very similar to the KBr-disk spectra of the corresponding compounds. Extensive libraries ($>150\,000$ entries) of reference spectra of standards prepared in this way are available commercially. The only compounds that cannot be readily identified in this manner are molecules with very strongly hydrogen-bonding groups or for analytes exhibiting polymorphism. For trace analytes containing O–H or N–H groups, the best results on library searching are usually found by examining only the spectral region below 2000 cm^{-1} and eliminating the region containing the strong, broad O–H and N–H stretching modes from the search.

Prognostication

Online IR spectrometry is proving to be an important way of identifying molecules eluting from a gas chromatograph. Light-pipe-based systems are the simplest, least expensive and most reliable, but often prove to have inadequate sensitivity for the identification of minor components. Of the two deposition-based techniques, the direct-deposition approach has LODs that rival those of benchtop GC-MS systems and has the great advantage of producing spectra that are directly comparable with KBr-disk reference spectra, of which there are over 150 000 available in digital form (i.e. suitable for computerized library searching). Thus one can forecast an increasing use of systems based on this principle in the future. It is also noteworthy that interfaces between FT-IR spectrometers and both supercritical-fluid and liquid chromatographs based on the same principle have been described.

See also: **II/Chromatography: Gas:** Detectors: General (Flame Ionization Detectors and Thermal Conductivity Detectors); Detectors: Mass Spectrometry; Detectors: Selective; Gas Chromatography-Ultraviolet.

Further Reading

Bourne S, Haefner AM, Norton KL and Griffiths PR (1990) Performance characteristics of a real-time direct deposition GC/FT-IR system. *Analytical Chemistry* 62: 2448–2452.

Griffiths PR and de Haseth JA (1986) *Fourier Transform Infrared Spectrometry*, ch. 18. New York: Wiley-Interscience.

Herres W (1987) *HRGC-FTIR*: *Capillary Gas Chromatography – Fourier Transform Infrared Spectroscopy*; *Theory and Application*. Heidelberg: Huethig.

Norton KL and Griffiths PR (1995) Comparison of direct deposition and flow-cell gas chromatography-Fourier transform infrared spectrometry of barbiturates. *Journal of Chromatography A* 703: 383–392.

Reedy GT, Ettinger DG, Schneider JF and Bourne S (1985) High resolution gas chromatography/matrix isolation infrared spectrometry. *Analytical Chemistry* 57: 1602–1609.

White R (1990) *Chromatography/Fourier Transform Infrared Spectroscopy and its Applications*. New York: Marcel Dekker.

Gas Chromatography–Mass Spectrometry

See **II / CHROMATOGRAPHY: GAS / Detectors: Mass Spectrometry**

Gas Chromatography–Ultraviolet

V. L. Lagesson and L. Lagesson-Andrasko,
GC–UV Center, Linköping, Sweden

During recent decades much interest has been focused on hyphenated analytical techniques. Gas chromatography (GC), liquid chromatography (LC), mass spectrometry (MS) and Fourier transform infrared (FTIR) spectrophotometry have been arranged online, usually in a series. For example a GC separation directly combined with IR or MS is established and widespread. The combination considerably increases the degree of selectivity and identification possibilities. This is also applicable for ultraviolet (UV) absorption spectrophotomery, but GC–UV has been largely overlooked. The interest concerning UV absorption spectrophotometry for analytical purposes has been directed towards the liquid phase for the vast majority of studies involving UV absorption because of its frequent use as a detector for high performance liquid chromatography (HPLC).

However, the first attempt to utilize UV absorption detection combined with GC was made by Kaye in

the early 1960s. He used a Beckman DK2 spectrophotometer and, in order to reach the far UV region, the instrument was purged by nitrogen. He recorded spectra of various substances in the vapour phase by means of a high speed mechanical scanner and a fast recorder in the wavelength range of 165–220 nm. His article from 1961 concerning analytical applications of UV spectroscopy includes a list of 256 references. The oldest reference was from 1932, but the first analytical application of UV absorption in the gas phase, which reported the determination of ammonia in nitrogen and in air, was from 1956.

At that time there were highly limited possibilities for handling large numbers of full scan data. Interest during this period was also increasingly focused on GC–MS and later also on GC–FTIR. These circumstances probably led to the lack of interest concerning the GC–UV hyphenation for a long time. Novotny published work on GC–UV in 1980 in connection with the introduction of Perkin Elmer GC–55 UV detector. The detection was carried out at various single wavelengths. This instrument was, for some reasons, withdrawn from the market shortly afterwards.

From about the mid-1980s there has been a gradual increase in interest in GC–UV. Most of the instrumental techniques described use commercially available spectrophotometers working in either a direct or remote configuration. With these conventional instruments there is no possibility of measuring at wavelengths shorter than 190 nm. A new instrument, GC–UV Inscan 175 spectrophotometer, was introduced on the market in 1996. This instrument has been used for spectral recordings of reference substances and a spectral library of about 1000 gas-phase UV spectra in the wavelength region of 168–330 nm has been established for the first time.

Tables 1 and **2** present the development of GC–UV in terms of the spectrophotometric and chromatographic conditions and specifications found in the literature. The various subjects discussed in these works are, for example, the influence of temperature on the noise level and the signal-to-noise ratios at various wavelengths. A number of examples of analysis, applications and determinations of isomers have been published. No review articles or monographs have yet been written about GC–UV. However, there is a thesis, mainly dealing with this subject and its development until 1992, and a popular science article was published in 1996 (see Further Reading).

Gas-phase UV Spectrophotometry

The spectral region of the UV electromagnetic absorption of interest to the analytical chemists extends from about 160 to 330 nm. Molecules in which all valence shell electrons are involved in single bonds, such as the straight chain saturated hydrocarbons, show absorption maxima in the region of 160–170 nm. Their spectra are observed only as 'end absorptions' because of instrumental limitations. The other groups of nonaromatic hydrocarbons are bathochromic-shifted and possess their absorption edges in the range of 190–200 nm. This is one aspect of the importance of measuring the absorption of the UV light in the gas phase because there is no solvent wavelength cutoff at 190–200 nm. The other important aspect is that the spectra are not influenced by solvent effects and therefore well defined. There are also no shifts in λ_{max} values and the bands are sharp in comparison with the relatively broad bands observed in the liquid phase, where their shapes depend on the degree of interaction between solvent and solute. Furthermore, in liquids, it is only very rarely that separation of vibrational bands is possible because the solvent effect generally tends to obscure the vibrational structure. By measurements in the vapour phase, these drawbacks are eliminated, which makes the UV spectra in the gas phase highly suitable for computer-based identifications of unknowns against a spectrum reference library. An example of the reproducibility of spectral details is shown in **Figure 1**, where a spectrum, taken from an analysis of cigarette smoke, is normalized and overlaid on the reference spectrum of isoprene. The absorbance spectra as well as the first derivatives are plotted. Derivatives of absorption spectra are preferably used in order to enhance spectral details. Derivatives of spectra can also be utilized in order to make selective determination of specific functional groups.

A study of molecular UV absorption spectra between 168–330 nm in the gas phase, for about 1000 organic compounds has demonstrated the importance of the short UV wavelengths for analytical purposes. About 70% of the 1000 spectra registered have absorption maxima at wavelengths shorter than 190 nm and their intensities are up to 100 times higher than those of the absorption bands at longer wavelengths. In addition to the high sensitivity of detection, the lower wavelength region is the spectral range, where the amount of details used for identification purposes increases considerably. Moreover, most of the functional groups in compounds not considered UV-absorbing, such as alkanes, ethers, aldehydes and ketones, display detailed spectra in this region.

The influence of temperature on the shape of spectra has been studied in the range of 15–205°C. A slight broadening effect on spectral absorption bands (0.3 nm) and the vibrational structure (maximally 1.4 nm) with increased temperature was observed. These effects are however, considered to have

Table 1 The development of GC–UV: instrumental conditions

Author (year)	*Instrument principle*	*Separation column*	*Separation conditions*	*Flow cell configuration*
Kaye (1962)	Beckman DK-2, modified and N_2-purged	1.8 m, i.d. 3.2 mm, packed column	Injection volume: 30 μL Flow (He): 189 mL min^{-1}	Path length: 1, 5, 10 cm Volume: 1.5–3 mL
Kaye (1964)	Beckman DU, modified and N_2-purged	1.8 m, i.d. 3.2 mm, packed column	Injection volume: 30 μL Flow (He): 123 mL min^{-1}	Path length: 1 cm Volume: 1.5 mL
Novotny (1980)	Perkin-Elmer GC-55 variable wavelength monitor	30 m, i.d. 0.7 mm, UCON 50 HB2000, capillary column	Injection volume: 0.1 μL	Path length: 1.12 cm Volume: 50 μL
Adams (1984)	Tracor Model 970 in a remote configuration. 240 nm and 260 nm bandpass filters	2 m, i.d. 2 mm, packed column 3% OV101 on 100/120, Supelcoport	Injection volume: 5 μL Flow (N_2): 30 mL min^{-1} 150°C, 2 min; 10°C min^{-1}, 250°C	Path length: 1.6 cm Volume: 200 μL
Lagesson (1984)	Varian Cary UV-Vis spectrophotometer	8 cm, i.d. 1.5 mm, packed column (10 μm particles), DDP, OV101	Injection volume: 1 μL Flow (N_2): 10 mL min^{-1} ~ 90°C	Path length: 9.5 cm Volume: 170 μL
Kube (1985)	HP 8450A, photodiode array	1.8 m, i.d. 6 mm, packed column 5% SP-1200, 1.75%, Bentone-34	Injection volume: 0.2–0.5 μL Flow (He): 60 mL min^{-1}	Path length: 12.5 cm Volume: 22 mL
Lagesson (1989)	HP 8452A, photodiode array, 324 diodes	8 cm, i.d. 1.5 mm, packed column (10 μm particles), DCQF1	Injection volume: 1 μL Flow (N_2): 15 mL min^{-1} start 70°C, ramp 15°C min^{-1}	Path length: 9.5 cm Volume: 170 μL
Bornhop (1991)	Rapid-scanning LC detector, Linear Instruments	30 m i.d. 0.53 mm, 1.0 μm, B-210, capillary column	Flow (He): 5 mL min^{-1}	Path length: 1.2 cm Volume: 85 μL
Bornhop (1992)	Rapid-scanning LC detector, Linear Instruments	25 m i.d. 0.32 mm, 0.4 μm, SE-52, capillary column	Injection volume: 0.5 μL, 1 : 100 Flow (He)	Path length: 1.2 cm Volume: 85 μL
Hackett (1995)	Remote detection using fibreoptics 206HR detector, Linear Instruments	30 m, i.d. 0.32 mm, 0.25 μm, DB5, capillary column	Injection volume: 1 μL splitless Flow (He): 30 cm s^{-1}	Path length: 1.2 cm Volume: 85 μL
Sanz-Vicente (1996)	HP 8451, photodiode array	4 m, i.d. 1/8 in, packed column, 5% SE-30, Chromosorb W HP	Injection volume: 30 μL	Path length: 1 cm Volume: 70 μL
Sanz-Vicente (1998)	HP 8451, photodiode array	4 m, i.d. 1/8 in, packed column, 5% SE-30, Chromosorb W HP	Injection volume: 50 μL	Path length: 1 cm Volume: 70 μL
Lagesson-Andrasko (1998)	INSCAN 175 GC-UV spectrophotometer, photodiode array, 1024 diodes, N_2-purged	8 cm, i.d. 1.5 mm, packed column	Injection volume: 1 μL Flow (N_2): 15 mL min^{-1}	Path length: 9.4 cm Volume: 170 μL
Lagesson (2000)	INSCAN 175 GC-UV spectrophotometer, photodiode array, 1024 diodes, N_2-purged	30 m, i.d. 0.32 mm, 0.25 μm, Hp-5, capillary column	Injection volume: 1 μL Flow (N_2): 3 mL min^{-1}, make-up flow 7 mL min^{-1}	Path length: 9.4 cm Volume: 170 μL

References:
Kaye W (1962) *Analytical Chemistry* 34: 287–293.
Kaye W and Waska F (1964) *Analytical Chemistry* 36: 2380–2381.
Novotny M, Schwende FJ, Hartigan MJ and Purcell JE (1980) *Analytical Chemistry* 52: 736–740.
Adams KA, Debra L, Van Engelen and Thomas LC (1984) *Journal of Chromatography* 303: 341–349.
Lagesson V, Lagesson-Andrasko L (1984) *Analyst* 109: 867–870.
Kube M, Tierney M and Lubman DM (1985) *Analytica Chimica Acta* 171: 375–379.
Lagesson V (1989) *Analytical Chemistry* 61: 1249–1252.
Bornhop DJ and Wangsgaard JG (1991) *Journal of High Resolution Chromatography* 14: 344–347.
Bornhop DJ, Holousek L, Hackett M and Wang H (1992) *G.C., Rev. Sci. Instrum.* 63: 191–201.
Hackett M, Wang H, Miller GC and Bornhop DJ (1995) *Journal of Chromatography A* 695: 243–257.
Sanz-Vicente I, Cabredo S, Sanz-Vicente F and Galban J (1996) *Chromatographia* 42: 435–440.
Sanz-Vicente I, Cabredo S and Galban J (1998) *Chromatographia* 48: 542–547.
Lagesson-Andrasko L, Lagesson V and Andrasko J (1998) *Analytical Chemistry* 70: 819–826.
Lagesson V, Lagesson-Andrasko L, Andrasko J and Baco F (2000) *Journal of Chromatography A* 867: 187–206.

Table 2 The development of GC–UV: instrumental specifications

Author (year)	*λ range (nm)*	*Bandwidth (nm)*	*Noise level*	*Detection limits*	*Data collection and handling*
Kaye (1962)	165–220		3×10^{-4} AU	10 ng naphthalene	Strip chart recorder
Kaye (1964)	160–210	0.08	3×10^{-4} AU	10 ng naphthalene	Sanborn Model 60-1300 dual-channel high speed recorder; scanning speed: 6 s
Novotny (1980)	Recordings at wavelengths: 205, 210, 220, 260 and 280			0.3 ng naphthalene	Strip chart recorder
Adams (1984)	Recordings at wavelengths: 240 and 260	~ 20	1.6×10^{-4} AU	43 ng naphthalene 8–94 ng polycyclic aromatics	Digital integrator
Lagesson (1984)	Single wavelength recordings Spectral scanning after carrier gas stop	0.25–3.5	5×10^{-4} AU	0.5 ng carbon disulfide	Strip chart recorder
Kube (1985)	226–350	2	2×10^{-4} AU	530 ng benzene	Printer
Lagesson (1989)	190–510	2	2×10^{-4} AU	80 pg mesitylene	PC data handling
Bornhop (1991)	195–360	5	2×10^{-5} AU		IBM model 50
Bornhop (1992)	192–360	5	2×10^{-5} AU	0.2 ng coumarin	IBM model 50
Hackett (1995)	192–360	2	2×10^{-5} AU	90 pg naphthalene	IBM model PS2 55 SX, 206 software, Linear Instruments
Sanz-Vicente (1996)	190–300	2	3×10^{-4} AU	15 ng mesitylene	Integration time: 0.5 s Data handling by means of a program in BASIC
Sanz-Vicente (1998)	190–250	2	3×10^{-4} AU	40 ng phenol	Integration time: 0.5 s Data interpretation by means of a program in BASIC
Lagesson-Andrasko (1998)	168–330	0.7 and 1.7	4×10^{-5} AU		Data collection: Instaspec II, Oriel Corp Data handling: Grams/386, Galactic Industries
Lagesson (2000)	168–330	1.7	4×10^{-5} AU	0.5–3 pg naphthalene	Data collection: Instaspec II, Oriel Corp Data handling: Grams/386, Galactic Industries

References: As shown in Table 1.

negligible influence on spectral searching for unknowns, especially if the reference spectrum and the unknown spectrum are registered at similar temperatures.

Instrumentation

The various parts of a GC–UV instrumental set-up are shown in **Figure 2**. This particular equipment consists of a remote configuration between the gas flow cell and a commercially available UV spectrophotometer (LC detector). For this arrangement fibre-optics were utilized.

The only commercial instrument, the GC–UV INSCAN 175 spectrophotometer, contains a purge gas flow system, which takes up the concept from Keye, in order to prevent oxygen and water vapour from entering the UV light path of the instrument. Nitrogen gas has a negligible absorption at wavelengths longer than 140 nm. Therefore dry and pure nitrogen can be used as the purge gas, which permits recordings at wavelengths shorter than 190 nm, which is the limit if air is present in the optical path. The lowest limit of the spectral scale (168 nm) is dependent on the quartz optics and the diode array. The additional available wavelength range of 168–190 nm is of considerable importance for the performance characteristics of the instrument. It places the GC–UV into a general method of analysis because all organic compounds and most of the inorganic gaseous molecules give rise to detailed spectra of high intensities in this range.

Light Pipes

From Table 1 it can be seen that the geometry of the gas flow cells used differs considerably, with path

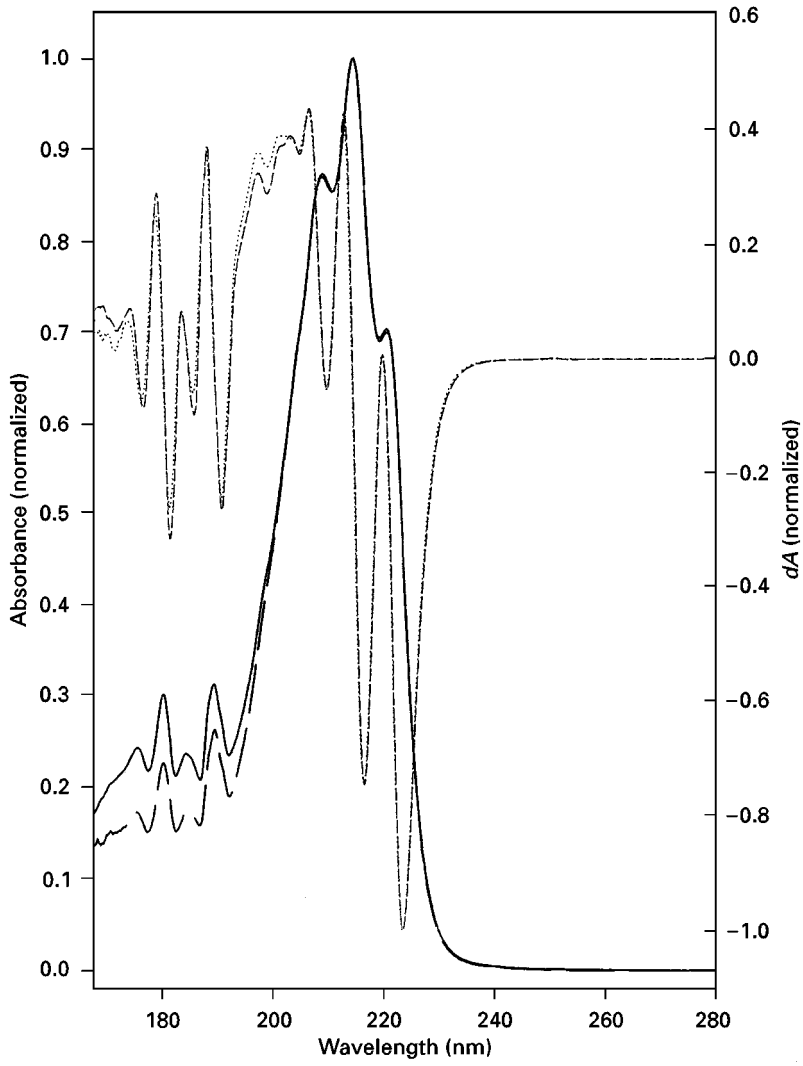

Figure 1 The reference spectrum for isoprene and a spectrum recorded at the analysis of 200 μL cigarette smoke. Both absorption spectra are normalized and overlaid together with their first derivatives. ——, Unknown absorbance; – –, reference absorbance; ----, unknown *dA*; . . . . , reference *dA*.

lengths varying from 1 cm up to 12.5 cm and volumes ranging from 70 μL up to 22 mL. Optimization of the gas flow cell involves keeping a low volume for a good chromatographic resolution. At the same time, the path length and the light throughput should be maximized. These optimization factors are the same as for GC–FTIR, where an internally gold-coated gas flow cell is used. A total reflection is obtained at the gold-coated walls, leading to a high light throughput in gas flow cells about 10 cm long and with an internal diameter usually ~ 1 mm. Because of the use of internal reflection, these gas flow cells are called light pipes. For GC–UV it was realized, at an early stage, that an internal coating was not necessary and an ordinary glass tubing gave a high light throughput due to a total reflection of UV light on the internal glass walls.

A useful rule is that the optimum performance of a GC–UV system in terms of signal-to-noise and band dispersion is obtained from a light pipe with an effective volume equivalent to the volume of a 'typical' GC peak, described by the peak width at half the maximum amplitude. Typical light pipe volumes currently employed for GC–FTIR vary from 50 to 200 μL and these figures should also be valid for GC–UV light pipes.

Figure 3 shows a light pipe configuration that consists of a gas flow cell with a built in micro gas chromatograph together with the light pipe. In addition to the use of this internal micro GC, the cell can easily be linked to an external capillary GC by means of a heated transfer line, as shown in the figure. The 10 cm long gas chromatographic column, which can also be directly connected to a one-stage thermal

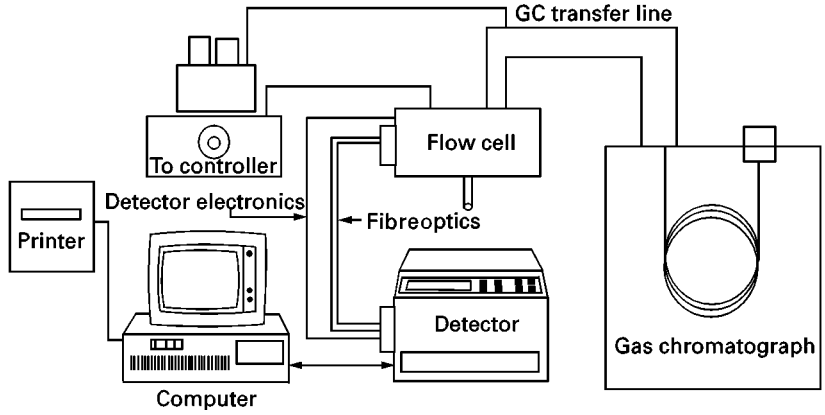

Figure 2 Block diagram for a GC-UV system. Reproduced from (1992) Capillary gas chromatography. *Rev. Sci. Instrum.* 63(1): 192.

desorption unit or to a gas loop injector, is preferably used for fast separations of gaseous and relatively volatile molecules.

Spectrophotometric Detection and Recording

Earlier work involved measurements at a single wavelength while recent spectrophotometric detection involves full spectral scans covering the whole chromatographic retention time scale. The results are obtained in three dimensions – wavelength, absorbance and retention time. Such a result is shown in **Figure 4**, where the wavelength scale follows the *x*-axis, the absorbance values the *y*-axis and the retention time goes along the *z*-axis. This particular sample is cigarette smoke injected by means of a loop injector (200 μL) on the micro gas chromatograph shown in Figure 3. UV spectra of compounds in the cigarette smoke are measured by means of an array of 1024 diodes, which cover a wavelength range from 168 to 330 nm. The spectrometer employed has a band width 1.7 nm or less in order to record the finer spectral details. The diode array detectors usually have a minimum exposure time of 0.02 s. The measuring exposure time must be below a level where a saturation of the diodes occurs. Typically, the exposure time is ~ 0.1 s. A number of these exposure values are measured and their average is calculated. The absorbance values at any retention time are then calculated for every diode representing a wavelength. The number of the exposure values are chosen according to the desirable chromatographic resolution.

Data Acquisition and Handling

A full scan GC–UV analysis generates a considerable amount of data. These data, which are calculated as absorbance values, easily exceed 10^6 measuring points, when capillary column separation with spectral recording every 2 s is employed. However, the use of modern computer technology makes the handling of a large number of measuring values possible. Various calculations and mathematical functions can be applied to the measuring data. Besides the simple functions, interactive subtraction, baseline corrections, various orders of derivatives, rotation (90°), damping functions and cuts at selected wavelengths can be applied.

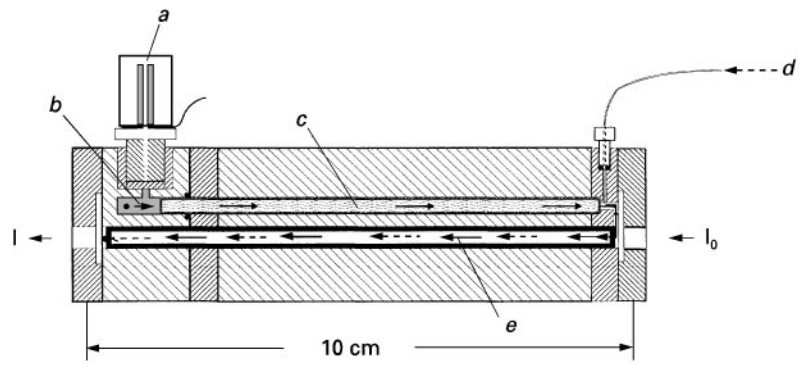

Figure 3 A 10 cm long gas flow cell for GC-UV measurements containing a built-in micro gas chromatograph and a light pipe *a*, Injector; *b*, injector chamber with carrier gas inlet; *c*, separation column; *d*, inlet from external GC; *e*, light pipe.

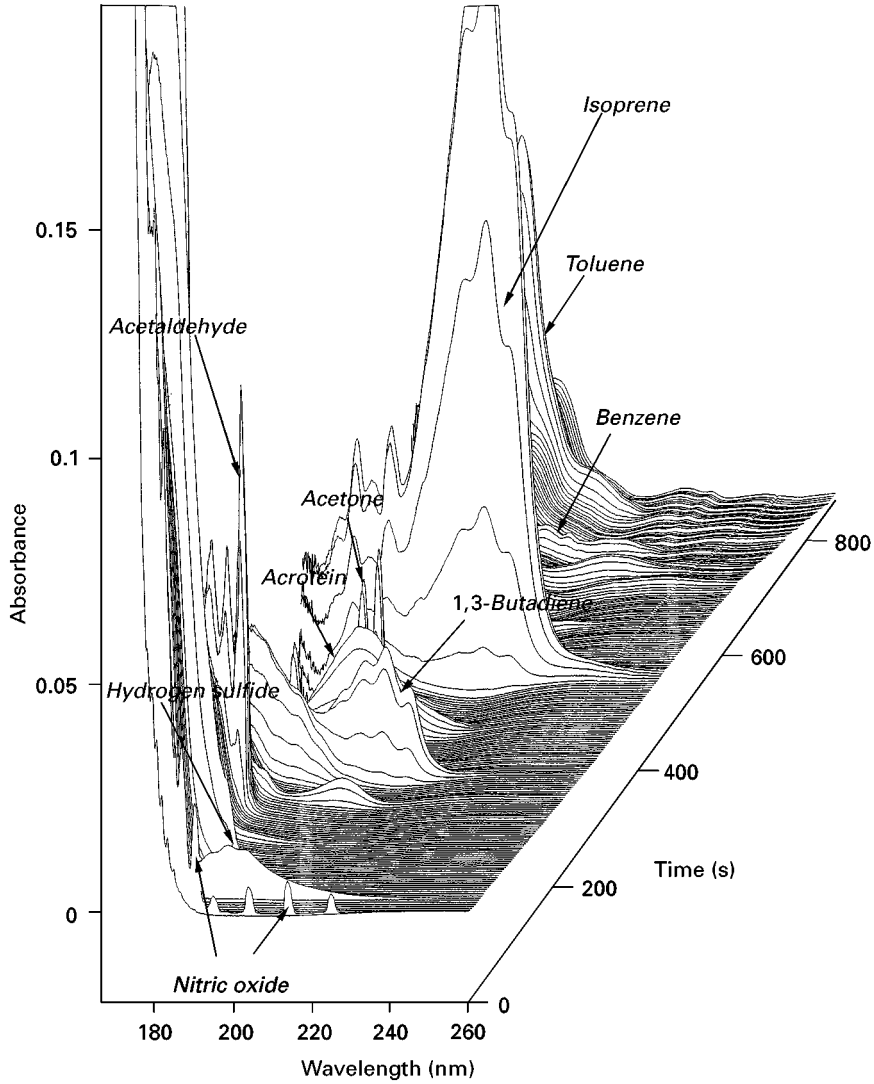

Figure 4 Results of cigarette smoke analysis obtained with the GC-UV method with the micro gas chromatograph, which is especially suitable for analysis of the most volatile compounds in cigarette smoke. The wavelength scale follows the *x*-axis, the absorbances the *y*-axis, and retention time the *z*-axes.

During an analysis the recording follows the axes shown in Figure 4 and, in order to monitor the chromatographic sequence, the data are turned 90° to get the retention time along the *x*-axes. Chromatograms can now be studied at any chosen wavelength, or for the average absorptions within a chosen wavelength region.

The gas-phase UV spectra are well defined and most of them contain a fine structure. In order to enhance the spectral details, derivatives of the absorption spectra are preferably utilized. When forming chromatograms the negative values obtained upon derivation are not convenient to handle and, to avoid this problem, the absolute values of the derivatives can be used. **Figure 5** shows the results from an analysis of a polychlorinated biphenyl (PCB, Arochlor 1248) sample. The presentation mode of the measured values is the same as for Figure 4, but the second derivatives with absolute values of the recorded absorption spectra are drawn for the retention times between 800 and 1600 s. The spectral details of the congeners and isomers concerning this group of related compounds appear quite clearly. Various types of graphical views can be carried out in order to suit certain presentations of results. One example of such a view is a contour plot, which is an effective way to treat the results. In **Figure 6** a contour plot is created from the analysis of a petroleum product. The advantage of these type of presentations is that compounds with close retention times appear as nonsymmetrical contour lines, which makes it possible to 'see' the hidden peaks. Another advantage is that

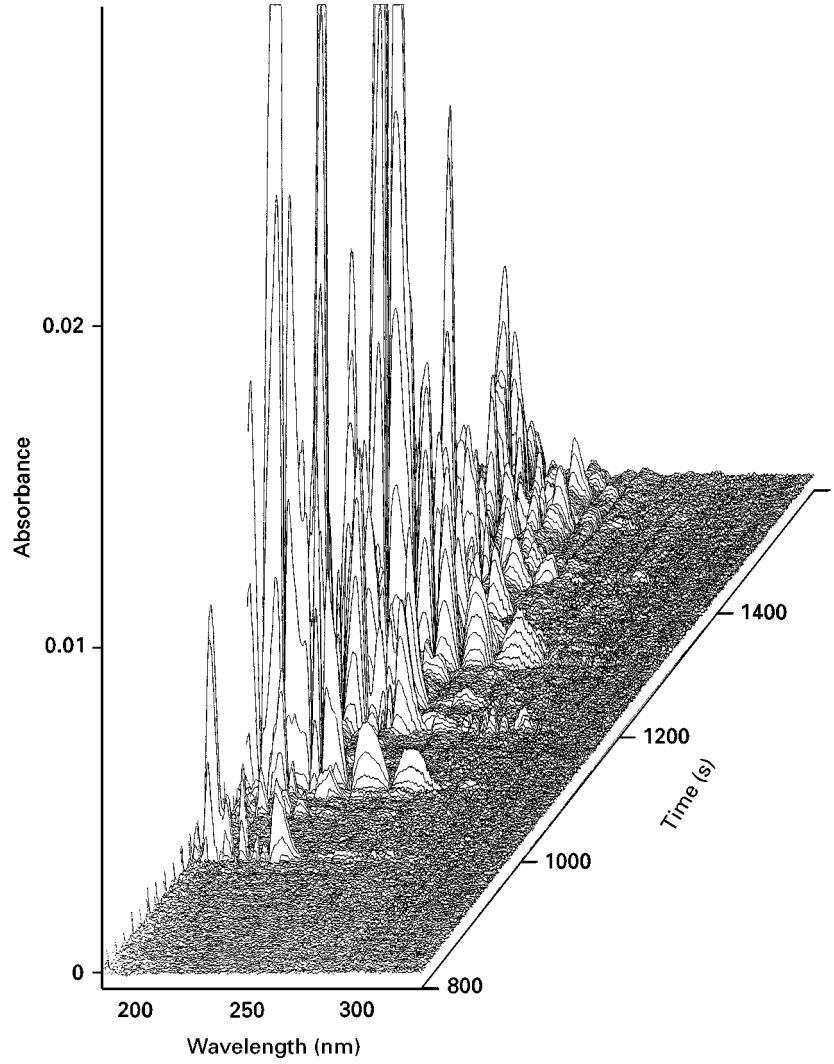

Figure 5 The result from a retention time of 800 s up to 1600 s is shown in a three-dimensional plot of the absolute values of second derivatives of absorption spectra collected at the analysis of a PCB sample.

compounds possessing the same functional group can often be directly shown.

Accuracy and Precision

To describe a position in the absorption spectrum the wavelength is used as the locating unit. This puts a high demand on the spectrophotometric measurements, especially accuracy, precision and reproducibility, of the wavelength. The weekly calibration of the wavelength scale of GC–UV INSCAN 175 spectrophotometer, using the spectral lines from a mercury–argon pen lamp, always gave the same wavelength values of the spectral lines measured in the region of 168–330 nm. The 1024 element photodiode array covers the scale from 166.7 to 330.0 nm. This gives a value of 0.16 nm per diode, which is to be considered as an ultimate limit of resolution. The reproducibility was measured for different bands of 1-hexene (λ_{max} 178.7 nm), 1-hexadecene (λ_{max} 177.9 nm) and 1-iodopropane (the band at λ: 177.6 nm, at λ_{max}: 182.7 nm and the band at λ: 199.4 nm) for 1 year. The standard deviation values were in the range of 0.05–0.15 nm, i.e. all were lower than the distance between two diodes (0.16 nm).

Sensitivity and Detection Limits

The discrepancy in sensitivity of the GC–UV method, given by detection limits in Table 2, can primarily be derived from the differences in the geometry of the gas flow cell and from the separation columns (packed or capillary) used.

In comparison with the infrared wavelength region, the absorptivities are up to 1000 times higher in the UV wavelength region. Also, the fact that the noise level could be kept equal to or lower than for FTIR detectors ought to imply a considerably more favourable signal-to-noise ratio. The specification concerning the noise level, along the time scale, given

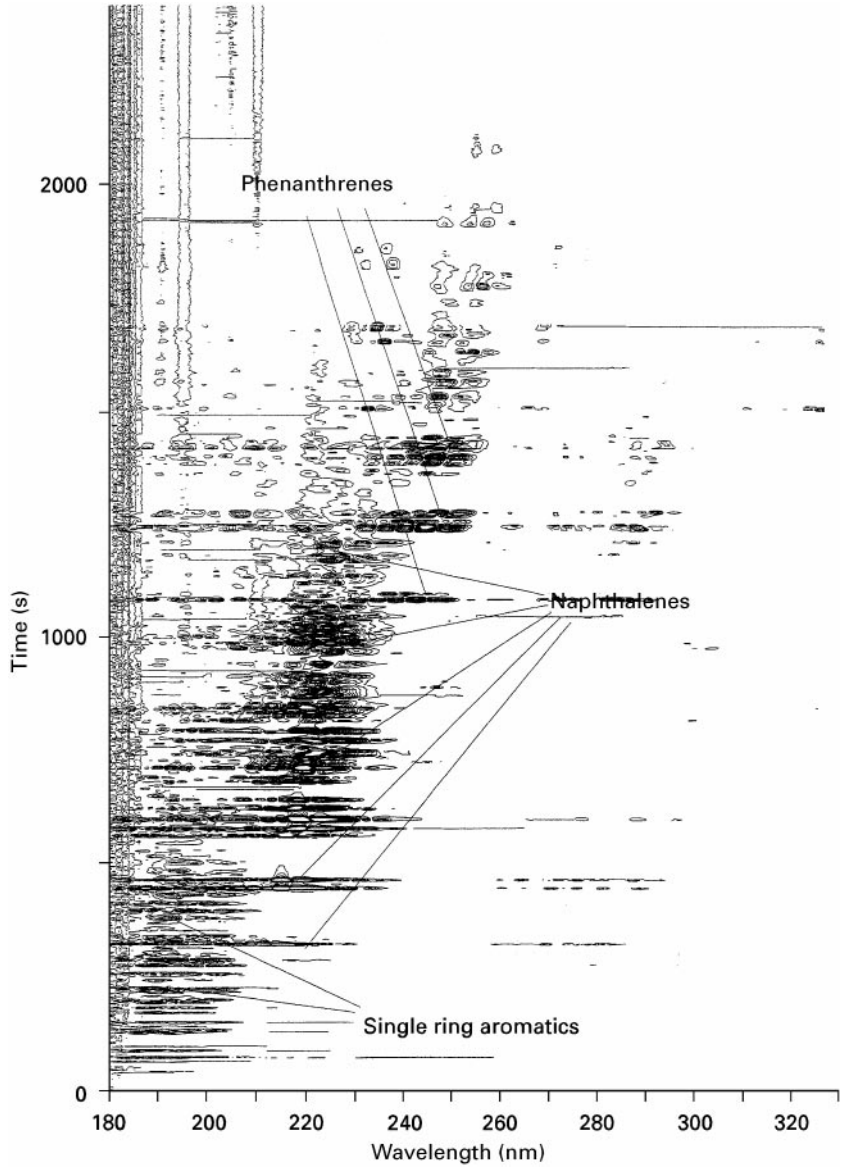

Figure 6 A contour plot showing the result obtained at the analysis of a petroleum product: the second derivatives are plotted and, as indicated, the single, double and polyaromatic compounds appear clearly.

for the GC–UV Inscan 175 spectrophotometer, is about 0.5×10^{-4} peak to peak.

For a detection limit defined as the amount giving rise to an absorption of 1.5×10^{-4} AU, and expressed as the minimum amount of the compound per second that could be detected, the following values were calculated: perchloroethylene 55 pg s^{-1}, naphthalene 3.3 pg s^{-1}, mesitylene 8.9 pg s^{-1}, carbon disulfide 4.8 pg s^{-1}, acetone 49 pg s^{-1} and benzene 5.4 pg s^{-1}.

The noise level can be lowered by smoothing and by taking the average absorption values within a wavelength range. However, it has been shown that this noise reduction is most effectively obtained using average derivatives values. The derivatives are in these cases differentials with a rather large gap value (2–6 nm) along the wavelength scale. The noise level obtained, using this mode, was $\sim 1 \times 10^{-5}$ AU peak to peak, which gives a calculated detection limit for naphthalene of ~ 0.5 pg s^{-1}.

The limit of quantification (MIQ: minimum identification quantity) is usually defined as the lowest quantity when the hit rate of the unknown is still found among the first five proposals. This depends on the size of the spectrum library and, at this stage, the available reference spectrum library is probably not large enough to make any closer estimations. However, clear identifications can be made in the mid pg range, provided that the compound possesses a functional group with relatively high absorptivity values (e.g. aromatics). For the GC–UV method the

introduction of an additional sensitivity level, namely a minimum of classification quantity (MCQ), appears to be desirable. The suggestion is to define MCQ as the minimum quantity necessary for giving the right functional group at the first library search proposal.

Qualitative Analysis

The identification of an unknown is commonly carried out by comparison with a library of reference gas-phase spectra. The absorption process of an atom or a molecule in the gas phase is free from any influence, which reproduces not only the unique character of the electronic transitions, but also of the accompanying simultaneous changes in the vibrational states. This gives rise to spectral shapes which are strictly defined and, in most cases, accompanied by fine structures. Therefore the UV spectra are well suited for identification by means of a computer-based spectral search against a reference spectrum library. A spectrum library of ~ 1000 gas-phase UV spectra recorded in the wavelength region of 168–330 nm has been established. A commercially available IR search program has been used with success for identification. Because of the relatively small size of this library, the identification possibilities are limited. Nevertheless, identification of classes of compounds can most often be directly pointed out. The compounds containing the same functional group show a number of characteristic similarities, but at the same time clear differences between individuals within a group are observed. The exceptions are cases when various straight alkyl chains are involved. The spectra of acetophenone and propiophenone, for example, are hard to distinguish from each other.

Determination of Specific Functional Groups

The reference spectrum library mentioned above has made it possible to identify ~ 50 functional groups due to their characteristic spectral appearances. These characteristics allow the assignment of a specific functional group in a compound without access to any reference spectrum. The specific functional groups can, for example, be exposed in a contour plot shown in Figure 6, where the measuring data (second derivatives) for single, double and polyaromatic compounds are outlined quite clearly. Specific chromatograms can be obtained for these aromatic groups by taking the average absorption in appropriate wavelength ranges.

Another example of specific detection is shown in **Figure 7**, where 6 mg of a dust sample was analysed by means of GC–MS and GC–UV. In both cases the analysis involved a thermal desorption before the gas chromatographic separation and in both cases the same type of capillary column and the same temperature programme were used. Figure 7A shows the chromatogram from the GC–MS total ion signal and Figure 7B–D shows the GC–UV chromatograms obtained at the wavelength ranges indicated. The chromatograms were calculated using the absolute values of the first derivatives of absorption spectra. Identifications were carried out by means of GC–MS for the peaks indicated 1–5 with following results: (1) hexanal; (2) heptanal; (3) octanal, (4) nonanal and (5) decanal. The nonaromatic straight chain aldehyde group has a characteristic sharp UV absorption edge at 187 nm. Therefore a specific detection of nonaromatic straight chain aldehydes can be made in the 187–190 nm wavelength range, as shown in the figure. The next GC–UV trace shows the chromatogram from the average values in the 187–220 nm range. This gives a less specific chromatogram. Naphthalene was identified at the indicated position (6) by means of a search against the gas-phase UV reference spectra library. The same library was used for the identifications of benzaldehyde at position (7) and 2-furaldehyde at position (8). The spectrum of 2-furaldehyde has a dominating absorption profile between 230 and 270 nm and, consequently, it only appears in the 238–244 nm wavelength trace.

The experiences of combining results from GC–MS and GC–UV have recently been explored and there are indications of valuable possibilities. The characteristic complementary qualities for GC–UV compared to GC–MS allow specific determinations – determinations of specific functional groups and also of structural isomers, which are difficult to distinguish by means of MS.

Isomers

There are numerous examples of structural isomers in chemistry and isomers of a certain compound have different physical and chemical as well as physiological properties. Thus, for example in the field of toxicology, some isomers possess toxicity which differ by several orders of magnitude.

Ninety-five groups of various isomeric compounds have been investigated and in all cases the GC–UV method was able to distinguish clearly between structural isomers. However, when the analysis involves various straight or branched alkyl chains the identification is complicated. For difficult identifications like these derivative functions can be applied in order to enhance differences in spectral details and thus distinguish between isomers not resolved by comparing the absorbance spectra alone. Some groups, like nonaromatic halogenated hydrocarbons and nonaromatic alcohols, show minimal differences. Nevertheless, they are still distinguishable and the first derivatives of their spectral curves give clear shifts of ~ 2–3 nm in the absorption maxima and minima.

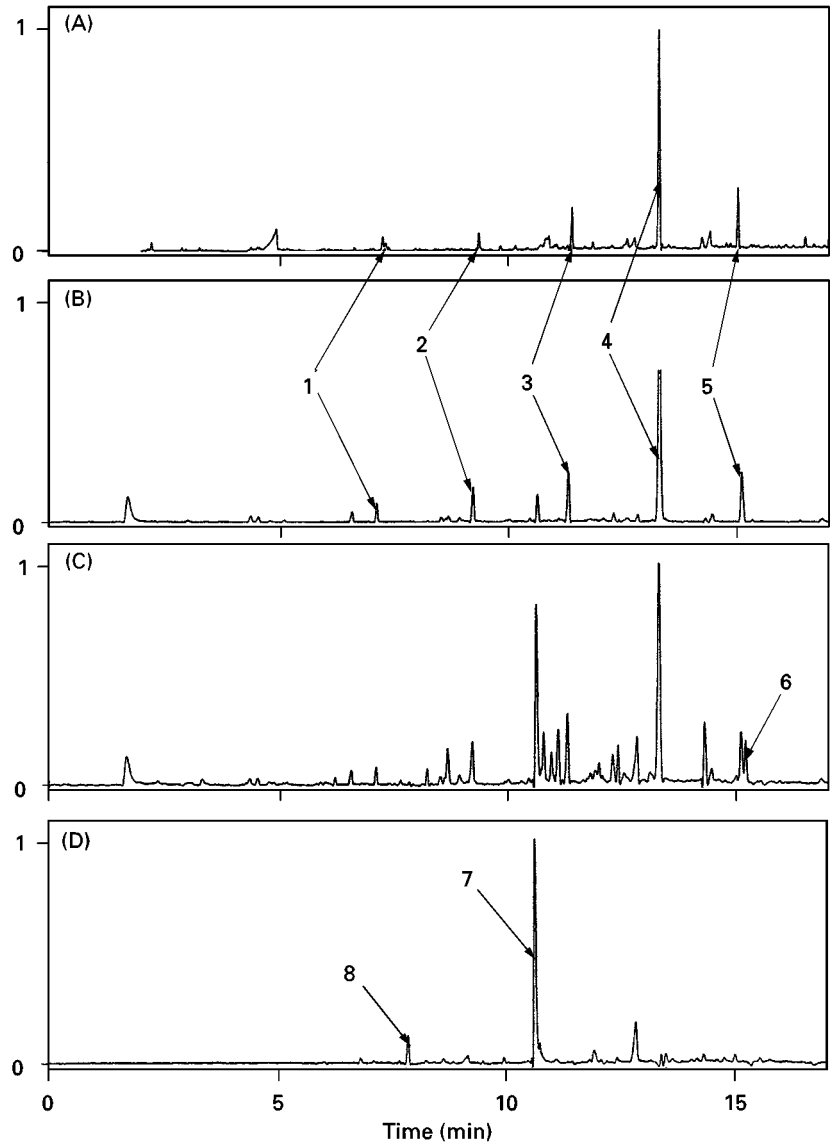

Figure 7 Four chromatograms after the analysis of a dust sample. (A) The upper trace shows the total ion current (TIC) obtained from the analysis of 10 mg dust by means of GC-MS linked to the thermal desorption unit. The next three traces show the chromatograms based on first derivatives for (B) 187–190 nm, (C) 187–220 nm and (D) 238–244 nm wavelength ranges from the analysis of 6 mg dust by means of GC-UV. The peaks indicated 1–5 were identified using GC-MS and the peaks indicated by 6–8 by GC-UV. The identification results are given in the text.

Quantitative Analysis

A linearity of detector response over a range of $\sim 10^4$ for aromatic hydrocarbons in the vapour phase has been reported. Similar linear responses were observed for more polar aromatic compounds (coumarin and phenols) and no deviations from Lambert–Beer's law were found in the range of the mass loading limits imposed by the capillary column employed. Also the linearity for nitric oxide standards has been studied in the range of 10–1800 ng at the wavelength of 213.5 nm. The standards were prepared from a standard gas tube containing 99% nitric oxide. Standard concentrations in nitrogen were prepared from the tube using Tedlar bags and gas-tight syringes. The standard curves were linear in the range studied.

Studies of day-to-day variation and repeatability have been carried out at a temperature of 110°C using a GC–UV Inscan 175 spectrophotometer linked to a dynamic dilution system for the standard concentrations and a 200 μL loop injection. The compounds determined were methanethiol and diethyl sulfide. The within-day relative standard deviations (RSD) were 2.3% ($n = 7$) for diethyl sulfide at a concentration of 82 p.p.m. and 3.0% ($n = 7$) for methanethiol at 79 p.p.m. The between-days deviations were measured for 3 months ($n = 36$). The RSD values were

determined for the slope of the standard curves, with concentrations between 80 and 2000 p.p.m.

These between-days RSD values were 4.0% for diethyl sulfide, and 5.0% for methanethiol. These results include the errors arising from the dynamic dilution system used. In this case a photo diode array type detector was employed, which has the advantage of having a low wavelength drift.

Applications

GC–UV is a general method of analysis with numerous possible application areas. So far, the method has been little used and most investigations have been concerned with the fundamentals of the analytical principle. Nevertheless, a number of works have been published, for example the determinations of nitric oxide adsorbed on mineral fibres and isoprene and acetone determinations in exhaled breath. A method, using GC–UV for the determination of alcohols, denoted as GC–GPMAS (gas chromatography with gas-phase molecular absorption spectrometry) has been reported. These are short reports concerning determinations of single, double and polyaromatics in petroleum products, volatile compounds at low concentrations in air, irritants adsorbed on dust particles, determinations of compounds present in cigarette smoke, identifications of compounds in flavour samples, analysis of methanethiol, diethyl sulfide and hydrogen sulfide in paper industry, and identifications of congenes and isomers of polychlorinated biphenyls (PCBs) and polychlorinated naphthalenes (PCNs).

Future Developments

UV absorption spectra are basically electronic spectra which arise from transitions between electronic states and are accompanied by simultaneous changes in the vibrational and rotational states. Thus, an absorption spectrum is a function of the whole structure of a molecule and an expression for its fundamental chemical properties. UV absorption spectra in the gas phase are very well defined and can be denoted as fingerprints of organic as well as inorganic compounds. They have considerably higher absorptivities than their counterparts in the infrared wavelength region and are very well suited for computer-based spectral search systems. The size of reference spectra presently available is much smaller compared with that available for GC–FTIR and particularly for GC–MS. Future development of the GC–UV method will include continuous extension of the reference spectrum library.

One of the main advantages of UV gas-phase spectra might be to make detailed classification of functional groups. At present ~ 50 groups with characteristic features can be identified. However, this will certainly be extended and will also include a number of groups with mixed functionalities.

Concerning further instrumental development, recordings of spectra at lower wavelengths than 168 nm will probably be possible. Another instrumental development that can be expected is matrix isolation and direct deposition techniques similar to the ones developed for GC–FTIR measurements. Furthermore, the GC–UV spectrophotometer will, in the near future, be adapted to online measurements in industrial process monitoring and control.

See also: **II/Chromatography: Gas:** Derivatization; Detectors: Mass Spectrometry; Detectors: Selective; Gas Chromatography-Infrared.

Further Reading

Brown RA and Pearl TD (1979) Chapter 15. In: Altgelt KH and Gouw H (eds) *Chromatography in Petroleum Analysis*. New York: Marcel Dekker.

Lagesson V (1992) *Micro Gas Chromatographic Separation combined 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, Department of Analytical and Marine Chemistry and Department of Occupational Medicine, Göteborg, 1992.

Lagesson V and Lagesson-Andrasko L (1996) *Reaching New Peaks*. Analysis Europa.

Gas–Solid Gas Chromatography

J. de Zeeuw, Varian-Chrompack, Middelburg, The Netherlands

Introduction

Gas–solid chromatography (GSC) has been used since the earliest days of gas chromatography and preceded gas–liquid chromatography. Through this early work the limitations of GSC were well recognized and, although the advantages of GSC were also apparent, it was quite some time before reliable and reproducible GSC columns became commercially available. There are many methods in the literature describing the application of GSC to specific analyses, for example the UK Institute of Petroleum method