



# Advanced GC-MS-SIM Method for Simultaneous Determination of Bisphenol-A and Phthalic Acid Esters (PAEs) in Seawater

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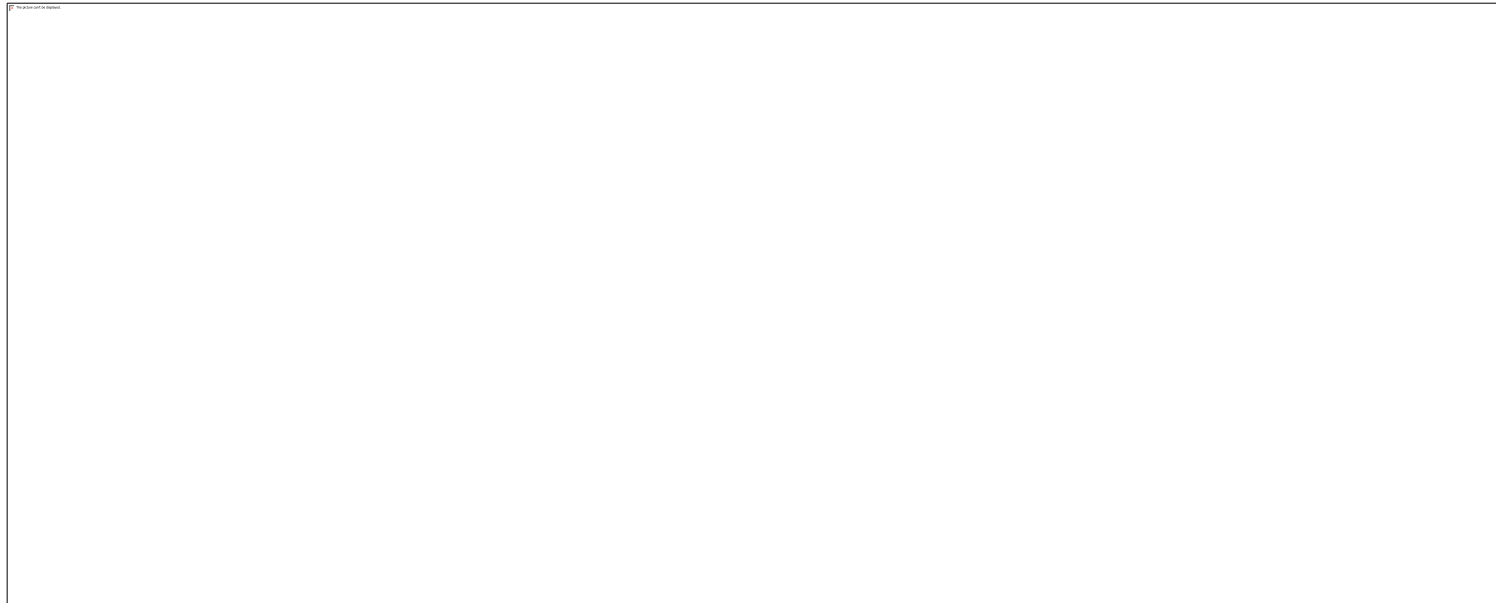


# Overview

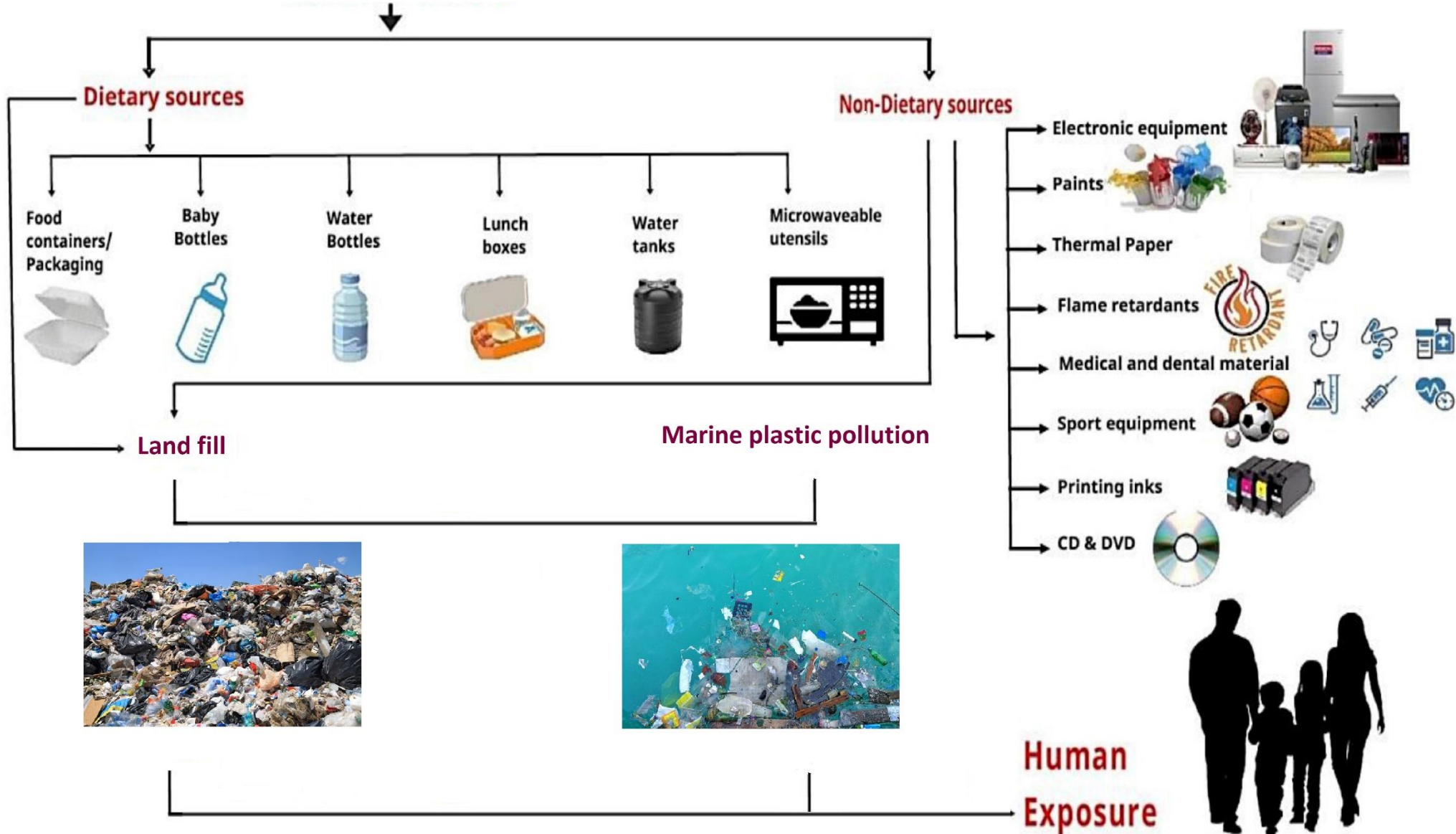
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# 1. Introduction

- Seawater is essential for drinking and plays a big role in areas with unique environmental and health challenges [1]. In Qatar, where there's not much freshwater, they mainly turn seawater into drinking water through a process called desalination [2]. Qatar has three primary desalination plants, one in Ras Abu Fontas south of Doha and two in Ras Laffan to meet the country's water supply needs using multi-stage flash distillation (MSF).



# Sources of BPA and PAEs



## 2. Goal of this study

- To develop very sensitive analytical method by GC-MS-SIM.
- To applied the developed analytical method to investigate concentration level of BPA and PAEs (DBP, BBP and DEHP) in Qatar marine.

# -Seawater Sampling

- Surface seawater samples were collected in three different locations-Qatar in May 2022; Ras Abu Fontas (1), Katara (2) and Al Khor (3), three sampling points were taken per location.



**1**



**2**



**3**

# -Extraction Steps



**1.** 45 mL of seawater



**2.** 2 mL of DCM



**3.** 50 µl of HCl



**4.** Subjected to ultrasonic bath



**5.** The DCM layer was separated



**6.** 50mg of sodium sulfate was added



**7.** Microcentrifuge were vortexed



**8.** Ready to analysis

### 3. Results and Discussion

- Developed analytical method for PAEs were done firstly by the SCAN mode in order to determine retention time for each PAEs, then by the SIM mode for quantification. SIM quantitation ions of (DBP, BPA, BBP, and DEHP) are shown in Table 1.
- **Table 1.** SIM Quantitation Ions For BPA, DBP, BBP and DEHP.

| Compound | $M_w$  | $R_t$ | Fragments (m/z)  |     |       |     |
|----------|--------|-------|------------------|-----|-------|-----|
|          |        |       | 1 (Quantitative) | 2   | 3     | 4   |
| DBP      | 278.34 | 10.09 | 149              | 150 | 76.1  | 223 |
| BPA      | 228.29 | 11.18 | 213              | 119 | 228   | 85  |
| BBP      | 312.36 | 11.93 | 149              | 91  | 206.1 | 104 |
| DEHP     | 390.56 | 12.64 | 149              | 167 | 57.1  | 104 |

- $M_w$ : molecular weight (g/mol),  $R_t$ : retention time (min).



## - Validation of Analytical Method

- **Linearity:** The linearity was assessed by prepared five different concentrations in dichloromethane at 2,50, 10, 25, 100 and 250 µg/L with three replicates (n=3). The linear regression equation was calculated by the least squares method and summarized in Table 2.
- **Table 2.** Regression analysis of calibration curves for PAEs by proposed method

| Compound | t <sub>R</sub> (min) | calibration equation | R <sup>2</sup> | RSD% | LOD  | LOQ  |
|----------|----------------------|----------------------|----------------|------|------|------|
| DBP      | 10.1                 | Y=2978.8x-10847      | 0.9999         | 0.55 | 0.09 | 0.24 |
| BPA      | 11.2                 | Y=724.67x-26833      | 0.9995         | 0.94 | 0.43 | 1    |
| BBP      | 11.9                 | Y=1789.6x-55768      | 0.9996         | 0.81 | 0.33 | 0.92 |
| DEHP     | 12.7                 | Y=3197x-148431       | 0.9994         | 0.60 | 0.93 | 2.65 |

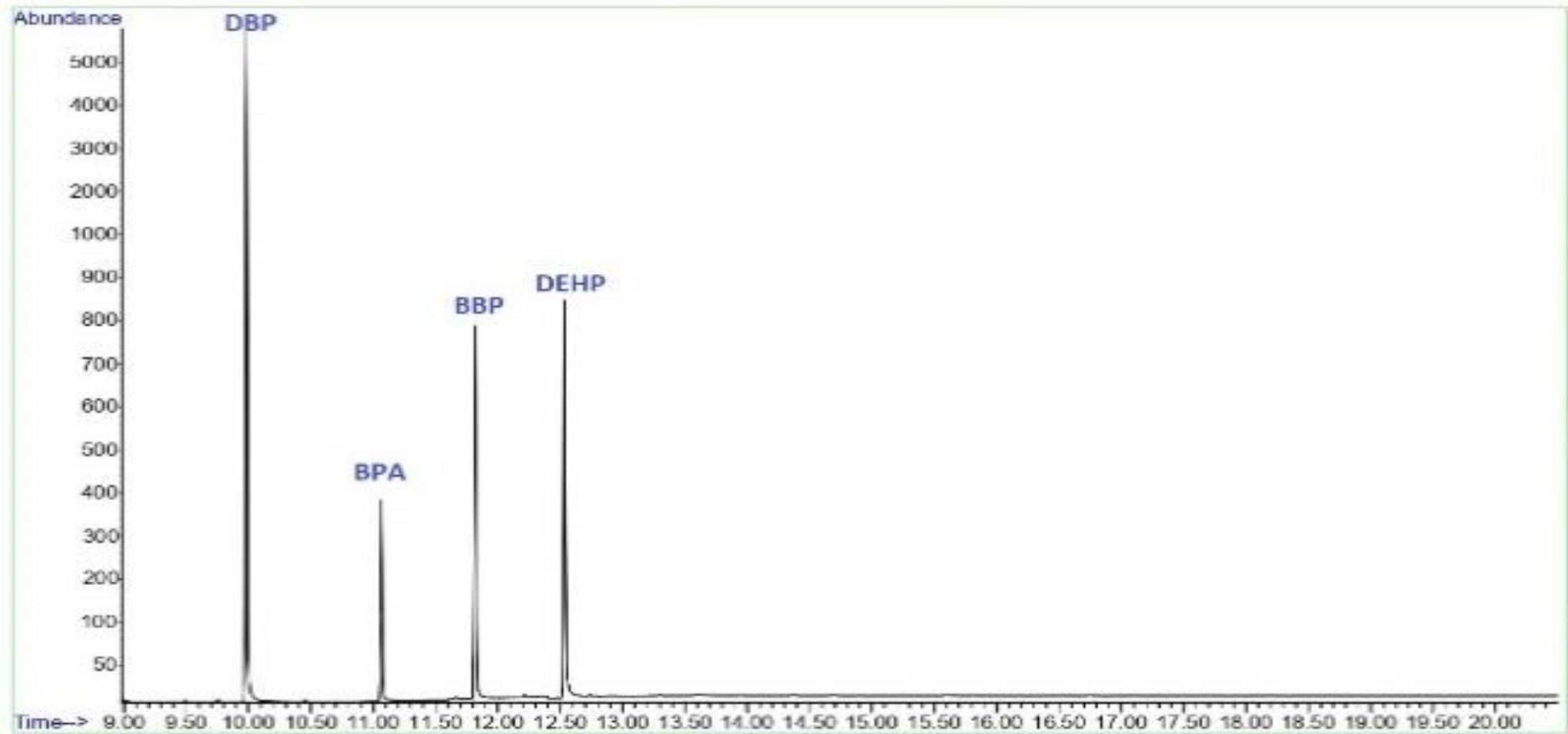
- R<sup>2</sup>: correlation coefficient, RSD: relative standard deviation.

**Sensitivity:** LODs in this study for DBP, BPA, BBP and DEHP by GC-MS-SIM were lower (0.09, 0.43, 0.33 and 0.93)  $\mu\text{g/L}$ , respectively compared with previous publications [8,9].

**Recovery:** The accuracy was performed to verify the effectiveness of the extraction step, was achieved at three spiked levels (5, 20 and 50)  $\mu\text{g/L}$  with three replicates (n=3). The results are summarized in Table 3.

**Table 3.** Accuracy of developed method.

| Spiked level<br>( $\mu\text{g/L}$ ) | Average Recovery (% $\pm$ SD) |                 |                 |                 |
|-------------------------------------|-------------------------------|-----------------|-----------------|-----------------|
|                                     | DBP                           | BPA             | BBP             | DEHP            |
| 5                                   | 94.04 $\pm$ 3.4               | 80.90 $\pm$ 8.2 | 98.14 $\pm$ 6.1 | 99.62 $\pm$ 5.7 |
| 20                                  | 91.04 $\pm$ 2.9               | 96.18 $\pm$ 5.7 | 90.28 $\pm$ 4.8 | 91.22 $\pm$ 4.4 |
| 50                                  | 103.7 $\pm$ 2.9               | 96.59 $\pm$ 5.5 | 88.95 $\pm$ 4.7 | 97.82 $\pm$ 3.5 |



**Figure 1.** Typical chromatogram of DBP, BPA, BBP and DEHP at (25  $\mu\text{g}/\text{L}$ ) using GC-MS-SIM with spitless mode

## Real Samples Analysis

- The developed method was employed for quantitative analysis in seawater samples, and the results are displayed in Table 4.
- Table 4.** concentrations of DBP, BPA, BBP and DEHP (ng/L) in three different locations-Qatar

| L        | DBP       |           | BPA       |           | BBP      |          | DEHP      |           |
|----------|-----------|-----------|-----------|-----------|----------|----------|-----------|-----------|
|          | ١         | ٢         | 1         | 2         | 1        | 2        | ١         | ٢         |
| <b>1</b> | 5.9±0.01  | 5.8±0.01  | 1.9±0.01  | 1.0±0.01  | 1.1±0.02 | 1.2±0.03 | 7.1±0.02  | 7.2±0.03  |
| <b>2</b> | 24.4±0.01 | 24.5±0.02 | 3.7±0.02  | 6.2±0.02  | 6.2±0.01 | 6.0±0.01 | 16.2±0.06 | 16.0±0.06 |
| <b>3</b> | 17.8±0.02 | 17.7±0.02 | 14.7±0.01 | 12.9±0.01 | 2.0±0.02 | 2.2±0.01 | 32.4±0.07 | 32.9±0.05 |

## 4. Conclusion and Recommendations

- This study provides an important role quality control studies of BPA, DBP, BBP and DEHP in marine environment of Qatar. The present method showed good linearity and high correlation coefficients. In addition, the recoveries were 80.9–103.7% with good precision ( $n = 3$ , RSD: 2.9–8.9%) for seawater samples spiked at 5, 20 and 50  $\mu\text{g/L}$  levels. This simple, accurate and highly sensitive method is expected to have potential applications in seawater samples.
- Generally, **results in this study confirmed that seawater in Qatar is safe and under MCL** allowable level established by EC for BPA is 0.1  $\mu\text{g/L}$  and by FDA for DEHP is 6.0  $\mu\text{g/L}$ .

## 5. Acknowledgements

- The analysis by GC–MS was accomplished in the Central Laboratories unit, Qatar University. The contents herein are solely the responsibility of the author.

## 6. References

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