



Možnosti stanovení složek bioplynů, rozpouštědel a degradačních produktů polymerů plynovou chromatografií s detekcí ve vakuové UV oblasti

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The Commercialization of Light



Overview of Molecular Spectroscopy



Vacuum Ultraviolet Detector for GC





Schug et al., Anal. Chem. 2014, 86, 8329-8335.

VUV: A Gap in The Analytical Toolbox



"The excitation <u>energies associated with</u> electrons forming <u>most single bonds are</u> sufficiently high that absorption occurs in the so-called <u>vacuum</u> <u>ultraviolet</u> region (λ <185nm), where components in the atmosphere also absorb strongly. <u>Because of</u> <u>experimental difficulties associated with the</u> <u>vacuum ultraviolet region, most</u> <u>spectrophotometric investigations of organic</u> <u>compounds have involved longer wavelengths than</u> <u>185nm</u>."

> <u>Principals of Instrumental Analysis,</u> by Douglas Skoog, Sixth Edition, 2006



Characteristics of VGA-100 (VGA-101)





- Universal and selective detection
- Unique, class similar spectra
- Optical differentiation of isomers
- Deconvolution of coeluting analytes
- Automated classification and speciation of mixtures
- Good quantitative performance



Permanent gas analysis

Thermal runaway of Li-ion and Li-M batteries

- Universal and selective detection
- Unique, class similar spectra
- **Optical differentiation of isomers**
- **Deconvolution of coeluting analytes**
- Automated classification and speciation of mixtures
- Good quantitative performance

Alkanes vs. Aromatics 1.20 Naphthalenes Linear Alkane Monoaromatic (210-240 nm) (180-200 nm) (125-160 nm) Benzene 1.00 Octane Normalized Absorbance Toluena



Note: The absorbance of e.g benzene at 180 nm is 10 000 more intense than at the typical 254 nm in HPLC

Bai et al., Revised

0.20

0.00

Library search and Unambiguous Compound Identification





No ghost components in the library match list

Similar But Very Distinct

Visual similarities are easily distinguished in the fitting routine; minor differences are significant



The chi-squared distribution is the distribution of a sum of the squares of *k* independent standard normal random variables The chi-squared distribution is used in the common tests for goodness of fit of two criteria of gualitative data,





- Universal and selective detection
- Unique, class similar spectra
- Optical differentiation of isomers
- (Spectral) Deconvolution of coeluting analytes
- Automated classification and speciation of mixtures
- Good quantitative performance



Polychlorinated biphenyls in Aroclor mixtures

Qiu et al., J. Chromatogr A 2017, 1490, 191-200.

Deconvolution

- Total absorption is proportional to the product of the concentration and the absorption cross section
- Co-elution is a sum of these products
- Linear regression allows for easy deconvolution of the compound concentrations; even for co-eluting compounds





Spectral Deconvolution of m&p Xylene



Fast GC-VUV Analysis of Terpene Isomers Additional selectivity which makes chromatographic separation less stringent



Summary:

- Terpenes have VUV spectra that are distinct
 - ø Includes structural isomers and co-eluting analytes
- VUV spectral identification of terpene isomers allows the chromatographic compression of GC runtimes
 - ø Can shorten GC runtimes by 2 3X or more
- Natural and forced co-elutions are deconvolved by VUV software
 - ø Eliminates inaccuracy inherent to dropping vertical integration lines to quantitate



- Universal and selective detection
- Unique, class similar spectra
- Optical differentiation of isomers
- Deconvolution of coeluting analytes
- Automated classification and speciation of mixtures (compositional analysis
- Good quantitative performance

Time Interval Deconvolution (TID)



PIONA analysis of finished gasoline (ASTM D8071)

Walsh et al., Anal. Chem. 2016, 88, 11130 - 11138.

PIONA Compound Characterization using VUV PIONA+

- Compositional Analysis of gasoline type samples
- Each PIONA compound class displays distinct spectral features
 - ø Enables straightforward compound class identification and quantitation
- PIONA compounds can be speciated through C6, and class identification >C6 using VUV PIONA⁺
 - ø Flexibility to vary chromatographic conditions
 - Ø Specific analytes such as individual oxygenates or aromatics belonging to the BTEX complex



- ASTM Method D8071 provides information that historically required the use of several ASTM methods or more comprehensive methods.
 - Ø A single-column GC-VUV separation method with a total runtime of <u>34 minutes</u>.
 - ø ASTM approved for PIONA compound analysis in finished gasoline
 - ø No special setups, traps, pre-column tuning, or calibration requirements
 - ø Automated VUV PIONA+ analysis and reporting

Group plus Compound Identification



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- Universal and selective detection
- Unique, class similar spectra
- Complementarity to MS
- Deconvolution of coeluting analytes
- Automated classification and speciation of mixtures
- Good quantitative performance

Instrumental Detection Limits

Paraffin IDLs averaged 41 pg on column

PAH IDLs averaged 28 pg on column

Terpene IDLs averaged 28 pg on column

FAME IDLs averaged 34 pg on column

Fragrance allergen [A], [B], and [C] IDLs averaged 35, 44, and 36 pg on column

Combined Class 2 & 3 Solvents



Analyzing Untargeted Unknowns by GC-VUV: Hangover Pain Relief



Summary:

- Applied GC-VUV residual solvents method to over-the-counter hangover medicine
- Detected an unexpected compound in the sample injected through static headspace
- Identified the unknown analyte as ethanol using VUV spectral library matching



Water Quantitation with GC-VUV



UV ANALYTICS

Introducing the SVGA-100



Streaming Gas Analysis Instrument



Ethylene / Acetylene Analysis



Formalin Headspace – No Separation Case

- Formalin solution headspace was sampled continuously
- Absorption cross sections for water, methanol, and formaldehyde was applied to total absorption



Additional Thoughts

- No vacuum
- Robustness
- Reproducibility of spectra
- Fast GC
 - Spectral vs. chrom resolution



- Universal and selective detection
- Unique, class similar spectra
- Optical differentiation of isomers
- Deconvolution of coeluting analytes
- Automated classification and speciation of mixtures
- Good quantitative performance

What's Next?

- GC-VUV/MS: parallel detection
- VUV is complementary to MS

Thank you for your attention!



Science in a new light

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