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Multivariate-Assisted Solid Phase Extraction Procedure for Simultaneous Preconcentration and Assessment of UV-Filters in Wastewater Prior to UV-Vis Spectrophotometric Determination

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Additional information is available at the end of the chapter

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Abstract

Determination of emerging pollutants such as UV-filters in environmental samples is very important because they have been proven to have harmful effects on human and aquatic life. In this study, a simple, fast and inexpensive method combining solid phase extraction (SPE) and UV spectrophotometry was developed for simultaneous preconcentration and determination of benzophenone and sulisobenzone in wastewater samples. The effect of factors affecting the preconcentration of UV-filters was optimized using univariate and multivariate approach. Under optimized conditions, the limits of detection (LOD), limits of quantification (LOQ) and preconcentration factors were in the range of 0.15–0.28 and 0.50–0.93 $\mu\text{g L}^{-1}$, 50–55, respectively. The dynamic linear range was up to 250 $\mu\text{g L}^{-1}$ for benzophenone and sulisobenzone. In addition, the intra- and inter-day precisions were 3.1–3.3 and 4.5–5.2%, respectively. The developed method was successfully applied to determine UV filters in wastewater samples attaining satisfactory recoveries over the range of 99.3–100.7%. The concentration of the target pollutants in wastewater samples ranged from 6.83 to 85.67 $\mu\text{g L}^{-1}$.

Keywords: solid phase extraction, emerging organic pollutants, UV-filters, response surface methodology, UV-Vis spectrophotometry, endocrine disruptors

1. Introduction

Ultraviolet filters are chemical agents that are used in a variety of cosmetics, specifically those used for sun protection such as sunscreen lotions, creams and sprays [1]. These compounds often contain single or multiple aromatic structures (**Figure 1**), sometimes conjugated with

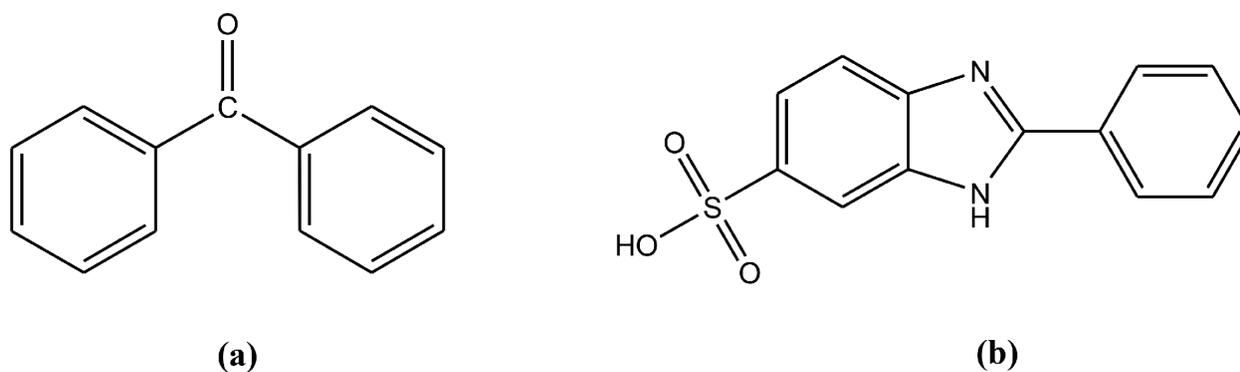


Figure 1. Chemical structures of (a) benzophenone and (b) sulisobenzone.

carbon-carbon double bonds and carbonyl moieties [2]. The presence of these functional groups affords UV filters the ability to absorb photons and rapidly return to the ground state by thermally emitting the energy through vibrational relaxation [3]. This makes the compound to be able to mitigate the deleterious effects of UV radiation [1, 2].

After application, UV-filters are washed off and enter the aquatic environment directly or indirectly via wastewater effluent and recreational water systems [4]. They are also used as sun blocking agents in materials such as plastics, adhesive and rubber, this suggests that these compounds can also leach into the environmental matrices [5–7]. The amount and type of UV-filter used depends on the desired degree of protection, however combined concentrations should not exceed 10% with other organic or inorganic UV-filters [8].

The main concern of the presence of these compounds is their potential toxicity and their effects as xenohormones (effect on reproductive activity) [9, 10]. These effects include estrogenic activity [11], effects on cell proliferation by 4-methylbenzylidene camphor (4-MBC), benzophenones, and octyl methoxycinnamate (OMC) [12]. Several studies have shown hormonal disruption in both in vivo and in vitro test systems in fish and mammals [13–16]. It has also been recently shown that besides estrogens, there are other hormonal targets affected by UV-filters in fish and mammals [17, 18].

A number of detection techniques have been used to quantify UV-filters in environmental water samples. These include techniques high performance liquid chromatography (HPLC) with UV or mass spectrometry detection [19, 20], HPLC-MS/MS [21], gas chromatography-mass spectrometry (GC-MS) and GC-MS/MS [22, 23]. However, the levels of these compounds in environmental waters are usual in the $\mu\text{g L}^{-1}$ range. Therefore, sample cleanup/preconcentration techniques such stir-bar sorptive extraction [20], pressurised liquid extraction [1], dispersive liquid-liquid phase extraction [24], solid phase extraction [25], among others, have been used to improve sensitivity, LODs and to remove interferences prior to quantification with the different analytical techniques.

Solid phase extraction is one of the most established preconcentration techniques used for the simultaneous extraction and analysis of organic compounds [26]. Mainly silica bonded phases such as C18 were formerly used for SPE, however recently modified and tuned solid phases can be used to achieve more specificity [27]. Advantages of SPE include the potential of simultaneous extraction, reduced labour and cost. Of the advantages of solid phase extraction, scientists are mostly attracted to the possibility of using reduced amount of organic solvents and the fact that SPE is highly tuneable with regards to the adsorbents used [28].

Thus the aim of this study was to develop a multivariate assisted solid phase extraction method for the simultaneous preconcentration of UV- filters in wastewater samples prior to their spectrophotometric quantification. The main advantage of the method relies on the use of multivariate optimization approach which led to the reduction of the number of experiments and analysis time as well as the use of a simple, fast and cost effective instrumentation. UV-Vis spectrophotometry was chosen due its simplicity and high availability. The factors (such as sample pH, flow rates, eluent and adsorbent types) affecting the preconcentration step method were optimized using univariate and multivariate approach. The developed SPE/spectrophotometric method was applied to the preconcentration and determination of two UV filters from the wastewater samples collected from Daspoort wastewater treatment plant (WWTP) in Pretoria, Gauteng, South Africa. According to our literature search there are limited reports on the application of UV-Vis spectrophotometry for quantification of UV filters [29]. In addition, to the best of our knowledge, the application of SPE/UV-Vis spectrophotometry for simultaneous preconcentration and determination of Benzophenone and sulisobenzene has been reported for the first time.

2. Experimental

2.1. Materials and reagents

Benzophenone (Reagent plus, 99%), sulisobenzene (5-benzoyl-4-hydroxy-2-methoxy-benzenesulfonic acid) (HPLC, $\geq 97.0\%$) and acetonitrile (for HPLC Plus) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Ethyl acetate was purchased from Merck (Merck, Darmstadt, Germany), ethanol and methanol were purchased from Associated Chemical Enterprises (Johannesburg, South Africa). Stock solutions of benzophenone and 5-benzoyl-4-hydroxy-2-methoxy-benzenesulfonic acid (10 mg L^{-1}) were prepared in ultra-pure water (Direct-Q® 3UV-R purifier system, Millipore, Merck). Working standards of $100 \text{ } \mu\text{g L}^{-1}$ were prepared daily by diluting appropriate volumes of the stock solution in ultra-pure water. The ion exchange resins used in this study as packing materials were Dowex 1x8 (Chloride form) (Sigma Aldrich).

2.2. Instrumentation

A Shimadzu UV-2450 high performance single monochromator UV-VIS spectrophotometer (Shimadzu Corporation, Tokyo, Japan) was used for all analysis of the samples. Solid phase extraction (SPE) was carried out in a VacMaster-24 sample SPE station (VacMaster, Biotage, Sweden). The latter was used to control the sample loading and elution flow rate in the range of $1\text{--}3.0 \text{ mL min}^{-1}$. An OHAUS starter 2100 pH meter (Pine Brook, NJ, USA) was used for pH adjustments of the reagents and to measure the pH of samples

2.3. Sampling and sample collection

Influent (after sediment removal) and effluent wastewater samples were collected from Daspoort wastewater treatment plant (WWTP, Pretoria, Gauteng, south Africa). The samples were collected in pre-cleaned 500 mL glass bottles. The samples were then refrigerated at 4°C .

Factors	Low level (-1)	Central point (0)	High level (+1)
Sample pH	4	7	10
Sample flow rate (SFR) (mL min ⁻¹)	2	3.5	5
Eluent flow rate (EFR) (mL min ⁻¹)	1	2	3

Table 1. Factors and levels used in 2³ factorial design for extraction and preconcentration of UV filters.

2.4. Solid phase extraction procedure

The columns were prepared according to [30]. Briefly, polyethylene columns of diameter 1.0 cm and 6 cm in height were used for preconcentration. Slurries of 0.5 g of Dowex 1x8 in double distilled deionized water were prepared and packed to columns to heights of about 1 cm. A porous frit was placed at the bottom of the column and at the top of the packing material to hold and confine the adsorbent within the designated capacity/volume. The columns were washed with 6 mL of double distilled deionized water followed by conditioning with 3 mL organic solvent (methanol, ethanol, ethyl acetate or mixture of methanol and acetonitrile) and then 3 mL of double distilled deionized water. Due to the scarcity of reference materials for UV-filters, a commercial sunscreen lotion was used as a reference material for the validation of the SPE/UV method. An appropriate amount of the sunscreen lotion was accurately weighed and dissolved using a small volume of methanol (2 mL) and made to the mark with double distilled deionized water and used for validation experiments.

An aliquot (10 mL) of model solution containing benzophenone and sulisobenzone at a concentration of 100 µg L⁻¹ was passed through a packed column at a flow rate of 2–5 mL min⁻¹. After percolating the synthetic samples through, the cartridges were washed with 3 mL double distilled deionised water. Then retained analytes were eluted with 2 mL organic solvents. The optimization of the solid phase extraction method was carried out using a 23 full factorial design involving three variables such as pH, sample flow rate (SFR) and eluent flow rate (EFR). Maximum, central point and minimum levels are presented in **Table 1**. The second step of the optimization strategy involved the application of a response surface methodology (RSM) based on a central composite design. All the experiments were carried out in random order and the experimental data was processed by using the Minitab 17 software program.

3. Results and discussion

3.1. Optimization of separation and preconcentration method

3.1.1. Selection of adsorbent and eluent type: univariate approach

Selection of the adsorbent and eluent type was achieved by packing columns using the ion exchange adsorbent (Dowex 1x8). Each experiment was done in triplicates for each solvent type and adsorbent combination. The flow rates and the sample pH were fixed at 2 mL min⁻¹

for both the sample loading and elution and 7, respectively. The results obtained are presented in **Figure 2**.

Selection of the adsorbent and eluent was done using the absorbance of benzophenone and sulisobenzone at the wavelengths of 260 and 220 nm, respectively. Since the absorbance is directly proportional to concentration, a higher absorbance can be related to higher concentration. Thus, from the univariate optimization, the most effective adsorbent and eluent combination was found to be Dowex 1x8 and methanol (**Figure 2**). This combination was further used for the optimization of the solid phase extraction procedure for both benzophenone (UV-01) and sulisobenzone (UV-02).

Due to the overall charge of adsorbents, the extraction and preconcentration of the analytes was possible by means of ionic interactions. Dowex 1x8 has an overall positive charge, thus the negatively charged analytes could interact with the positive charges of the adsorbent. This resulted in higher absorbances and Dowex 1x8 resin was selected as the suitable adsorbent for further studies.

The polarity of the solvent was the contributing factor on the elution of the analytes, the more polar solvent resulted in better elution from the SPE column, and hence higher absorbances for methanol were observed when used in combination with Dowex 1x8. This was a consequence of the methanol having the ability to displace the analytes from the positively charged Dowex 1x8 adsorbent. The 1:1 mixture of acetonitrile and methanol also had promising results, but did not perform better than the methanol alone. Acetonitrile could not be used for this study even though it is more polar than methanol, there are dangers associated with the use of pure acetonitrile like the risk of cyanide poisoning as a result of its decomposition products.

Experimental conditions; mass of adsorbent 0.5 g, sample volume 10 mL at $100 \mu\text{g L}^{-1}$, eluent volume 2 mL, pH 7, flow rates 2 mL min^{-1} . MeOH = methanol, ACN = acetonitrile, EtOH = ethanol.

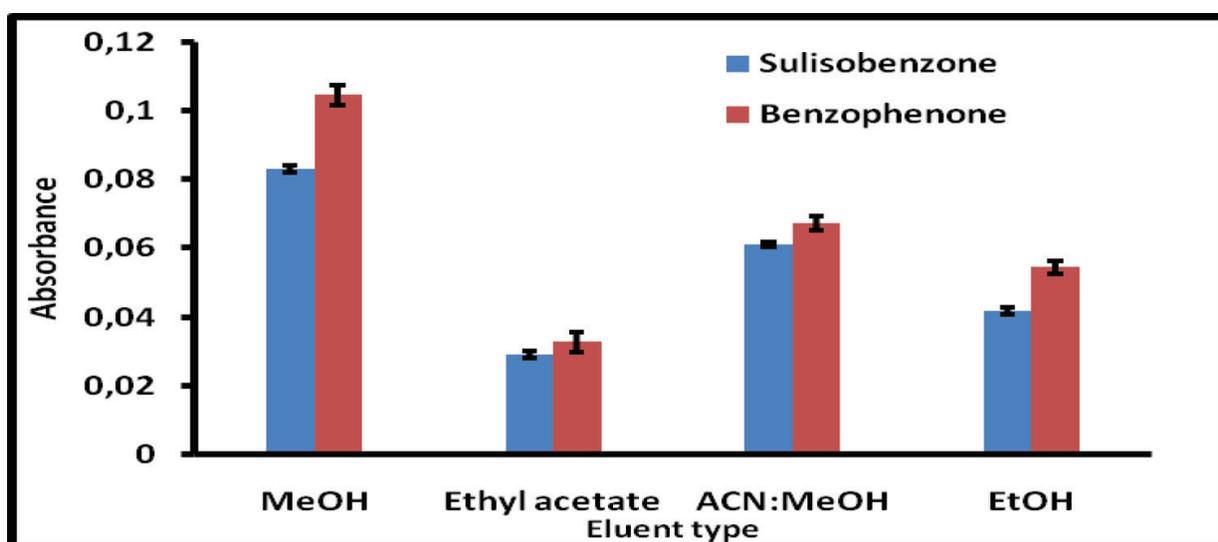


Figure 2. Selection of suitable adsorbent and eluent combination in model aqueous solution.

3.1.2. Optimization of the SPE operation parameters: Multivariate approach

In order to achieve quantitative preconcentration of analytes by SPE system, the optimization of the most influential parameters, such as sample pH, sample and eluent flow rates, was carried out using 2^3 full factorial design and response surface methodology (RSM) based on a central composite design. Two level full factorial design (FFD), involving 11 experiments was used for screening of the significant factors for the extraction and preconcentration of UV filters. **Table 2** presents the factorial design matrix and the analytical responses (expressed as average percentage recovery, %R) obtained in each experiment. Analysis of variance (ANOVA) reproduced in the form of Pareto chart was used to investigate the significance of the effects SPE procedure. The Pareto chart of main effects and their interactions produced are shown in **Figure 3**.

It can be seen from **Figure 3** that for simultaneous preconcentration of UV filters, sample pH and EFR and their interactions were statistically significant. The effect of sample flow rate on the analytical response (%R) was not significant at 95% confidence level. The overall results obtained for the screening step indicated that sample pH and EFR required further optimization. Whereas, sample flow rate was fixed at 3.5 mL min^{-1} .

A central composite design matrix consisting of 14 experiments and analytical response based on each of the experimental runs (**Table 3**) was used for further optimization of the SPE method. The analysis of variance (ANOVA) of the predicted response surface quadratic model for the recoveries of UV filters was obtained. The ANOVA results were analysed using quadratic equations (not included) for the models to illustrate the dependence of the analytical response with respect to the evaluated main effects [31].

The 3D response surface plots (**Figure 4**) were used to access the interactive relationship between individual variables (sample pH and EFR) and analytical response [31]. Based on

Expt.	pH	SFR (mL/min)	EVR (mL/min)	UV-01 (%R)	UV-02 (%R)
1	4	2	1	34.39	33.7
2	10	2	1	39.63	39.1
3	4	5	1	51.01	53.5
4	10	5	1	72.71	75.4
5	4	2	3	12.22	16.0
6	10	2	3	8.84	9.1
7	4	5	3	11.58	10.6
8	10	5	3	10.24	17.6
9	7	3.5	2	83.55	72.8
10	7	3.5	2	78.88	77.5
11	7	3.5	2	81.08	78.6

Table 2. Two level (2^3) full factorial design matrix and analytical response.

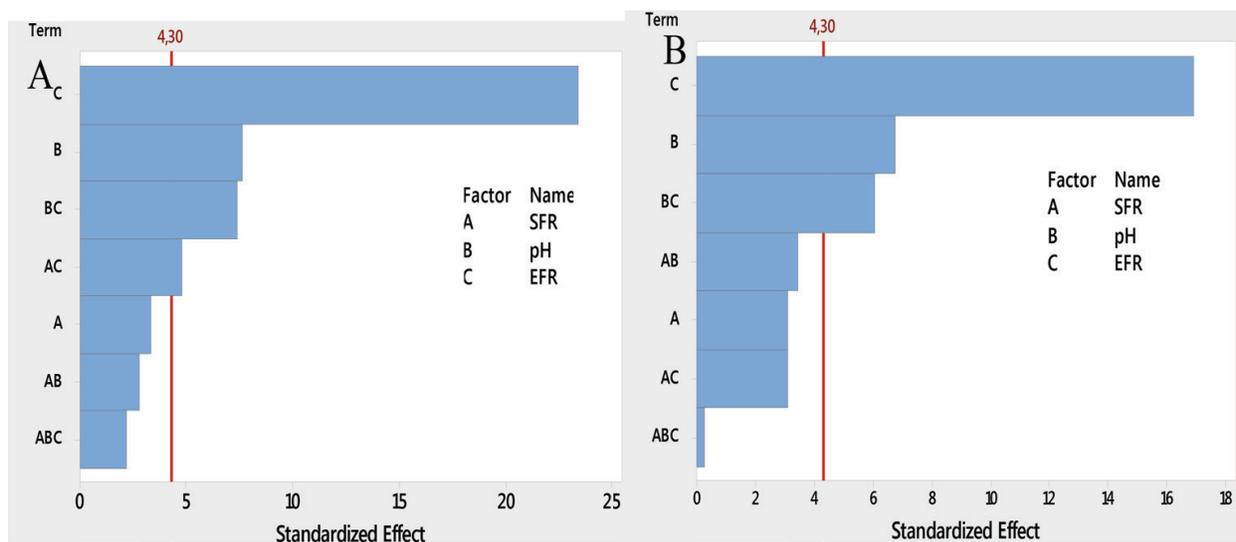


Figure 3. Pareto charts of standardized effects for variables in the preconcentration of (A) benzophenone and (B) sulisobenzone.

quadratic equations and 3D surface response plots, the calculation indicated that pH = 7.5 and EFR = 2 mL min⁻¹ provided maximum retention and recovery of the studied analytes. Therefore, the results obtained from both designs, illustrated that the optimum conditions that led to quantitative extraction and preconcentration of UV filters were 7.5, 3.5, 2 mL min⁻¹ for sample pH, sample and eluent flow rates, respectively.

Sample	pH	SFR (mL/min)	EFR (mL/min)	UV-01 %R	UV-02 %R
1	4	3.5	1	66.1	63.4
2	10	3.5	1	65.7	44.5
3	4	3.5	3	49.7	16.6
4	10	3.5	3	25.9	19.2
5	7	3.5	2	61.3	51.9
6	7	3.5	2	54.8	59.2
7	7	3.5	2	49.7	49.7
8	2.8	3.5	2	78.8	49.6
9	11.2	3.5	2	42.0	66.0
10	7	3.5	0.5	100.1	103.1
11	7	3.5	3.4	32.2	17.4
12	7	3.5	2	75.0	81.5
13	7	3.5	2	74.8	82.0
14	7	3.5	2	75.1	81.8

Table 3. Central composite design matrix and analytical response.

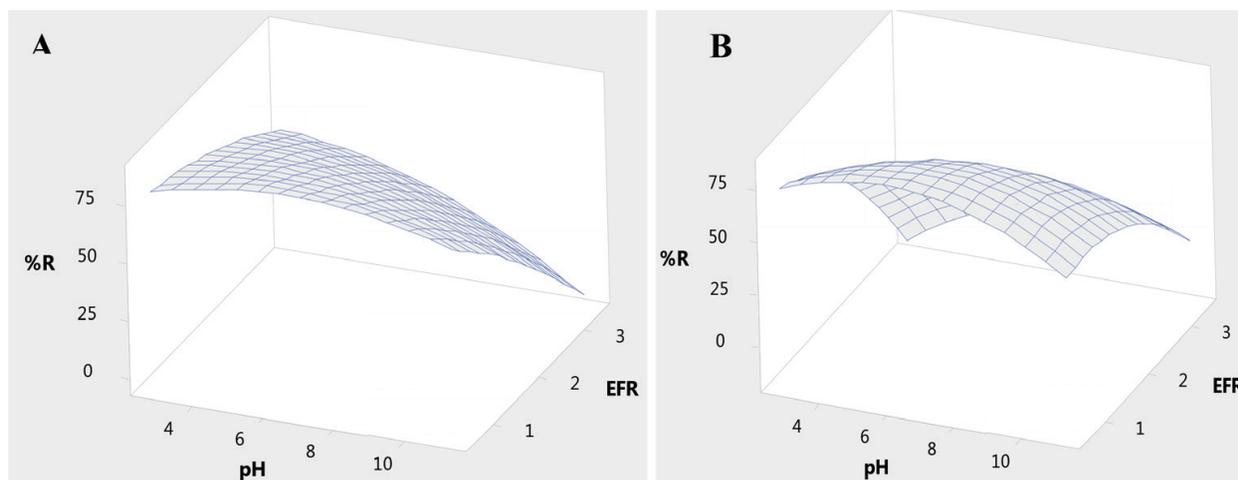


Figure 4. Response surfaces obtained for (A) benzophenone and (B) sulisobenzene after extraction and pre-concentration by SPE.

The effect of pH on the extraction and pre-concentration of UV filters can be seen from **Tables 2** and **3**. Acidic pH resulted in lower recoveries. This is because benzophenone and sulisobenzene have pKa values of 7.5 and 7.6, respectively, meaning that in acidic pH they are more likely to accept H⁺ ions resulting in lower recoveries as they end up with an overall positive charge. In more alkaline conditions (pH 10), the analytes are easily displaced on the adsorbent, resulting in little or no adsorption.

The central pH (7) showed the highest recoveries for both UV-filters. This is a result of the interaction of the analytes' negative charge with the positive charges of the adsorbent prior to elution with methanol.

The optimum conditions obtained by the multivariate approach were confirmed experimentally. Under these conditions (7.5, 3.5, 2 mL min⁻¹ for sample pH, sample and eluent flow rates, respectively), quantitative recoveries ranging from 96 to 98.6% were obtained. These recoveries were compared with the predicted recoveries values (95.6 and 98.1% for benzophenone and sulisobenzene) obtained using the RSM model. It was then concluded that the results obtained by RSM model were valid since there was no significant difference at a 95% confidence level between the experimental and predicted values.

3.2. Analytical performance

Under the determined optimum experimental conditions, the analytical performances of the developed method for pre-concentration and determination of UV-filters were investigated. The calibration curves were obtained after a set of standard solutions (0 to 350 µg L⁻¹) was processed using the described SPE procedure. The concentrations of the analytes in the eluent solutions were quantified with the aid of a UV spectrophotometer. The limits of detection and quantification were calculated using the expressions: $LOD = 3Sd/b$ and $LOQ = 10Sd/b$, where Sd is the standard deviation of 10 replicate measurements at lower concentrations of calibration curves and b is the slope of each calibration curves. Dynamic linear ranges (DLR), correlation coefficient (R^2), enrichment factor (EF), LOD and LOQ for benzophenone were determined to be LOQ-250 µg L⁻¹, 0.9990, 50, 0.28 µg L⁻¹ and 0.93 µg L⁻¹,

respectively. Whereas for sulisobenzone, the DLR, R^2 , LOD, LOQ, and EF were found to be $LOQ=250 \mu\text{g L}^{-1}$, 0.9991, $0.15 \mu\text{g L}^{-1}$, $0.50 \mu\text{g L}^{-1}$ and 55, respectively. Furthermore, the intra-day (repeatability; $n = 10$) and interday (reproducibility; $n = 7$ working days) precisions of the SPE method, expressed in terms of relative standard deviation (% RSD), ranged 3.1–3.3 and 4.5–5.2%, respectively. The analytical performance of the proposed method was compared to other methods that reported in the literature **Table 4**. It can be seen that the performance of the current method was comparable or better than those reported in the literature. In addition, the LODs obtained using the current method were lower compared to [25, 32].

3.3. Validation and application

The accuracy of the SPE/UV procedure was evaluated using a sunscreen lotion with a sulisobenzone content of 1.75% (w/w). The recovered sulisobenzone was $1.69 \pm 0.07\%$ (w/w) meaning that the percentage recovery was 96.6%. Therefore, the determined values by SPE/UV were in the acceptable range. In addition, the accuracy and matrix effects were investigated by analysing spiked real waste water samples and the results are shown in **Table 5**. From the recoveries shown in **Table 4**, it can be seen that the SPE/UV procedure described was not affected by the matrix effects as the recoveries for both benzophenone and sulisobenzone ranged from 99.3 to 100.7%.

As seen on **Tables 5 and 6**, there was a significant amount of both UV filters on the influent. This can be explained by the fact that the Daspoort waste water treatment plant treats domestic waste water. Therefore as explained by [37], personal care products are usually applied to

Analyte(s)	Matrix	Analytical method	DLDLR ($\mu\text{g L}^{-1}$)	LOD ($\mu\text{g L}^{-1}$)	EF	% RSD	Refs.
Octicrylene	Wastewater	MEPS-GC-MS	0.25–20	0.081	-	7	[33]
Benzophenone-3	Water	CE-ESI-MS	300–20000	150	3400	1.5–6.5	[25]
Benzophenone-3	Water	SBSE-LC-MS/MS	0.005–0.5	0.0009	-	3–7	[34]
Benzophenone-2	Human serum	DLLME-UPLC-MS/MS	0.6–40	0.2	-	1.9–13.1	[35]
Benzophenone-3	Sea water	DLLME-GC-MS	0.1–0.5	0.03	262	<15	[25]
Benzophenone	Tap water	DDA-IL-DLLME	0.002–1.5	0.0013	-	3.5–5.3	[32]
Benzophenone	Sunscreen	SPE-GC-MS	10–2000	4.4	25.3	4.6–5.5	[36]
Benzophenone and sulisobenzone	Wastewater	SPE-UV/vis	0.50–250	0.15–0.28	50 and 55	3.1–5.2	Current work

MEPS = microextraction in packed syringe, CE-ESI = capillary electrophoresis-electro spray ionisation, SBSE-LC-MS/MS = stirbar sorptive extraction-liquid chromatography tandem mass spectroscopy, DLLME-UPLC = dispersive liquid-liquid microextraction-ultra pressure liquid chromatography, GC-MS = gas chromatography-mass spectroscopy, SPE = solid phase extraction, DDA-IL = double dispersant assisted-ionic liquid, UV/vis = ultraviolet-visible spectrophotometry.

Table 4. Comparison of the analytical figures of merit of the current method and those reported in the literature.

Sample	Added ($\mu\text{g/L}$)	Benzophenone		Sulisobenzene	
		Found ($\mu\text{g/L}$)	% R	Found ($\mu\text{g/L}$)	% R
Influent 1	0	85.8 \pm 1.3		69.4 \pm 1.2	
	50	135.3 \pm 2.3	99.3	119.7 \pm 3.5	100.7
	100	186.3 \pm 2.5	100.6	169.4 \pm 4.2	100.0
Effluent 1	0	6.83 \pm 0.92		19.8 \pm 0.9	
	50	56.7 \pm 1.2	99.8	69.6 \pm 1.3	99.7
	100	106.9 \pm 3.1	100.0	119.1 \pm 2.7	99.3

Table 5. Analysis of wastewater samples (influent and effluent) spiked and unspiked from Daspoort (Pretoria, Gauteng, South Africa) wastewater treatment plant.

Samples	Months	Benzophenone		Sulisobenzene	
		SPE/UV	SPE/HPLC	SPE/UV	SPE/HPLC
Influent	August	78.6 \pm 1.2	79.4 \pm 1.5	56.3 \pm 2.1	58.0 \pm 1.8
	September	155.3 \pm 2.4	157.2 \pm 2.2	171.3 \pm 3.1	172.2 \pm 2.8
	October	327.3 \pm 4.3	328.9 \pm 4.0	337.3 \pm 3.6	337.6 \pm 3.6
Effluent	August	18.5 \pm 0.7	19.5 \pm 0.5	14.5 \pm 0.7	15.1 \pm 0.5
	September	57.9 \pm 1.3	59.0 \pm 1.5	23.6 \pm 0.9	24.2 \pm 0.8
	October	134.5 \pm 1.5	135.1 \pm 1.2	45.3 \pm 0.5	46.0 \pm 0.2

Table 6. Analysis of influent and effluent over from Daspoort (Pretoria, Gauteng, South Africa) wastewater treatment plant a period of 3 months.

the skin and later washed off into drains which are connected to wastewater treatment plants. From wastewater treatment plants, the water is discharged into rivers [3]. This has resulted in the occurrence of UV-filters in surface waters [22], sediments [38, 39], drinking water and even fish [4, 12, 40].

The presence of UV-filter in different water bodies does not only have an effect in humans as suspected endocrine disrupters [18]. Their effects spans into aquatic life, as reported by [3], benzophenone can cause cell membrane impairments in fresh water protozoa. Benzophenone was also found in other fresh water species in percentages ranging from 50 to 80% by [41].

The described method was applied in the analysis of real water samples collected over a period of three months as expressed in **Table 6**. The influent and effluent samples were collected over two seasons, namely winter (one month) and spring (two months). From **Table 6**, it was observed that between the three months, October showed the highest concentrations for both the influent and effluent. This was because it was significantly warmer during spring when compared to August. It is also worthy to note that the concentrations of benzophenone were higher than those of sulisobenzene. This could be the consequence of the degradation of sulisobenzene during the water treatment process. This is possible because benzophenone

forms the backbone of sulisobenzone, this means that when the sulisobenzone loses the methoxy and sulfonic acid side chains, traces of the benzophenone can remain in the water.

The described SPE/UV procedure was compared with a reference method, SPE/HPLC method using the same extraction conditions. The obtained results from the SPE/UV methods were comparable with the SPE coupled with HPLC method. According to the paired student t-test, there was no significant difference between the two methods at 95% confidence level. Therefore, the SPE/UV procedure can be utilised as a rapid, cheap and effective method for the determination of UV-filters in water samples.

4. Conclusions

The combination of SPE and UV-Vis spectrophotometry offers a simple, inexpensive and selective procedure for the assessment of UV-filters in wastewater samples. With the aid of multivariate optimisation of key parameters in the solid phase extraction procedure, it was possible to achieve satisfactory analytical performance. Real sample analysis showed that as explained by [27], wastewater treatment plant processes are not exhaustive enough to completely remove emerging organic pollutants. There were still some traces of benzophenone and sulisobenzone found in the effluent which is released into the nearby river. This means that the flora and fauna in the river is exposed to these potentially toxic compounds. Thus, the next step would be to study the distribution of these UV-filters in the river where the effluent is released into.

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