Fibre-optic UV Systems for gas and vapour analysis

Hanns Simon Eckhardt1,3, Karl-Friedrich Klein1, Bernd Spangenberg2, Tong Sun3, Kenneth T.V. Grattan3
1University of Applied Sciences Giessen-Friedberg, Wilhelm-Leuschner-Str, 13, 61169 Friedberg, Germany
2University of Applied Sciences Offenburg, Badstrasse 24, 77652 Offenburg, Germany
3City University London, Northampton Square, London, EC1V 0HB, United Kingdom
Hanns-Simon.Eckhardt@iem.fh-friedberg.de

Abstract. The identification and quantification of compounds in the gas phase becomes of increasing interest in the context of environmental protection, as well as in the analytical field. In this respect, the high extinction coefficients of vapours and gases in the ultraviolet wavelength region allow a very sensitive measurement system. In addition, the increased performance of the components necessary for setting up a measurement system, such as fibres, light sources and detectors has been improved. In particular the light sources and detectors offer improved stability, and the deep UV performance and solarisation resistance of fused silica fibres allow have been significantly optimized in the past years. Therefore a compact and reliable detection system with high measuring accuracy is developed. Within this paper possible applications of the system under development and recent results will be discussed.

1. Introduction

The analysis of gas and vapor phase samples can be carried out by a variety of instrumental methods, which include gas chromatographic and optical methods /1/. Depending on the composition of the sample, the required accuracy and time resolution, and finally the desired grade of automation a suitable method needs to be considered. In the case of an unknown or very complex sample the detection system needs to separate, identify and quantify the compounds in the matrix. For these requirements the analytical chemistry often utilizes gas chromatographic separation with an additional identifying detector. Techniques such as optical absorption measurements in the infrared (GC-FTIR), which can identify the structure, mass spectroscopy (GC-MS) which can identify compounds by their ions mass/charge ratio, or atomic emission detectors (GC-AED), which identify atoms within a compound by their emission have been developed and utilized.

For mixtures with a limited number of known substances the system needs to separate the substances sufficiently for determining their concentrations. The separation of the substances can be carried out either by the retention time of the substances in a gas chromatic separation and a quantitative detection system or by different characteristic absorption bands in an optical measurement.

The development of a stable measurement system in the UV wavelength region, allowing stand-alone analysis or hyphenation with analytical techniques is well founded by the stronger UV-absorption bands, compared to the infrared wavelength region /2,3/, which allow either higher
sensitivity or a shorter absorption path length of the measuring system. In addition, improved fibers for the transportation of UV light, powerful and stable broadband light sources and fast data acquisition systems extend the possibilities for applications. In the case of hyphenation the measurement system can be implemented with an upstream gas chromatograph, and due to the non-destructive measurement connected with additional detectors downstream (e.g. a FID or MS detector).

2. Measurement Technique and System

2.1. Measurement of Gas chromatographic effluent

A schematic design of the setup for the measurements is shown in Fig. 1: The major components of the detection system consisting of a 30W deuterium light source, imaging optics, incoupling and outcoupling fiber, a gas flow cell, and a spectrometer. For the use with a Gas chromatographic separation, the transfer line and the gas flow cell needs to be temperature controlled to avoid condensation of the vapor phase compounds in the gas chromatographic effluent. With this measurement setup the components can be analyzed both by their retention time, as well as by their absorption behavior. For the determination of the detectors performance a reference mixture was prepared The components in the mixture are shown in Table 1, with their molecular weight, CAS number and boiling point temperature.

The spectra of all components were either available by a database comprising approx. 1600 UV spectra /4/, or were measured within the measurement system. The spectra of all compounds used during the measurements are shown in figure 2. The spectral absorption of the components shows that they can be separated by their spectral absorption in the wavelength range.

Figure 1 Detection system with an upstream gas chromatographic separation

Figure 2. Absorption spectra of different gases

Figure 3 shows a 3-dimensional diagram obtained by UV detection after a gas chromatographic separation of the reference sample, composed of absorption spectra over time. The first absorption peak measured starts after approx. 50s: carbon disulfide is detected due to the related UV-spectrum. In the following section, no substance is available and detected; the baseline separation offers a good opportunity to distinguish between those components. After that, the following substances can be detected: ethylbenzene (143 s), bromobenzene (200 s), and butyrophenone (350 s).

Both isomers of decahyronaphtalene were detected with significantly lower absorption at 275 s and 310 s. Although Diphenyl sulfoxide was in the mixture, no absorption peak was detected; however, this substance was unstable in this mixture and therefore not detectable with the reference method (GC-MS) as well.

2.2. Optical fibres in UV wavelength region
The spectral behavior of the gas flow cell strongly influences the performance of the measurement system. Up to now, the existing UV detection systems, which perform measurements in the deep ultraviolet wavelength range below 200nm, mostly not contain fiber optics. Reasons might be the increasing basic attenuation of the fibers for lower wavelengths and, in addition, the solarization behavior of the fibers which might limit the stability of the measurement system.

| Component                  | CAS   | Mass [g/mol] | BP [°C] |
|----------------------------|-------|--------------|---------|
| Ethylbenzene               | 100-41-4 | 106.17       | 136     |
| Bromobenzene               | 108-86-1 | 157.01       | 156     |
| cis-decahydronaphtalene    | 493-01-6 | 138.25       | 195     |
| trans-decahydronaphtalene  | 493-02-7 | 138.25       | 186     |
| Buthyrophenone             | 495-40-9 | 148.2        | 220     |
| Diphenylsulfoxide          | 945-51-7 | 202.27       | 206     |
| Carbon disulfide           | 75-15-0  | 76.14        | 46.5    |

However, the improved fiber material in the case of fused silica specialty fibers, and the development of hollow core waveguides offer the opportunity to utilize fiber optics in this wavelength region. The hollow core waveguide, which was developed for the transportation of UV laser light /5/, can be used for producing a fiber optic absorption cell with a long path length and low volume compared to existing light pipe techniques for gas analyses. The minimum wavelength is given by the gas in the core, mainly. As shown in previous publications, a system with a single Hollow-Core-Waveguide (HCW) as an absorption cell has been built up and characterized /6/.

![Figure 3](image-url) Figure 3. 3 dimensional view of GC-UV measurement

![Figure 4](image-url) Figure 4. Measurement of the basic attenuation of an all silica fibre with a cut-back measurement

In the case of fused silica fibers the performance of the measurement system can be optimized by a selection of the fiber material in case of the basic attenuation. Fig. 4 shows a measurement result of a cutback measurement for spectral attenuation in the wavelength range below 250nm. Within this figure the influence of the systems dynamic behavior on the measurement is clearly seen, during the cut-back measurement. For the exact determination of the basic attenuation a series of cut-backs need to be done. In this case the longest length measured was 12m. In addition, lengths of 8, 4, 2 and 0.5m were measured. When the spectral attenuation is calculated from this length, taking the 0.5m sample as a reference, different absorptions can be observed on the same fiber: The black plot shows the calculated basic attenuation from a cutback from a 12 m sample down to 0.5 m. With every additional measurement the attenuation of the fiber comes closer to the dotted calculated absorption of the fiber.
The dynamic range of the system used is the reason for this “measurement error”. The longer fibers do not transport sufficient light in this wavelength range and therefore an "absorption peak", which is shifting to DUV wavelengths, can be observed.

In addition the behavior of the fibers in terms of solarization was improved significantly, cutting the UV induced loss by more than a factor of two, depending on the fiber diameter /7/.

![Figure 5. Absorption spectra of benzene with different spectral resolution](image1)

![Figure 6. Stability measurement according to an ASTM measurement at 185 nm wavelength](image2)

3. Characterization of the systems performance

3.1. Characterization of new UV-spectrophotometer

As described in previous publications /8,9/ either the wavelength range or the optical behaviour of the commercially available spectrophotometers was limiting the performance on their use in gas analysis. However, recently the development of a high resolution fiber-optic spectrometer for the analysis of gas absorption bands has been completed. Two prototypes have been realized. Both prototypes covering a wavelength region of about 120nm have been set up for different mean wavelengths. In addition reference measurements for spectroscopic systems have been carried out to determine the spectral performance of the polychromators used /9/. These tests included measurement of the spectral resolution of the detection system, and in addition the stray light behaviour. As there is no standardized procedure for photometric systems designed for gas analysis, a standard practice for photometric detectors was used. The main difference is, that the spectrophotometer is tested with a fibre-optic cuvette holder and reference samples. In the case of spectral behaviour this could be carried out with an absorption measurement of toluene in hexane, or a measurement of benzene in the gas phase. In the case of the stray light measurement a sodium iodide solution with a cut-off wavelength of 260nm was used.

The result of the spectral resolution can be seen in figure 5, where a fine structure of benzene in the wavelength range between 230 and 270nm is clearly visible (black plot). The determined spectral resolution is approximately 0.5nm. For comparison an absorption measurement with a spectral resolution of 1nm is shown (black plot). In addition to that a stray light behaviour of 2.5 AU was determined.

3.2. Stability of measurement system

The stability of the measurement system is given by the stabilities of the components used. There are influences which can be determined by measuring only one part of the system, like spectral stability over temperature, but measurements of drift and noise for every component are not necessarily useful. At this time the stability measurements are carried out for a system set-up in a climate chamber to evaluate influence of temperature changes on measurement precision. First results show that the
wavelength drift within the spectrometer are smaller than one pixel on the diode array, with a temperature change of 40°C. The noise and drift measurements are carried out following a best practice method, the ASTM-standard /10/ where the noise is calculated in windows of 1 minute in a total measuring time of 15 minutes. At room temperature a measurement series has been carried out, giving a drift of 4 to 10 mAU for wavelengths between 185 and 200 nm. These results seem to be a little bit high compared to prior tests with spectrophotometric systems carried out beforehand. One reason might be the unhoused read out electronic of the diode array or a not sufficiently stable power supply for this electronic. Further tests will be carried out to determine appropriate characteristic of the system in a housing.

4. Summary
Absorption spectroscopy in the ultraviolet wavelength region is a useful tool to gather data of gaseous samples. This technique might be used successfully to identify compounds eluting from a gas chromatographic separation in applications like food safety, environmental research or the estimation of hazards on the human body. In addition to that the system can be used in stand alone applications to analyse gases to quantify components in a mixture, e.g. hazardous compound in the environmental field /11/, disease markers in exhaled breath /12/, or the analysis of tobacco smoke /13/. The properties of the measurement system have been optimized in the case of the wavelength region and stray light properties of the newly developed spectrophotometer. In addition the fibre based sensor cell approach offers high flexibility of the measurement setup.

References
[1] J. Hogan: "Specialty Gas Analysis", Wiley-VCH, New York (1996)
[2] V. Lagesson: "Micro gas chromatographic separation cobined with UV- and IR-spectrophotometric detection/identification with applications within the occupational hygiene field using diffusive and active sampling followed by a direct thermal desorption technique”, PHD thesis, University of Göteborg & University of Linköping, Sweden (1992)
[3] H.S. Eckhardt, K. Behler, M. Frank, K.T.V. Grattan, K.-F. Klein, R. Kötschau, U. Schröder: “Further improvements of high-precision gas-analysis in DUV-region”, SPIE-proc. Vol. 5317, p. (San Jose, Jan.2004)
[4] www.gc-uv.com
[5] Y. Matsuura, M. Miyagi: “Hollow fiber delivery system of ArF and KrF excimer laser light”. SPIE-proc. Vol. 3596,pp. 2-7 (San Jose, Jan. 1999)
[6] R. Kötschau, H.S. Eckhardt, K.-F. Klein, K. Behler, and G. Hillrichs: "Gas analysis in the UV region using a long-length hollow core waveguide", SPIE-proc. Vol. 4957 pp. 134-141 (2003)
[7] V. Khalilov, K.-F. Klein, J. Belmahdi, R. Timmerman, G. Nelson: “High-OH fibers with higher stability in the UV-region”. Proc. SPIE, Int. Soc. Opt. Eng. BiOS’06, Vol. 6083, paper 6083-08 (2006)
[8] H.S. Eckhardt, K.T.V. Grattan, K. Graubner, K.-F. Klein, T. Sun "Fiber-optic based gas sensing in the UV region", SPIE-proc. 60830A (2006)
[9] H.S. Eckhardt, H. Dominick, K. T. V. Grattan, K. Graubner, K.-F. Klein, B. Spangenberg, and T. Sun: " Fiber-optic detection device for GC-UV", Proc. SPIE Vol. 6433, (2007)
[10] ASTM E684-93: "Standard Practice for Testing Fixed-Wavelength Photometric Detectors used in Liquid Chromatography"
[11] A. Nilsson: "Novel technique for analysing volatile compounds in indoor dust : application of gas chromatography - UV spectrometry to the study of building-related illness" Linköping University medical dissertations, 0345-0082, Linköping, Sweden (2004)
[12] A.W. Jones, V. Lagesson, C. Tagesson: "Determination of isoprene in human breath by thermal desorption gas chromatography with ultraviolet detection”, Journal of Chromatography B, vol. 672 pp. 1-6 (1995)
[13] Hatzinikolaou, D. G.; Lagesson, V.; Stavridou, A. J.; Pouli, A. E.; Lagesson-Andrasko, L.; Stavrides, J. C.: " Analysis of the Gas Phase of Cigarette Smoke by Gas Chromatography Coupled
with UV-Diode Array Detection”, Anal. Chem. A., 2006; 78(13); 4509-4516