A review on analytical methods of petroleum hydrocarbons in water and sediment of aquatic systems

Zongkai Yue1, Qirang Shi1, Jia Ai1, Shitao Peng1, Xinyu Miao2* and Zhiyong Wang1*

1 Key Laboratory of Environmental Protection Technology on Water Transport, Ministry of Transport, Tianjin research institute for water transport engineering, M.O.T., Tianjin, 300456, China
2 Tianjin Key Laboratory of Hazardous Waste Safety Disposal and Recycling Technology, College of Environmental Science and Engineering, Tianjin University of Technology, Tianjin 300384, China

Corresponding author’s e-mail: wangzhiyong@tiwte.ac.cn

Abstract. In this paper, the research progress on the extraction and analysis methods of petroleum hydrocarbon in water and sediment were reviewed. The principle, application scope, advantages, disadvantages and applications of various extraction methods and determination methods are summarized systematically. At present, liquid-liquid extraction is the most commonly used method to extract petroleum hydrocarbons (PHCs) in water samples, while Soxhlet extraction and ultrasonic extraction are the most commonly used methods to extract PHCs in sediment samples. Gas chromatography is the main development direction to determine the concentration of specific components of PHCs.

1. Introduction

The presence of petroleum hydrocarbons (PHCs) contaminant in water and sediment environments causes significant environmental impacts and poses a substantial hazard to both human and other forms of life in the aquatic environments[1]. PHCs will enter aquatic systems in a relatively high concentration and cause pollution and mainly composed of three types of compounds: alkanes, olefins, and aromatics, which contaminant characterize vast majority of organic compounds and by-products[2-4]. The alkane component can be divided into the following categories: n-alkanes (straight chain alkanes), isomeric alkanes (branched chain alkanes), cycloalkanes, and the complex mixture which difficult distinguished[5]. PHCs are generally less soluble in water and readily adsorbed onto particulate matter, and then subsequently scavenged to the bottom sediment, which causes PHCs have characteristic of persistence and recalcitrant nature in the aquatic environments[6].

Different PHCs have different microbial degradation rates due to their different hydrocarbon types and contents. The biodegradation rate of different PHCs will decrease with the increase of the molecular weight of the PHCs[7,8]. Generally, Aromatic hydrocarbons are generally less biodegradable than aliphatic hydrocarbons[9].

Monitoring of PHCs can not only assess the pollution status of aquatic systems, but also can be used to track the source of pollutants. However, the existing extraction methods of PHCs are different in the applicable scope, extraction solvents and calibration standards obtained by different extraction methods are sometimes difficult to compare[10]. Hence, in this paper, the methods of extracting and
analyzing PHCs in water and sediment are summarized, the advantages, disadvantages and application range of these methods are compared.

2. Methods for Extraction
In the process of detecting and analyzing the specific content of PHCs in water and sediment, the extraction of PHCs is an important prerequisite for the subsequent analysis. At present, even though a large number of researchers are carrying out this detection, the detection results are not objective. Generally, PHCs are extracted with specific organic solvents, transferred to the organic phase of organic solvents, and then purified for quantitative analysis[2, 10].

2.1. Water Samples
Extraction is a unit operation in which the components of the system have different solubility in the solvent to separate the mixture. Liquid-liquid extraction (LLE) is the most commonly used method to extract PHCs in water samples, which is a method of transferring a solute substance from one solvent to another by means of the difference in solubility or partition coefficient of a substance in two mutually insoluble or slightly soluble solvents (such as methylene chloride, acetone, etc.)[11,12]. Of course, there are also other methods, such as continuous LLE [13], solid phase extraction [14], vortex extraction[15], and microextraction [16]. The LLE technology is the most widely used method for now and the samples can obtain good recovery rate (75% to 103%)[11], however, LLE technology will use huge amount of organic phase of extraction solvent consumption.

Continuous liquid-liquid extraction technique can make use of organic solvent, and continuous cycle compared with the traditional LLE technology, the recovery rate was guaranteed and the consumption of organic solvent was reduced, but the extraction time is longer (18 to 24 hours), and the process of heating extraction parts will cause the volatile organic compounds were degraded[13], therefore, continuous liquid-liquid extraction technique is suitable for latex[13].

Solid-phase extraction (SPE) technology is a method that water samples through a contain filler (such as silica or alumina), PHCs were enriched in solid phase by column and then cleared into a small amount of organic solvent, this technology with characteristic as simply operated, low organic solvent consumption, high enrichment factor and emulsification[14]. But the extraction efficiency of SPE technology is not stable, and have disadvantages such as solid column is easily blocked by suspended matter in water[14,17].

2.2. Sediment sample
The extraction methods of PHCs from sediments mainly include ultrasonic extraction, microwave extraction, Soxhlet extraction, accelerated solvent extraction and supercritical fluid extraction (SFE). All of them adopt solid-liquid extraction and extract the components to be measured from the matrix with solvents.

Soxhlet extraction is still widely used as a classic method of extracting PHCs from sediments and often used as a control method for evaluating other methods due to its high extraction efficiency[18]. However, this method is time-consuming, generally required for 24 h or even 72 h, and the solvent consumption is large, the extraction process cannot be automatically controlled, so it is not suitable for rapid analysis of environmental samples in large quantities[18].

Ultrasonic extraction is one of the extraction methods of PAHs recommended by EPA (EPA Method SW-846 3550). Ultrasonic extraction makes use of multi-stage effects such as cavitation, emulsification and agitation generated by ultrasonic radiation to increase the molecular motion frequency and speed, so that the extracted components can be dissolved into the extractant more quickly, and at the same time, the solvent penetration can be increased, so that the extractant can better contact with the target molecules in the sediment, and the extraction efficiency can be effectively improved[19].

Microwave extraction is an extraction method that uses microwave energy to speed up the extraction process. Its advantage lies in the low amount of solvent and the ability to process multiple
samples simultaneously. The disadvantages of microwave extraction are as follows: excessively high local temperature may cause decomposition of target components to a certain extent, which may affect the extraction effect.

SFE as one of the methods to extract PHCs from sediments was recommended by the EPA. Extraction of target components in samples using supercritical fluid (Such as CO₂) as extractant[20]. The supercritical fluid has good fluidity and diffusion ability. The extraction agents are non-toxic and pollution-free. SFE can also be combined with gas chromatography, liquid chromatography and other analytical instruments to improve the speed of analysis[21].

Accelerating solvent extraction is a method that the extractant was heated and pressurized to improve its solubility and diffusion force, so as to improve the extraction efficiency and promote the extraction. Accelerated solvent extraction is not only faster and more efficient, but also has less solvent consumption, good selectivity to target components, no damage to component morphology, and little influence on matrix. However, This method is not widely used due to the high cost of instruments[22].

Each extraction technology has its advantages and disadvantages. To select the appropriate extraction method, the cost, time and complexity of operation should be considered comprehensively according to the requirements of analysis. The most commonly used method to extract PHCs from water samples is still liquid-liquid extraction because of its simple device and easy operation. Soxhlet extraction and ultrasonic extraction methods are currently widely used methods for they does not require expensive equipment.

3. Analytical Procedures

Choosing a rapid, accurate and effective detection method to evaluate the hydrocarbon pollution of water and sediment samples is of great significance for the prediction of petroleum hydrocarbon pollution, choosing appropriate treatment and remediation measures, and dealing with relevant oil spill compensation dispute cases.

3.1. Gravimetric Method
Gravimetric method is a method that extract petroleum hydrocarbon from sample with organic solvent, weigh the solvent after evaporation and calculate petroleum content. Gravimetric method is not limited by standard oil products, and do not require special testing instruments. However, the petroleum component which boiling point is lower than the extractant in the process of solvent evaporation were easily lost, so the components of PHCs cannot be determined separately and it is only suitable for the determination of high concentration petroleum hydrocarbon (The concentration in the water sample was 5-1000 mg/L, and the concentration in the sediment was >500 mg/kg)[23].

3.2. Infrared Spectrophotometry Method
Carbon tetrachloride is usually used as extractant to extract PHCs in the samples by infrared spectrophotometry, and the polar animal and plant oils and fats are removed by adsorbents such as magnesium silicate for determination. In petroleum hydrocarbon, functional groups such as -CH₂-, -CH₃, =CH- are absorbed by stretching vibration at 2930, 2960, and 3030 cm⁻¹, respectively[24]. In this method, olefin, alkanes, cycloalkanes, and aromatic hydrocarbons in PHCs can be determined by using the absorbance of PHCs at three wavelengths. Infrared spectroscopy can accurately measure the content of each component of PHCs, but this method is susceptible to the interference of non-hydrocarbon organic matter, such as the determination of petroleum hydrocarbon contaminated samples that are rich in animal fats, the result will be on the high side.

3.3. Ultraviolet Fluorescence Spectrophotometry
Ultraviolet fluorescence spectrophotometry is also one of the commonly used methods to detect petroleum hydrocarbon[25]. The aromatics and olefins in PHCs have conjugated double bonds and have characteristic absorption in the ultraviolet region of 215-260nm. Therefore, the PHCs can be
measured qualitatively and quantitively by ultraviolet spectrophotometry[25]. Due to the absorption of many extractants in the ultraviolet region of 225nm, it is very important to select the extraction solvent and the wavelength of determination. Ultraviolet spectrophotometry is one of the most commonly used methods for microbial degradation of PHCs due to its simple operation and good repeatability[25].

3.4. Fluorescence Spectrophotometry
Fluorescence spectrophotometry determination principle is under the irradiation of ultraviolet light with fluorescent effect in PHCs, aromatics by excitation and emission fluorescence quantitative, then according to the fluorescence intensity of fluorescence spectrophotometry can only determine the specific components of PHCs, the aromatic and olefin compound measurement effect is good, but, for alkanes, determination of hydrocarbon, accuracy is not high in the determination of PHCs[26].

3.5. Gas Chromatography
Gas chromatography is a widely used detection method for petroleum hydrocarbon[27]. It uses chromatographic column to separate different components of petroleum hydrocarbon and then enter detector for quantitative determination[28]. At present, GC-FID and GC-MS combined with capillary column, flame ion detector and mass spectrometer detector have high sensitivity and low detection limit, which can not only determine the total amount of petroleum hydrocarbon, but also determine the composition and concentration of each component, fingerprint analysis of petroleum hydrocarbon, judge the source of petroleum pollution and the degradation and degree of weathering of petroleum hydrocarbon. Therefore, GC has a tendency to gradually replace other methods.

4. Conclusion
The key to the analysis of petroleum hydrocarbon lies in the extraction of samples, especially the selection of extraction methods and extraction reagents. Among them, liquid-liquid extraction is commonly used for water sample extraction, while Soxhlet extraction and ultrasonic extraction are commonly used for sediment sample extraction. The determination of petroleum hydrocarbon concentration is divided into the determination of total petroleum hydrocarbon concentration and the determination of petroleum hydrocarbon component concentration. Gas chromatography has become the main development direction for the analysis of petroleum hydrocarbon because both are applicable. Infrared spectrophotometry can be used when the concentration is lower. Ultraviolet spectrophotometry and fluorescence spectrophotometry are mainly used to determine the components in the form of aromatics and olefin in PHCs.

Acknowledgments
This work was supported by the National Natural Science Foundation of China (21677065) and the Central-level Nonprofit Research Institutes Fundamental Research Funds (No. TKS20200411).

References
[1] Agency for Toxic Substances and Disease Registry (ATSDR), (1999) Toxicological Profile for Total Petroleum Hydrocarbon, US Department of Health and Human Services, Public Health Service, Atlanta, Ga, USA.
[2] Ahmed, O. E., Mahmoud, S. A., Mousa, A. E. M. (2015) Aliphatic and poly-aromatic hydrocarbons pollution at the drainage basin of Suez Oil Refinery Company. Current Science International, 4: 27-44.
[3] Ashok, A., Cusack, M., Saderne, V. (2019) Accelerated burial of petroleum hydrocarbons in Arabian Gulf blue carbon repositories. Science of the Total Environment, 669: 205-212.
[4] W. Weisman, Ed., (1998) Analysis of Petroleum Hydrocarbons in Environmental Media (Total Petroleum Hydrocarbon Criteria Working Group Series), vol. 1, Amherst Scientific Publishers, Amherst, Mass, USA.
[5] Wongnapapan, P., Wattayakorn, G., and Snidvongs, A. (1999) Petroleum hydrocarbon in seawater and some sediments of the South China Sea, Area I: Gulf of Thailand and East Coast of Peninsular Malaysia. Proceedings of the 1st Technical Seminar on Marine Fishery Resources Survey in the South China Sea, pp. 105-110.

[6] John, W., Farrington, Hideshige, T. (2014) Persistent Organic Pollutants (POPs), Polycyclic Aromatic Hydrocarbons (PAHs), and Plastics: Examples of the Status, Trend, and Cycling of Organic Chemicals of Environmental Concern in the Ocean. Oceanography, 27 (1): 196-213.

[7] Alis, A. M., Payus, C., Ali, M. M. (2015) Surface sediment analysis petroleum hydrocarbon and total organic carbon from coastal area of Papar to Tuaran, Sabah. Malaysian Journal of Analytical Sciences, 19 (2): 318-324.

[8] Wigger, P. E., Torkelson, B. E. (1997) Petroleum hydrocarbon fingerprinting: numerical interpretation developments. Proceedings of the International Petroleum Environmental Conference, San Antonio, Tex, USA.

[9] Revill, A. T., Carr, M. R., Rowland, S. J. (1992) Use of oxidative degradation followed by capillary gas chromatography-mass spectrometry and multi-dimensional scaling analysis to fingerprint unresolved complex mixtures of hydrocarbons. Journal of Chromatography A. 589(1-2):281-286.

[10] Agency for Toxic Substances and Disease Registry (ATSDR) (1999). Toxicological profile for total petroleum hydrocarbon. Atlanta, Ga, USA: US Department of Health and Human Services, Public Health Service.

[11] Morris, J. P. (2013) Residual diesel range organics and selected frothers in process waters from fine coal flotation [Master of Science Thesis in Mining and Minerals Engineering], Virginia Polytechnic Institute and State University.

[12] United States Environmental Protection Agency (US EPA). (1996) Separatory funnel liquid-Liquid extraction: Method 3510C [S]. Washington DC: Government Printing Press, 1996.

[13] United States Environmental Protection Agency (US EPA). (1996) Continuous liquid-liquid extraction: Method 3520C [S]. Washington DC: Government Printing Press.

[14] United States Environmental Protection Agency (US EPA). (2007) Solid-phase extraction: Method 3535A [S]. Washington DC: Government Printing Press.

[15] Cortes, J. E., Suspes, A., Roa, S. (2012) Total petroleum hydrocarbons by gas chromatography in Colombian waters and soils. American Journal of Environmental Sciences, 8 (4): 396-402.

[16] United States Environmental Protection Agency (US EPA). (2014) Organic compounds in water by microextraction: Method 3511 [S]. Washington DC: Government Printing Press.

[17] Xinchao, R., Zeyu, Y., Hongqin, X. (2013) Fast chemical fingerprinting analysis for biodiesel/diesel blends using commercial solid phase extraction (SPE) cartridge and gas chromatography-mass spectrometry (GC-MS). Analytical Methods, 5 (5): 1205.

[18] Dionex Corporation, (2011) Extraction of total petroleum hydrocarbon contaminants (diesel and waste oil) in soils by accelerated solvent extraction (ASE). Dionex Application Note 338.

[19] De Dobbeleer, I., Galbiati, F., Teli, L. (2016) Determination of total petroleum hydrocarbons in rubble and soils by accelerated solvent extraction and GC-FID. Poster Note 64829, Thermo Fisher Scientific.

[20] Weisman, W., Ed., (1998) Analysis of Petroleum Hydrocarbons in Environmental Media (Total Petroleum Hydrocarbon Criteria Working Group Series), vol. 1, Amherst Scientific Publishers, Amherst, Mass, USA.

[21] United States Environmental Protection Agency (US EPA). Separatory funnel liquid-Liquid extraction: Method 3560 [S]. Washington DC: Government Printing Press, 1996.
[22] Galbiati F., Teli,L. (2015) Determination of Total Petroleum Hydrocarbons in Rubble and Soils by Accelerated Solvent Extraction and GC-FID, Thermo Fisher Scientific.

[23] United States Environmental Protection Agency (USEPA), “Analytical method guidance for EPA method 1664a implementation and use (40 CFR part 136),” Office of Water 4303, 2000.

[24] Strother, T., Lowry, S., Bravo, B. (2013) Measurement of dispersed oil in water using an infrared analysis method. Application Note 52439, Thermo Fisher Scientific Inc.

[25] Matthew, M. (2009) A comparison study of gravimetric and ultraviolet fluorescence methods for the analysis of total petroleum hydrocarbons in surface water [M.S. thesis], Northeastern University, Boston, Mass, USA.

[26] Quick Results on Site (QROS), Hydrocarbon Analysis with QED, 2012, http://www.qros.co.uk/hydrocarbon_analysis.html.

[27] Becker, R., Koch, M., Wachholz, S. (2002) Quantification of total petrol hydrocarbons (TPH) in soil by IR-spectrometry and gas chromatography conclusions from three proficiency testing rounds. Accreditation and Quality Assurance, 7:286–289.

[28] Cortes, J. E., Suspes, A., Roa, S. (2012) Total petroleum hydrocarbons by gas chromatography in Colombian waters and soils. American Journal of Environmental Sciences, 8: 396–402.