



# Fast liquid chromatography–diode array detection assisted by chemometrics for quantification of seven ultraviolet filters in effluent wastewater

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## ABSTRACT

A fast chromatographic method is presented for simultaneous quantification of seven organic ultraviolet (UV) filters (benzophenone-3,4-methylbenzilidene camphor, octocrylene, 1-(4-tert-butylphenyl)-3-(4-methoxyphenyl)1,3-propanedione), ethylhexyl methoxy cinnamate, ethylhexyl salicylate and homosalate) in effluent wastewater samples. The UV filters were pre-concentrated by Bond Elut-ENV cartridges and separated on an ODS column (15 cm × 0.46 cm, 5 μm) in less than 2.5 min using a non-aqueous mobile phase of methanol–acetonitrile (50:50, v/v) with flow-rate of 1.5 mL min<sup>-1</sup>. Appropriate baseline correction through asymmetric least squares was applied to reduce the matrix of background signals in three way data. Then, second-order calibration based on multivariate curve resolution–alternating least squares (MCR-ALS) was implemented on the unfolded three-way data obtained from liquid chromatography with diode array detection (LC-DAD) through standard addition calibration method for handling co-eluted peaks, systematic and proportional errors. Recoveries ranging from 76% to 130% and %RSD values less than 11.2 for all UV filter shows the accuracy and precision of the proposed method in wastewater samples. In addition, statistical *t*-test as well as computed elliptical joint confidence region (EJCR) confirms the accuracy of the proposed method and indicates the absence of both constant and proportional errors in the predicted concentrations. This study demonstrates that coupling of the fast HPLC-DAD method with powerful algorithm of MCR-ALS can be considered as an efficient method for quantification of UV filters in highly contaminated samples of wastewaters where both time and cost per each analysis can be reduced significantly.

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## 1. Introduction

Organic UV filters such as 4-methylbenzilidene camphor (4-MBC), ethylhexyl methoxycinnamate (EMC), octylcrylene (OCR), and benzophenone-3 (BPN) are used in sunscreen creams, lotions and other personal care products. The crucial effect of these chemical compounds against some skin damages such as photo-induced immune suppression and carcinogenesis is well known [1]. Since these compounds are designed to mostly remain on the outer surface of the skin, therefore they are easily washed off during any contact with water like bathing, swimming, and entered into natural water resources through direct or indirect pathways [2]. Extensive usage of UV filters in sunscreens and other cosmetics along with increasing their shelf life and with continuous transfer to environment has produced a class of emerging contaminants during last decade [3]. So, screening of UV-filters has been received much attention in environmental studies. In addition, monitoring

of these chemical compounds in the influent and effluent wastewater samples is a useful way to study the removal efficiency of wastewater treatment plants [4].

The different drawbacks of organic UV filters to environment have been discussed previously [2]. The lipophilic character and relative persistency of some of these compounds which lead to their bio-accumulation, as well as their harmful effects, such as low birth weight, cellular damages, hormonal activity, and different allergies, have raised attentions to their environmental analysis [5–7].

For many years, most of the relevant analytical methods were focused on the determination of these compounds in commercial formulation of personal care products (PCPs) to attenuate the negative effects from sunlight exposure and to control the quality of procedures. Reverse-phase high performance liquid chromatography (RP-HPLC) with UV–vis detection was the method of choice for the identification and determination of UV filters in sunscreens in several studies [8–11]. According to high concentration of UV-filter compounds in such matrixes (at least at mg g<sup>-1</sup> level), most of the sample preparation methods applied for this purpose, were considered as clean-up techniques and were carried out without any need for sample enrichment. During the last few years, environmental impact of UV-filters as a class of emerging contaminants has

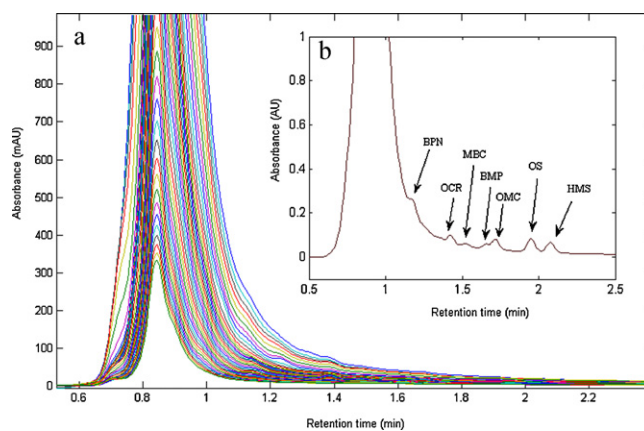
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been studied and various analytical procedures have been developed. In fact, because of bioaccumulation properties of UV filters, even low contamination level of UV-filters during an enough period of time, can lead to considerable health and environmental damages and so the trace analysis techniques seems to be inevitable [2]. Many extraction and clean-up procedures have been reported to obtain satisfactory results in different environmental samples [12–21]. HPLC with UV detector and diode array detection (DAD), gas chromatography–mass spectrometry (GC–MS) and liquid chromatography with tandem mass spectrometry (LC–MS) detection were chosen for qualitative and quantitative analyses of UV-filter compounds. In the LC separation of these compounds, some authors proposed the use of surfactant-modified hydro-organic eluents for satisfactory resolution of overlapping peaks [13,21]. In a review published in 2007, Giokas et al. explained all analytical methods for measuring UV filters in biological and environmental samples [2]. Also, in 2009, Richardson published a review on developments in water analysis for emerging environmental contaminants. One class of these compounds were devoted to UV filters and newly developed analytical methods were reviewed [3].

In the chromatographic analysis of complex environmental samples such as river and wastewaters, poor chromatographic resolution or partial peak separation between matrix constituents and the compounds of interest often occurs. In these cases, the analytes of interest can be quantified through univariate calibration by changing the experimental conditions, i.e., adding a reagent such as sodium sulfite to the sample before pre-concentration [22], optimization of mobile phase condition to longer run times or using an organic modifier in the mobile phase [23]. However these involve spending time and resources and strongly depend on the sample matrix. Also there is no guarantee to ensure that the separation will be complete. Second-order calibration methods that process three-way data are today useful alternatives to solve these types of problems. In fact, a large number of reports on the analysis of complex samples were presented using hyphenated chromatographic data and second-order calibration methods [24]. There are several second-order models with different trilinearity assumptions for multiway analysis, such as generalized rank annihilation method (GRAM) [25], alternating trilinear decomposition (ATLD) [26], self-weighted alternating trilinear decomposition (SWATLD) [27], parallel factor analysis (PARAFAC) [28], PARAFAC2 [29], multivariate curve resolution alternating least squares (MCR-ALS) [30,31], bilinear least squares (BLLS) [32], and unfolded partial least squares/residual bilinearization (U-PLS/RBL) [33]. Among these algorithms, PARAFAC2 and MCR-ALS allow deviations to the trilinearity of three-dimensional data. MCR-ALS is an excellent tool for modelling of LC–DAD data in case of retention time shift between chromatograms and also for exploiting the second-order advantage [34]. This method has been used for the analysis of various samples through recent years [35–39]. In fast LC methodology coupled with MCR-ALS modelling, we can imply studies such as the analysis of biocide mixture using short columns [40], determination of phenolic acids in strawberry samples using an organic modifier [41] and determination of dyes in beverages using a dramatic change in the mobile phase condition [42]. Recently, a fast chromatographic method using PARAFAC2 was proposed by the author for simultaneous quantification of four aflatoxins in pistachio samples [43]. The most important points in this field can be notified as reducing the time of analysis, the amount of consumed solvents and finally cost per analysis.

The major challenge in determination of UV filters is to provide reliable and matrix-free analytical methods for determination of these compounds in biological and environmental samples at low concentration levels [2]. In the present study, we proposed a new strategy based on a non-aqueous and fast LC with MCR-ALS modelling in combination with standard addition method for



**Fig. 1.** Chromatographic profile of a typical wastewater sample monitored at multiple wavelengths (every 3rd wavelength has been shown for more clarity) (a) and chromatogram belongs to the same sample spiked with seven UV filters (w-s6) measured at 305 nm (b). The analytes of interest are indicated.

quantification of seven UV filters among the mostly found compounds in wastewater samples. Fig. 1(a) shows the chromatogram of a real effluent wastewater sample, in multiple wavelengths, from a sewage treatment plant which is studied in this paper. The appearance of a high band at the beginning of the chromatogram (due to the organic components of the sample) and the co-eluted analytes is clear as shown in this figure. For better observation of the analytes, the chromatogram of a spiked sample is inserted in a new window and monitored at 305 nm. Chemical and trade name as well as abbreviated names of the UV filters which are used in this paper are given in Table 1.

## 2. Experimental

### 2.1. Chemicals and solvents

Benzophenone-3,4-methylbenzilidene camphor, octocrylene, 1-(4-tert-butylphenyl)-3-(4-methoxyphenyl)1,3-propanedione, octyl methoxy cinnamate, octyl salicylate and homosalate were all obtained from Merck (Germany) in their pure form. HPLC-grade methanol (MeOH), acetonitrile (ACN), ethyl acetate (EA) and dichloromethane (DCM) were from Merck. Sodium chloride and hydrochloric acid (32%) which were used in sample preparation and pH adjustment, respectively, were of analytical reagent quality from Merck. Ultrapure water was obtained from a Milli-Q water purification system from Millipore (USA). Filter reservoirs and polystyrene-divinylbenzene cartridges (Bond Elut-ENV) (6 mL, containing 500 mg of sorbent) were purchased from Varian (USA).

### 2.2. Instrumentation and software

An Agilent 1200 Series system equipped with a Rheodyne 7725 manual injector with a 20- $\mu$ L injection loop, a degasser system, a quaternary pump, a column oven, a Hewlett-Packard

**Table 1**  
Selected target UV-filters in the present study.

Abbreviation	Chemical name	Trade name	CAS reg. no.
BPN	Benzophenone-3	Eusolex <sup>®</sup> 4360	131-57-7
OCR	Octocrylene	Eusolex <sup>®</sup> OCR	6197-30-4
MBC	4-Methylbenzilidene camphor	Eusolex <sup>®</sup> 6300	38102-62-4
BMP	Methoxydibenzoylmetane	Eusolex <sup>®</sup> 9020	70356-09-1
OMC	Octyl methoxy cinnamate	Eusolex <sup>®</sup> 2292	5466-77-3
OS	Octyl salicylate	Eusolex <sup>®</sup> OS	118-60-5
HMS	Homosalate	Eusolex <sup>®</sup> HMS	118-56-9

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