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Simultaneous determination of 3,4-dimethoxybenzaldehyde and 3,4-dimethoxyphenylacetone in industrial waste waters by high-performance liquid chromatography–diode array detection

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Abstract

The environmental pollutants 3,4-dimethoxybenzaldehyde (DMB) and 3,4-dimethoxyphenylacetone (DMPA) were separated and quantitatively determined in treated and untreated industrial waste waters on a porous graphitized carbon column using HPLC with diode array detection (DAD). It was established that the detector response is linear in a wide range of injected quantities for both pollutants, and the logarithm of the capacity factor depends linearly on the concentration of acetonitrile in the eluent. The relative standard deviation of the retention time, peak height and peak area was lower than 1% in the normal and lower than 3% in the lowest concentration range. Peak purity tests indicated that the method separates well DMB and DMPA from other impurities present in the waste waters. Both aerobic and anaerobic treatments markedly decreased the concentration of DMB and DMPA in industrial waters and HPLC combined with DAD proved to be an adequate analytical procedure to follow such changes.

Keywords: Dimethoxybenzaldehyde; Dimethoxyphenylacetone; Water analysis; Environmental analysis

1. Introduction

The growing concern about environmental protection considerably increased the requirements for reliable and accurate analytical methods of environmental pollutants [1]. Due to their high separation capacity and sensitivity various chromatographic techniques such as gas–liquid [2,3] and high-performance liquid chromatography (HPLC) [4,5] and—to a lesser extent—thin-layer chromatography [6,7] and capillary zone electrophoresis [8,9] have been successfully used in environmental analysis. As the concentration of pollutants is generally low the use of more sensitive hyphenated techniques in the environmental analyis is rather a rule than an exception [10,11]. HPLC has been frequently used for the determination of various pollutants in water (glufosinate [12], phenoxyalkanoic acids and other acidic herbicides [13], hydroxy-*s*-triazines [14], fenamiphos and folpet [15], organophosphorus pesticides [16], sulfonylureas [17], phenylurea herbicides and their corresponding anilines [18], atrazine [19], rotenone [20], and various polar pesticides [21]). A wide variety of supports have been tested and used in the HPLC analysis of environmental pollutants. Besides the traditional reversed-phase supports [22,23] nitrile-, amino- [24] and nitro-bonded stationary phases [25], porous graphitized carbon (PGC) [26–28], etc, have also been used for the separation and quantitative determination of various environmental pollutants. Due to its considerable advantages HPLC combined with diode array detection (DAD) has also found application in the environmental analysis increasing the reliability of solute identification and

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the sensitivity of detection of solute with different absorption spectra in one run [29–32]. As the sensitivity of a simple HPLC–DAD system is moderate, on-line enrichment [33,34] and direct large volume injection and coupled column technique [35–37] have been frequently used to decrease the detection limit of polar pesticides to a limit of 0.1 μg/L.

The objectives of our investigation were the development of a HPLC–DAD method for the separation and quantitative determination of 3,4-dimethoxybenzaldehyde (DMB) and 3,4-dimethoxyphenylacetone (DMPA) in industrial waste waters, the study of the effect of aerobic and anaerobic treatments on the decomposition rate of DMB and DMPA and the assessment of the suitability of PGC support for the analysis.

2. Experimental

The samples of waste water were taken at a pharmaceutical plant before treatment and after aerobic and anaerobic treatments. The samples were filtered through a G3 glass filter to remove solid particles and then 5 g sodium chloride was added to each 100 ml sample. The addition of the sodium chloride was motivated by the fact that salt decreases the solubility of the pollutants in the water phase (salting-out effect). Each 100 ml sample was extracted 3 times with 10 ml chloroform. The collected chloroform phases were evaporated to dryness at room temperature in nitrogen atmosphere and the solide residue was dissolved in 1 ml methanol. This solution was used for the HPLC analysis. The separation and quantitative determination of DMB and DMPA were carried out on a PGC column (Shandon Hypercarb 100×4.6 mm I.D., particle size 7 μm; Shandon Scientific, Cheshire, UK) because these solutes are not well separated on a traditional octadecylsilica column.

The HPLC–DAD system consisted of an ISCO model 2350 HPLC pump and an ISCO model 2360 gradient programmer (Isco, Lincoln, NE, USA), a Rheodyne injector with a 20 μl sample loop (Rheodyne, Cotati, CA, USA), a Waters 991 photodiode array detector (Millipore Waters, Milford, MA, USA), a NEC Power Mate SX/16 computer (NEC Technologies, Boxborough, USA) and a Waters 5200 printer plotter (Millipore Waters, Milford, MA, USA). The detection wavelength range was 200–230 nm, the absorption maximum of DMB and DMPA being 203 and 228 nm. The determination of the calibration curve and the qualitative evaluation was carried out at these two wavelengths. The linearity of the calibration curve was checked by injecting both pollutants in the range of 10 μg–5 ng per injection. To compare the reliability of the determination of peak height and peak area both parameters were separately used for the calibration. The flow-rate was 0.6 ml/min. The experiments were carried out at room temperature (22–24°C). Each determination was run in quadruplicate and the relative standard deviations of the retention time, peak height and peak area were calculated. Eluents were the mixtures of water and acetonitrile in various concentrations. Acetonitrile was choosed as organic modifier because of its low UV absorbance. To determine the robustness of the method the separation was carried out at 75.0, 77.5, 80.0, 82.5 and 85% (v/v) acetonitrile concentrations and linear relationship was calculated between the logarithm of the capacity factor (k') and the acetonitrile concentration in the eluent:

$$\log k' = \log k'_0 + bC \quad (1)$$

where log k' is the logarithm of capacity factor; log k'_0 is the logarithm of capacity factor extrapolated to zero acetonitrile concentration in the eluent (intercept, related to the retention capacity of the column); b is the change of log k' value caused by unit change (1%, v/v) of acetonitrile concentration (slope, related to the specific surface area of solutes in contact with the PGC surface); and C is the acetonitrile concentration in the eluent (%, v/v). The separation factor was also calculated at each acetonitrile concentration.

The peaks of DMB and DMPA on the chromatogram of waste water extracts were identified by comparing the retention time and UV absorption spectra with those of authentic standards and by the method of standard addition. The efficiency of separation was checked by the peak purity test carried out at the maximum of absorbance. The qualitative evaluation was carried out according to the calibration curves taking into consideration the

result of peak purity test. The detection limit of the method was determined by using water samples spiked with the pollutants at various concentrations.

3. Results and discussion

The pollutants were not well separated on an octadecylsilica column (250×4 mm I.D.), the retention times being 7.33 (DMB) and 7.46 (DMPA) in water–methanol (1:1 v/v), and 9.42 (DMB) and 9.46 (DMPA) in water–methanol (3:2 v/v). This result is somewhat surprising because the calculated hydrophobicity of DMB and DMPA differ considerably and a good separation can be excepted in reversed-phase conditions. We assume that the electron withdrawing capacity of substituents may influence the apparent hydrophobicity of the compounds resulting in irregular retention behaviour.

PGC showed excellent separation characteristics the peaks of DMB and DMPA are well separated from each other (Fig. 1); the peaks of DMB and DMPA are well separated from each other. Good linear relationships were found between the injected quantity of pollutants and both the peak height and peak area:

$$ng_{DMB} = -5.54 \cdot 10^{-3} + (1.22 \pm 0.04) \cdot 10^{-1} \cdot \text{peak height}$$
$$r_{calc} = 0.9887 \quad (2)$$

$$ng_{DMB} = -4.10 \cdot 10^{-3} + (1.44 \pm 0.05) \cdot 10^{-1} \cdot \text{peak area}$$
$$r_{calc} = 0.9813 \quad (3)$$

$$ng_{DMPA} = -3.96 \cdot 10^{-3} + (1.02 \pm 0.01) \cdot \text{peak height}$$
$$r_{calc} = 0.9914 \quad (4)$$

$$ng_{DMPA} = -1.15 \cdot 10^{-2} + (4.43 \pm 0.76) \cdot 10^{-2} \cdot \text{peak area}$$
$$r_{calc} = 0.9876 \quad (5)$$

Eqs. 2–5 are higly significant the significance level being in each instance over 99.9% (see r_{calc} values). This result indicates that both the peak height and peak area can be successfully used for the qualitative determination of DMB and DMPA. However, the correlation coefficients were higher for peak height than for peak area therefore Eqs. 2 and 4 were used for the quantitative evaluation of the DMB

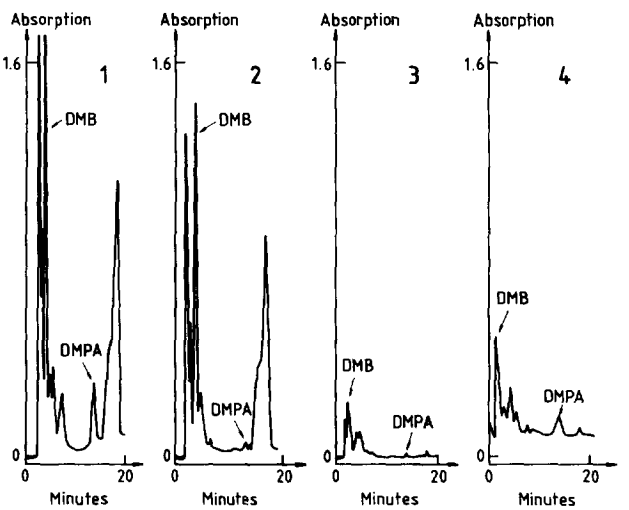

Fig. 1. Chromatograms of 3,4-dimethoxybenzaldehyde (DMB) and 3,4-dimethoxyphenylacetone (DMPA) extracted from industrial waste waters. 1 = waste water influx; 2 = waste water efflux after 15 h aerobic treatment; 3 = waste water efflux after 24 h aerobic treatment; 4 = waste water efflux after anaerobic treatment.

and DMPA contents of waste waters. The log k, values depended linearly on the concentration of acetonitrile (C) in the eluent:

$$\log k'_{DMB} = 1.56 - (6.12 \pm 0.01) \cdot 10^{-2} \cdot C$$
$$r_{calc} = 0.9953 \quad (6)$$

$$\log k'_{DMPA} = 0.61 - (7.10 \pm 0.06) \cdot 10^{-2} \cdot C$$
$$r_{calc} = 0.9915 \quad (7)$$

The significant relationships between the log k' value and the acetonitrile concentration in the eluent indicates that both DMB and DMPA show regular retention behaviour also on PGC column. The separation factor was over 1 in each eluent system proving the adequate robustness of the method. The mean values of the relative standard deviations of the determination of retention time, peak height and peak area for the highest and lowest concentrations were 0.49–2.28%; 0.90–0.99%, 0.88–2.90%, respectively. The low values of the relative standard deviations indicate the stability and reliability of the HPLC–DAD system. The matching values of the peak purity tests varied between 97.89–99.70%. This result indicates that both DMB and DMPA are well separated from the other impurities present in the waste waters and it proves again the suitability of the method for the separation and quantitative determination of these pollutants in waste waters. The detection limit of the method was 1.0 μg/L and 2.5 μg/L for DMB and DMPA, respectively. This discrepany may be due to the different specific absorption capacity of DMB and DMPA.

The DMB and DMPA content of waste waters are complied in Table 1. The data in Table 1 clearly show that both aerobic and anaerobic treatments are suitable to decrease considerably the content of DMB and DMPA in industrial waste waters. It can be further concluded from the data that the HPLC–DAD method using porous graphitized carbon column offers considerable advantages making possible the separation and quantitative determination of DMB and DMPA which is not possible by using traditional octadecylsilica support generally used in the analysis of environmental pollutants.

Table 1
The content of 3,4-dimethoxybenzaldehide (DMB) and 3,4-dimethoxyphenylacetone (DMPA) in industrial waste waters (ppb)

No. of water sample	DMB		DMPA	
	Mean	R.S.D	Mean	R.S.D.
1	875	0.63	837	0.48
2	260	0.95	718	0.67
3	367	1.12	128	1.34
4	50	2.46	70	1.89

R.S.D. = relative standard deviation. 1 = waste water influx; 2 = waste water efflux after 15 h aerobic treatment; 3 = waste water efflux after 24 h aerobic treatment; 4 = waste water efflux after anaerobic treatment.

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