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Absorbance detector for high-performance liquid chromatography based on light-emitting diodes for the deep-ultraviolet range

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ABSTRACT

A HPLC-detector has been designed which employs light-emitting diodes in the deep-UV-range below 300 nm as wavelength specific radiation sources and special UV-photodiodes for measuring the signal. A monochromator is therefore not needed. The design features a beam splitter and a reference photodiode, precision mechanics for adjustment of the light beams and electronics for stabilization of the LED-current. The processing of the photodiode currents is carried out with a high performance log-ratio amplifier which allows direct absorbance measurements. The optical and electronic performance of the detector was characterised and high precision over several absorbance units was obtained. Testing of analytical separation methods in isocratic as well as gradient modes employing UV-detection at 255 and 280 nm showed a very similar performance to a commercial photodiode-array detector used in the fixed wavelength mode in terms of linearity, precision and detection limits. The chief advantages of the new device are small size, low power consumption, and low cost.

1. Introduction

Light-emitting diodes (LEDs) for the visible and infrared regions have been available for many years and are used for diverse applications. Compared to conventional incandescent and discharge lamps, they feature low power consumption and high efficiency, high stability and long life times, but also relatively narrow emission bands of typically about 30 nm width. These widths are well matched to the absorption bands of molecules and, as Flaschka et al. [1] demonstrated already in 1973 with early red LEDs, the construction of very simple but powerful instruments and detectors is possible by combination of the LEDs with inexpensive solid state photodetectors. Monochromators are not needed as the wavelength selectivity is inherent to the radiation sources. A multitude of designs and analytical applications making use of LEDs as light sources and photodiodes as detectors for absorbance, fluorescence and turbidity measurements, chemical sensing, and quantification in separation methods has been reported since. LED-based analytical instruments, in particular devices designed for field measurements, are produced commercially. A recent comprehensive review on analytical applications of LEDs appears not to be available, but Dasgupta et al. presented an overview of flow-through detectors based on LEDs in 2003 [2], O'Toole and Diamond reviewed absorption sensors utilizing LEDs in 2008 [3], and Xiao et al. reviewed LED-based detection in capillary electrophoresis in 2007 [4].

LEDs for the UV-range have been more elusive, and while devices emitting at 370 nm have been available for a number of years, for the deep-UV-range below 300 nm such emitters have only recently been developed. This is due to difficulties caused by the relatively high energy of the short wavelengths concerned. On the other hand this spectral region is of particular interest for analytical chemistry because many species absorb light in this range, but not at longer wavelengths. In particular, absorption detection in the UV-range for HPLC is a very widely used analytical method. Due to the lack of devices for the deep-UV-range few reports on LED-based detectors for HPLC have appeared, and these have been limited to special applications concerning longer wavelengths [5–9].

A first report on a detector for HPLC using an LED emitting at 255 nm originating from our research group appeared in 2008 [10]. It clearly showed the potential of the device for this application. However, while simple, the device had a significant shortcoming, the response was proportional to transmittance, rather than absorbance, and thus not linear with concentration. Herein an improved design, giving direct absorbance readings, is reported along with a study of its performance. In addition to the LED emitting at 255 nm, the use of a second device radiating at 280 nm has now also been studied, and applications for the two different deep-UV LEDs are demonstrated. The two wavelengths are of particular interest in HPLC as many methods have been developed using these. This originates from the use of low pressure mercury lamps (the line at 253.7 nm is a native emission line, while the band at 280 nm is

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derived from this line using a phosphorescent compound enclosed in the lamp [11]). While the mercury lamps are not widely used anymore, in particular the 254 nm line has become a *de-facto* standard for many applications also when employing other light sources.

2. Materials and methods

2.1. Instrumentation

The UV-LEDs (UVTOP280TO39BL and UVTOP255TO39BL) were obtained from Sensor Electronic Technology (Columbia, SC, USA) and the UV-photodiodes (SG01L-C) were products of Sglux Solgel Technologies GmbH (Berlin, Germany). The beam splitter (G344312000) was obtained from Qioptiq Photonics (Munich, Germany) and the micromanipulators (NT38-526) were sourced from Edmund Optics Germany (Karlsruhe, Germany). The flow-through cuvette designed for detection in HPLC (178.313-QS) was sourced from Hellma (Müllheim, Germany). The log-ratio amplifier (LOG102) was a product of Texas Instruments (Austin, TX, USA). Separations were carried out on an Agilent 1100 HPLC system which includes a photodiode-array detector (DAD) (Agilent, Waldbronn, Germany) using separation columns from Phenomenex (Torrance, CA, USA, Aqua C18, 5 μm, 250 mm × 4.6 mm) or Agilent (ZORBAX Eclipse XDB D8, 5 μm, 150 mm × 4.6 mm) as indicated. The signals from both, the LED-detector and the commercial detector, were digitized using an e-corder ED401 data-acquisition system (EDAQ, Denistone East, NSW, Australia) and the Chart software package (EDAQ) running on a personal computer. Absorption spectra and reference absorbance values were measured with a conventional UV/Vis-spectrophotometer from Perkin-Elmer (Lambda 20, Perkin-Elmer Switzerland, Schwerzenbach, Switzerland).

2.2. Reagents

Water used throughout had a resistivity ≥15 MΩ cm and was obtained from a NANO-Pure water purification system (Barnstead, IA, USA). All chemicals were either of analytical grade or HPLC gradient grade. Acetonitrile (ACN) was obtained from Fisher Scientific (Loughborough, UK) and methanol (MeOH) as well as trifluoracetic acid (TFA) from J.T. Baker (Deventer, Holland). Tetrabutylammonium hydrogen sulfate, benzoic acid, L(+)-ascorbic acid, salicylic acid sodium salt and nicotinamide were purchased from Acros (Morris Plains, NJ, USA). KH_2PO_4, NaOH, DL-tryptophan, 4-methylbenzoic acid, thiamine, folic acid, riboflavin, caffeine, naproxen and nicotinic acid were obtained from Fluka (Buchs, Switzerland) and 4-hydroxybenzoic acid, homovanilic acid, vitamin B_{12}, paracetamol (acetaminophen) and diclofenac sodium salt were sourced from Sigma–Aldrich (Buchs, Switzerland). The cold medicine analysed was a commercially available effervescent tablet and contained ascorbic acid, paracetamol and caffeine as active ingredients.

2.3. Procedures

All solutions were degassed in an ultrasonic bath and filtered through 0.2 μm nylon filters (BGB Analytik AG, Boeckten, Switzerland) before analysis. The fundamental characterisation of the detector was carried out by filling the cell with standard solutions prepared in methanol/water, 40/60 (v/v). The HPLC-separations were carried out with a column temperature of 25 °C and the bandwidth of the commercial DAD used in the monochromatic mode was set to 4 nm.

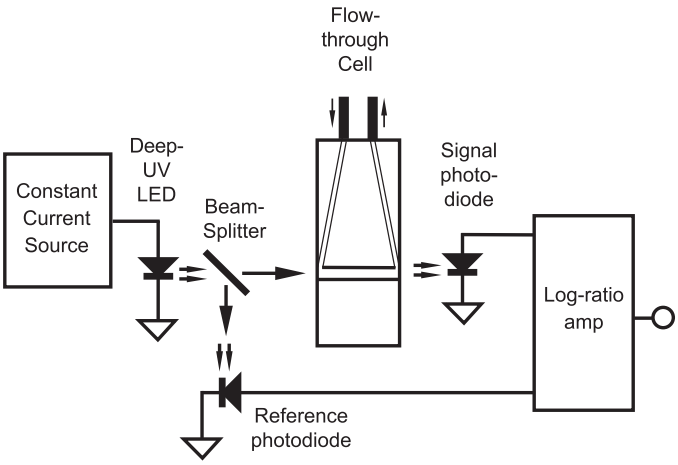

Fig. 1. The design of the detector.

2.4. Estimation of absorbance values

The absorbance, A, of Lambert–Beer's law is given by $A = \log(I_0/I)$, where I_0 and I are the light intensity before and after passage through the sample respectively. In practice the intensities have to be determined with detectors that convert I_0 and I into electrical currents, i_0 and i, via a sensitivity coefficient S. For non-monochromatic light sources the term has to be expanded in order to account for the spectral dependences of the light source, I_0, of the molar absorptivity coefficient, ε, and of the sensitivity, S, of the detectors, across the relevant wavelength range. The absorbance is then thus given by the following expression:

$$A = \log \frac{i_0}{i} = \log \frac{\int_{\lambda_0}^{\lambda_1} S(\lambda) I_0(\lambda) d\lambda}{\int_{\lambda_0}^{\lambda_1} S(\lambda) I_0(\lambda) 10^{-\varepsilon(\lambda) bc} d\lambda}$$

An estimation of expected absorbance readings was carried out accordingly by numerical integration. The relative $I_0(\lambda)$ and $S(\lambda)$ values were read from corresponding plots in the data sheets for the LED and the photodiode respectively, and the values of $\varepsilon(\lambda)$, were obtained from the measured absorbance spectra for the compounds of interest. A wavelength interval of 2 nm was used.

3. Results and discussion

3.1. Design

A sketch of the set-up is given in Fig. 1 and the complete circuitry in Fig. 2. The new design is based on an integrated log-ratio amplifier in surface mount technology which gives an output voltage (V_O) dependent on two input currents (i_1 and i_2) as defined by the following equation: $V_O = \log(i_1/i_2)$. The two currents are derived proportionally from radiation intensity (I) using special UV-photodiodes. One of the sensors is employed to measure a reference intensity (I_0), and thus the output voltage of the amplifier is directly related to absorbance (A) according to $A = \log(I_0/I)$. A signal of 1 V corresponds to an absorbance of 1, or, in other words, equals 1 AU (absorbance unit). Note, that although the wavelength specificity is essentially given by the emitter, the use of detectors with built-in filters to block longer wavelengths is desirable to eliminate background signals due to spurious weak intensities which were found to be present outside the emission band of the LED [10]. The photodiodes employed are designed to measure weak levels of the UVC-range (<280 nm) and thus incorporate an optical filter to eliminate radiation at longer wavelengths. These are new products which have a higher maximum spectral sensitivity than the device

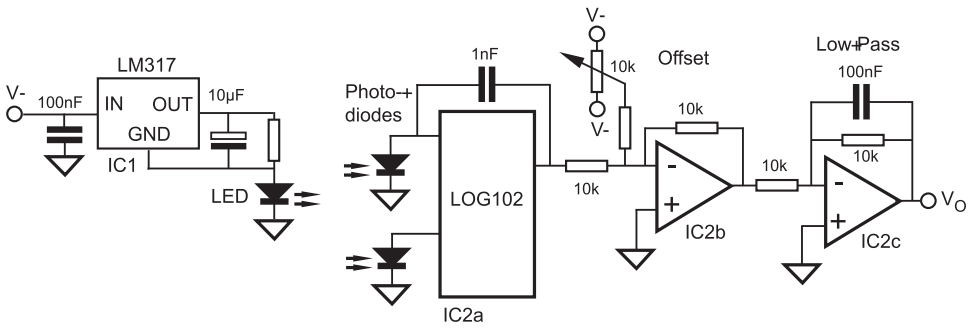

Fig. 2. Circuitry.

previously employed [10] (110 mA W^{-1} as opposed to 19 mA W^{-1}). A simple offset circuitry (and low pass filtering) is provided based on auxiliary operational amplifiers which are also part of the integrated circuit package of the device. The offset allows to correct for an imbalance of the intensities on the two photodiodes for geometric reasons. A further improvement in the circuitry compared to our earlier design [10] is the use of a constant current source for driving the LED, rather than a simple current limiting resistor. Besides the ability to measure absorbance values (rather than signals related to transmittance) the new circuitry was therefore designed to be more stable, because both, the referenced approach and current stabilization, should compensate for changes in the emitted intensity mainly expected due to temperature fluctuations.

The components are arranged around the commercial flow-through cell which was designed for the small volumes in HPLC detection and has a standard optical path length of 1 cm. The UV-LED is mounted on a micromanipulator stage in order to optimize its position in front of the window of the cell such that maximum intensity is obtained on the signal photodiode. A beam-splitter arranged in a 45°-angle allows the generation of the reference signal. Note that the splitting ratio is 20%:80%, *i.e.*, only 20% of the intensity is diverted towards the reference photodiode. The entire assembly, including the electronic circuitry, is housed in a dye-cast metal case with the dimensions of 140 mm × 102 mm × 73 mm. The LED draws a current of 25 mA, and the power consumption of the complete circuitry was measured to be about 500 mW. In contrast, a deuterium lamp as used in a conventional detector consumes several tens of watts of electrical power.

3.2. Optical and electronic performance

The basic characteristics of the device were first evaluated on its own, *i.e.*, not in operation as an on-line detector in HPLC, in order to determine its fundamental performance characteristics. First the electronic noise was determined by measuring the maximum deviation of the signal for a dry cell over a period of 20 s. The data for the two LEDs with emission bands at 280 and 255 nm is shown in Table 1 and indicates good values in the low µAU-range. Detectors in chromatography are generally used with an electronic low-pass filter which is set to an appropriate cut-off frequency in order to remove high frequency noise. As is true for any detector, the noise level was of course found to be dependent on the amount of electronic filtering applied by the data acquisition system, the lower the cut-off frequency, the lower the noise level. Values similar to the ones reported for the experimental device were also observed for the commercial (photodiode array-) detector of the HPLC system used for this study and indeed the manufacturer quotes a value of 20 µAU for short term noise at 254 nm [12]. The drift of the detector was also evaluated for both wavelengths and at different times and values between 0.3 mAU/h and 5 mAU/h were obtained. Presumably this slight instability is mostly due to residual temperature sensitivity (gentle warming with a hot air gun confirmed an effect of temperature), and therefore these values vary with environmental conditions. Again, the performance in this regard was also found to be comparable with what was observed with the commercial detector of the HPLC-system used. The manufacturer states a value of 2 mAU/h at 254 nm [12].

The detector was then further tested by filling the cell with standard solutions of substances absorbing in the relevant ranges around 280 and 255 nm. The calibration curves are shown in Fig. 3. It is evident that a linear response was obtained up to the highest concentrations measured for 3 of the compounds, namely for tryptophan (280 nm) as well as for benzoic acid and 4-hydroxybenzoic acid (both at 255 nm), while for the 4th compound (ascorbic acid measured at 280 nm) a curvature is evident. The fact that a linear response over a large range was obtained for tryptophan, benzoic acid and hydroxybenzoic acid demonstrates, first of all, that the set-up indeed delivers absorbance values according to Lambert–Beer's law. Secondly, the fact that it was possible to measure extremely high absorbances of up to 3, proves that neither significant stray light is present, nor a significant dark current on the photodiodes, as both would lead to non-linearity, *i.e.*, lowered absorbance readings at the high end. Even higher absorbance readings may be possible but this was not tested as not relevant. Note that, while this indicates an excellent performance of the device, for detection in HPLC such extensive ranges are rarely ever needed and are in fact not accessible with the commercial detector used for comparison. The reason for the non-linearity of the response to ascorbic acid must be due to spectral reasons and not to stray light or similar effects. The absorbance spectra of the 4 compounds are given in Fig. 4 together

Table 1
Electrical and optical performance of the detector.

Performance parameter	Deep-UV-LED used			
	280 nm		255 nm	
Baseline noise low pass filtered with 20 Hz cut-off[a]	52 µAU		61 µAU	
Baseline noise low pass filtered with 1 Hz cut-off[a]	7.5 µAU		16 µAU	
	Tryptophan	Ascorbic acid	4-Hydroxy-benzoic acid	Benzoic acid
Correlation coefficient, *r* (absorbance range tested)	0.9999 (32–2780 mAU)	0.9998 (18–535 mAU)	0.9997 (3.5–3132 mAU)	1.0000 (8.3–2767 mAU)
Absorbance values (conventional spectrophotometer)	659 mAU (657 mAU)	671 mAU (562 mAU)	381 mAU (783 mAU)	874 mAU (895 mAU)

[a] Maximum deviations for a period of 20 s for a dry cell, filtering was implemented digitally using the facility of the software for the data-acquisition system employed.

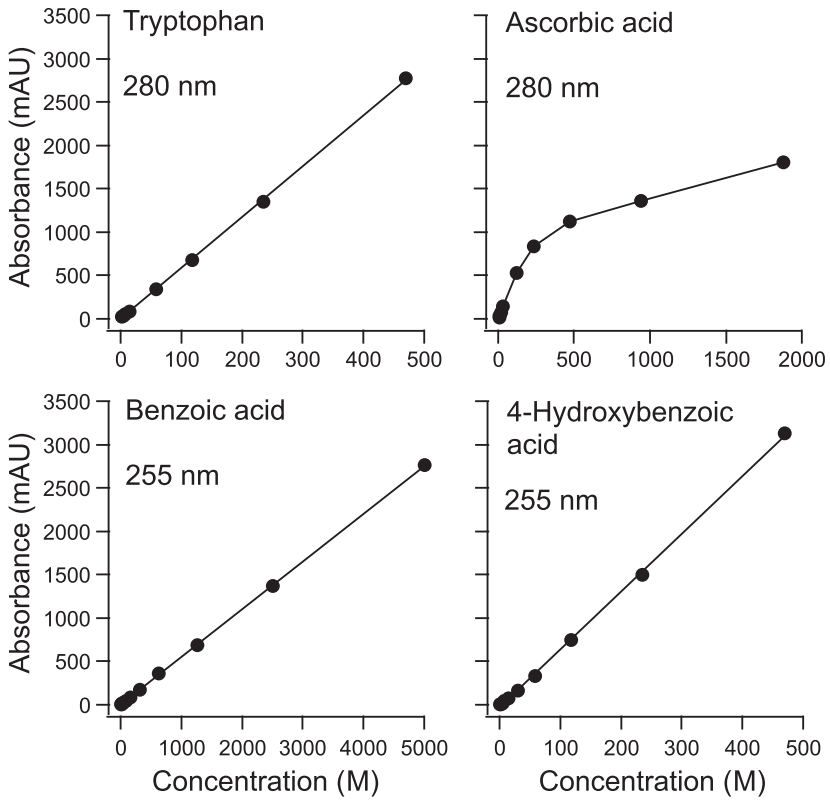

Fig. 3. Plots of absorbance *vs.* concentration for 4 selected compounds. Concentration ranges: tryptophan, 1.831–468.8 μM; benzoic acid, 4.883–5000 μM; L(+)-ascorbic acid, 3.662–1875 μM; 4-hydroxybenzoic acid, 0.458–468.8 μM.

with the emission spectrum of the 280-nm LED. A consultation of the spectra reveals that for ascorbic acid the absorptivity in the region of 280 nm is changing sharply. As Lambert–Beer's law is only strictly obeyed for monochromatic light, and indeed curved responses are generally obtained when the absorptivity is not constant across the actual wavelength band employed (see for example [13]), the behaviour is not unexpected. The bandwidth of the LEDs is approximately 12 nm (data sheet available from the supplier), while the bandwidth of the commercial detector employed can be adjusted in the range from 1 nm to 16 nm when using the diode array detector in the monochromatic mode. It is possible to estimate the absorbance readings obtained for non-monochromatic light sources by considering the spectral variations of the source, absorbing compounds and detector across the wavelength range. The modelled results for tryptophan and ascorbic acid for the 280 nm-LED are given in Fig. 5 together with the actually measured values. The procedure is detailed in the experimental section. While the fit is not perfect, the linear and non-linear calibration curves measured for tryptophan and ascorbic acid respectively are clearly predicted. The deviations between the measured and calculated values at the high end for ascorbic acid must be due to the limited quality of the spectral data available for the LED and the photodiode (as we were not able to measure this data ourselves, this had to be gleaned from small scale plots in the data sheets for the components). Please note, that for the lower absorbance readings relevant for detection in HPLC, even for ascorbic acid, the non-linearity is negligible, and thus this is not a limitation in the application of the device. Correlation coefficients obtained for the 4 species are given in Table 1.

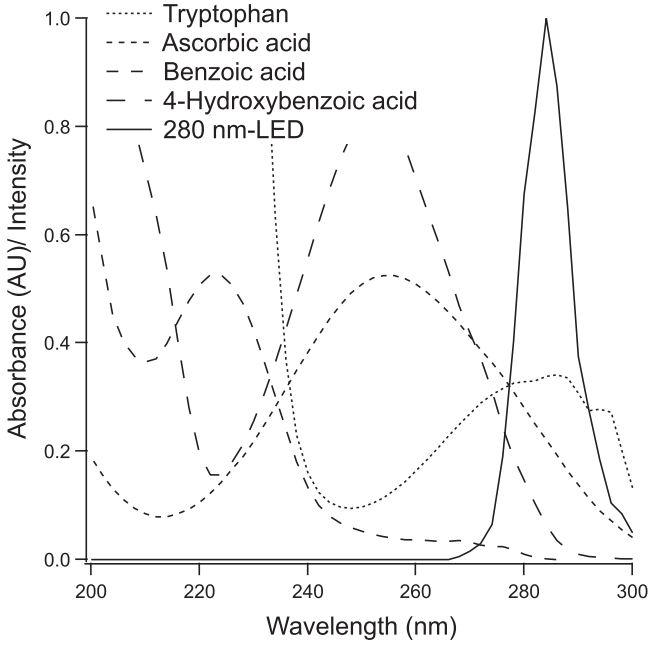

Fig. 4. Spectra of the 4 selected compounds and emission spectrum of the 280 nm-LED.

The absorbance values obtained with the new device for 4 solutions (one for each of the standards) were compared with the readings from a conventional UV-Vis spectrophotometer. The values are given in Table 1. The readings are close for two of the compounds (tryptophan and benzoic acid measured at 280 and 255 nm respectively) but deviations are evident for the other two compounds (hydroxybenzoic acid and ascorbic acid). The reason for this must be the slight different optical characteristics (small variation in the peak wavelength of the LEDs for which the datasheet of the manufacturer states a tolerance of approximately ±5 nm, as

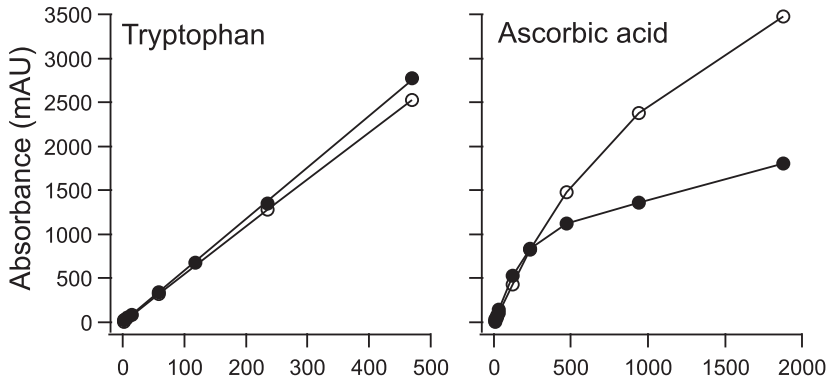

Fig. 5. Plots of absorbance *vs.* concentration for tryptophan and ascorbic acid measured with the LED emitting at 280 nm (full circles) and as predicted from the spectral data of light source, compounds and detector (open circles).

well as differences in bandwidth) as well as again the fact that for the two compounds with the strong deviations the spectra show pronounced variations in absorbance in the region of relevance.

3.3. Performance in HPLC

The detector was then tested for its intended application in a flow through mode using standard solutions. The cell was coupled to the HPLC system and peak areas were determined for the injection of standards of tryptophan for 280 nm and 4-hydroxybenzoic acid for 255 nm, using isocratic conditions. The quantitative data is given in Table 2 together with the values determined for the diode-array detector for comparison. Note that the measurements could not be done simultaneously. It was found that when arranging both detector in series, extra-column band broadening was introduced, so that a direct on-line comparison between the two devices was not possible. As is evident, good linearity was also obtained for the measurements of peak areas for both standards at the two wavelengths respectively. The detection limits can also be considered excellent and compare quite well with those obtained with the commercial photodiode array detector. Note that these LODs do not quite tally with the low noise levels reported in Table 1. The reason for this are small fluctuations of relatively low frequency which were found to occur on the chromatographic baseline and which determine the signal to noise ratio. These were observed for both, the experimental and the commercial detector, but were

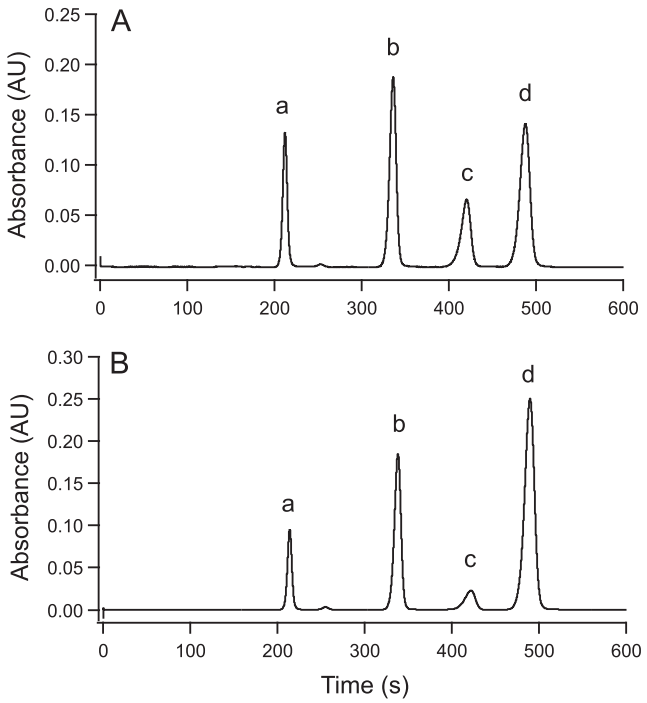

Fig. 6. Separation of aromatic acids, 255 nm: (A) deep-UV-LED detector, (B) commercial UV-detector. (a) Homovanilic acid, 0.31 mg/mL. (b) Sorbic acid 15.4 μg/mL. (c) Salicylic acid, 0.64 mg/mL. (d) 4-Methylbenzoic acid, 0.16 mg/mL. Column: Aqua C18, 5 μm, 250 mm × 4.6 mm. Mobile phase: 0.1% TFA in MeOH/H_2O (55:45 (v/v)). Flow rate: 1.0 mL/min. Injected volume: 10 μL.

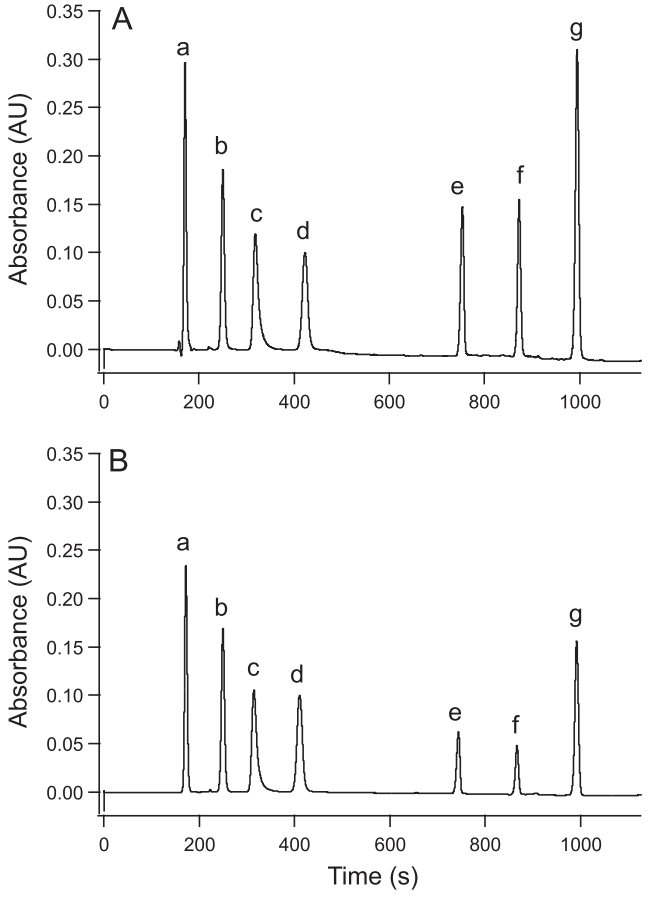

Fig. 7. Separation of water soluble vitamins, 255 nm: (A) deep-UV-LED detector, (B) commercial UV-detector. (a) Ascorbic acid, 48.4 μg/mL. (b) Nicotinic acid, 48.4 μg/mL. (c) Thiamine, 48.4 μg/mL. (d) Nicotinamide, 48.4 μg/mL. (e) Folic acid, 32.3 μg/mL. (f) Riboflavin, 0.16 mg/mL. (g) Vitamin B12, 21.5 μg/mL. Column: Aqua C18, 5 μm, 250 mm × 4.6 mm. Mobile phase: 0.05 M aqueous KH_2PO_4/MeOH, t = 0 min, 90:10 (v/v), t = 4 min, 90:10; t = 15 min, 50:50; t = 18 min, 50:50; flow rate, 1.0 mL/min. Injected volume: 20 μL.

Table 2
Performance parameters in HPLC.

Performance parameter	280 nm tryptophan		255 nm 4-HBA	
	LED-Det.	DAD	LED-Det.	DAD
Correlation coefficient for peak areas	0.9999 (1.8–450 μM)	0.9999 (1.8–450 μM)	0.9999 (0.46–470 μM)	0.9999 (0.46–470 μM)
Reproducibility for peak area[a] (RSD, $n = 12$)	0.18%	0.13%	0.13%	0.09%
LODs[b] in absorbance units	0.4 mAU	0.3 mAU	0.4 mAU	0.1 mAU
LODs[b] as concentration	0.4 μM	0.2 μM	0.1 μM	0.06 μM
Plate number, N	6700	6800	–	–

[a] Tryptophan: 1875 μM; 4-HBA: 80 μM.
[b] Corresponding to peaks which are 3 times as tall as the maximum baseline fluctuations over 5 times the width of the peak.

absent when testing the devices dry or with stationary solutions. It was also noted that this small baseline instability (for both detectors) also showed some relationship to the eluent composition. For pure water the baseline was found to be more stable. The reasons for these observations are not quite clear, but may at least partly be due to mechanical causes. Also compared for the two systems was the peak width. As evident, the plate numbers determined for an identical injection, as a measure for separation efficiency, are comparable for both systems, showing that the new detector does not introduce any extra band broadening. Note, that for the experimental cell this factor is of course determined by the geometry of the flow-through cuvette employed, and not related to the use of an LED as such.

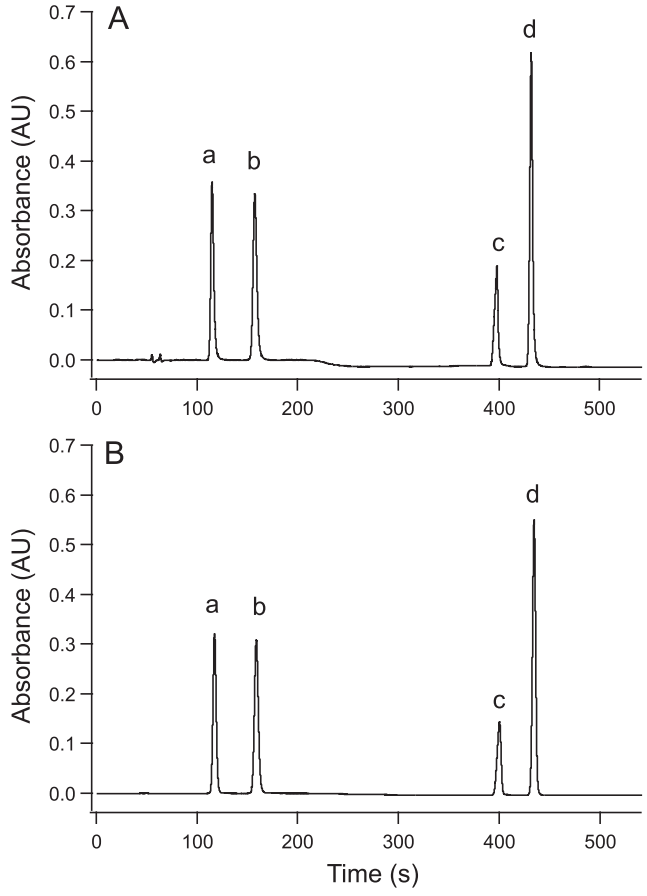

Fig. 8. Separation of analgesics, 280 nm: (A) deep-UV-LED detector, (B) commercial UV-detector. (a) Paracetamol, 0.25 mg/mL. (b) Caffeine, 0.075 mg/mL. (c) Naproxen, 0.125 mg/mL. (d) Diclofenac, 0.125 mg/mL. Column: Eclipse XDB C8, 5 μm, 150 mm × 4.6 mm. Mobile phase: 0.05 M aqueous KH_2PO_4/MeOH/ACN, $t = 0$ min, 80:10:10 (v/v/v); $t = 2$ min, 80:10:10; $t = 5$ min, 35:35:30; $t = 9$ min, 35:35:30; flow rate, 1.5 mL/min. Injected volume: 10 μL.

3.4. Examples of applications

The new detector was then further evaluated by running some separations in comparison with the commercial detector. The isocratic separation of some aromatic carboxylic acids detected at 255 nm is shown in Fig. 6. Note, that again the two chromatograms were not acquired concurrently, but sequentially after swapping the detectors. Some disparity in peak heights is evident. While the values for homovanilic acid and sorbic acid (the first two peaks) are relatively close, the peak for salicylic acid is more than twice as tall when measured with the LED-based detector, while the peak for 4-methylbenzoic acid is smaller for the new detector. These differences must again be due to variations of spectral nature between the two detectors, and do not indicate a shortcoming of the experimental device.

The chromatograms for several water soluble vitamins of Fig. 7A and B measured again at 255 nm show a similar pattern in that some differences in peak heights are evident. These separations were carried out by gradient elution, which illustrates that the LED-detector

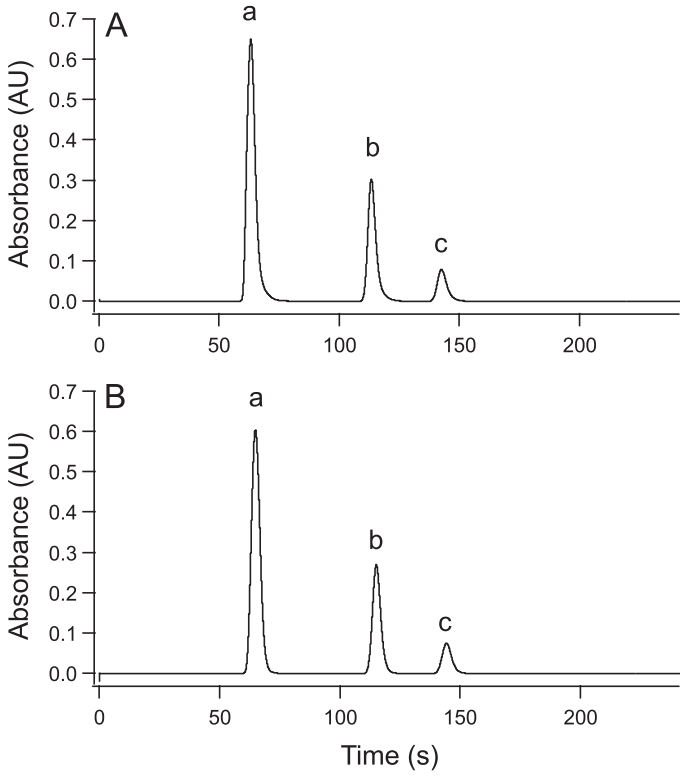

Fig. 9. Analysis of a cold medicine, 280 nm: (A) deep-UV-LED detector, (B) commercial UV-detector. (a) Ascorbic acid. (b) Paracetamol. (c) Caffeine. Column: Eclipse XDB C8, 5 μm, 150 mm × 4.6 mm. Mobile phase: MeOH/H_2O, 45:55 (v/v), flow rate 1.0 mL/min. Injected volume: 5 μL.

is also compatible with this mode of separation. Note that the baselines for both chromatograms are not quite as flat as for the isocratic separation of Fig. 6. These variations are more pronounced for the LED-detector than for the conventional device. It is thought that this is due to some susceptibility to changes of the refractive index of the eluent. Complete immunity to refractive index changes would require a perfectly collimated light beam passing perpendicularly through the wetted interfaces. No optimization in this regard was attempted for the experimental cell.

The separations shown in Fig. 8 of a standard mixture of analgesics demonstrates that the acquisition of chromatograms is also possible at 280 nm. This separation was also performed with a gradient elution, and again some deviations in the baseline are evident for the period when the eluent composition is changing, but this was somewhat more pronounced for the new detector. The two small unidentified peaks visible early in the chromatogram obtained with the LED are also present on the chromatogram acquired with the commercial detector, but are much smaller there and not discernable on the scale of the reproduction. This indicates that these may also be refractive index artefacts.

In Fig. 9, the analysis of a sample of a commercially available cold tablet containing paracetamol, caffeine and ascorbic acid is shown. These chromatograms were obtained with the 280 nm-LED and using isocratic separations. Except for a very slight difference in peak heights, the chromatograms are virtually undistinguishable.

4. Conclusions

The new device was found to give a performance in terms of linearity, precision and limits of detection which is comparable to that of a modern photodiode array detector (DAD) used in the monochromatic mode. A somewhat higher susceptibility to gradient effects was noted then for the commercial detector and some attention may therefore be needed when implementing methods with abrupt changes in eluent composition. The device was powered up for a total of several hundreds of hours, but, in contrast to our simpler earlier design [10], no deterioration of performance was noted. A flexibility in wavelength is possible as similar UV-LEDs for the wavelength range from 240 to 400 nm are available with peak wavelengths spaced at intervals between 5 and 10 nm. While not having the advantage of a DAD of allowing the acquisition of spectra this will not always be necessary, and on the other hand the cost of the new device is a fraction of that of conventional detectors.

Acknowledgement

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