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Identification of compounds and specific functional groups in the wavelength region 168–330 nm using gas chromatography with UV detection

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Abstract

A GC–UV instrumental set up with two different GC units has been used for determination of specific functional groups and compounds in complex mixtures. Separations have been made using a micro gas chromatograph built into a gas flow cell and by means of an external capillary gas chromatograph linked to the same gas flow cell. Four various applications (cigarette smoke, petroleum, dust, flavour) have been performed in order to demonstrate the potential of the GC–UV method. Gas phase UV spectra have been recorded in the region of 168–330 nm. Based on a gas phase spectrum reference library the identification of unknowns as well as the determination of specific functional groups have been achieved. A table showing the spectral shapes and positions of the absorption bands for 50 specific functional groups is presented. The advantage of using derivative spectra in order to amplify spectral details and improve selectivity is discussed. Regarding sensitivity, it has been found that identifications can be made in the mid-pg range and limit of detection for naphthalenes are at a level of 0.5–3 pg/s.

Keywords: UV detection; Detection, GC; Cigarette smoke; Flavours; Dust; Petroleum; Sensitivity

1. Introduction

Gas chromatography with ultraviolet detection (GC–UV) came to the attention of analysts in the early 1960s [1–3]. However, at that time the handling of large numbers of full scan data was limited. Interest at that time was more focused on GC–mass spectrometry (MS) and later on GC–Fourier transform (FT) IR. It was not until the early 1980s that the principle was rediscovered [4–8]. However, the detection was mostly made at single wavelength settings. Using a micro gas chromatograph built into a gas flow cell, single-wavelength monitoring was used for some applications [9,10]. The separation technique [11], used for these separations, is also for one of the applications used in the present investigations. From the mid-1980s until today an increasing interest in full scan GC–UV [12–20] can be observed. The subjects discussed in these works are the influence of temperature on the noise level and the signal-to-noise ratios at various wavelengths. The instrumental techniques described were based solely on commercially available spectrophotometers and were working in either direct or remote configura-

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tion. Due to the use of conventional spectrophotometric set up there were no possibilities to measure at wavelengths below 190 nm. Examples of analysis shown concerned mainly determinations of aromatics, but also the determination of alcohols after derivatization to benzoates was demonstrated. Another subject of interest was the determination of isomers [12,13] of trimethylbenzenes and dichlorobenzenes.

A spectral library of ~1000 gas phase UV spectra as a basis for identification of compounds and determination of specific functional groups has been established for the first time [20]. The wavelength region recorded was 168–330 nm. This work also included investigations concerning the influence of temperature on shape and position of spectral curves. The target compounds chosen were 2,5-dimethylfuran and 1-iodobutane. The spectrum for 2,5-dimethylfuran was interpreted as electronic transitions accompanied by vibrational excitation while the distinct absorption bands of 1-iodobutane were interpreted as $n \rightarrow \sigma^*$ transitions. Normalised first derivative spectra of these compounds were recorded in the range 15 to 205°C with steps of 15 and 20°C. A slight broadening effect with increasing temperature was observed in both cases and slight wavelength shifts were noticed for some spectral details for 2,5-dimethylfuran. However, it was concluded that if the temperature difference at the recording of the unknown and the corresponding reference spectrum does not exceed 100°C the possibilities for identifications will not be limited. Studies were also carried out concerning the spectral appearances of isomers of propanol, dimethoxybenzaldehyde and dimethylphenol. To distinguish between structural isomers is regarded to be of great importance in view of the supplementary information that is gained in comparison with GC–MS.

Applications have been reported [21–23] where the instrumental GC–UV set up was similar to the arrangement presented here and combined with a direct one-stage thermal desorption procedure. These applications concerned determination of volatile compounds and gases in human breath, and nitric oxide adsorbed on mineral fibres.

In this paper, results from four applications are presented. The focus is the identification of compounds and, especially, the determination of specific functional groups. This is based on absorption or the lack of absorption bands, their shapes and positions. Regarding quantitative aspects the sensitivity is discussed. The use of the GC–UV method for quantitative measurements will be treated comprehensively in another paper.

2. Experimental

An Inscan 175 GC–UV spectrophotometer was combined with a HNU Model 321 capillary GC system. Fig. 1 presents the block diagram of this instrumental arrangement. The instrumental parts consisted of (a) gas flow cell with a built-in micro gas chromatograph [6], (b) a heated transfer line, (c) a spectrograph with a focal length of 120 mm with interchangeable gratings and a variable inlet slit linked to a 1024 element photo diode array detector, (d) a deuterium lamp, (e) the capillary column, and (f) a one-stage thermal desorption oven linked to the gas chromatographic separation, alternatively a loop injector. Regarding the gas flow cell the connection can easily be altered between the internal micro gas chromatograph and, through the heated transfer line, to an external GC system. The transfer line between the external GC system and the gas flow cell was arranged in two ways. For 0.25 and 0.32 mm capillary columns these were drawn directly to the connection site on the cell while 0.53 mm capillary columns were linked to a short (about 30 cm) piece of deactivated 0.32 mm capillary column which in turn was linked to the cell. The heated transfer line consisted of a resistance wire leading from inside the GC oven to the point were the capillary enters the gas flow cell. The capillary column is in close contact and in parallel with the wire. The capillary and the wire are kept together in a thermally isolated glass tubing. With this combined arrangement the internal gas flow of the cell is used as a make up flow, if necessary.

The samples (cigarette smoke, flavour, petroleum and dust) were analysed using both the built in micro gas chromatograph with an 8 cm long column, and by means of the external capillary gas chromatograph. Two types of capillary columns and one type of packed micro columns were employed and these together with the separation conditions used for the

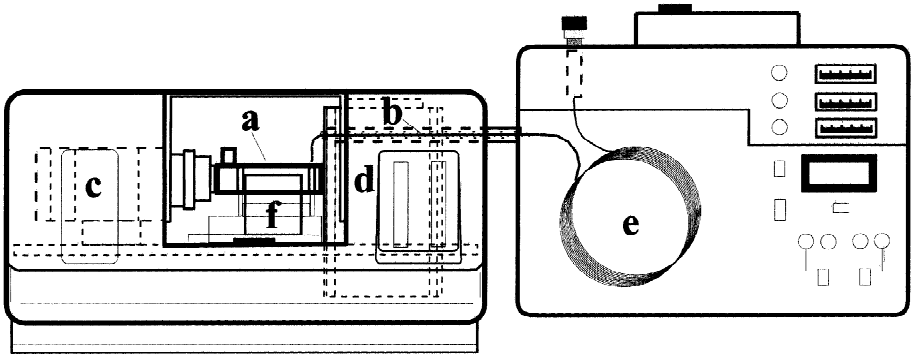


Fig. 1. Block diagram of the GC–UV configuration comprising interfacing with an external GC system: (a) gas flow cell with a built-in micro gas chromatograph, (b) a heated transfer line, (c) a spectrograph with a focal length of 120 mm with interchangeable gratings and a variable inlet slit linked to a 1024 element photo diode array detector, (d) a deuterium lamp, (e) the capillary column, and (f) one-stage thermal desorption oven linked to the gas chromatographic separation, alternatively a loop injector.

present investigations are summarised in Table 1, which also includes the conditions for UV detection.

The GC–UV instrument used is equipped with a simple one-stage thermal desorption unit. The temperature regulation for this unit can be set at constant temperatures up to 210°C. For the analysis of cigarette smoke the desorption oven was replaced by a sample loop injector (Valco) with a loop volume of 200 μl. For the flavour and the petroleum samples the ordinary syringe injections were used. Compounds adsorbed on dust were thermally desorbed and their vapours collected by means of solid-phase microextraction (SPME) on a polydimethylsiloxane (PDMS) fibre (Supelco).

A wavelength range between 168 nm and 330 nm was chosen by means of a micrometer screw in-

Table 1
Operational conditions

Application	Injection	Column	Separation conditions	Detector conditions
(1) Cigarette smoke	Gas loop, 200 μl,, injection temperature: ambient	8 cm, InsPW (10-μm particles of a polystyrene–divinylbenzene material similar to Porapak P type)	Nitrogen carrier: ~10 ml/min, Temperature program: from 40°C, ramp 8°C/min up to 130°C	Exposure time: 0.1 s, cycle time: 4 s BW: 1.7 nm (slitwidth, 0.3 mm), wavelength range: 168–330 nm, light pipe temperature: 40–130°C
(2) Flavour (''after shave'')	0.5 μl, split/splitless injector in splitless mode, injection temperature: 180°C	HP5, 30 m×0.32 mm I.D., 0.25 μm film thickness	Nitrogen carrier: ~3 ml/min; make up flow: ~7 ml/min, temperature program: 50°C, 3 min, 4°C/min to 100°C, 1 min, 5°C/min, 220°C	Exposure time: 0.1 s, cycle time: 2 s, BW: 1.7 nm (slitwidth, 0.3 mm), wavelength range: 168–330 nm; light pipe temperature: 150°C,
(3) Petroleum product dissolved in hexane	0.5 μl, split/splitless injector in splitless mode, injection temperature: 220°C	HP5, 30 m×0.32 mm I.D., 0.25 μm film thickness	Nitrogen carrier: ~3 ml/min; make up flow: ~7 ml/min, temperature program: 70°C, 1 min, 8°C/min to 130°C, 1 min, 5°C/min, 240°C	Exposure time: 0.1 s, cycle time: 2 s, BW: 1.7 nm (slitwidth 0.3 mm), wavelength range: 160–330 nm; light pipe temperature: 180°C
(4) Dust	SPME split/splitless injector in splitless mode 1 min, injection temperature: 250°C	CP-Sil 13 CB, 20 m×0.32 mm I.D., 1.2 μm film thickness	Nitrogen carrier: ~3 ml/min; make up flow: ~7 ml/min, Temperature program: 40°C, 8°C/min up to 130°C	Exposure time: 0.1 s, cycle time:2 s, BW: 1.7 nm (slitwidth, 0.3 mm), wavelength range: 173–330 nm; light pipe temperature: 140°C

fluencing the angle of the 1200 l/mm holographic grating. The slit width was 0.3 mm throughout the investigations which gave the bandwidth of 1.7 nm. An exposure time, integration time and a cycle time for the diodes control the spectral recordings. The exposure time was set to 0.1 s. The cycle times were either 4 s or 2 s depending on the efficiency of the column chosen. The integration times were set to the maximum possible in the cycle times used in order to optimise the signal-to-noise ratio.

The optical system of the GC–UV instrument was flushed with dry nitrogen (99.996%) at a rate of ~1 l/min, in order to prevent light absorption due to water vapour and oxygen. The same gas supply was also used as a carrier gas source. Before entering the instrumental system the nitrogen gas passed through a gas purifier (Molecular Sieve-Drierite, Altech). The light pipe of the gas flow cell had a volume of 170 μl and, in order to keep a good time resolution, the flow-rate through the cell was kept at ~10 ml/min. The capillary column separations required lower flow-rates and in these cases the internal flow of the cell was used as a make up flow. The operation temperature of the cell is controlled by a regulator, which can be temperature programmed. Various temperature programs can be used when the internal micro GC system is employed as well as for the external GC system. Data recordings and interpretations were carried out using a Grams 386 computer program (Galactic Industries) with the three-dimensional and IR search options. In order to enhance spectral details and improve selective determinations, first and second derivatives were in some cases calculated. These derivatives were calculated with the ''gap'' method which is a point difference method by defining the data interval used for calculating the derivatives. The IR search program was used with no modifications. The reference spectra building up the reference library were taken as absorption spectra and the number of data points were reduced from 1024 to 150 and covered the wavelength range from 170 nm up to 330 nm. When loading the reference spectra into the library and when searching an unknown spectrum against the library the spectra are automatically normalised. Generally an least squares algorithm was used for the search. Some data was also handled by a SigmaPlot, version 3.02 computer program (Jandel).

3. Results and discussion

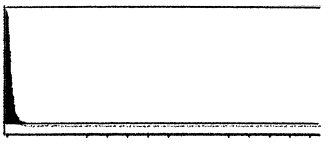
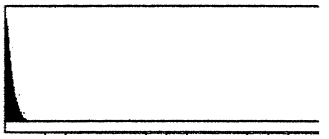
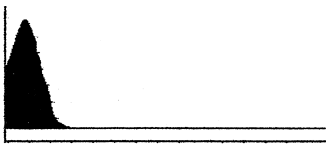
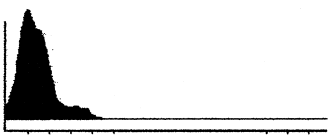
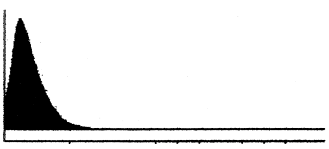
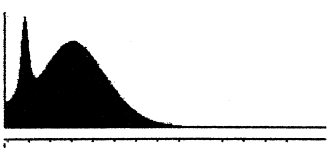
3.1. Characteristic wavelengths and derivatives of spectra

The wavelengths of absorption maxima and the characteristics of absorption regions for 50 specific functional groups are presented in Table 2. It can be seen, that the vast majority of the absorption maxima are at wavelengths shorter than 195 nm, which emphasises the importance of being able to register spectra in the short UV wavelength region. The characteristics of the various functional groups found are based on a number of compounds measured for each group (minimum 3). The table also demonstrates the individual shape and position of each specific functional group. Analogously to the characteristic frequencies in the IR spectra, the characteristic wavelengths can correspondingly be used for the UV spectra of compounds in the vapour phase. This, together with the feature of spectral shapes, can be correlated with specific functional groups. A qualified judgement of the relation between the spectrum of an unknown compound and the functional group can often be performed by a direct, visual inspection, and our experience is, that this can be made after a relatively limited training period.

The advantage of using UV spectrophotometry as a method for studying absorption characteristics of conjugated chromophores has been known for a long time. At the end of Table 2 the wavelengths of absorption maxima are given, and the characteristics of absorption regions found for eight groups of compounds are presented. The conjugated group are: dienes, α,β-unsaturated aldehydes, α,β-unsaturated acids and esters, diketones, aromatic aldehydes, aromatic esters and alkenylbenzenes. The spectral appearances due to the conjugated double bonds in the molecular structure are stable and dominating with low influences from other substituents.

In order to enhance the details of the recorded absorption spectra the derivatives of these spectra can preferably be used. However, these calculations give positive as well as negative values, which are not suitable when chromatograms are to be formed. Particularly, when the chromatograms are based on the average absorption in a relatively large wavelength region, the sum of the negative as well as the

Table 2
Characteristic absorption wavelengths and wavelength regions of specific functional groups

Functional group	λ_{max} (nm)	Characteristics of absorption region	Spectra shapes 170–330 nm
Non conjugated bonds			
1. Non-Aromatic Hydrocarbons			
1.1. Straight chain, saturated	<169	Sharp absorption edge at ~170 nm	
1.2. Branched, saturated	~169	Sharp absorption edge at 172–174 nm	
1.3. Straight chain, unsaturated	~178	Absorption starting at ~195 nm with two week knees up to λ_{max}	
1.4. Cyclic, saturated	~172	Sharp absorption edge at ~175 nm	
1.5. Cyclic, unsaturated	178–182	Skewed absorption at 170–215 nm with week knees	
2. Non-Aromatic Halogenated Hydrocarbons			
2.1 Straight chain chloro-substituted	177–179	Skewed absorption at 170–210 nm	
2.2. Straight chain bromo-substituted	169–177	Sharp absorption edge at 178.5 nm and weak absorption at 180–230 nm	
2.3 Straight chain double bromo-substituted at 1,2 and 1,1 positions	~178	Broad absorption band 170–230 nm with a narrow sharp absorption at ~178 nm.	

(*Continued on next page*)

Table 2 (*continued*)

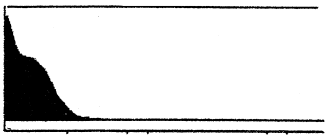
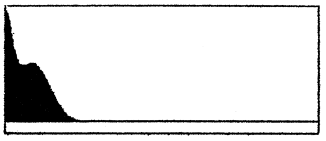
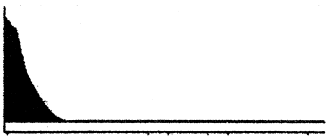
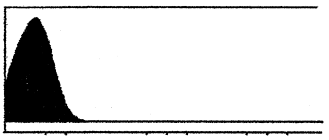
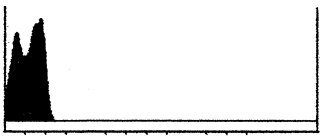
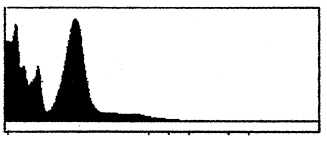
Functional group	λ_{max} (nm)	Characteristics of absorption region	Spectra shapes 170–330 nm
2.4 Straight chain iodo-substituted	~183 and ~200	6–8 sharp absorption regions at 170–200 nm, broad and week absorption 240–280 nm	
3. Non-Aromatic Alcohols			
3.1. Primary	~184 and <170	Absorption 170–200 nm with λ_{max} ~184 nm; for higher alcohols followed by an absorption at shorter wavelengths with no λ_{max} reached	
3.2. Secondary	~184 and <170	Absorption 170–200 nm with λ_{max}~184 nm; for higher alcohols followed by an absorption at shorter wavelengths with no λ_{max} reached	
3.3. Tertiary	<170	Absorption 170–200 nm with λ_{max}~184 nm; for higher alcohols followed by an absorption at shorter wavelengths with no λ_{max} reached	
3.4. Diols	<170	Absorption 170–200 nm no λ_{max} reached	
3.5. Cyclic	~185 and <170	Absorption 170–200 nm with λ_{max} ~185 nm, for higher alcohols followed by an absorption band at shorter wavelengths with no λ_{max} reached	
4. Non-Aromatic Ethers			
4.1. Saturated open chain ethers	~188 and 173–176	Sharp absorption edge at ~191 nm followed by two dominating absorptions	
5. Non-Aromatic Mercaptans and Sulphides			
5.1. Mercaptans	~204	Absorption 170–215 nm with λ_{max} at ~204 nm	

Table 2 (*continued*)

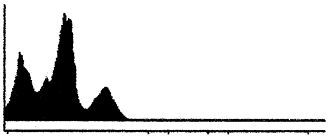
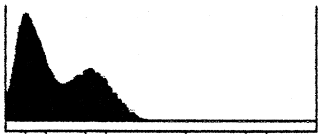
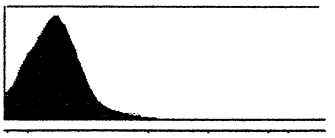
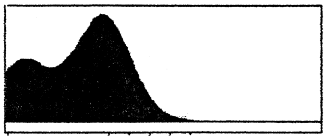
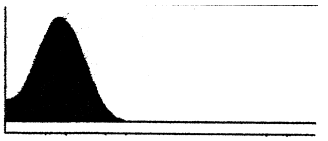
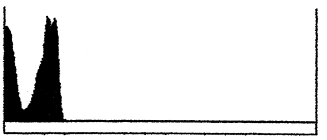
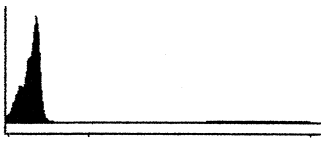
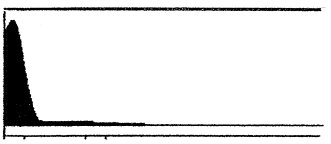
Functional group	λ_{max} (nm)	Characteristics of absorption region	Spectra shapes 170–330 nm
5.2. Sulphides	181–220	Series of sharp absorption regions between 170–230 nm	
6. Non-Aromatic Amines			
6.1.Primary	~180	Skewed absorption 170–200 nm, broad absorption 200–240 with λ_{max}~215 nm and with pronounced fine structure superimposed	
6.2. Secondary	~195	Broad absorption between 170–230 nm	
6.3. Tertiary	~210	Broad absorption between 170–250 nm	
7. Non-Aromatic Nitro Compounds			
7.1. Straight chain non-aromatic nitro compounds	~198	Broad symmetric absorption between 170–230 nm	
8. Non-Aromatic Ketones:			
8.1. Non-aromatic straight and cyclic ketons Straight and cyclic	~195 and ~176	Sharp absorption edge ~197 nm. Absorption triplet 183–200 nm; absorption 170–180 nm	
9. Non-Aromatic Aldehydes			
9.1. Straight chain non-aromatic aldehydes	~184	Sharp absorption edge ~186 nm. Absorption triplet 170–188 nm	
10. Non-Aromatic Carboxylic Acids			
10.1. Saturated open chain non-aromatic carboxylic acids	~174	Absorption between <170–185 nm; formic acid blue shifted	

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Table 2 (*continued*)

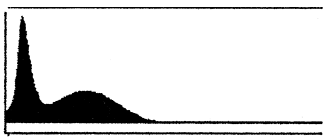
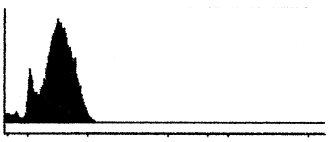
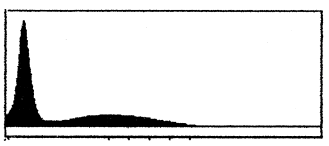
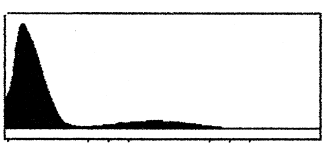
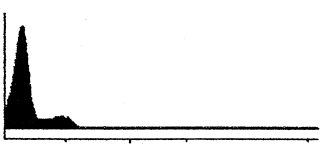
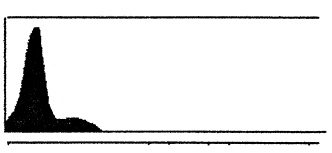
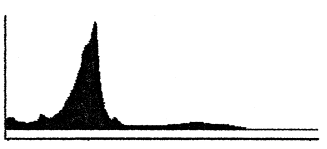
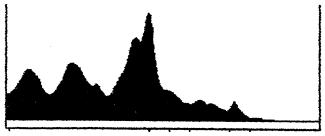
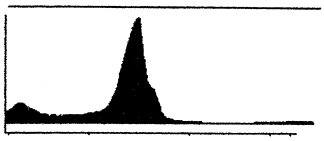
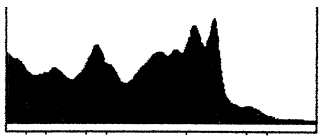
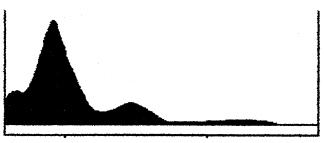
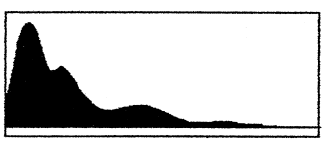
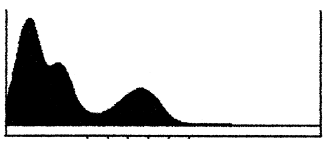
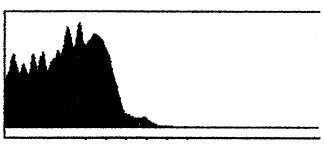
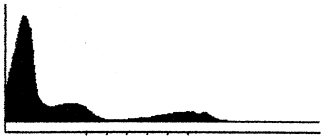
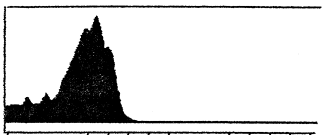
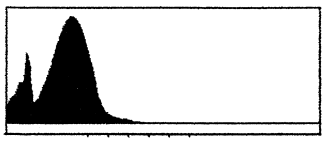
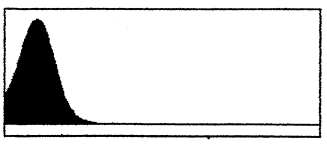
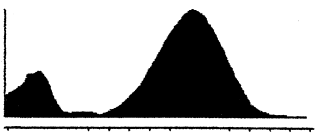
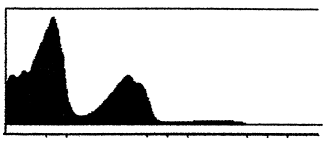
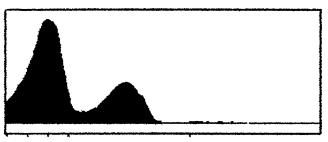
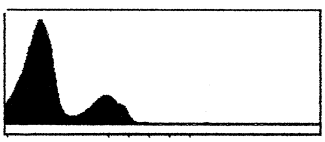
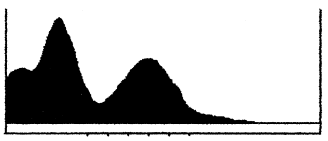
Functional group	λ_{max} (nm)	Characteristics of absorption region	Spectra shapes 170–330 nm
11. Non-aromatic esters			
11.1. Formates	~177	Absorption 170–188 nm, weak absorption 190–240 nm with signs of superimposed fine structure	
11.2 Acetates, propionates, butyrates, malonates, succinates, caproates	170–177	Absorption 170–187 nm, broad absorption 190–240 nm	
12. Non-Aromatic Anhydrides			
12.1. Carbon disulfide	~196	Absorption with sharp details 180–215 nm	
12.2. Open chain	~177	Absorption 170–187 nm, broad absorption 190–260 nm	
13. Non-aromatic acid halides:			
13.1. Saturated non-aromatic acid halides	~178	Skewed absorption 170–200 nm, broad absorption 210–280 nm	
14. Aromatic Hydrocarbons			
14.1. Benzene	~178	Absorption 170–185 nm, plateau 185–205 nm	
14.2. Alkyl substituted	184–194	Absorption 185–205 nm, plateau 195–215 nm	
14.3. Naphthalenes	>209 nm	Main absorption 180–230 nm, red shifted upon substitution, minor absorption 230–300 nm	

Table 2 (*continued*)

Functional group	λ_{max} (nm)	Characteristics of absorption region	Spectra shapes 170–330 nm
14.4. Phenanthrenes	~239	Absorption ~180 nm, ~200 nm, ~235 nm, ~280 nm; slightly red shifted upon substitution	
14.5. Anthracenes	~235	Main absorption 220–250 nm.	
14.6. Benzanthracenes	~274	Detailed absorption spectra 170–310 nm.	
15. Aromatic Alcohols and Phenols			
15.1. Phenols	184–202	Absorption 170–205 nm, plateau 195–215 nm, absorption band 260–280 nm	
15.2. Catechols	187–200	Absorption 170–205 nm, plateau 195–215 nm, absorption 260–280 nm	
16. Aromatic Amines:			
Single ring anilines	191–197	Absorption 170–210 nm, absorption 210–250 nm, week absorption 275–305 nm	
17. Aromatic Nitro Compounds:			
17.1. Aromatic nitro compounds Ring nitro	176–182	Three to four broad absorption regions 170–280 nm	
18. Aromatic Polycyclic Ketones:			
18.1. Benzophenones	~182	Three broad absorption regions 170–280 nm	
19. Five-Membered Aromatic Heterocycles:			
19.1. Furans	203–206	Series of sharp absorption regions 170–230 nm superimposed on a broad skewed absorption	

(*Continued on next page*)

Table 2 (*continued*)

Functional group	λ_{max} (nm)	Characteristics of absorption region	Spectra shapes 170–330 nm
20. Six-Membered Aromatic Heterocycles:			
20.1. Pyridines	172–180	Absorption 170–185 nm, 185–205 nm and 240–280 nm, spectral appearance similar to single ring aromatic hydrocarbons but with a λ_{max} at considerably lower wavelengths	
Conjugated bonds			
1. Dienes	>208	Triplet main, red shifted upon carbon chain substitution	
2. α,β-Unsaturated Aldehydes	>195	Absorption 180–210 nm, sharp absorption ~175 nm; red shifted upon increase in carbon chain length	
3. α,β-Unsaturated Acids and Esters	~186	Absorption 170–210 nm	
4. Diketones	~260	Main absorption 225–295 nm, absorption 170–195 nm	
5. Aromatic Aldehydes	193–200	Absorption 170–210 nm, absorption with weak knee 210–250 nm, weak absorption 260–300 nm	
6. Aromatic Ketones	185–190	Absorption with knee 170–220 nm, broad absorption 220–240 nm	
7. Aromatic Esters	~186	Absorption with knee 170–200 nm, broad absorption 200–230 nm	
8. Alkenylbenzenes	193–195	Absorption 180–215 nm, absorption with weak knee 215–260 nm	

positive derivative values gives results which are difficult to interpret. For certain applications we therefore have used the absolute values of the derivatives.

Fig. 2 shows the absorption spectrum for 1-methylnaphthalene (A), together with the second derivative spectrum (B), and the absolute values of the second derivative spectrum (C). As can be seen from this figure, the spectral details are considerably sharpened upon derivation, and become a improved base for a selective detection. The calculated derivatives are actually differentials with various gap values along the wavelength scale. For a large gap value the signal-to-noise ratio becomes more favourable, but finer spectral details are obscured. The gap values applied were 2 nm for highest selectivity measurements and 4 nm for best signal-to-noise measurements.

3.2. Analysis of cigarette smoke using GC–UV with micro separation columns

The cigarette smoke from a conventional filter cigarette was taken by means of a gas tight glass syringe. The smoke was injected using a loop injector in direct connection with the built in micro gas chromatograph of the gas flow cell. The operational conditions are presented in Table 1, No 1. The separation was in this case carried out on a packed column with a carrier gas flow of 10 ml/min and with a temperature program starting at 40°C with a temperature ramp of 8°C/min up to 130°C. The separation column (Ins PW, Inscan AB) is suitable for separations of volatile compounds. The micro GC system has the advantage of giving selective separations by means of a large number of various 8 cm long columns, which are easy to replace. The support

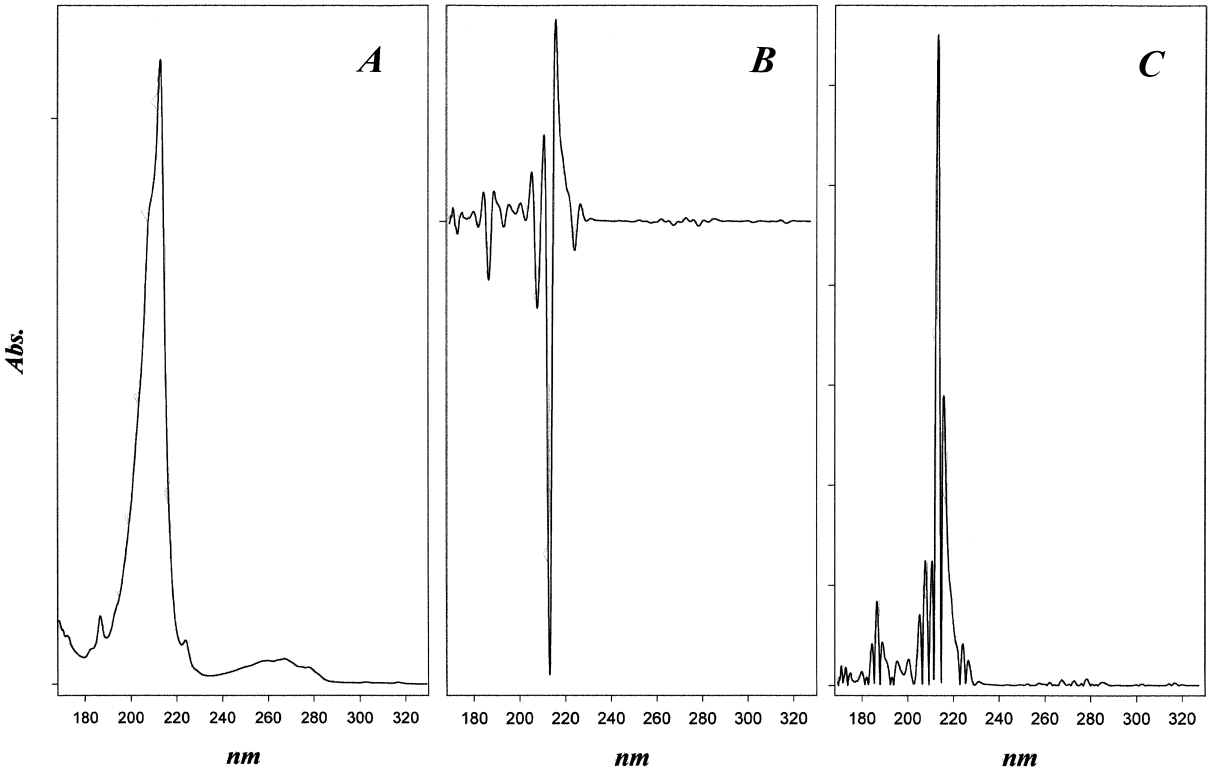


Fig. 2. Absorption and derivative spectra of 1-methylnaphthalene: (A) absorption spectrum, (B) second derivative spectrum, (C) second derivative spectrum with absolute values after an injection of ~0.5 μl of petroleum product. The separation column was HP5, 30 m×0.32 mm I.D., 0.25 μm film thickness, and the spectra were recorded at a bandwidth of 1.7 nm.

materials and the stationary phases can be chosen and combined in numerous ways in order to adapt a column for the application at hand. These short columns give fast separations because their capacity factor rises very fast. However, the efficiency of the short column is limited and the number of theoretical plates is usually less than 1600.

Fig. 3 illustrates the type of data that is obtained with the GC–UV method employed. In this three-dimensional plot the collected spectra follow the wavelength scale along the *x*-axis, the light absorbance values along the *y*-axis, and the separation time follows the *z*-axis. These results are analogous to those obtained with a HPLC system connected to a photo diode array detector. The spectra appearing along the time scale are nitric oxide, hydrogen sulphide, acetaldehyde, 1,3-butadiene, acrolein, acetone, isoprene, benzene and toluene. The figure demonstrates the presence and importance of spectral details at short wavelengths not seen in liquid phases and the determination of the organic as well as the inorganic compounds in the sample.

3.3. Analysis of a flavour using GC–UV linked with capillary separation columns

In order to take advantage of the high efficiency of capillary columns, the gas flow cell has recently been modified so, that it can be directly linked to an external GC system by means of a heated transfer line. Although the spectral details can be used for determination of unresolved chromatographic peaks, there are often a need for high efficiency separations when dealing with complex samples.

In Fig. 4A a chromatogram obtained from the analysis of a flavour sample (‘‘after shave’’) is shown. Experimental conditions for this analysis are presented in Table 1 No. 2. The chromatogram is based on the average of second derivative absorption spectra between 185 and 220 nm (gap value 4 nm). The figure also shows an expanded part of the chromatogram from a retention time of 3 min up to 10 min. Identification of the peak marked by an arrow will be discussed in Section 3.6. In Fig. 4B the data from the same analysis are projected in a three-dimensional mode, where the second derivatives of the collected spectra with absolute values are presented. The plot shows several sharp details and the patterns marked by arrows indicate phenolic structures.

3.4. Analysis of a petroleum using GC–UV linked with capillary separation columns

One example of application, where selective determinations are desirable is analysis of single-, double- and polyaromatic rings in petroleum products. Fig. 5A shows a contour plot of the result obtained after the analysis of a petroleum sample where the absolute values of second derivatives were used. Experimental conditions for this analysis are presented in Table 1 No. 3. The various aromatics can be observed where the single aromatic rings dominate in the wavelength region from ~188 nm up to 203 nm, the double aromatic rings from ~210 nm to 229 nm, and the polyaromatics from ~240 nm to 259 nm. Chromatograms formed by taking the average absorption in these wavelength regions are shown in Fig. 5B. The selective detections were considerably improved in comparison with the averages of plain absorption spectra. The three absorption regions of these aromatics are partly overlapping. The largest overlap is between the double rings and the single rings. About 10% of the peak area from chromatogram of the double rings ‘‘spills over’’ to the peak area of the single rings. However, this occurs in well defined retention time regions. The wavelength ranges chosen were rather broad, because the naphthalenes show bathochromic shifts with increasing of substitution by methyl groups.

3.5. Analysis of compounds adsorbed on dust particles using GC–UV linked with capillary separation columns

The sharp well defined adsorption edges for non-aromatic ketones, ethers and aldehydes can be used for selective determination. Fig. 6 shows overlaid chromatograms recorded at the analysis of a dust sample. The dust particles were thermally desorbed at 150°C and the desorbed compounds were collected by means of SPME (PDMS fibre). The trapped sample was injected at 250°C on to a capillary separation column. The other experimental conditions are reported in Table 1 No. 4. The chromatogram drawn with a solid line shows the first deriva-

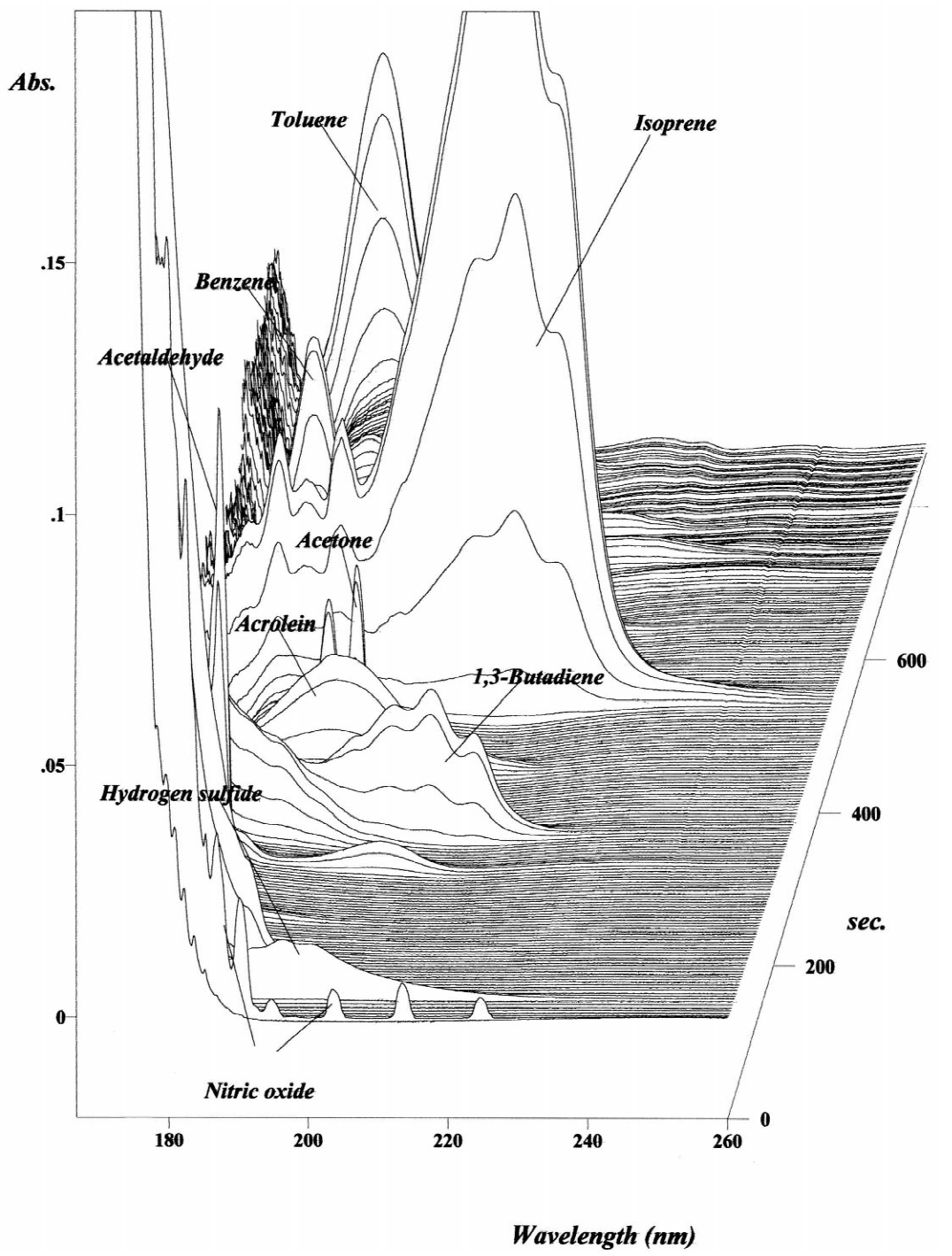


Fig. 3. Three-dimensional plot of spectra/gas chromatograms from analysis of 200 μl cigarette smoke using the internal micro separation column and loop injection. The separation column was InsPW (10-μm particles of a polystyrene–divinylbenzene material similar to Porapak P type), and the spectra were recorded at a bandwidth of 1.7 nm. *x*-Axis: the wavelengths, *y*-axis: the absorbance values, *z*-axis: the retention time. Some of the identified compounds are indicated in the figure.

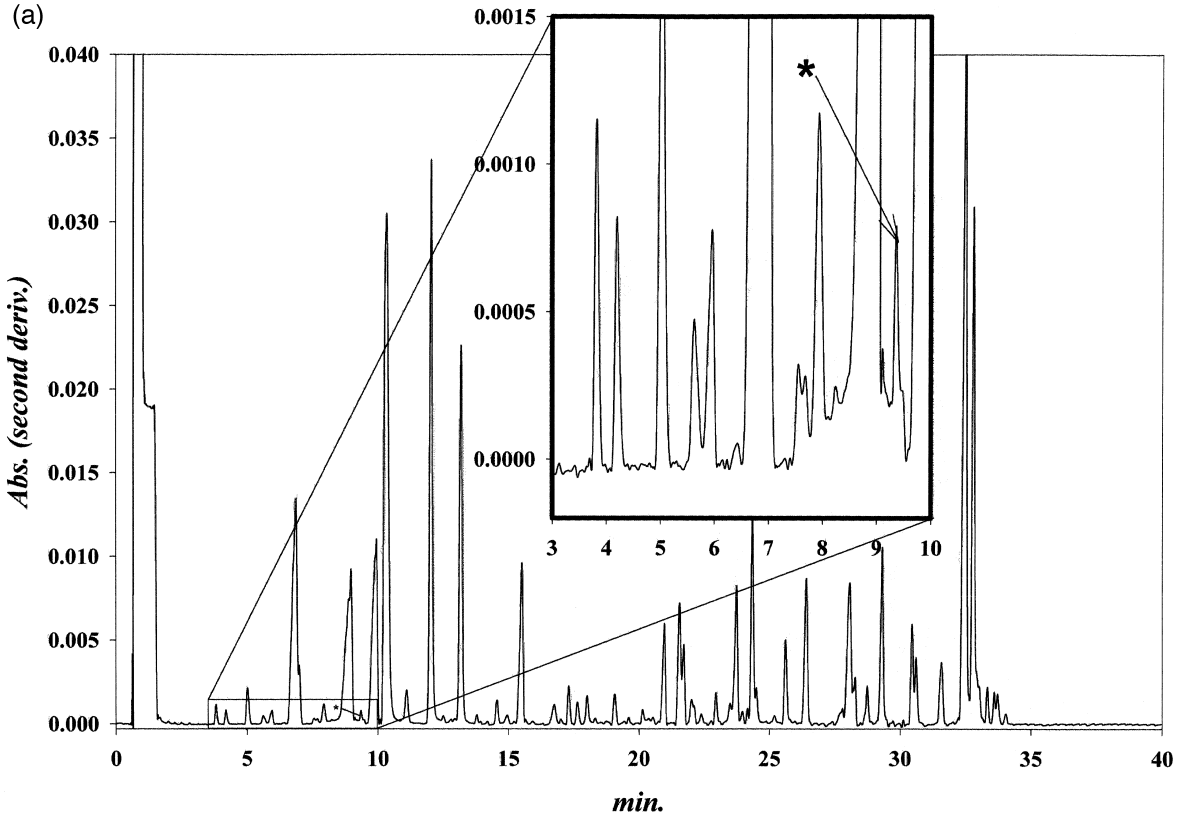


Fig. 4. (A) Chromatogram obtained after the analysis of ~0.5 μl flavour sample. The separation column was HP5, 30 m×0.32 mm I.D., 0.25 μm film thickness, and the spectra were recorded at a bandwidth of 1.7 nm. The chromatogram is based on the average between 185 and 220 nm of the second derivatives of collected spectra. The expanded view concerns the retention time between 3 and 10 min and the identification of the peak marked with an arrow is shown in Fig. 7B. (B) Three-dimensional plot of spectra/gas chromatograms after the analysis of ~0.5 μl flavour sample. The separation column was HP5, 30 m×0.32 mm I.D., 0.25 μm film thickness, and the spectra were recorded at a bandwidth of 1.7 nm. *x*-Axis: the wavelengths, *y*-axis: the absorbance values, *z*-axis: the retention time. Derivatives, which are actually differentials, have a gap value of 2 nm along the wavelength axis. Recorded spectra marked with arrows indicate phenolic structure.

tives of spectra with the average absorption between 185.8 and 187.3 nm and with a gap value of 2.0 nm. The dotted line chromatogram is obtained from the first derivative spectra with the average absorption between 190 and 220 nm and with a gap value of 4.0 nm. The 185.8–187.3 nm range chromatogram is arranged in order to specifically register the sharp absorption edges for non-aromatic aldehydes, while the 190–220 nm range can be considered as relatively unspecific. The peaks with corresponding spectra, which were identified as non aromatic straight chain aldehydes, are marked (a), (b) and (c) in the expanded regions in the figure. Notice that at the marked peaks (b) and (c) of two aldehydes, there are two very close peaks which were hidden when the range of 190–220 nm was plotted. Concerning peak (c) the hidden peak is only 2 s apart. The compound adjacent to (b) was determined as a phenone and the compound adjacent to the aldehyde (c) as propiophenone.

3.6. Identification

The gas phase spectra are well suited for identification purposes with computer-based search against a reference library of known spectra. In Fig. 7A a search result is shown concerning an unknown component in a cigarette smoke. The search was

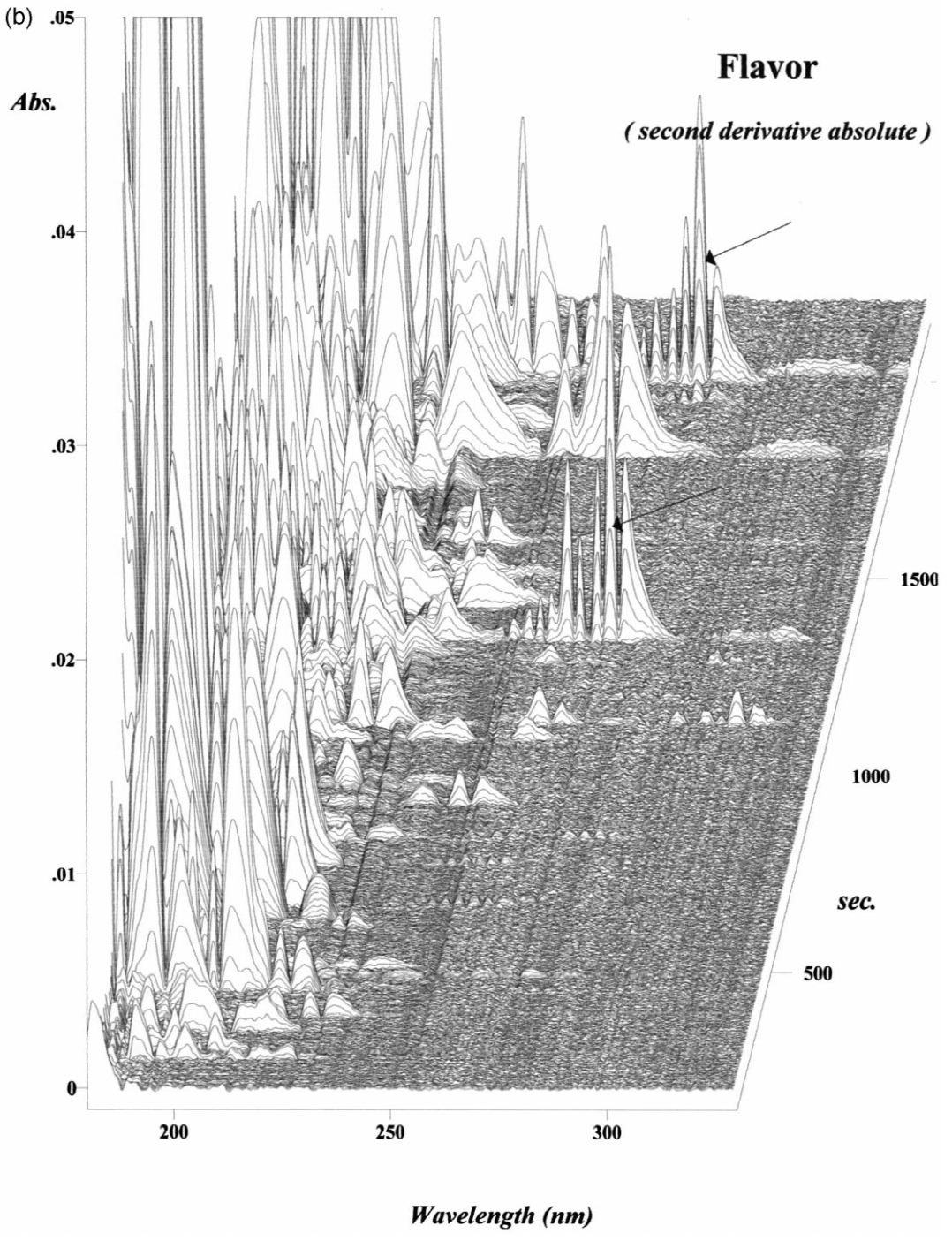


Fig. 4. (*continued*)

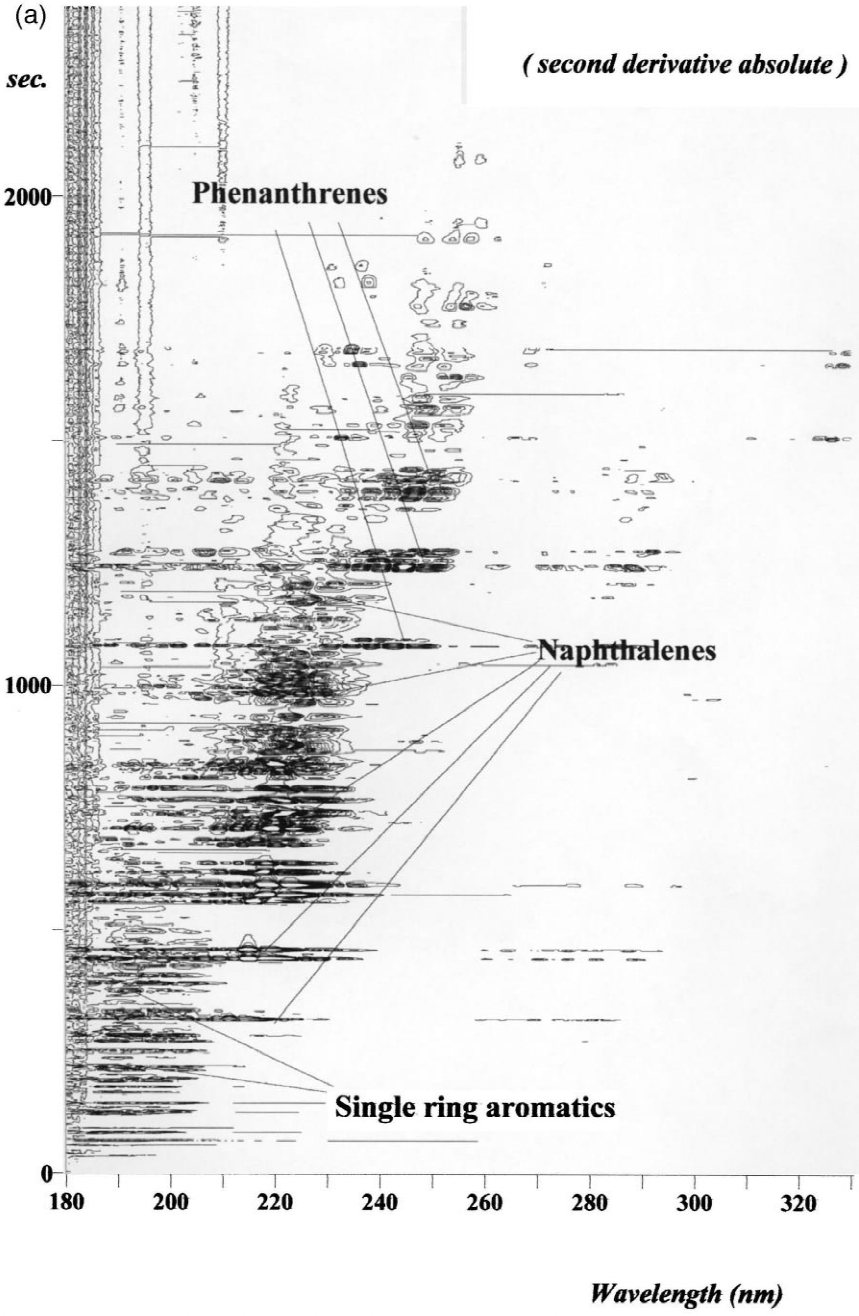


Fig. 5. (A) Contour plot of the results received after analysis of ~0.5 μl petroleum product. The separation column was HP5, 30 m×0.32 mm I.D., 0.25 μm film thickness, and the spectra were recorded at a bandwidth of 1.7 nm. Second derivative values with absolute values are used for the recording. The clear signs of single-, double- and polyaromatic compounds were indicated. The red shift upon degree of substitution can be noticed for the naphthalenes. (B) Chromatogram obtained after analysis of ~0.5 μl petroleum product. The separation column was HP5, 30 m×0.32 mm I.D., 0.25 μm film thickness, and the spectra were recorded at a bandwidth of 1.7 nm: (a) average absorbance values between 188 and 203 nm, (b) average absorbance values between 210 and 229 nm, (c) average absorbance values between 239 and 257 nm.

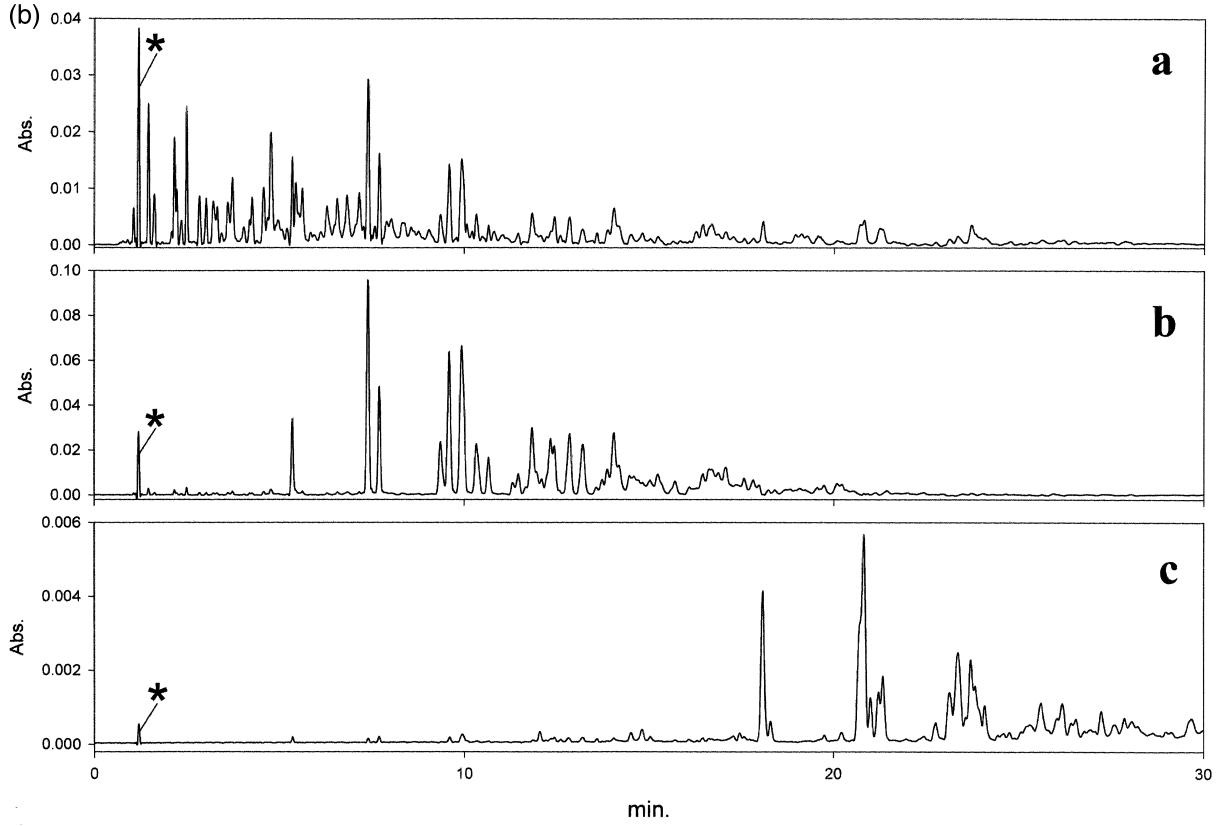


Fig. 5. (*continued*)

performed by means of a least-square algorithm. The five closest alternatives, arranged after hit rate order, are shown below the figure showing the unknown spectrum and the reference spectrum overlaid. The spectra are slightly shifted in order to illustrate the correspondence. As discussed earlier, the functional groups (substituents?) often have a strong influence on the appearance of the spectra, especially if conjugation is present. In such a case the search result can be as shown in Fig. 7B. This search concerned a compound present in the flavour sample showed earlier (Fig. 4A and B), and the peak for the compound of interest is marked in the expanded region of the chromatogram. The results gives the best hit rate for ethylbenzoate. However, looking at the alternatives, the hit rates for these are very close, but they all clearly point at the same functional group, namely an aromatic single ring conjugated with a carboxyl group.

3.7. Sensitivity

The noise levels expressed as absorbance units appear in two directions, namely along the wavelength axis and along the retention time axis. The noise level (peak-to-peak) along the wavelength axis depends on the integration and cycle time for the diodes and the degree of damping that can be applied without loosing spectral details. Generally it can be kept at about $0.5 \cdot 10^{-4}$ AU in the wavelength range of 180–330 nm. Noise along the retention time axis consists, to a considerable extent, of instrumental noise which is coming mainly from the temperature regulation of the light pipe. This level is slightly

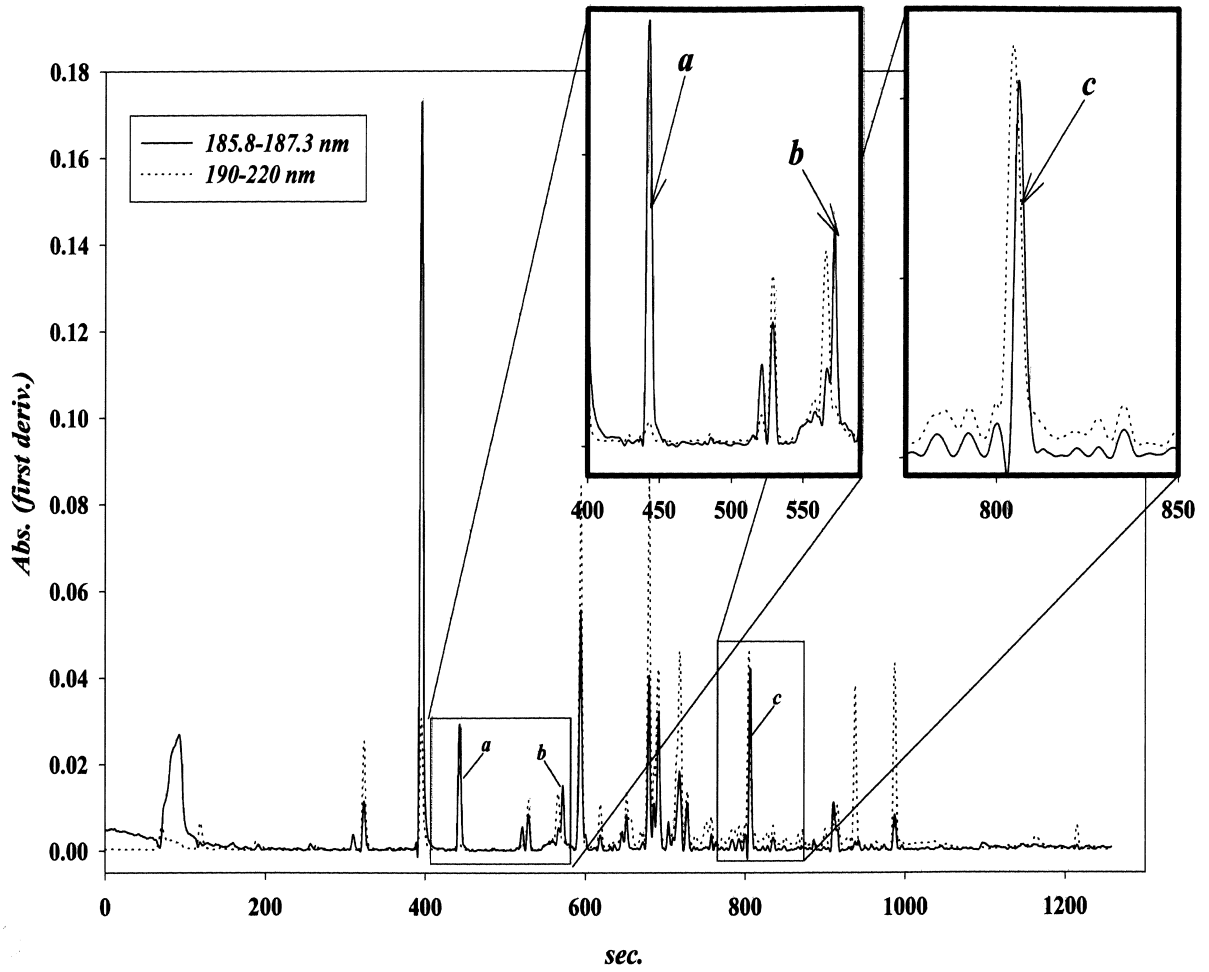
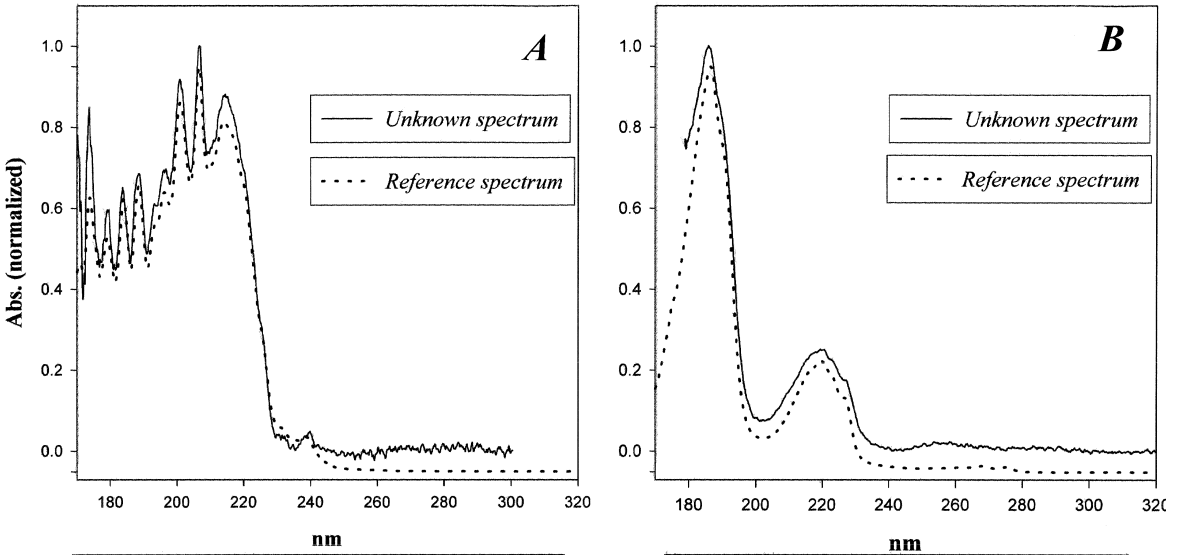


Fig. 6. Overlaid chromatograms recorded after the analysis of compounds adsorbed on a dust sample. The separation column was CP-Sil 13 CB, 20 m×0.32 mm I.D., 1.2 μm film thickness, and the spectra were recorded at a bandwidth of 1.7 nm. The solid line chromatogram calculated from the first derivatives of collected spectra in the 185.8–187.3 nm wavelength region represents a specific detection tuned for non aromatic straight chain aldehydes. Dotted line chromatogram calculated from the first derivatives of collected spectra in the 190–220 nm wavelength range represents an unspecific detection. The aldehydes identified are shown as peak (a), (b) and (c) in the expanded views of the chromatogram.

improved by taking the averages within a broader wavelength range. However, when applying the absolute values of first and second derivatives of spectra the noise levels are considerably improved and approaches $1 \cdot 10^{-5}$ AU for averages over suitable wavelength ranges.

Calculated detection limits, defined as three-times the standard deviation of noise, were made for naphthalene at a light pipe temperature of 120°C. Depending on experimental conditions these values ranged from 0.5–3 pg/s. The minimum identification quantity (MIQ) is defined as that the hit rate of the unknown should be found among the first five proposals. This obviously depends on the size of the spectrum library. However, for the GC–UV method our experience is, that clear identifications can be made in the mid-pg range provided that the compound belongs to a functional group with relatively high absorptivity values (e.g., aromatics). For the GC–UV method the introduction of an additional



Number	Hit Quality	Identification
1	0.0004614	2,5-Dimethylfuran
2	0.0060746	Triethylamine
3	0.0065821	N,N-Diethylethylenediamine
4	0.0073356	2,3,6-Trichlorobenzaldehyde
5	0.0088427	1-Methylpyrrolidine

Number	Hit Quality	Identification
1	0.0005075	Ethyl benzoate
2	0.0005229	iso-Amyl benzoate
3	0.0006305	Benzoic acid ethyl ester
4	0.0006459	Methyl benzoate
5	0.0008151	tert-Butyl peroxybenzoate

Fig. 7. Computer-based search results for (A) minor component present in cigarette smoke and (B) compound present in the flavour sample shown in Fig. 4A at the marked peak in the expanded view of the chromatogram.

sensitivity level, namely a minimum classification quantity (MCQ), appears to be desirable. This could, as a suggestion, be defined as the minimum quantity that needs for determination of the right functional group should appear on the first library search proposal.

4. Conclusion

GC linked with UV spectrophotometric detection, optimised for gas phase measurements, has proven to be a versatile and powerful GC–UV method of analysis. The library of gas phase UV spectra of compounds constitute a detailed and well defined base for a computer search concerning determination of specific functional groups and individual compounds even in complex mixtures such as cigarette smoke, flavour or petroleum. The spectral characteristics, which are presented for 50 specific functional groups, show that the feature and position of spectral shapes, can be correlated with specific functional groups. Analogously to the characteristic frequencies in the IR spectra, the characteristic wavelengths can correspondingly be used for the UV spectra of compounds in the vapour phase. However, in order to fully exploit all the information available for interpretations of an unknown spectrum, more knowledge has to be gathered about the relationship between structure and spectral appearances. Especially concerning mixed functionalities there is a need for considerably more studies.

The low detection, classification and identification limits show the good sensitivity of the GC–UV method. A comparison between GC–UV and GC–FT-IR concerning selectivity seems appropriate. Both the methods are spectrophotometric with similar types of light pipe arrangements. They also share the same advantages of being able to distinguish structural isomers and to determine specific functional groups and compounds in complex mixtures. The light pipe geometry is in the present investigations close to what is common for GC–FT-IR instrumentation. A complication is that the sensitivi-

ty varies to a considerable extent between various groups of compounds in the UV-wavelength region as well as in the IR-wavelength region. However, the sensitivity in UV is up to three-orders of magnitude higher than in IR [2,24] for groups of compounds like aromatics and groups containing conjugated double bonds. Consequently, the sensitivities for GC–UV are considerably more favourable.

The results that have been obtained in this study, together with the earlier published and unpublished applications concerning environmental air analysis, determinations of nitric oxide adsorbed on mineral fibres and dusts, analysis of breath samples, analysis of polychlorinated biphenyls and polychlorinated naphthalenes, determinations of single-, double- and polyaromatics in petroleum products, analysis of flavours, and so on, leads us to strongly believe that GC–UV will be in near future established as an important method of analysis.

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