Miniaturized solid-phase microextraction coupled with gas chromatography-mass spectrometry for determination of endocrine disruptors in drinking water

Mereke Alimzhanova a,b,*, Madina Mamedova a,b, Kazhybek Ashimuly b, Alham Alipuly b, Yerlan Adilbekov b

a al-Farabi Kazakh National University, Faculty of Physics and Technology, 71 al-Farabi Ave., 050040 Almaty, Kazakhstan
b Center of Physical Chemical Methods of Research and Analysis, al-Farabi Kazakh National University, 050012 Almaty, Kazakhstan

* Corresponding author.
E-mail address: alimzhanova.mereke@gmail.com (M. Alimzhanova).

https://doi.org/10.1016/j.fochx.2022.100345
Received 20 January 2022; Received in revised form 11 May 2022; Accepted 21 May 2022
Available online 23 May 2022

ABSTRACT

A simple and rapid method based on miniaturized solid-phase microextraction (mini-SPME) followed by gas chromatography–mass spectrometry was developed to identify eight endocrine disruptors (atrazine, diethylstilbestrol, hexestrol, estrone, estradiol, ethinylestradiol, norgestrel, and megestrel) in drinking water samples. Extraction parameters was optimized and further analyses was performed using them. The optimum temperature for the determination of endocrine disruptors in water was 80 °C; the optimum extraction and preincubation times were 60 and 20 min, respectively. The studied linear range of endocrine disruptors was 10.0–1000 μg mL⁻¹. The limit of detection ranged from 0.020 to 0.087 μg mL⁻¹. The correlation coefficient (r²) was 0.96–0.99. This research introduces a novel method for detecting analytes at extremely low concentrations, as well as the possibility of combining several detection technologies to give high-accuracy qualitative and quantitative determination of endocrine disruptors in aqueous samples.

ARTICLE INFO

Keywords:
Endocrine disruptors
Water
Miniaturized SPME
Hormone
Pesticide

Introduction

The most important component of public health is the quality of drinking water, as poor-quality drinking water can affect many aspects of human existence. The absence of contaminants in drinking water is the most important criteria for ensuring its safety. According to (Wee et al., 2021), contamination of drinking water with endocrine-disrupting compounds (EDCs) is a growing problem globally.

The presence of endocrine disruptors in water may be due to contamination of spring water, contamination during production and bottling, or migration of substances from the packaging. Possible sources of contamination include unintentionally introduced substances because of the technological process. These are contamination and decomposition products from closures, sealing materials for them, pipe materials, pump systems, storage containers, cleaning and disinfecting agents. A significant group of pollutants are pesticides, humic substances and phthalates (Gonsioroski et al., 2020).

The Endocrine Society defines endocrine disruptors as “exogenous (unnatural) chemicals or mixtures of chemicals that interfere with any hormone action”. Hormones, in turn, are biologically active substances of organic nature that are produced in specialized cells of the endocrine glands that enter the blood, bind to the receptors of target cells, and have regulatory effects on metabolism and physiological functions (Gore et al., 2014).

EDCs are chemicals that disrupt the endocrine system, interacting with it as endogenous hormones. EDCs block hormone receptors and can ultimately disrupt physical development (Münze et al., 2017). Infertility, thyroid dysfunction, infection susceptibility, autoimmune illness, and heart disease have all been linked to high levels of EDCs in humans (Köck-Schulmeyer et al., 2013).

Currently, more than 200 substances are known that have a detrimental effect on the endocrine system. Among them are hormones (diethylstilbestrol, hexestrol, estrone, estradiol, ethinyl estradiol, norgestrel, and megestrel), parabens, pesticides (atrazine), and phthalates (bisphenol A). These substances are found in many everyday objects and can easily enter our body (De Coster & Van Larebeke, 2012). Sanfilippo et al. (2010) identified trace endocrine disruptors, hormones (17-estradiol (E2), diethylstilbestrol (DES), 4-hydroxytamoxifen), phenolic

CONTACT Yerlan Adilbekov
b Center of Physical Chemical Methods of Research and Analysis, al-Farabi Kazakh National University, 050012 Almaty, Kazakhstan (Yerlan Adilbekov).
compounds, and phthalates (bisphenol A (BPA), di (2-ethylhexyl) phthalate (DEHP), 4-oclyphenol (OF), and 4- n-nonylphenol (4-n-NP)) in ultrapure water samples for laboratory use by gas chromatography-mass spectrometry (GC-MS). Carles et al. (2021) studied and compared the effect of atrazine and nitrates on fetal growth and development; however, they found no evidence that atrazine-contaminated water had a negative impact on prenatal development. However, the results of other studies (Almberg et al., 2018; Chevrier et al., 2011) suggested that exposure to EDC-contaminated water led to the birth of small for gestational age (SGA) or low birth weight (LBW) babies.

Other researchers (Hugo et al., 2009; Ying, 2012) reported that EDCs pose the highest risk for women during pregnancy or for fetuses during their early development, when organs and the nervous system are just beginning to form, leading to the possibility of preterm delivery. One of the most serious examples of this is diethylstilbestrol (DES), a synthetic estrogen drug (Thomas Zoeller et al., 2012). DES has been associated with a variety of side effects in women exposed during pregnancy and their fetuses. Endocrine diseases due to DES can manifest decades later and not only in the first, but also in the second and third generations (Petricovic et al., 2002).

The problem of developing methodological approaches for identifying endocrine disruptors in drinking water samples is of relevance. Analysis of the existing methodological base for the determination of endocrine disruptors in water samples showed that solid-phase microextraction coupled with gas chromatography mass analysis was taken as the basis (Gibson et al., 2010; Tan et al., 2008).

Various researchers have identified endocrine disruptors using various solid-phase microextraction (SPME) methods. Bisphenol A was identified in drinking water by solid-phase extraction (SPE) and ultra-performance liquid chromatography-tandem mass spectrometry (UPLC-MS/MS) (Moid AlAmmari et al., 2020). Steroids (estrona, estradiol and diethylstilbestrol) in water were analyzed by direct immersion SPME-GC-MS-MS (Chopra et al., 2014). Nonylphenol and octylphenol in water were determined using SPME and comprehensive two-dimensional gas chromatography with a flame ionization detector (Moreira et al., 2015).

These techniques enable the identification of selected analytes in extremely low concentrations, and the combination of various detection methods enables both the high-accuracy qualitative and quantitative determination of endocrine disruptors in aqueous samples (Magi et al., 2010).

The current study aimed to identify endocrine disruptors in drinking water samples using for the first time miniaturized solid-phase microextraction (mini-SPME) in combination with gas chromatography mass spectrometry method. The advantage of gas chromatography is its ability to effectively separate many components of the analyzed mixture. The use of mass spectrometry detection substantially expands the spectrum of compounds that can be determined by gas chromatography (Diaz-Cruz et al., 2003).

Compared with the SPME method, in our proposed mini-SPME method, 2 mL vials are used, and only a small amount of the target analyte, 1 mL, is required. When using the mini-SPME method, the time to reach equilibrium between the liquid phase and the fiber is considerably shorter, which increases the total analysis quality. This method will be useful for the efficient, rapid and inexpensive determination of endocrine disruptors in drinking water samples. With this proposed sample preparation method, toxic organic solvents are not required, making it a green method of analysis.

Materials and methods

Reagents and samples

EDC standards atrazine, diethylstilbestrol, estradiol, ethinylestradiol, norgestrel, hexestrol, estrone, megestrol was used in this study (Meryer, China). Distilled water obtained by electric bidistiller BE-4 (Livam, Russia). Helium gas, (≥99.995%) in 40 L bottles, max. pressure 150 bar (Orenburg, Russia).

The process of choosing the optimal parameters of mini-solid phase microextraction for extracting analytes from water was carried out on real samples of drinking water.

Sample preparation

We added standard of an endocrine disruptor (atrazine, diethylstilbestrol, estradiol, ethinylestradiol, norgestrel, hexestrol, estrone, or megestrol) each weighing 0.01 g in a 20 mL vial. 10 mL of methanol is added to the vial with a pipette to obtain an initial solution with a concentration of 1000 mg mL⁻¹. Then, we shook and placed it in an ultrasonic bath to ensure the complete dissolution of substances. Calibration solutions are prepared from the stock solution (C = 1000 mg mL⁻¹).

In volumetric flasks, with a volume of 5 mL, 50, 250, 1250, 2500 μL we added from the stock solution (to obtain calibration solutions with concentrations of 10, 50, 250 and 500 μg mL⁻¹, respectively), and brought to the mark with methanol.

The methanol has been evaporated off for mini solid-phase microextraction analysis. From each calibration solution 0,1 mL was taken to 2 mL vials. Then the the methanol was at room temperature. Each calibration solution was prepared in four parallel steps. After evaporation, 1 mL of water was added, set in an ultrasonic bath for mixing and transfer of analytes to the aqueous phase.

Equipment

The extraction coating was injected using a MultiPurpose Sampler (Gerstel, Germany) into the sample injection device of a gas chromatograph with a 7890A/5975C mass spectrometric detector in splitless mode. Chromatography was performed using a DB-35MS capillary column with a length of 30 m, an inner diameter of 0.25 mm, and a film thickness of 0.25 μm. The carrier gas (helium, grade “A”) was supplied at a constant rate of 1.0 mL min⁻¹.

Desorption of analytes was carried out at a temperature of 270 °C for 20 min. The temperature of the column thermostat was programmed from 80 °C (exposure 1 min) to 200 °C (exposure 5 min) with a heating rate of 30 °C min⁻¹, and up to 300 °C (exposure 5 min) with a heating rate of 5 °C min⁻¹. The analysis time is 35 min. The MSD interface temperature was 320 °C, the temperature of the quadrupole was 180 °C, and the ion source temperature was 230 °C. Detected in the ion-scanning mode in the range of mass numbers m/z 50–950 a.m.u.

Agilent MSD ChemStation software (version 1701EA) was used to control the gas chromatograph system and the system for recording and processing chromatographic data. The data processing included the determination of the retention times of the test substance, the heights and areas of the peaks, as well as the processing of the spectral information obtained using the mass spectrometric detector. To decode the obtained mass spectra, the Wiley 11th edition and NIST’02 libraries were used.

Results and discussion

Optimization of extraction parameters

Design of the experiments was based on the SPME protocol developed by Pawliszyn (Pawliszyn, 2012; Risticovic et al., 2010). Selection of fiber coating, extraction time and temperature, preincubation and desorption time are all main factors in optimizing SPME conditions for different samples. In water analysis, the extraction process determines a lot of the key parameters, such sensitivity, repeatability, reproducibility, precision and accuracy, limits of detection, quantification, and linearity (Abdula’uf & Tan, 2015).

2
Selection of the optimal extraction time

The choice of the optimal extraction time is one of the important factors in achieving the maximum efficiency of the extraction of the studied components from the sample (Cháfer-Pericás et al., 2007; Mousa et al., 2013; Pawliszyn, 2012). The extraction time is set in accordance with the saturation of the analyzed compounds on the extraction coating of the fiber sufficient for identification by the mini-SPME GC–MS method.

During the optimization, the following extraction times were applied: 5; 10; 20; 30 and 60 min. Extraction temperature was 80 °C. Incubation and desorption times were set as both at 20 min. Initial temperature of the GC oven was set at 80 °C, exposure time at the initial temperature was 1 min. Followed by heating up to temperature 200 °C at the rate of 30 °C min⁻¹, exposure time at the final temperature 300 °C at the rate of 5 °C min⁻¹. Results of analysis of EDCs at different extraction times are presented in Fig. 1.

For the determination three EDCs and five endocrine steroid hormones by direct immersion solid-phase microextraction in aqueous and biological environmental samples were optimized (Yang et al., 2006). The extraction time was set at 120 min, the incubation temperature was 45 °C. With an increase in the extraction time to 120 min, the reactions of all target compounds increased and reached a near-equilibrium state.

The trace endocrine disrupting chemicals using multiple monolithic fiber solid-phase microextraction (MMF-SPME) utilizing polymeric ionic liquid-based adsorbent were studied (Pei et al., 2017). Also here, an increase in the extraction time shows an increase in the peaks of the target analytes. Hence, an optimal extraction time of 50 min was chosen here.

Therefore, in this study as seen on Fig. 1, an increase of extraction time from 5 to 60 min leads to an increasing of response by approximately 10 times of endocrine disruptors. However, an increase in extraction time will lead to an unstable analytical signal for estradiol, the highest peak of which is reached at 20 min, but the result shows that there is no large peak difference between 20 and 60 min. Thus, based on the data it was concluded that the 60 min is the optimal time of extraction, as it provides adequate detection of endocrine disruptors.
Selection of the optimal preincubation time

The preincubation time is necessary for the sample to reach the required extraction temperature, as well as to establish equilibrium between the gas and liquid phases during headspace-solid phase microextraction (Pawliszyn, 2012; Risticevic et al., 2010), whereas in the direct immersion-solid phase microextraction (DI-SPME) equilibrium takes place between fiber and sample matrix (Zhang et al., 2018), which is the same for the mini-SPME. The preincubation time has a significant effect on the process of solid-phase microextraction of organic compounds 3, 5, 7, 10, 20, and 30 min were tested to determine the optimal preincubation time for EDCs from drinking water samples (Fig. 2).

As shown by the results of the experiments, an increase in the preincubation time has a less effect on the extraction of EDCs, except for atrazine and hexestrol. The pre-incubation time of 20 min allows achieving the required equilibrium and sensitivity in the analysis of EDCs, so further analyzes are effective to perform at 20 min.

Selection of the optimal fiber type and temperature

Extraction coating is one of the most important parameters of solid phase microextraction. The composition and thickness of the extraction coating have a significant effect on the selectivity of mini-solid-phase microextraction of organic compounds from samples and the sensitivity of the method. The following extraction coatings were tested to determine the target analytes content in drinking water samples:

- 100 μm polydimethylsiloxane (PDMS);
- 50/30 μm divinylbenzene/carboxen/polydimethylsiloxane
- (DVB/CAR/PDMS);
- 85 μm polyacrylate (PA).

As a result, it was found that the greatest response EDCs provides an extraction coating based on 50/30 μm DVB/CAR/PDMS. This may be due to its multicomponent composition, which allows the extraction of a wider range of analytes (Fig. 3a).

The research (Risticevic et al., 2010) showed the PDMS and PA is an adsorption fibers that allows the main extraction of volatile and polar semi-volatile compounds with molecular weights from 30 to 225 and 80 to 300 respectively. Since these target analytes are compounds with rather high molecular weights 215–312 g mol⁻¹, as it is seen from the Fig. 3a fibers based on PDMS and PA do not provide the recovery of such compounds.

Optimization of temperature was carried out on drinking water samples contaminated with standards of endocrine disruptors. The extractive coating was exposed in a sample and held for 60 min at temperatures of 30°C, 40°C, 50°C, 60 and 80°C (Fig. 3b).

The experimental results, presented in the form of a graph of the dependence of the peak area of analytes on the extraction temperature, showed that with an increase in the temperature from 30 to 80 °C, the degree of extraction of the analytes under study increases. Mousa et al. (2013) endocrine disruptors have a high boiling point of 154–200 °C therefore, temperatures significantly higher are required for the extraction from the drinking water samples. A temperature of 80 °C for endocrine disruptors provides maximum response and increases their concentration by 10 times. Thus, the optimal extraction temperature providing the greatest response to endocrine disruptors is 80 °C. It is not recommended to increase the extraction temperature above 80 °C, as high pressure is formed in the vial, which can cause the vial to crack or explode.

A simple and rapid method based on miniaturized solid-phase microextraction (mini SPME) technique followed by gas chromatography-mass spectrometry (GC-MS) was developed by the
simultaneous determination of 8 endocrine disruptors in drinking water. The mass concentrations of atrazine, diethylstilbestrol, hexestrol, estrone, estradiol, ethinyl estradiol, norgestrel, and megestrel were determined by gas chromatography with mass spectrometric detection in combination with mini-solid-phase microextraction in the concentration range of endocrine disruptors from 10 to 1000 μg mL⁻¹. The limit of detection was found in the range of 0.020–0.087 μg mL⁻¹. The correlation coefficient was found in the range 0.96–0.99 (r²) (Table 1).

The results of the study showed that the miniaturized-SPME (mini-SPME) coupled with gas chromatography-mass spectrometry makes it possible to determine endocrine disruptors in drinking water samples. During the optimization, it was concluded that fiber based on DVB/CAR/PDMS is the best option for the recovery of target analytes. Incubation time is necessary for the sample to reach the required equilibrium, the response of the peak of endocrine disruptors increased ten times, however it is not recommended to exceed this temperature. The previous incubation time is necessary for the sample to reach the required equilibrium temperature as well as to establish equilibrium between the gas and liquid phases. So the optimum pre-incubation time was established at 20 min and extraction time of 60 min. Linear range of endocrine disruptors from 10 to 1000 μg mL⁻¹. The limit of detection was found in the range of 0.020–0.087 μg mL⁻¹. The correlation coefficient was found in the range 0.96–0.99 (r²).

Table 1

| Analyte          | Linear range | r²    | LOD  |
|------------------|--------------|-------|------|
| Atrazine         | 10–1000      | 0.9992| 0.020|
| Diethylstilbestrol| 10–1000      | 0.9791| 0.037|
| Hexestrol        | 10–1000      | 0.9976| 0.024|
| Estrone          | 10–1000      | 0.9619| 0.027|
| Estradiol        | 10–1000      | 0.9841| 0.025|
| Ethinyl Estradiol| 10–1000      | 0.9785| 0.025|
| Norgestrel        | 10–1000      | 0.9757| 0.053|
| Megestrel         | 10–1000      | 0.9612| 0.087|

Conclusions

The results of the study showed that the miniaturized-SPME (mini-SPME) coupled with gas chromatography-mass spectrometry makes it possible to determine endocrine disruptors in drinking water samples. During the optimization, it was concluded that fiber based on DVB/CAR/PDMS is the best option for the recovery of target analytes. Incubation time is necessary for the sample to reach the required equilibrium temperature as well as to establish equilibrium between the gas and liquid phases. So the optimum pre-incubation time was established at 20 min and extraction time of 60 min. Linear range of endocrine disruptors from 10 to 1000 μg mL⁻¹. The limit of detection was found in the range of 0.020–0.087 μg mL⁻¹. The correlation coefficient was found in the range 0.96–0.99 (r²).

Conflict of interests

Authors declare no conflict of interests.

References

Abdurauf, I. B., & Tan, G. H. (2015). Design of experiment in the development of spme method for the determination of pesticide residues in fruits and vegetables. Sample Preparation, 2(1). https://doi.org/10.1515/sampre-2015-0005

Almberg, K. S., Turyk, M. E., Jones, R. M., Rankin, K., Freels, S., & Stayner, L. T. (2018). Atrazine contamination of drinking water and adverse birth outcomes in community water systems with elevated atrazine in Ohio, 2006–2008. International Journal of Environmental Research and Public Health, 15(9), 12–15. https://doi.org/10.3390/ijerph15091889

Carles, C., Alfony-Lluty, M., Dupuis, A., Rabouan, S., & Migeot, V. (2021). Comparison of the effect on fetal growth of a mixture of atrazine and nitrates in drinking water and of active tobacco exposure during pregnancy. International Journal of Environmental Research and Public Health, 18(1), 1–15. https://doi.org/10.3390/ijerph18010020

Chávez-Pérez, C., Herrera-Hernández, R., & Campilo-Falcó, P. (2007). In-tube solid-phase microextraction-capillary liquid chromatography as a solution for the screening analysis of organophosphorus pesticides in untreated environmental water samples. Journal of Chromatography A, 1141(1), 10–21. https://doi.org/10.1016/j.jchroma.2006.11.105

Chevrier, C., Limon, G., Monfort, C., Rouget, F., Garlantézec, R., Petit, C., ... Cordier, S. (2011). Urinary biomarkers of prenatal atrazine exposure and adverse birth outcomes in the pelage birth cohort. Environmental Health Perspectives, 119(7), 1034–1041. https://doi.org/10.1289/ehp.1104775

Chopra, S., Gomes, P. C. F. L., Dhandapani, R., & Snow, N. H. (2014). Analysis of Steroids using Solid Phase Microextraction-Gas Chromatography-Mass Spectrometry-Mass Spectrometry (SPME-GC-MS-MS). Scientia Chimica, 6(2), 105–116. https://doi.org/10.15229/sc.2014.024

De Costa, S., & Van Larebeke, N. (2012). Endocrine-disrupting chemicals: Associated disorders and mechanisms of action. Journal of Environmental and Public Health, 2012, 1–12. https://doi.org/10.1155/2012/716708

Díaz-Cruz, M. S., López de Alda, M. J., López, R., & Barceló, D. (2003). Determination of estrogens and progestogens by mass spectrometric techniques (GC/MS, LC/MS and LC/MS/MS). Journal of Mass Spectrometry, 38(9), 917–923. https://doi.org/10.1002/jms.529

Gibson, R., Durán-Alvarez, J. C., Estrada, K. L., Chávez, A., & Jiménez Cisneros, B. (2010). Accumulation and leaching potential of some pharmaceuticals and potential endocrine disruptors in soils irrigated with wastewater in the Tula Valley, Mexico. Chernosphere, 81(11), 1437–1445. https://doi.org/10.1016/j.chemosphere.2010.09.006

Gnosiorowski, A., Mourikes, V. E., & Flaws, J. A. (2020). Endocrine disruptors in water and their effects on the reproductive system. International Journal of Molecular Sciences, 21(6). https://doi.org/10.3390/ijms21061929

Gore, A. C., Crews, D., Doan, L. L., & Merrill, M. L. (2014). IPen-Intro-Edc-V1_9e-En-Web-Pdf-December.

Hugo, O.-A., Jane, F., Leighanne, H., & Cristina, C. (2009). Drinking-water herbicide exposure in Indiana and prevalence of small-for-gestational-age and preterm delivery. Environmental Health Perspectives, 117(10), 1619–1624. https://doi.org/10.1289/ehp.0900784

Kopp-Schulmeier, M., Villagraza, M., López de Alda, M., Céspedes-Sánchez, R., Ventura, F., & Barceló, D. (2013). Occurrence and behavior of pesticides in wastewater treatment plants and their environmental impact. Science of the Total Environment, 458–460, 466–476. https://doi.org/10.1016/j.scitotenv.2013.04.010

Magi, E., Scapolla, C., Di Carro, M., & Liscio, C. (2010). Determination of endocrine-disrupting compounds in drinking waters by fast liquid chromatography-tandem mass spectrometry. Journal of Mass Spectrometry, 45(9), 1003–1011. https://doi.org/10.1002/jms.1781

Martínez, C., Ramírez, N., Gómez, V., Pocurtull, E., & Borrell, F. (2013). Simultaneous determination of 76 micropolutants in water samples by headspace solid phase
Selective solid-phase microextraction and gas chromatography-mass spectrometry. Talanta, 116 (2013), 937-945. https://doi.org/10.1016/j.talanta.2013.07.055

Mold AlAmari, A., Rizwan Khan, M., & Ağel, A. (2020). Trace identification of endocrine-disrupting bisphenol A in drinking water by solid-phase extraction and ultra-performance liquid chromatography-tandem mass spectrometry. Journal of King Saud University - Science, 32(2), 1634–1640. https://doi.org/10.1016/j.jsus.2019.12.022

Moreira, M. A., André, L. C., Ribeiro, A. B., Da Silva, M. D. R. G., & Cardenal, Z. L. (2015). Quantitative analysis of endocrine disruptors by comprehensive two-dimensional gas chromatography. Journal of the Brazilian Chemical Society, 26(3), 531–536. https://doi.org/10.5935/0103-5053.20150009

Mousa, A., Basheer, C., & Rahman AlArfaj, A. (2013). Application of electro-enhanced solid-phase microextraction for determination of phthalate esters and bisphenol A in blood and seawater samples. Talanta, 115, 308–313. https://doi.org/10.1016/j.talanta.2013.05.011

Münze, R., Hannemann, C., Orlinskiy, P., Gunold, R., Paschke, A., Foit, K., … Liess, M. (2017). Pesticides from wastewater treatment plant effluents affect invertebrate communities. Science of the Total Environment, 599-600, 387–399. https://doi.org/10.1016/j.scitotenv.2017.03.008

Pawliszyn, J. (2012). 2 - Theory of solid-phase microextraction (J. B. T.-H. of S. P. M. Pawliszyn (ed.); pp. 13–59). Elsevier. 10.1016/B978-0-12-416017-0.00002-4.

Petrovic, M., Eljarrat, E., Pérez De Alda, M. J., & Barceló, D. (2002). Recent advances in the mass spectrometric analysis related to endocrine disrupting compounds in aquatic environmental samples. Journal of Chromatography A, 974(1–2), 23–51. https://doi.org/10.1016/S0021-9673(02)00907-X

Ristic, S., Lord, H., Greñekti, T., Arthur, C. L., & Pawliszyn, J. (2010). Protocol for solid-phase microextraction method development. Nature Protocols, 5(1), 122–139. https://doi.org/10.1038/nprot.2009.179

Sanfilippo, K., Pinto, B., Colombini, M. P., Bartolucci, U., & Reali, D. (2010). Determination of trace endocrine disruptors in ultrapure water for laboratory use by the yeast estrogen screen (YES) and chemical analysis (GC/MS). Journal of Chromatography B: Analytical Technologies in the Biomedical and Life Sciences, 878 (15–16), 1190–1194. https://doi.org/10.1016/j.jchromb.2010.03.025

Selvaraj, K. K., Shanmugam, G., Sampath, S., Joakim Larsson, D. G., & Ramaswamy, B. R. (2014). GC-MS determination of bisphenol A and alkylphenol ethoxylates in river water from India and their ecotoxicological risk assessment. Ecotoxicology and Environmental Safety, 99, 13–20. https://doi.org/10.1016/j.ecoenv.2013.09.006

Serrano, J., Kolansczyk, R. C., Tapper, M. A., Lahren, T., Dęgner, N., Hammermeister, D. E., … Kubatová, A. (2019). Characterization and analysis of estrogenic cyclic phenone metabolites produced in vitro by rainbow trout liver slices using GC-MS, LC-MS and LC-TOF-MS. Journal of Chromatography B: Analytical Technologies in the Biomedical and Life Sciences, 1126–1127(May), Article 121717. https://doi.org/10.1016/j.jchromb.2019.121717

Tan, B. L., Hawker, D. W., Müller, J. F., Tremblay, L. A., & Chapman, H. F. (2008). Stir bar sorptive extraction and trace analysis of selected endocrine disruptors in water, biosolids and sludge samples by thermal desorption with gas chromatography-mass spectrometry. Water Research, 42(1–2), 404–412. https://doi.org/10.1016/j.watres.2007.07.052

Thomas Zoeller, R., Brown, T. R., Doan, L. L., Gore, A. C., Skakkebaek, N. E., Soto, A. M., … Vom Saal, F. S. (2012). Endocrine-disrupting chemicals and public health protection: A statement of principles from the Endocrine Society. Endocrinology, 153 (9), 4097–4110. https://doi.org/10.1210/en.2012-1422

Wee, S. Y., Aris, A. Z., Yusoff, F. M., & Praveena, S. M. (2021). Tap water contamination: Multiclass endocrine disrupting compounds in different housing types in an urban settlement. Chemosphere, 264, Article 128488. https://doi.org/10.1016/j.chemosphere.2020.128488

Yang, L., Lan, C., Liu, H., Dong, J., & Luan, T. (2006). Full automation of solid-phase microextraction/on-fiber derivatization for simultaneous determination of endocrine-disrupting chemicals and steroid hormones by gas chromatography-mass spectrometry. Analytical and Bioanalytical Chemistry, 386(2), 391–397. https://doi.org/10.1007/s00216-006-0631-y

Ying, G. G. (2012). Endocrine disruptive chemicals. What? Where? In Analysis of endocrine disrupting compounds in food. 10.1002/9781118346747.ch1.

Zhang, L., Gionfriddo, E., Acquaro, V., & Pawliszyn, J. (2018). Direct immersion solid-phase microextraction analysis of multi-class contaminants in edible seaweeds by gas chromatography-mass spectrometry. Analytica Chimica Acta, 1031, 83–97. https://doi.org/10.1016/j.aca.2018.05.066

Zhao, J. L., Ying, G. G., Wang, L., Yang, J. F., Yang, X. B., Yang, L. H., & Li, X. (2009). Determination of phenolic endocrine disrupting chemicals and acidic pharmaceuticals in surface water of the Pearl Rivers in South China by gas chromatography-negative chemical ionization-mass spectrometry. Science of the Total Environment, 407(2), 962–974. https://doi.org/10.1016/j.scitotenv.2008.09.048