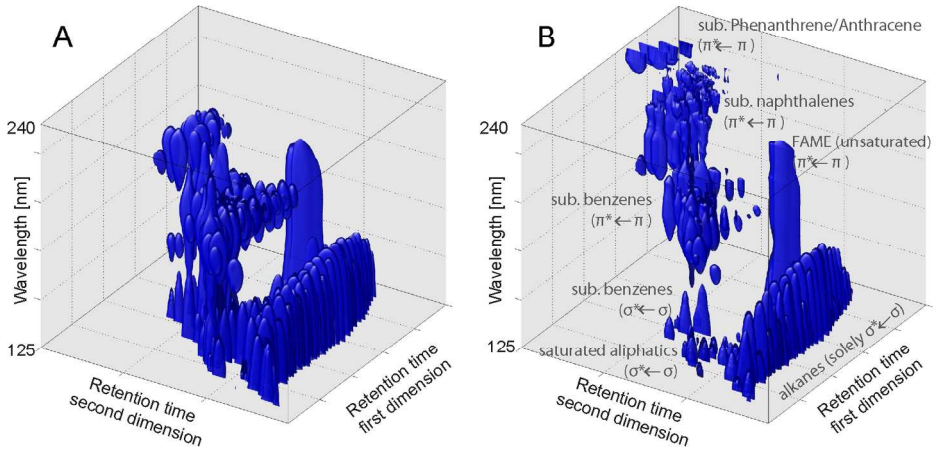

Three-dimensional illustration of B7 Fuel analyzed with GC×GC-VUV. (A) Raw VUV-spectra are arranged along the Z axis. Only the highest absorption regions are depicted. For details see text. (B) Same matrix as (A) but each VUV-spectrum was normalized to 1. The normalization makes also compounds with lower concentrations visible (here the condensed ring aromatics)
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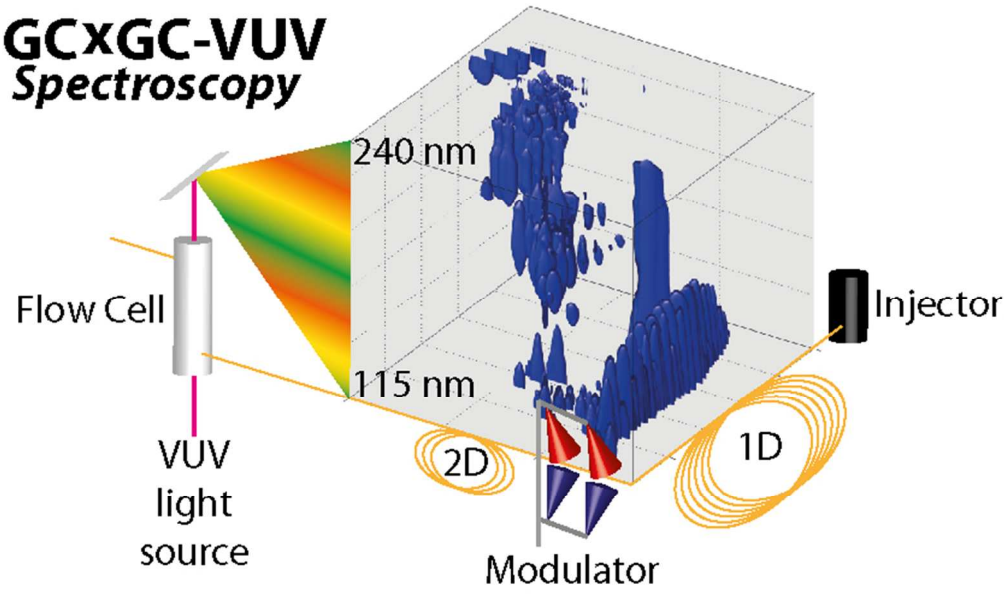

TOC Graphics
70x41mm (300 x 300 DPI)