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APPLICATION OF GC×GC-VUV FOR THE ANALYSIS OF ALTERNATIVE FUELS AND FEEDSTOCKS

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01 | INTRODUCTION

In recent years, the trend towards other feedstocks as a substitute for crude oil has increased for various reasons. The focus is on pyrolysis oils, especially those made from end-of-life plastics. The composition of this raw material can vary greatly and differs significantly from fossil sources. In this context, numerous projects have already been started in recent years. This is a challenge in many respects, not least for chemical analysis. Sophisticated techniques such as GC×GC-TOFMS or high-resolution mass spectrometry (HRMS) are required to obtain a detailed overview of the often very complex compositions. In view of certain analytical questions, it is essential to consider new approaches. Vacuum UV was introduced as a new detection option for gas chromatography several years ago. Today, GC-VUV is an established technique in the routine analysis of gasoline, jet fuel and diesel. It has also been shown in various publications that VUV is also a suitable detection option for two-dimensional gas chromatography. The combination of both techniques provides a powerful and versatile instrument for analytical chemistry. A few years ago, a proof-of-concept project was put on hold again for lack of suitable software for data processing. Now the project is restarted in view of the possible application of different software and its applicability as suitable analysis method of alternative and synthetic fuels and their feedstock. In the presented work, the possibilities of applying the combination of GC×GC and VUV detection for a comprehensive analysis of plastic pyrolysis oil are to be investigated.

02 | INSTRUMENTATION

A GC×GC system consisting of a reversed-phase column combination (1st column: 60 m 50% phenyl-methylpolysiloxane; 0.2 mm ID; 0.2 µm df; 2nd column: 20 m 100% polydimethylsiloxane; 0.25 mm ID; 0.1 µm df) and an INSIGHT® flow modulator from SepSolve is used to develop a suitable analysis method. This system is optimized for the analysis of conventional middle distillates and is used in routine analysis. Instead of the FID, a VUV detector model VGA 100 from VUV Analytics is now used for detection in this method development. While the GC×GC system is controlled using the software Chromspace® from the company SepSolve and data recording is achieved by the software VUVision™ Wfrom the company VUV Analytics, data processing must be carried out using third-party software: the software GC Image™ from Zoex Corporation. This software not only enables data import and processing, but also offers access to a VUV database with reference spectra. Similar approaches have previously been published in scientific journals [1,2].

GC Columns	1st Column	2nd Column
Type	AS-17	ZB-1HT
Length	60 m	20 m
Inner Diameter	0.2 mm	0,25 mm
Film thickness	0.2 µm	0.1 µm
Carrier Gas	He	He
Flow	1.5 ml/min	25-15 ml/min
Oven Program	35 - 300°C; 2°C/min	
Split Ratio	100:1	
Injection Temp.	300°C	
Injection Volume	1 µm	

VUV Parameter	
Instrument	VGA 100
Wavelength Range	125 - 240 nm
Acquisition Rate	50 Hz
Makeup Gas Pressure	1.0 psi
Flowcell Temperature	295°C
Transferline Temperature	295°C

03 | ANALYSIS OF PYROLYSIS OIL

Pyrolysis oils are undoubtedly one of the most complex and demanding samples in the field of petrochemical analysis. For several years, however, refineries and the chemical industry have increasingly focused on them as a possible substitute for fossil crude oil. The range in terms of composition is enormous compared to conventional crude oils. In particular, pyrolysis oils from biogenic sources such as algae, wood or sewage sludge are extremely complex and difficult to characterize without sophisticated techniques such as high-resolution mass spectrometry. In contrast, the composition of plastic-based pyrolysis oils is more straightforward and can be characterized using modest analysis methods. The analysis focuses, among other things, on the identification and quantification of oxygen- and nitrogen-containing compounds. However, given the large number of isomeric compounds, simultaneous assignment and accurate quantification is a major challenge. While a detailed identification of individual compounds and compound classes using GC×GC-MS is easily feasible, quantification here is usually only approximately due to being based on area percent. A possible alternative to this can be provided by measurement using GC×GC-VUV. Measuring the absorption of UV light in a wavelength range between 125 and 240 nm makes it possible to record characteristic spectra of individual compounds and assign them to different compound classes. The VUV spectra database can still be significantly expanded compared to MS databases, but the GC Image™ software offers the option of automatically assigning substance classes based on their spectra by defining characteristics for certain substance classes in the "CLIC Expressions" tool. One aspect of the current method development is the qualitative and quantitative analysis of phenolic compounds. For this purpose, the middle distillate fraction of a pyrolysis oil was measured with both GC×GC-MS and GC×GC-VUV and the respective analysis results were compared (Figure 1).

Figure 1: Chromatogram of a flow modulation GC×GC-VUV measurement of the middle distillate fraction of a typical pyrolysis oil. The enlarged area shows compounds that could be identified as phenols using the CLIC expression tool. Also included is an overlay of measured spectra and reference spectra from the VUV library.
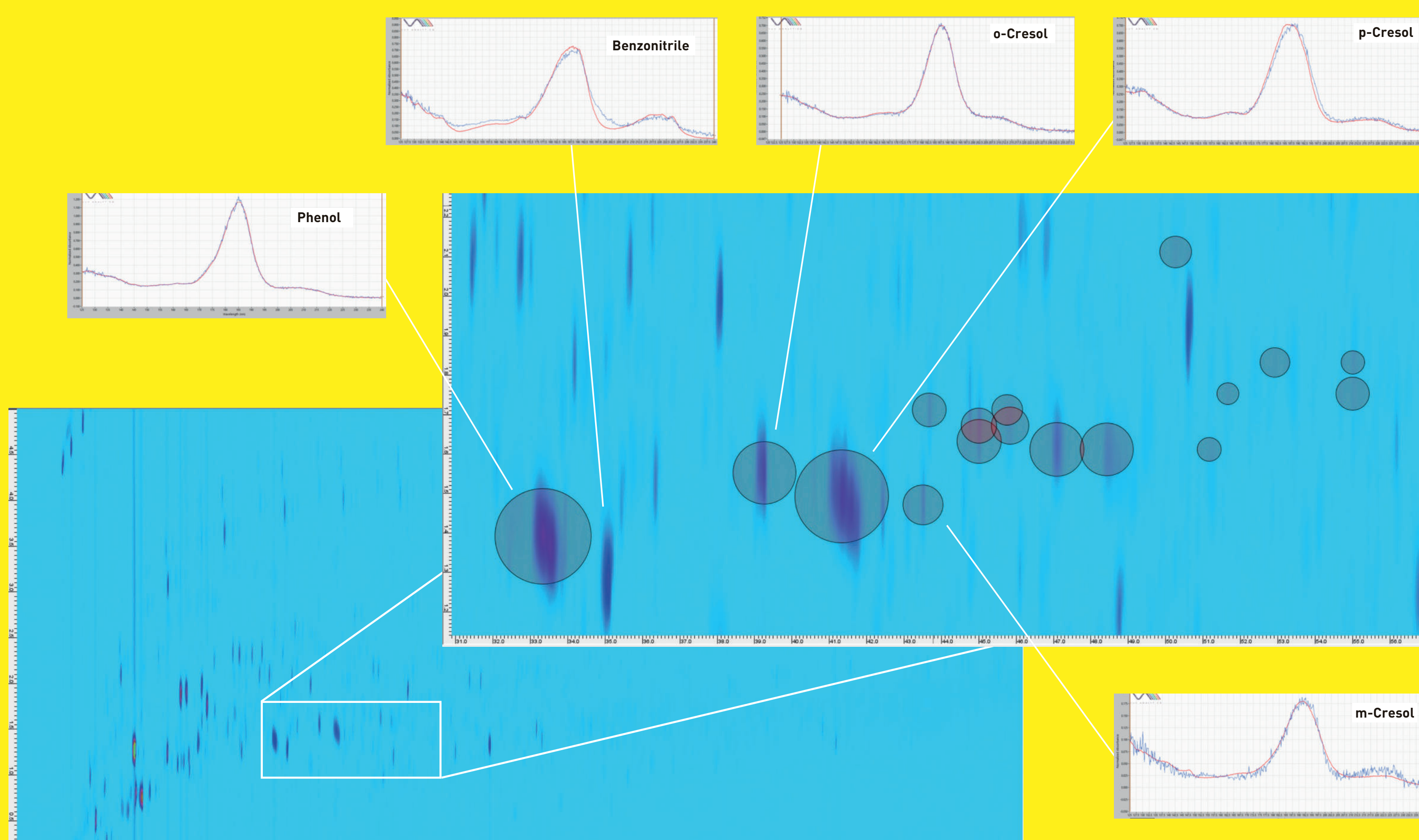
04 | DATA PROCESSING

As already mentioned, the data processing is carried out in the software GC Image™. Thanks to a corresponding plug-in, the extensive data can easily be imported into the software and processed. Basic data processing includes baseline correction and single compound (blob) detection. In a further step, detected blobs can be divided into different substance classes based on the elution pattern and their characteristic absorption. By application of the "CLIC Expressions" evaluation tool an automated selection of certain compound classes based on previously defined criteria is possible. Basic information has been published elsewhere [3]. In contrast to MS data, wavelength ranges are used instead of characteristic mass fragments or their relative intensities. The applied functions within CLIC Expressions are the relative intensity from 180 – 190 nm as well as retention times in both dimensions. Retention times were additionally applied to distinguish from other aromatic compounds, the applied wavelength range is a rather unspecific criterion. Figure 1 also shows the spectra of benzonitrile for comparison. The refinement of the applied expressions for phenols and other compounds classes is currently still in progress.
Example CLIC Expression "Phenols":
(RELATIVE("180-190")>500)&(RETENTION(1)>30)&(RETENTION(2)<=(RETENTION(1)*0.045))
& (RETENTION(2)>=RETENTION(1)*0.019+0.6

05 | COMPARISON TO GC×GC-TOFMS

The same sample from Figure 1 was also measured applying a GC×GC-TOFMS and evaluated using automated evaluation tools in Visual Basic Script implemented in the ChromaTOF® software. Since a detailed comparison of the two measurements and evaluations would go beyond the scope of this publication, a comparison initially only focuses on phenolic compounds. The main components could be clearly assigned in both methods. Precise quantification methods are still the central task of method development, therefore only a semi-quantitative data based on area or volume, respectively, can be presented. This shows that the proportion of phenolic compounds is estimated to be higher using GC×GC-VUV, although more individual compounds were detected with GC × GC-TOFMS. A detailed comparison and an exact quantification are therefore absolutely necessary in the course of method development.

Compound/ Compound Class	GCxGC-TOFMS[%Area]	GCxGC-VUV[%Volume]
Phenol	1.60	2.03
p-Cresol	1.83	1.90
o-Cresol	0.43	0.70
m-Cresol	0.02	0.19
Total	4.98	8.12
Number of single compound	26	17

Table 1: a comparison between the semiquantitative results in area and volume percent, respectively. The total numbers of compounds assigned using scripts is also specified.

06 | CONCLUSION & OUTLOOK

The development of comprehensive analysis methods using GCxGC-VUV is still in its infancy. However, the combination of these two versatile techniques offers the possibility of introducing a new, powerful instrument for both research and routine applications in analytical chemistry. Currently, analysis methods for specific substances and substance classes can already be created. In the further course of method development, this should be extended to a qualitative and quantitative full analysis of alternative and synthetic fuels and feedstocks.

REFERENCES

[1] Gröger, T. et al., A Vacuum Ultraviolet Absorption Array Spectrometer as a Selective Detector for Comprehensive Two-Dimensional Gas Chromatography: Concept and First Results. Analytical Chemistry, 2016, 88, 6, 3031 – 3039
[2] Lelevic, A. et al., Quantitative Analysis of Hydrocarbons in Gas Oils by Two-Dimensional Comprehensive Gas Chromatography with Vacuum Ultraviolet Detection. Energy Fuels, 2021, 35, 17, 13766 – 13775
[3] Stephen E. Reichenbach et al., Computer language for identifying chemicals with comprehensive two-dimensional gas chromatography and mass spectrometry; Journal of Chromatography A; 1071 (2005) 263 - 269

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