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Detection of imidacloprid and Bisphenol-S by Solid Phase Extraction (SPE) coupled with UV-VIS spectrometer and LC-MS

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ABSTRACT

Solid-phase extraction (SPE) and UV/Vis-spectrometer are acknowledged as economical and efficient technique analytical techniques and applied in analyzing target organic compounds in water and other aqueous samples. The present study suggested imidacloprid (at 270nm) and bisphenol-S (at 259nm) can be detected and quantitatively measured via UV-vis spectrometer. The assay was linear with a good coefficient of correlation for both imidacloprid (R^2= 0.9992) and bisphenol-S (R^2 = 0.9996). Based on SPE coupled with UV-spectrometer, the recovery of IMP and BS were achieved at 93-97% and 86-116% respectively, which are close to that achieved by SPE coupled with liquid chromatography-mass spectrometer (LC-MS) analysis; 84-102% for imidacloprid and 83-92% for bisphenol-S.

Keywords: *analysis of emerging micropollutant; solid-phase extraction (SPE); UV-Vis spectroscopy; liquid chromatography-mass spectrometer (LC-MS*
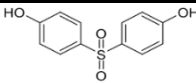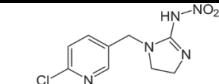
1. INTRODUCTION

Emerging micropollutants (EMPs) can be defined as predominantly synthetic and naturally occurred chemicals presented in various water sources, which are deleterious to human health and ecosystem through the food chain. Recently, EPMs have been frequently detected in natural water sources at the global scale, but the monitoring, regulation and efficient remediation of EMPs are insufficient to meet increasing demands derived from both human health and ecological security [1-6]. Imidacloprid (IMP) is one of the most common neonicotinoids pesticides, which has been widely detected in wastewater effluent and raw water (rivers & wetlands) at 10 µg/L to 100 µg/L [7-12]. IMP exhibited the aquatic toxicity, especially onto aquatic invertebrate, arthropods and neurological toxicity to pollinator (e.g. the population of honey bees and birds). Population reduction in honey bees and birds were observed due to their exposure in IMP contaminated areas [10, 13-15]. Bisphenol-S (BS) has been introduced as a safe replacement to bisphenol-A in various industrial products, However, recent researches show that BS also exhibits a potentially high endocrine negative effect on human and aquatic species based on fatal mouse tests; in some cases, BS could even possess higher toxicity than bisphenol-A and other bisphenol analogues [16-19].

To monitor EMPs and problematic pharmaceuticals residues in different water sources, development of reliable analytical techniques and procedures are urgent. Liquid-liquid extraction (LLE) and solid phase extraction (SPE) are two commonly applied methods for the sample preparation before analysis, but various studies reported that SPE has apparent advantages over the LLE at prospect of high recovery, pre-concentration factor, low consumption of organic solvents, simplicity, easy automation and operation [20-21]. UV-visible spectrometer is a relative time-saving and cost-saving and portable instrument to detect and measure target contaminant in the prepared model waste-water among analytical techniques. Besides, gas chromatograph-mass spectrometer (GC-MS) and liquid-chromatograph-mass spectrometer (LC-MS) have been widely applied because of their higher accuracy, sensitivity and selectivity compared to SPE-UV spectrometer despite higher economic cost [22].

Table 1. Basic chemical and physical properties of bisphenol-S and imidacloprid [23-26]

Chemicals	Bisphenol-S	Imidacloprid
Chemical strcuture		
CAS No.	80-09-1	138261-41-3
Molecular Mass (g/L)	250.27	255.66
Pka	8.00	11.12
LogP	1.2	0.56
Water solubility (mg/mL)	1.1	0.58-0.61

This research aims to develop methods which can achieve detection and determination of bisphenol-S and imidacloprid in model wastewater sample by applying SPE and UV-spectrometer and liquid chromatographic-mass spectrometer (LC-MS). Primary objectives include 1) To study valid SPE method of re-concentration of IMP and BS in test sample preparation, which for quantitative and qualitative analysis of the concentrations. 2) To compare SPE recovery results derived from UV-spectrometer and LC-MS analysis in order to validate the experimental methods and to confirm the usability of SPE-UV spectroscopy method in the analysis of IMP and BS in aqueous solutions.

2. MATERIALS AND METHODS

2.1. Chemical and Materials.

Bisphenol-S (>98%) and Imidacloprid (98%) were purchased from Sigma-Aldrich (UK). Their chemical and physical properties can be viewed in Table 1. HPLC-grade methanol (>99%) was purchased from Acroes (UK). Acetonitrile (ACN) and 98% formic acid were obtained from Fisher Scientific (UK). Deionised water was prepared through the ELGACAN B114 water deioniser with a C114 cartridge (ELGA Labwater). For establishing calibration curves, reagent (50:50 (v/v) MeOH/CAN) was mixed with a given amount of bisphenol-S and imidacloprid separately to make 20mg/L stock solutions. For the test solutions, stock solutions of bisphenol-S (20mg/L) and imidacloprid (20mg/L) were prepared separately with deionised water, which was applied to prepare the test solutions (100 µg/L, 10 µg/L) respectively. Stock solution and standard solution samples were stored in the refrigerator (<4°C), and need to be used within one week. 200 mL and 500 mL of 100 µg/L test solutions and 1000 mL of 10 µg/L test solutions were prepared by dosing stock solution (20mg/L in deionised water) of bisphenol-S and imidacloprid into tap water, as shown in Table 2.

Table 2. Description of the prepared test solution and theoretical information of elutes.

Simulated test solution			After extraction	
C. (µg/L)	Vol. (mL)	Replication (n)	Elute Vol. (mL)	Elute Conc. (mg/L)
100	200	x3	10	2
100	500	x3	10	5
10	1000	x3	10	1

2.2. Solid Phase Extraction.

Solid-phase extraction (SPE) method was applied to collect the target compounds dissolved in the prepared test solution. Strata-X 33µm polymeric reversed-phase columns (pore size 88A, surface area 818m^2/g and particle size 28µm; sorbent mass 200 mg/6 mL) were applied as SPE cartridge in this study. 1L conical flask, plastic cock, rubber corks and plastic tubes were assembled as an SPE device for condition, loading and washing of test water solution, and the elution was completed in glass manifold with pressure meter connect onto FB 70155 rotary vacuum pump (Fisher Brand), purchased from Fisher Scientific. Volumetric flask, plastic connectors, rubber corks, plastic tubes were assembled to build an extraction device. Strata-X reverse-phase cartridge (200 mg/6 mL) was applied for extraction of each prepared test solution under low pressure provided by the vacuum pump. Each cartridge was pre-conditioned with mix reagent (50:50 (v/v) MeOH/ACN) followed by washing with 30 mL of pH 7.0 deionised water. Then the sample was loaded and extracted under vacuum through the SPE cartridge at the flow rate of 10 mL/min. Subsequently, the SPE columns were rewashed with 30 mL deionised water then dried for 20min under full vacuum condition. Bisphenol-S and imidacloprid were eluted with mix reagent (50:50 (v/v), MeOH/ACN) and collected into the 10 mL conical flask, adding mix reagent in the conical flask and reconstitute the volume to 10 mL. Due to the interference of methanol-dissolved extracts in LC-MS analysis and high concentration of target compounds in SPE extracts which is beyond the maximum detection limitation, the 1 mL collected SPE extracts were dried at 30-35 °C with the heating evaporator. Afterwards, reconstituted to 1 mL with the mix of ACN/H2O (v/v 20/80), then 1/10 aliquot of reconstituted samples were transferred to LC-MS vials, and then adding up to 1 mL with ACN/H2O (v/v 20/80) in order to prevent contamination of LC column. The real quantity of targetting compounds was calculated based on the dilution factors.

2.3. Spectra and Calibration Curve.

Spectra files and standard calibration curves are two prerequisite tools in the analysis by UV-vis spectrometer. For establishing the spectra of bisphenol-S and imidacloprid, three samples with serial concentrations were prepared, which respectively is 4mg/L, 6mg/L and 8mg/L. Then the spectra were built under scanning mode of GENESYS™ 10S UV-Vis Spectrophotometer (Thermo Scientific), the highest peak and corresponding identification UV-wavelength were determined based on spectra. For establishing the UV absorbance calibration curve of bisphenol-S and imidacloprid, 17 calibrating points were decided in this case, which range from 0-10mg/L. 17 calibration standard samples were prepared by serial dilution of stock solution (20mg/L in 50/50 v/v, MeOH/ACN), and concentrations are 0.1mg/L, 0.2mg/L, 0.3mg/L, 0.4mg/L, 0.6mg/L, 0.8mg/L, 1mg/L, 1.2mg/L, 1.4mg/L, 1.6mg/L, 1.8mg/L, 2mg/L, 4mg/L, 6mg/L, 8mg/L, 10mg/L, respectively. Based on each scatter derived from 17 calibration spots, linearity coefficient (R^2) and the coefficient equation were calculated, and the measured UV-absorbance intensity of each sample can be converted into the concentration of the target compounds. After the measurement method established as stated above, then transferring a portion of samples into quartz made cuvette (Fisher Scientific) and insert into UV-Vis Spectrophotometer to measure the UV-absorbance.

2.4. LC-MS Analysis.

The LC-MS instrument employed to analyze IMP and BS was Acquity Premier XE system, which consists of ACQUITY ultra-performance liquid chromatography (UPLC). Chromatography column applied is High Strength Silicate column (C18. 100 x 2.1mm, 2.6 um particles, Thermo Accucore). The Mobile Phase was a mixture of solvent A and Solvent B, solvent A was made of HPLC-grade methanol, and Solvent B was made of 0.1% formic acid in deionised water. For analysis of imidacloprid and bisphenol-S, the equilibration started with elution of 100% solvent B at 0.2 mL/min flow rate for 1min. Then elution of solvent B is introduced at 1min and linearly increase to 100% throughout 7min and always remain this elution till 8 min 30 seconds, at which solvent A decrease to 0% at 9th min, then the elution consist till the 17min when the elution end at this time. The injection volume of the sample was 250uL with the running time of overall 17min. The detected retention time of imidacloprid and bisphenol-S are at 7.31 min, 6.01 min respectively. The m/z of precursor ion of imidacloprid and bisphenol-S are 256.0595 and 251.0372, and identifying m/z of product-ion of imidacloprid and bisphenol-S in mass spectra are 209.0587, 156.9953 respectively (

Table **3**). A 7-points and 9-points calibration curve for LC-MS analysis was respectively established based on detected mass spectra response against the prepared standard solution of IMP and BS, as shown in

The difference % was commonly employed as an indicator which able to reasonably evaluate the precision and validity of the calibration curve, on account of the particular working mechanism of mass spectra. In the present study, the calibrating point with difference % lower than 20% was rational and applied for establishing the calibration curve.

Table **4**. IMP and BS standard solutions were prepared by serial dilution of 2mg/L of BS and IMP stock solution in methanol. Difference % means the bias that is referring to the concentration of prepared standard solutions in comparison with the target concentration.

| Bisphenol-S | 6.01 | 251.0372 | 156.9953 |

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Table **4**. The details of standard solution for established LC-MS calibration curve of IMP and BS.

Imidacloprid			Bisphenol-S		
Target Conc. (µg/L)	Prepared Conc. (µg/L)	Difference %	Target Conc. (µg/L)	Prepared Conc. (µg/L)	Difference %
1	1.1	6.3	2.5	2.8	12.9
2.5	2.7	6.5	5	4.3	-13.7
10	11.4	14.1	10	10.8	8.1
25	28.3	13.3	25	26.5	6.1
50	39.6	20.8	50	50.4	0.7
100	99	-1.1	100	118.8	18.8
250	244.1	-2.4	250	277.1	10.9
			500	482.3	-3.6
			1000	986.6	-1.3

Table **3**. The detected retention time, characteristic m/z parent ion and product ion m/z of IMP, BS and AZM.

Chemicals	Retention T. (min)	Precursor ion (m/z)	Product ion (m/z)
Imidacloprid	7.31	256.0595	209.0587

3. RESULTS

3.1. Scanning Spectra and Calibration Curve of BS and IMP.
As Figure 1 shows, the highest absorbance peak of imidacloprid was detected in spectra; which is 270 nm (Fig. 1, left) and consisted with the identifying wavelength reported previously [27-28]. Due to that the highest peak presents the highest absorbance; thus, the 270nm was applied for detecting the imidacloprid in water samples. For bisphenol-S, highest absorbance appeared at 259 nm (Figure 1, right), it was thus applied as the detecting wavelength for bisphenol-S, which also consistent with the characteristic absorbance peak recorded in previous studies [29-30].

Calibration curve of bisphenol-S and imidacloprid were built with 17-round detection of absorbance (Table 5). Figure 2 shows calibration curves for the absorbance vs the corresponding concentration range, and they exhibit high linearity between absorbance and concentration in the standard samples ($R^2 >$ 0.998).
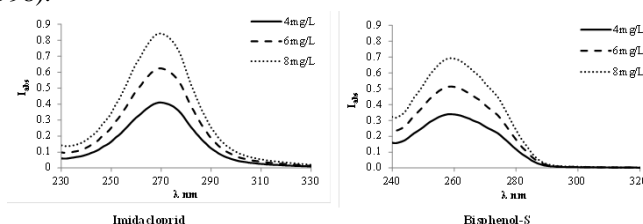

Figure 1. Spectra of imidacloprid (λmax $= 270$nm) (left) and bisphenol-S (the λmax$= 259$nm) (right).

Table 5. Concentration of prepared calibration standard samples against measured UV absorbance.

Bisphenol-S (4,4'-Sulfonyldiphenol) (λmax = 259nm)		Imidacloprid (λmax = 270 nm))	
Concentration (mg/L)	Absorbance (λ_{max} = 259)	Concentration (mg/L)	Absorbance (λ_{max} = 270)
0	0 ± 0.000	0	0 ± 0.000
0.1	0.011[a] ± 0.000[b]	0.1	0.003 ± 0.001
0.2	0.021 ± 0.001	0.2	0.016 ± 0.000
0.3	0.031 ± 0.000	0.3	0.025 ± 0.001
0.4	0.041 ± 0.001	0.4	0.036 ± 0.001
0.6	0.060 ± 0.001	0.6	0.061 ± 0.001
0.8	0.073 ± 0.001	0.8	0.087 ± 0.001
1.0	0.094 ± 0.001	1.0	0.107 ± 0.001
1.2	0.110 ± 0.001	1.2	0.129 ± 0.001
1.4	0.132 ± 0.001	1.4	0.155 ± 0.000
1.6	0.146 ± 0.001	1.6	0.182 ± 0.001
1.8	0.164 ±0.001	1.8	0.203 ± 0.001
2	0.180 ± 0.001	2	0.223 ± 0.001
4	0.344 ±0.001	4	0.411 ± 0.001
6	0.519 ± 0.002	6	0.626 ± 0.001
8	0.703 ± 0.001	8	0.866 ± 0.003
10	0.854 ± 0.002	10	1.085 ± 0.003

Note: [a]Mean absorbance (n = 4); [b]Standard error (n = 4)

3.2. SPE Recovery Study.

Table 6 shows that calculated SPE recoveries obtained from the analysis of UV-vis spectrometer and LC-MS. Recoveries obtained from UV-spectrometer were calculated through equation-1 shown below. For SPE of highly concentrated samples (100 µg/L), mean recoveries of imidacloprid and bisphenol-S are 86-103% and 93-94% respectively via UV-vis spectrometer test, which is presented among the acceptable range from 80 to 120%. For SPE of low concentrated samples (10 µg/L), the 116% and 97% mean recoveries were respectively obtained for bisphenol-S and imidacloprid based on UV-vis spectrometer test, which is also presented among the acceptable range from 80% to 120%.

$$Recovery\% = \frac{Mass\ extracted\ from\ model\ water}{Mass\ added\ in\ model\ wastewater\ beofre\ extracrtion} \times 100$$
(Eq.1)

As Table 6 shows above, SPE recoveries tested by applying LC-MS analysis are 83-92% and 84-102% respectively for bisphenol-S and imidacloprid, which are presented in the acceptable range from 80% to 120%. In comparison, it can be observed that LC-MS derived recoveries are consistent with results derived from the study using UV-vis spectrometer. By applying pair t-test via Minitab 17, the p-value is 0.012, which indicate no significant difference presented between recoveries based on SPE-UV spectrometer and LC-MS ($p < 0.05$). In terms of detection and quantification of IMP and BS in the test solution, it can be suggested that UV-vis spectrometer can achieve equivalent measuring performance as LC-MS. Besides, a comparison study has been conducted between recoveries of present study and recoveries derived from previous studies, as Table 7 shows below.
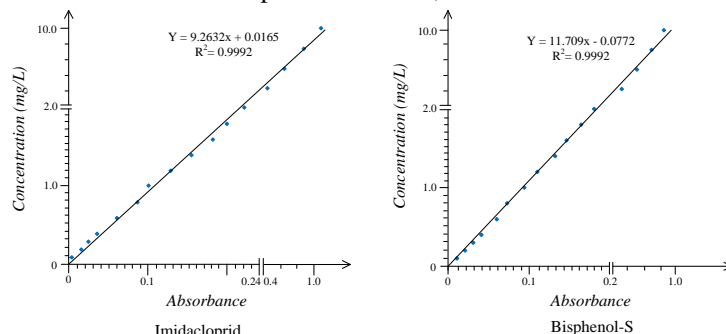

Figure 2. Calibration curves of imidacloprid and bisphenol-S with a range from 0 to 10mg/L.

Table 6. Details of model wastewater samples and recovery % of bisphenol-S and imidacloprid.

				UV-VIS spectrometer					
	Model test solution			**Bisphenol-S**			**Imidacloprid**		
Conc. (µg/L)	Volume (mL)	Total mass (µg)	Replication	Reconstituted volume after SPE (mL)	Recovery (%)	Mean Recovery (%)	Reconstituted volume after SPE (mL)	Recovery (%)	Mean Recovery (%)
100	200	20	x 2	10	78-95	86	10	92-96	94
100	500	50	x 3	10	99-105	103	10	86-104	93
10	1000	10	x 3	10	107-121	116	10	87-114	97

				LC-MS					
	Model test solution			**Bisphenol-S**			**Imidacloprid**		
Conc. (ug/L)	Volume (mL)	Total mass (µg)	Replication	Reconstituted volume after SPE (mL)	Recovery (%)	Mean Recovery (%)	Reconstituted volume after SPE (mL)	Recovery (%)	Mean Recovery (%)
100	200	20	x 2	10	74-91	83	10	86-99	93
100	500	50	x 3	10	88-98	92	10	73-94	84
10	1000	10	x 3	10	81-97	90	10	94-113	102

Table 7. Comparison of SPE recovery% in the present study to the SPE recovery% in previous studies.

Reference	Samples Categories	Analytical Methods	Recovery%
	Bisphenol-S		
This study	Tap water	UV-Spectrometer	86-116 (n=8)
This Study	Tap water	LC-MS	83-92 (n=8)
[20]	Tap water	UHPLC-MS	89.8-91.4 (n= 18)
[21]	River water	LC-ETMS	86.9-107.3 (n=6)
[21]	Wastewater	LC-ETMS	90-101.8% (n=6)
[19]	River water Lake water	LC-MS/MS	95-96% (n=7)
	Imidacloprid		
This study	Tap water	UV-Spectrometer	93-97 (n=8)
This study	Tap water	LC-MS	84-102 (n=8)
[22]	Tap water	HPLC-DAD	82-115 (n = 10)
[31]	Tap water Groundwater Reservoir	HPLC-UVD	87.5%-109.8% (n=9)
[32]	Tap water	HPLC	85-92 (n=9)

4. CONCLUSIONS

IMP and BS in test solutions can be measured via solid-phase extraction (SPE)-UV-vis spectrometry at detection limit of 10 µg/L, with 93-97% and 86-116% recoveries. Consistent results were validated by SPE-LC-MS tests, with acceptable recoveries obtained (84-102% for IMP, 83-92% for BS). For this situation, it can be concluded that SPE coupled with UV-vis spectrometer could be a reliable technique for detecting and quantifying imidacloprid and bisphenol-S in water samples at concentration range greater than 10 µg/L. This study suggests that the SPE-UV-vis spectrometry could be an alternative to the SPE-LC-MS and

other high-cost techniques for analyzing the target organic compounds in the aqueous phase.

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6. ACKNOWLEDGEMENTS