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Selectable-power photoreactor for flow-injection analysis systems and high-performance liquid chromatography post-column photochemical derivatization[1]

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Abstract

A new design for a post-column photochemical reactor is presented, differing from those described in the literature in that different working powers (between 8 and 40 W) may be selected in order to improve detection and linearity of response. The application of the device in post-column photoderivatization of phenolic aldehydes both in high-performance liquid chromatography with UV–Vis or fluorescence detection (isocratic and gradient elutions) and in flow-injection analysis systems is discussed. Use of selectable-power photoreactors such as the one described here allows optimum conditions to be selected for each analyte. Moreover the coil length may be reduced.

Keywords: Post-column reactors; Derivatization, LC; Flow-injection analysis; Photoreactor selectable power; Phenolic aldehydes

1. Introduction

Over the last twenty years photochemical reactors have been widely used and their basic advantages compared with post-column chemical derivatization systems have been shown [1–3]. However, the number of reactors available on the market is rather limited and many researchers have built their own photoreactors, once a suitable method for preparing the reaction coil was described [4–6]. Both the commercial devices and those developed in the laboratory usually have a low-pressure mercury cylindrical tube lamp around which the coil is placed, knitted in such a way that the extra-column band broadening is minimized.

This kind of reactor has proved useful but its applications are limited by the available radiation power as a consequence of the coil geometry in relation to that of the light source itself.

In order to achieve maximum efficiency and selectivity of the photoreaction, a light source should

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be chosen which generates radiation with wavelengths close to the wavelength of the absorption maximum of the analyte. Mercury tube lamps have proved useful in many applications [7–9]. A second important factor is the radiation intensity. In principle, as the photon flow increases, the reaction time required to achieve an appropriate detection level may decrease. However, high intensities may cause photodecomposition of the analytes or of their initial photoproducts, or photoreactions other than those of interest. Thus, a balance must be found between the intensity of the radiation source and the systems efficiency, depending on the aim of the analysis. Other factors must also be considered. For example, 10-W lamps are geometrically unsuitable to use in compact commercially available photoreactors which guarantee a higher level of reproducibility than the laboratory-built reactors. On the other hand, 8-W lamps found in commercial photoreactors lack sufficient power to achieve some types of photoreactions of analytical interest.

The easiest way to increase the radiation power, starting from commercial lamps with a suitable geometry, is to simply increase the number of lamps which illuminate the reaction coil. There are reports on the use of two lamps illuminating quartz [10] or PTFE [11] coils.

Here we present a new type of photoreactor designed and developed in our laboratory, which uses five 8-W commercial mercury tube lamps. The main feature of this prototype is the ability to select different working powers (between 8 and 40 nominal watts) by means of simultaneous, independent or sequential connection of the five available lamps. In this way, we can select the most suitable light power for each analyte in each case, and achieve maximum efficiency without causing photodecomposition reactions which are undesirable or which compete with the photoreaction mechanism of the analyte under study. Moreover, since the system efficiency increases with increasing radiation power, the length of the reaction coil may be decreased – thus making the knitting technique used less critical – resulting in reduced band broadening and improved signal-to-noise ratio.

As a model system to study the characteristics of the proposed photoreactor device, we have chosen a group of twelve polyphenolic aldehydes whose enhanced detectability compared to polyphenolic acids using post-column photoderivatization has already been shown [12].

2. Experimental

2.1. Solvents and reagents

All of the standards of the 12 polyphenolic aldehydes used in this study were of 97–99% purity from Merck (Darmstadt, Germany) and Fluka (Buchs, Switzerland). All solutions were prepared in methanol (HPLC-grade, Merck)–water (purified with a Milli-Q system; Millipore, Milford, MA, USA) (1:1) in the 10–125 ppm range.

Methanol and HPLC-grade water both containing formic acid (95%, Merck) were used as mobile-phase components in all cases. In flow-injection analysis (FIA) and HPLC isocratic modes 3-methoxy -4-hydroxybenzaldehyde (vanillin) was used as model analyte. For HPLC gradient experiments, mixtures of all studied analytes at various concentration levels were eluted using the multisegmented gradient described in a previous paper [12]. The injection volume was always 10 μl.

2.2. Apparatus and chromatographic conditions

The experimental set-up consisted of a pump (Waters, Model 600), a universal injector (Waters, Model U6K), a reversed-phase chromatographic column (Waters, Novapack C_{18}, 15 cm×3.9 mm I.D., 4 μm particle size) and a second injection valve (Model 7010, Rheodyne, Cotati, CA, USA) fitted with a 10-μl loop (used for injections in FIA mode), a laboratory-made photoreactor (described in the next paragraph) and a pair of detectors in series: a diode-array detector (Waters, Model 990+) and a programmable fluorescence detector (PU4027, Philips, Cambridge, UK) having independent data acquisition and control systems. The specific conditions of each analysis are specified in the Results and Discussion Section or in the figure captions.

2.3. Design of the photochemical reactor

The reactor is made up of a commercial knitted tubing coil of PTFE (10 m×0.33 mm I.D; Astec

89502, Tecknokroma, Barcelona, Spain) placed around a low-pressure mercury cylindrical tube lamp (8 W) (General Electric G8T5). Four more lamps of the same kind are placed around the capillary at perpendicular axes. These lamps emit most of their radiation within the spectrum line of 254 nm, close to absorbtion maximum of the compounds tested.

Each lamp is turned on or off by a switch on the outside of the reactor. A neon pilot light shows the condition of each lamp, allowing those which remain switched on during each experiment to be controlled.

The lamp located inside the reaction coil is controlled by the main switch of the reactor. To enhance the radiation of the lamps the inside of the case that holds the reactor is built from curved sheets of sanded steel. Two fans – inlet and outlet – ensure efficient dissipation of the heat generated in the system. Fig. 1 shows a diagram of the experimental device and an outline of the construction of the photoreactor.

3. Results and discussion

3.1. Optimization of the photoreactor

After carrying out some initial tests, we observed that the peak levels obtained as a result of the photoreaction showed measurable variations depending on whether the reactor had been turned on immediately before the analyte injection or had been on for some time.

Fig. 2 shows this influence for a series of five consecutive injections in the FIA mode of a methanolic solution of vanillin, carried out with the reactor at variable power but subjecting the device to stabilization by turning on the five lamps for increasing periods (3–15 min) before selecting the working power (turning off the lamps not used in each case). Fig. 2 shows that a stabilization period of 15 min is sufficient to achieve reproducible results regardless of the working power.

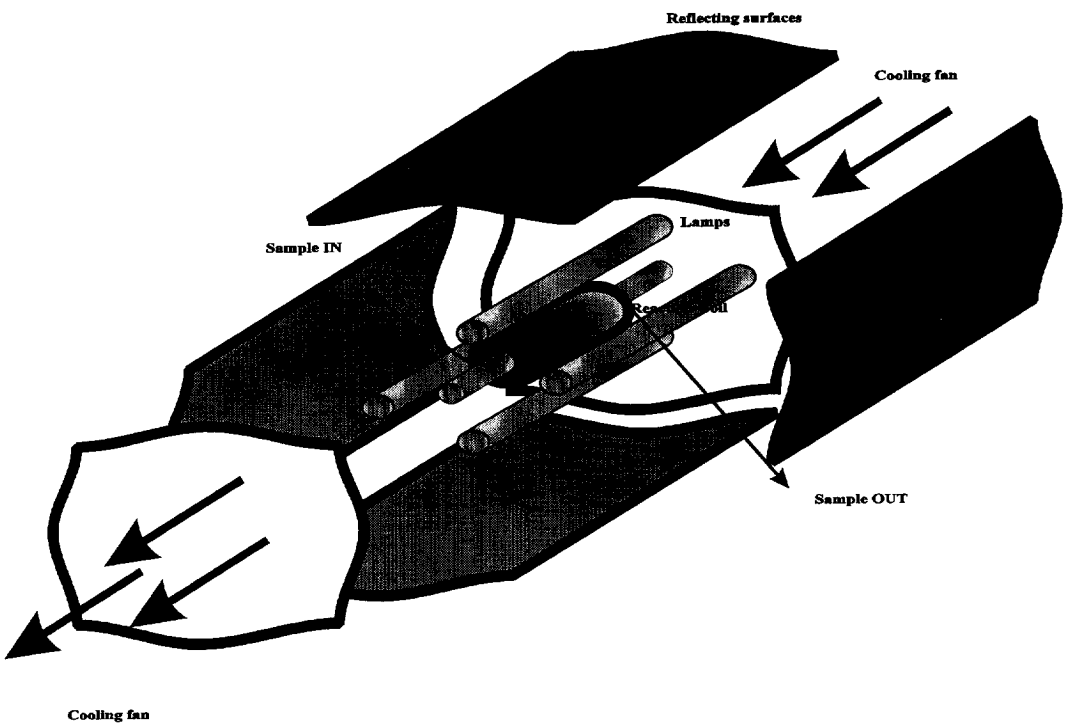

Fig. 1. Exploded view of the selectable-power photoreactor.

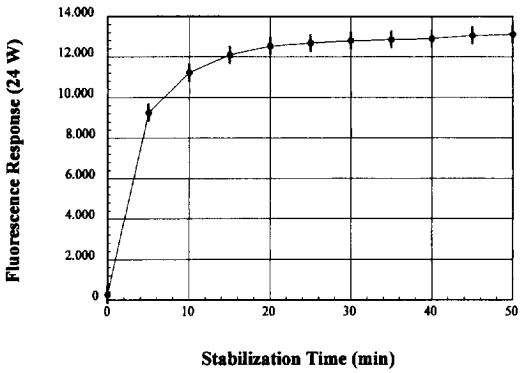

Fig. 2. Example of the stabilization time of the fluorescence response of vanillin at 24 W (FIA mode).

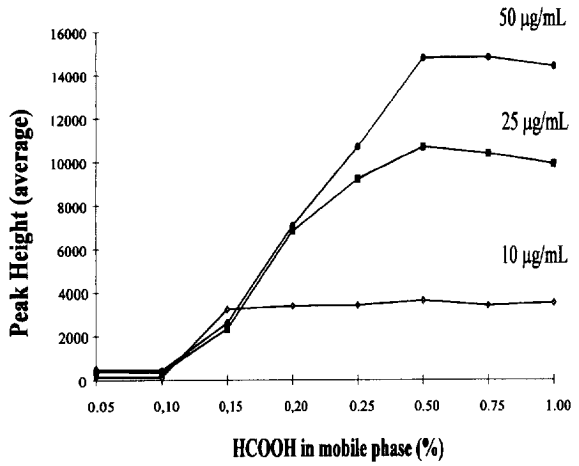

Fig. 3. Variability of the fluorescence response of vanillin in terms of formic acid percentage in mobile phase (average of five injections in FIA mode).

As the chromatographic system usually requires a stabilization period of more than 15 min, switching-on of the device at the same time the chromatographic system is started is more than sufficient to ensure stability of the photoreactor.

3.2. Effect of formic acid percentage in the mobile phase

The effect of the type of acid added to the mobile phase to separate the phenolic aldehydes on the performance of the photoreaction has been reported previously [13]. The photoreaction of phenolic aldehydes is optimized when formic acid is used to acidify the mobile phase. It has also been established that the proportion of acid has an important effect on the extent of the photoreaction. Fig. 3 shows the effect of the percentage of formic acid in the mobile phase on peak height for five injection series in the FIA mode for various standard vanillin solutions. In all cases the mobile-phase flow-rate was constant at 1 ml/min. We can clearly see that no photoreaction occurs if the amount of formic acid in the mobile phase is less than 0.1% and that the extent of the reaction increases as the proportion of formic acid increases, reaching a maximum at 0.5%. It has to be noted that this effect is not only important from the point of species detectability, but also particularly with respect to the linearity of the photoreactor response. Thus, for formic acid percentages of ca. 0.15% the response is independent of the vanillin concentration in the injected solution.

Higher percentages are sufficient to achieve complete photoreaction of the most diluted but not of the most concentrated sample. For percentages higher than 0.5% the response remains constant or is slightly lower, which is probably due to fluorescence quenching in the detector by the acid.

According to our previous experiments [14], the most probable, although not fully confirmed, hypothesis for the photoreaction mechanism is the photoreduction of the phenolic aldehydes by intermolecular hydrogen-atom abstraction to give the corresponding short-lived radical alcohols, the formic acid acting as hydrogen donor as well as obstructing intramolecular hydrogen-atom abstraction. This mechanism would be similar to the ones proposed by Turro [15] and by LaCourse and Krull [16]; however, we could not detect stable dimers as photoproducts. According to published data [15,17] intermolecular hydrogen-atom abstraction from alcoholic solvents to aldehydes and ketones cannot occur in the case of hydroxyl substituents in the 2 or 4 position where intramolecular hydrogen-atom abstraction dominates, thus inhibiting photoreaction. However, in the presence of acids photoreaction takes place because electrons of the donor groups become unavailable. The substantial effects exhibited by the nature and concentration of the acid in the mobile phase tend to confirm these hypotheses

although a more detailed study would be necessary to fully understand the photoreaction mechanism affecting all species considered.

3.3. Sample analysis in FIA systems

As some of the working variables seem to clearly affect the linearity of the response in the fluorescence of the photoproducts, we proceeded to study these effects. To do so we employed FIA systems (the chromatographic column is, in this case, used only as a damper for the pump pulse and samples are injected through the second injection valve in the system). As model analyte for these tests vanillin was chosen. Injections in triplicate were used for solutions of various analyte concentrations (ranging from 25 to 125 μg/ml) for each light power available in the device (8, 16, 24, 32 and 40 nominal watts) and varying the methanol percentage in the mobile phase (from 20 to 50%) including 0.5% formic acid. Peak-height and area values were measured for each series of injections and the average value corresponding to the three injections was calculated (R.S.D. values are given in Table 1). Fig. 4 graphically summarises these results. Linearity of response does not occur at 8 W (one lamp only) but increases with the methanol proportion. This increase can be observed at all powers; however, graphs show that the linearity of response increases with power and only at 32 and 40 W the system behaves in a suitable way for analysis. At intermediate powers, linearity is generally improved when the methanol proportion is low. These conclusions are important as this type of compound may not be resolved in

Table 1
Relative standard deviation (% R.S.D.) of the vanillin injections with different percentage of MeOH in mobile phase and varying photoreactor power (FIA mode)

	Peak height (μg/ml)					Peak area (μg/ml)				
	25	50	75	100	125	25	50	75	100	125
8 W										
20% MeOH	1.62	0.11	0.89	0.18	1.47	1.31	0.08	0.94	0.71	1.20
30% MeOH	0.34	1.00	0.59	0.64	0.84	0.30	0.58	0.45	0.14	0.69
40% MeOH	2.55	1.31	1.24	1.09	0.91	2.60	0.91	0.89	1.26	0.77
50% MeOH	1.28	0.81	0.89	0.85	0.66	0.97	0.36	1.12	1.24	0.76
16 W										
20% MeOH	0.78	0.12	1.77	0.61	0.50	0.21	2.06	0.68	0.36	0.31
30% MeOH	0.19	0.72	0.32	0.70	0.19	0.12	0.62	0.28	0.44	0.16
40% MeOH	0.06	0.52	0.27	0.22	1.19	0.15	0.39	0.24	0.10	0.88
50% MeOH	0.49	0.35	0.15	0.30	0.54	0.69	0.37	0.31	0.52	0.47
24 W										
20% MeOH	0.55	0.48	0.14	0.63	0.43	0.49	0.65	0.30	0.45	0.48
30% MeOH	0.78	0.67	0.46	0.60	0.63	0.64	0.53	0.23	0.34	0.36
40% MeOH	0.50	0.49	0.15	0.52	0.28	0.53	0.35	0.06	0.41	0.31
50% MeOH	0.63	0.22	0.65	0.10	0.43	0.23	0.07	0.58	0.19	0.39
32 W										
20% MeOH	0.95	0.52	0.27	0.59	1.02	0.83	0.19	0.13	0.46	1.31
30% MeOH	0.36	0.19	0.28	0.53	0.48	0.24	0.09	0.34	0.57	0.27
40% MeOH	0.65	0.41	0.74	0.42	0.61	0.54	0.53	0.61	0.46	0.45
50% MeOH	0.67	0.44	0.43	0.37	0.14	0.64	0.69	0.28	0.45	0.32
40 W										
20% MeOH	0.22	0.42	0.72	0.62	0.53	0.25	0.69	0.72	0.52	0.40
30% MeOH	0.12	0.73	0.80	0.51	0.24	0.18	0.43	0.42	0.61	0.21
40% MeOH	0.52	0.45	0.13	0.47	0.13	0.54	0.46	0.29	0.52	0.12
50% MeOH	0.52	0.49	0.47	0.39	0.17	0.69	0.85	0.52	0.31	0.13

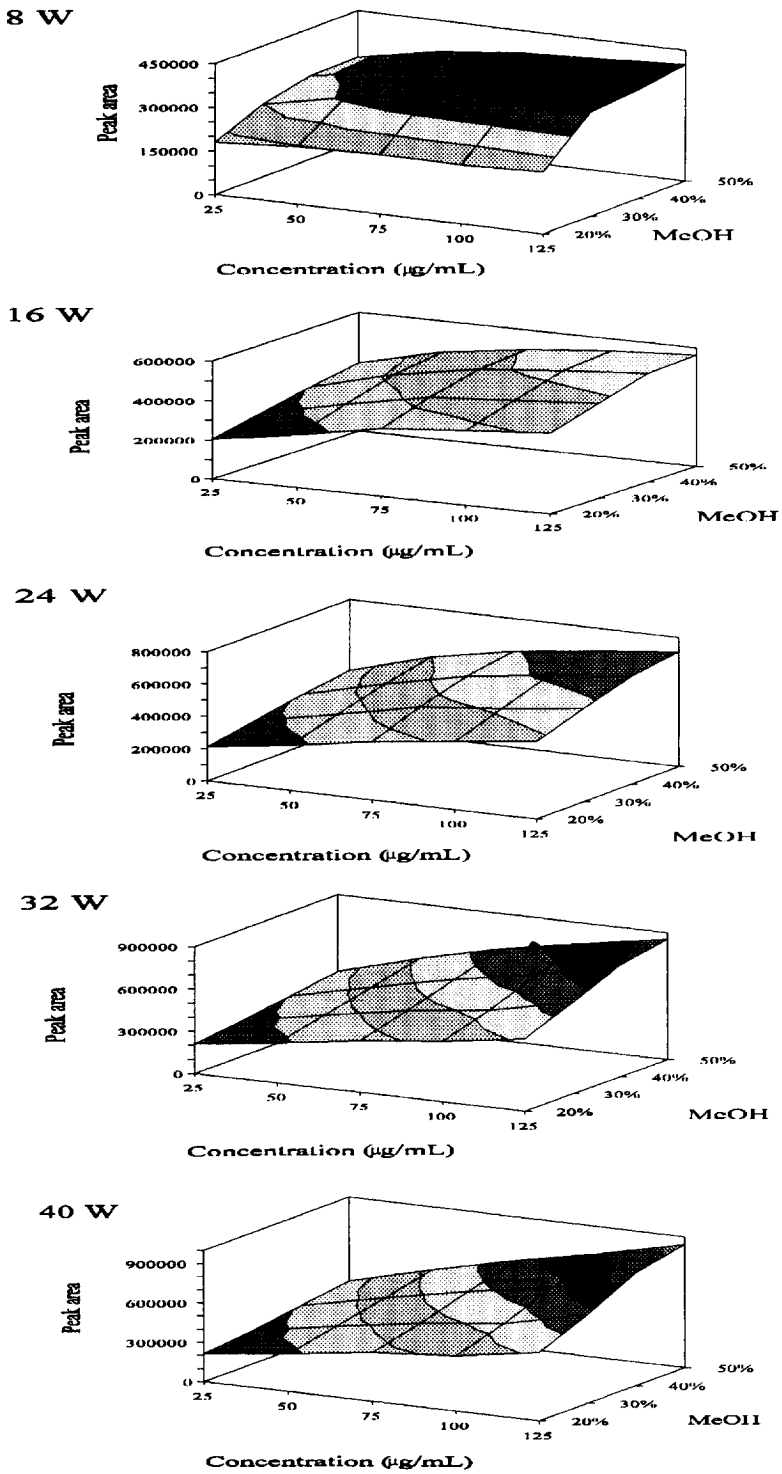

Fig. 4. 3-D graphs showing the fluorescence response of vanillin vs. proportion of methanol in the mobile phase, with the five power values available. FIA mode.

Table 2
Results of the vanillin calibrations with different percentages of MeOH in mobile phase and varying photoreactor power after linear regression (FIA mode)

	Peak height			Peak area		
	R^2	Intercept	Slope	R^2	Intercept	Slope
8 W						
20% MeOH	0.6373	5999	−2.65	0.8897	178 367	297.57
30% MeOH	0.2661	9001	8.13	0.8510	242 602	1045.06
40% MeOH	0.0325	9625	1.25	0.8655	280 083	870.96
50% MeOH	0.5763	9147	7.03	0.9126	278 377	1066.98
16 W						
20% MeOH	0.8860	6387	55.67	0.9628	164 858	2105.53
30% MeOH	0.7821	8738	49.52	0.9345	223 501	2255.02
40% MeOH	0.7431	10 543	46.68	0.9315	273 551	2438.92
50% MeOH	0.6776	11 885	32.10	0.9252	318 969	2149.55
24 W						
20% MeOH	0.9871	5731	81.76	0.9959	146 222	2726.28
30% MeOH	0.9543	7672	90.89	0.9773	202 288	3112.91
40% MeOH	0.9084	9707	91.80	0.9683	254 128	3518.42
50% MeOH	0.8409	1190	978.23	0.9534	304 193	3441.43
32 W						
20% MeOH	0.9973	5336	95.10	0.9977	135 928	3020.25
30% MeOH	0.9948	6169	120.31	0.9952	159 056	3873.86
40% MeOH	0.9936	7435	140.01	0.9986	189 248	4820.39
50% MeOH	0.9608	10 113	141.47	0.9894	256 210	4944.64
40 W						
20% MeOH	0.9942	5335	97.39	0.9933	135 053	3035.54
30% MeOH	0.9934	5845	130.37	0.9905	148 495	4121.79
40% MeOH	0.9955	6584	163.68	0.9919	168 720	5356.08
50% MeOH	0.9934	8782	176.64	0.9984	224 545	5748.87

HPLC using isocratic elution but requires binary gradients. Therefore, in practical situations, the methanol percentage should be varied throughout the testing and it is necessary to ensure the linearity of response of this factor if the mechanism and photoreaction are to be used for quantitative purposes. Table 2 gives the calibration curves for vanillin in the FIA mode, confirming previous conclusions.

3.4. Isocratic elutions

Although we have previously mentioned that the group of phenolic aldehydes considered in this study may not be resolved isocratically, experiments were carried out using vanillin as a model analyte. Elutions were carried out with a methanol percentage of 50% in the mobile phase, 0.5% formic acid and 1.0 ml/min mobile-phase flow-rate. In this case, 10-μl samples were injected through the U6K universal injector. Fig. 5 shows the results of these experiments (R.S.D. values for three injections series are given in Table 3). These results seem contradictory to those previously presented for injections in FIA systems. Although the behaviour of the photoreaction is linear in all working conditions, the expected effect of the photoreactor power does not occur here and apparently one lamp alone achieves the same efficiency as the five together. These results can be understood when comparing analyte concentration in chromatographic bands vs. flow-injection bands. The data for the FIA system in Fig. 4 – for 50% methanol in the mobile phase and using only one lamp (8 W) – indicate that there is a quasi-linear

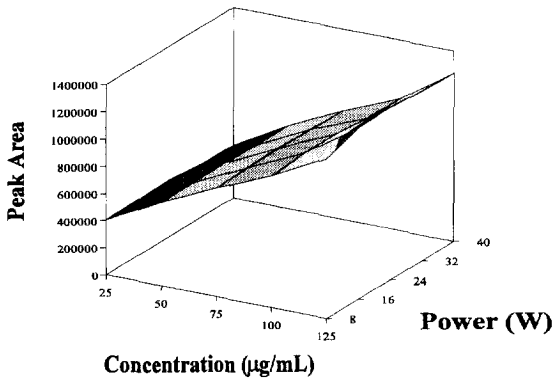

Fig. 5. 3-D graph showing the fluorescence response of vanillin vs. selected power in the photoreactor. Methanol proportion was constant at 50%. Isocratic elution; flow-rate, 1 ml/min.

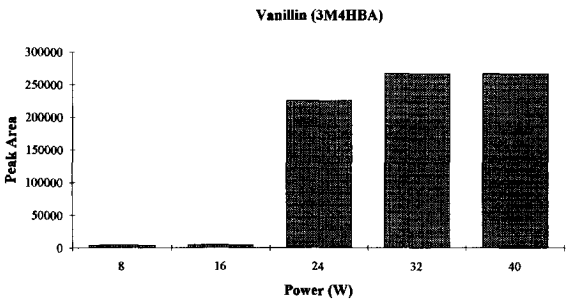

Fig. 6. Intensity of the fluorescence response of vanillin vs. selected power in the photoreactor, for a 1-m PTFE coil. Methanol proportion was constant at 50%. Isocratic elution; flow-rate, 1 ml/min.

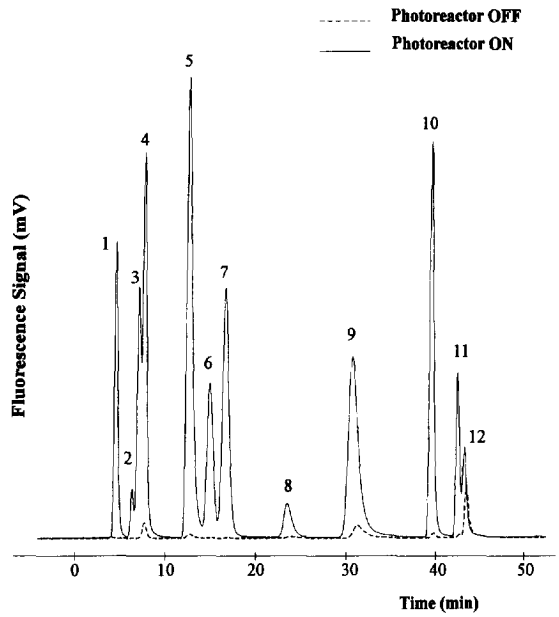

Fig. 7. Overlaid fluorescent chromatograms of a mixture of twelve phenolic aldehydes (75 μg/ml) obtained with the photoreactor turned off and on (40 W). Gradient elution; solvent, water–methanol. Peaks: 1=3,4-dihydroxybenzaldehyde (protocatechualdehyde): 34DHBA; 2=2,5-dihydroxybenzaldehyde: 25DHBA; 3=4-hydroxybenzaldehyde: 4HBA; 4=3-hydroxybenzaldehyde: 3HBA; 5=2-hydroxybenzaldehyde (salicylaldehyde): 2HBA; 6=4-hydroxy-3-methoxybenzaldehyde (vanillin): 3M4HBA; 7=3-hydroxy-4-methoxybenzaldehyde (isovanillin): 3H4MBA; 8=2-hydroxy-3-methoxybenzaldehyde (*o*-vanillin): 2H3MBA; 9=3-methoxybenzaldehyde (*m*-anisaldehyde): 3MBA; 10=3,4-dimethoxybenzaldehyde (veratraldehyde): 34DMBA; 11=2,4-dimethoxybenzaldehyde: 24DMBA; 12=3,5-dimethoxybenzaldehyde: 35DMBA.

Table 3
Relative standard deviation (% R.S.D.) of the vanillin injections with 50% of MeOH in mobile phase and varying photoreactor power (isocratic elution)

	Peak height (μg/ml)					Peak area (μg/ml)				
	25	50	75	100	125	25	50	75	100	125
8 W	1.94	1.28	1.32	2.04	0.30	0.37	0.20	0.28	0.77	1.41
16 W	2.12	1.33	1.03	1.94	0.38	0.31	0.20	0.34	0.26	0.22
24 W	1.47	0.69	0.72	1.98	1.38	0.15	0.05	0.24	0.33	0.37
32 W	0.98	0.77	0.52	1.59	0.80	0.11	0.10	0.05	0.14	0.89
40 W	1.42	1.67	0.31	0.84	1.06	0.08	0.25	0.10	0.05	0.64

Table 4
Results of the calibrations for 12 phenolic aldehydes varying photoreactor power after linear regression (gradient elution)

	8 W			16 W			24 W			32 W			40 W		
	R^2	Intercept	Slope	R^2	Intercept	Slope	R^2	Intercept	Slope	R^2	Intercept	Slope	R^2	Intercept	Slope
34DHBA	0.9659	8412.5	2059.9	0.9942	12065	2040.4	0.9629	28417	1700.1	0.9736	3738.4	2117.7	0.9741	21597	1923.3
25DHBA	0.9900	−3161	282.84	0.9753	823.5	258.75	0.9733	−1158	327.88	0.9478	−1893	339.45	0.9673	−525.7	350.41
4HBA	0.9793	12947	1719.3	0.9972	16753	1684.7	0.9744	24634	1559.1	0.9715	15079	1663.7	0.9761	19354	1637.4
3HBA	0.9689	15260	3537.7	0.9937	15461	3521.8	0.9737	39186	3002.4	0.9485	16314	3306.8	0.9706	25905	3271.4
2HBA	0.9919	13749	4701.3	0.9915	65501	4170.4	0.9769	25617	5207	0.9930	−13012	5879.8	0.9735	12058	5723.3
3M4HBA	0.9886	30365	1450.2	0.9908	33637	1416.9	0.9849	37701	1479.6	0.9924	16993	1730.1	0.9917	23281	1721.2
3H4MBA	0.9764	14236	3232.5	0.9949	18986	3184.7	0.9730	39949	2806.8	0.9749	6058.8	3352	0.9753	25543	3157.1
2H3MBA	0.9729	−7053	401.96	0.9752	−4500	439.34	0.9638	−6012	508.42	0.9686	−3686	525.95	0.9595	−8333	636.07
3MBA	0.9916	−19154	4145.1	0.9849	38817	3396.9	0.9820	−4506	4066.7	0.9874	−10067	3948.6	0.9722	−16339	4062.8
34DMBA	0.9621	90854	1861.7	0.9483	29596	2951	0.9822	74121	2271.5	0.9624	90993	2242.1	0.9821	65233	2629.7
24DMBA	0.9893	31453	802.06	0.9810	16471	1063.9	0.9833	27862	924.23	0.9928	33222	859.32	0.9775	21377	1028
35DMBA	0.9529	−1133	700.41	0.3652	26416	293.4	0.9854	2760.4	722.58	0.9383	−11287	859.03	0.9506	−3269	850.63

relation for low analyte concentrations. As the concentration increases, this linearity is lost because the available photon flow is insufficient to complete the photoreaction within the residence time of the chromatographic band in the photoreactor. The linearity range increases with radiation intensity, and (logically) with the residence period, because the probability of interaction with the available photons increases. In the case of isocratic elutions, band broadening in the column causes much wider sample areas during the time the chromatographic band passes through the photoreactor than when working in the FIA mode. As a result, the analyte concentration (for equivalent injections) in the band decreases and the photoreaction is more efficient. Moreover, the coil used in these experiments is quite long (10 m) which allows a sufficiently long residence period to favour complete photoreaction even with low radiation powers.

From the above it may be concluded that, given the possibility to increase the photon flow, the coil length can be reduced. Fig. 6 clearly shows the effect of the use of a much shorter coil (1 m). In this case, at least 24 W are necessary to achieve a measurable photoreaction and the response is stable at more than 32 W. According to Selavka et al. [5], the use of appropriately designed knitted open tubular (KOT) reactors reduces the extra-column band-broadening to negligible values, irrespective of the tube length used in the PCR construction. Nevertheless, laboratory-knitted short PCRs would be less critical and, in any case, a small reduction in band-broadening should be expected. Our data indicate a peak width (for vanillin) of 115±1.5 s using a 10-m commercial KOT compared to 95±1.3 s for a 1-m laboratory-made loosely knitted coil.

3.5. Gradient elutions

Fig. 7 shows the gradient separation of the phenolic aldehydes considered. The separation of these species and their selective detection compared to the phenolic acids which usually accompany them in real samples of food and agricultural products has previously been shown [12,13], as well as the detection limits and relative standard deviations of the peak height for the species producing signals in the fluorescence detector after the photoreaction [12]. It should be noted that the peak width does not increase proportionally with elution time (as in isocratic separations) and therefore not all chromatographic bands are equally diluted in the process. The results obtained with the 10-m coil suggest that the photoreaction is complete, or almost so, at any power applied starting from 8 W (only one lamp turned on) although there are, in fact, variations in linearity and slope of the calibration curves obtained for each compound at different powers, as shown in the

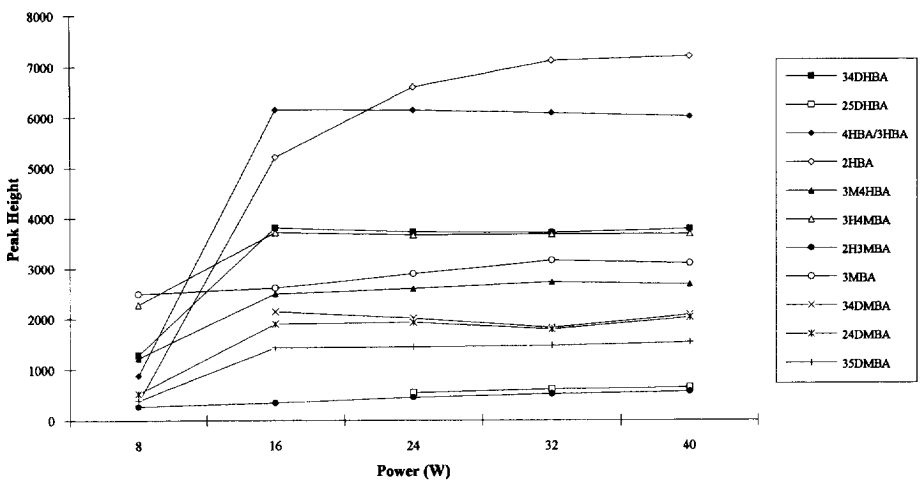

Fig. 8. Intensity of fluorescence response of twelve phenolic aldehydes vs. selected power in the photoreactor for a 1-m PTFE coil. Gradient elution.

calibration data given in Table 4. In any case, the use of shorter coils again shows the effect of the radiation power on the extent of the photoreaction. This effect can be seen in Fig. 8 for a 1-m coil. Some peaks are not detected at a power lower than 16 W. Others exhibit a huge power effect, particularly between 8 and 16 W, while for other compounds this effect is less important. Salicylaldehyde even shows an increase in the extent of the photoreaction for powers higher than 16 W which only stabilises at 32 W. This means that the detection limits reported elsewhere [12] can be improved up to seven-fold for compounds like salicylaldehyde (2HBA) using four or five lamps, up to six-fold for 3HBA and 4HBA and two-fold for vanillin (3M4HBA) and isovanillin (3H4MBA) using only 16 W, while the remaining species more or less have the same detection limits as those achieved with a single 8-W lamp photoreactor.

4. Conclusions

The use of selectable-power photoreactors allows adaptation of the photoreactor conditions according to the technique used (FIA or HPLC in isocratic or gradient mode) in a way that the maximum extent of photoreaction is achieved in each case and that a linear response is abtained that favours quantitative measurements. When using photoreaction as a HPLC post-column derivatization system, working with very short coils will preserve the chromatographic characteristics obtained in separation. However, for some photoreactions it may not be suitable to use excessive radiation powers which could compete with the process of analytical interest. The advantage of the device presented here is its versatility, as the radiation power may be selected independently, allowing working conditions to be precisely adjusted to each particular case.

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