chemosensors

Communication

Direct Determination of Three PAHs in Drill Cuttings Recycling Products by Solid-Surface 3D Fluorescence Coupled with Chemometrics

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Abstract: In this work, the feasibility of solid-surface three-dimensional fluorescence (SSTF) in combination with chemometrics to rapidly and directly determine three PAHs in drill cuttings recycling products was studied for the first time. Due to the nondestructive characteristics of SSTF and the "mathematical separation" of chemometric three-way calibration, neither time-consuming sample pretreatments nor toxic organic reagents were involved in the determination. By using the smart "mathematical separation" function of the parallel factor analysis (PARAFAC) algorithm, clear spectral profiles together with reasonable quantitative results for the three target PAHs were successfully extracted from the total SSTF signals of drill cuttings recycling products without the need for chromatographic separation. The linearity of the calibration models was good ($R^2 > 0.96$) and the average spiked recoveries of three target PAHs were between 88.1–102.7% with a relative standard deviation less than 20%. Nevertheless, given the green, fast, low-cost, and nondestructive advantages of the proposed strategy, it has the potential to be used as a fast screening approach and allow for a quick survey of PAHs in drill cuttings recycling products.

Keywords: solid-surface three-dimensional fluorescence; polycyclic aromatic hydrocarbons; chemometrics

Citation: Geng, T.; Liu, Z.; Guo, X.; Wang, Z.; Li, X.; Chen, W. Direct Determination of Three PAHs in Drill Cuttings Recycling Products by Solid-Surface 3D Fluorescence Coupled with Chemometrics. *Chemosensors* **2023**, *11*, 150. https://doi.org/10.3390/chemosensors11020150

Academic Editors: Hailong Wu and Tong Wang

Received: 20 December 2022
Revised: 10 February 2023
Accepted: 11 February 2023
Published: 20 February 2023

1. Introduction

With the development of the economy, the demand for petroleum is increasing significantly. In order to meet this demand, more and more petroleum should be exploited. However, during the exploration of petroleum, a large amount of waste is produced every year, such as waste drilling fluids and drilling cuttings, oil sludge, and landing crude oil [1–3]. Oil-based drill cuttings are the hazardous waste generated from oil and gas development, which accounts for 50–70% of the total amount of the abovementioned wastes [4,5]. For example, the annual amount of waste drilling cuttings generated in China alone is more than 3 million tons [6,7]. In order to dispose of these solid wastes, many of them are treated by some chemical or biological techniques and recycled into paving stones or construction bricks [8,9]. As is well known, the drilling solid wastes usually contain high levels of polycyclic aromatic hydrocarbons (PAHs) and have potential risks to the environment and living bodies [10]. Therefore, it is urgent to develop an inexpensive, effective, and user-friendly analytical method to monitor and assess the content of PAHs in drilling solid wastes recycling products.

Up until now, a lot of analytical strategies (mainly chromatographic methods, such as HPLC-UV [11,12], GC-MS [13,14], and GC×GC-TOFMS [15,16]) have been developed for determining the contents of PAHs in various environmental matrices. Generally, the chromatography-based methods provide good separation and low limits of detection. However, they tend to be expensive, a waste of time, and usually require tedious sample pretreatments [17]. Owing to the existence of aromatic rings in molecules, PAHs are intrinsically fluorescent, which makes fluorescence spectroscopy possible for their analysis [18]. Fluorescence spectroscopy has superior performance from the perspective of accuracy, cost, analytical speed, and the operator's safety and health. For example, Gu et al. [17] proposed a green chemometrics-assisted fluorimetric detection method for the direct and simultaneous determination of six PAHs in oil-field wastewaters, which was proven to be comparable with the classical GC-MS method. More recently, they proposed three- dimensional fluorescence spectroscopy coupled with chemical pattern recognition methods for tracing the sources of oilfield wastewater [19]. However, as for solid samples [20], traditional fluorescence spectrometry still faces complex sample extraction steps and may consume plenty of toxic organic reagents, which would lead to secondary pollution.

In considering the above, solid-surface three-dimensional fluorescence (SSTF) could be an attractive alternative method to analyze solid samples directly [21]. SSTF spectrometry offers a simple, fast, non-destructive form of measurement, without any sample preparation or extraction steps, which has been investigated extensively in food preparation [22] and pharmaceutical domains [23]. Structurally, SSTF data acquired from multiple solid samples consist of three dimensions: the excitation dimension, emission dimension, and sample dimension. This form of data structure enables SSTF spectrometry to achieve the accurate quantitative analysis of multiple components of interest in complex solid samples with unknown interferences when combined with chemometric three-way calibration algorithms, which is known as the "second-order advantage" [24,25].

The purpose of this work was to evaluate the feasibility of SSTF spectrometry coupled with chemometric three-way calibration for the rapid and direct determination of three common PAHs in drill cuttings recycling products. To achieve this goal, SSTF spectra of two kinds of drill cuttings recycling products, including pretreated waste drilling cuttings and their recycling product bricks, were acquired and analyzed using the chemometric three-way calibration algorithm: parallel factor analysis (PARAFAC). The analytical process of this strategy is illustrated in Figure 1, as reported by our previous work [17]. It was demonstrated that the combination of SSTF spectrometry with chemometric three-way calibration has the potential to offer a quick survey of PAHs in drill cuttings recycling products owing to its green, fast, low-cost, and nondestructive characteristics.

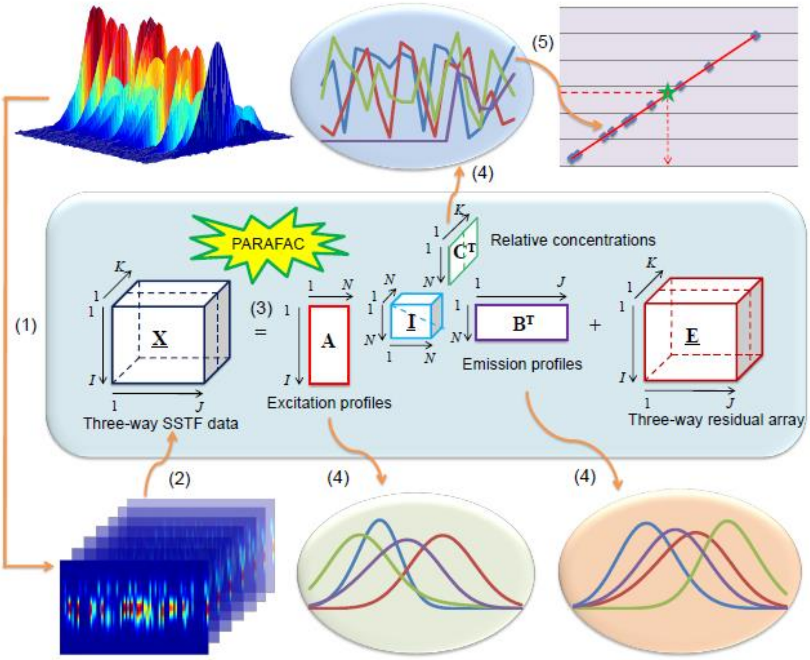

Figure 1. Schematic representation of SSTF spectrometry coupled with the PARAFAC algorithm for the rapid and direct determination of three common PAHs in drill cuttings recycling products.

2. Experimental

2.1. Chemicals and Reagents

The standard substances of three common PAHs, including anthracene (ANT), fluoranthene (FLA), and pyrene (PYR), were provided by Shanghai Aladdin Biochemical Technology Co., Ltd. (Shanghai, China); their mass purity was >99%. Two kinds of drill cuttings recycling products, including the pretreated waste drilling cuttings and their recycling product bricks, were sampled from an oil field in the southwest of China. Blank soils without any PAHs pollution were collected from local farmland in Jingzhou, China, and were confirmed by GC-MS method. Prior to analysis, the drill cuttings recycling products and blank soils were naturally dried, crushed by blender, and passed through a 120-mesh sieve.

2.2. Sample Preparation

To quantify the ANT, FLA, and PYR in drill cuttings recycling products, nine calibration samples (Cal01–Cal09) were prepared by diluting corresponding solid PAHs standards with blank soils using the grinding method. The calibration ranges of ANT and FLA were 0.5 to 4.5 mg g^{-1}, while the calibration range of PYR ranged from 2 to 10 mg g^{-1}. In addition, three prediction samples for each kind of drill cuttings recycling products were made by using their corresponding solid powders directly. Each kind of drill cuttings recycling product was prepared in triplicate, and the concentration of every target PAH was the mean value. Furthermore, to prove the accuracy of the proposed analytical method, three spiked samples (Sp01–Sp03) for each drill cuttings recycling product were constructed by adding low, middle, and high levels of solid PAHs standards to the prediction samples mentioned above. The concentrations of the three PAHs in the nine calibration samples and the three spiked drill cuttings recycling product samples are summarized in Table 1.

Table 1. Concentrations (mg g^{-1}) of three PAHs in nine calibration samples and three spiked drill cuttings recycling product samples.

Sample	ANT	FLA	PYR
Cal01	0.5	4.5	8
Cal02	1	4	5
Cal03	1.5	3.5	2
Cal04	2	3	9
Cal05	2.5	2.5	6
Cal06	3	2	3
Cal07	3.5	1.5	10
Cal08	4	1	7
Cal09	4.5	0.5	4
Sp01	1	3	3
Sp02	2	2	9
Sp03	3	1	6

2.3. Solid-Surface 3D Fluorescence Measurement

Solid-surface 3D fluorescence was measured by an F-7000 spectrofluorometer configured with a 5J0-0152 solid sample holder accessory (Hitachi, Tokyo, Japan). In order to obtain the SSTF spectra, the apparatus was run in 3-D scan mode with excitation range of 250 to 430 nm (3 nm interval) and emission range of 400 nm to 511 nm (3 nm interval). The scan speed was 30,000 nm min^{-1}, and PMT voltage was 500 V. Slit widths of excitation and emission were both set to 5 nm. In such a way, a three-way SSTF data array with a size of 62 (excitation) × 39 (emission) × 21 (sample) was obtained.

2.4. Chemometric Analysis

The SSTF spectra were recorded by FL solution software (Hitachi, version 4.0). In all situations, the raw SSTF spectra were transferred from FD3 format into MATLAB readable

.txt files for further data analysis. PARAFAC decomposition, regression, and prediction of three PAHs in drill cuttings recycling products were implemented using the in-house code.

3. Results and Discussion

3.1. SSTF Characteristics of Individual PAHs

Considering the adverse effects of Rayleigh and Raman scattering in the SSTF spectra, they must be eliminated before data analysis. In this study, the Raman scattering was firstly minimized by deducting the basal blank (i.e., blank soil) from all SSTF spectra. Then, the Rayleigh scattering was removed and modeled by the interpolation method. Figure 2 shows the STTF spectra of the third calibration sample before and after removing the Rayleigh scattering. As can be seen, it was successfully eliminated from the raw STTF spectra. Figure 3 shows the contour plots of the SSTF spectra of the solid standard ANT, FLA, PYR, and a mixture of them after removing the scattering. It can be clearly seen that ANT, FLA, and PYR have a wide excitation peak range of 250–400 nm and an emission peak at around 420, 460, and 440 nm. Moreover, the peak regions of the three PAHs are significantly overlapped (Figure 3A–C). Due to the high spectral overlap, it is very difficult to distinguish the presence of one specific PAH in the mixture (Figure 3D) without the assistance of deconvolution. Moreover, the PAHs usually co-existed with plenty of other unknown fluorescent interferences in drill cuttings recycling products, making the situation more complex.

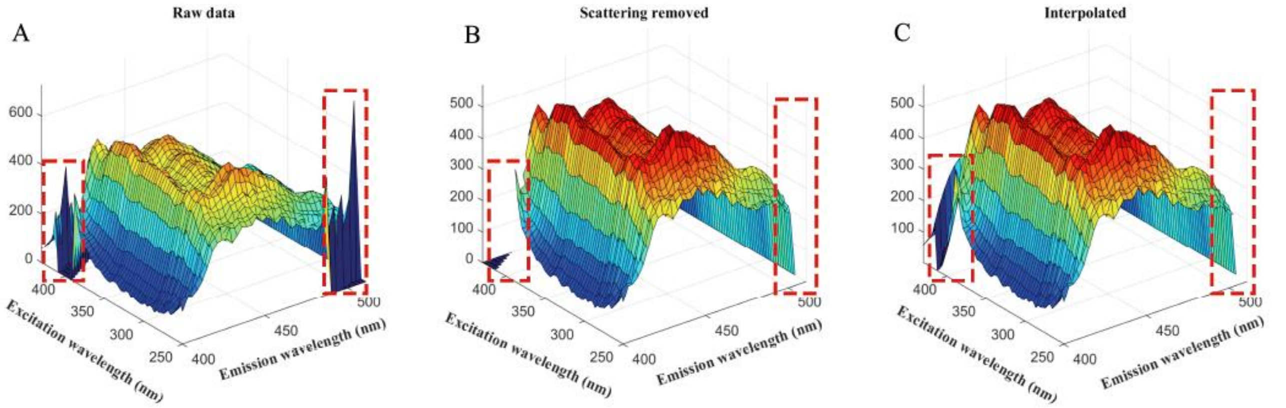

Figure 2. Removal of Rayleigh scattering (red dotted box) in STTF spectra of the third calibration sample. (**A**) Raw spectra with Rayleigh scattering; (**B**) gapped spectra with scattering removed; (**C**) repaired spectra modeled by the interpolation method.

In this case, a traditional solution is to apply the strategy named "separation followed by analysis"; that is, to first completely separate target PAHs by some necessary sample pretreatment procedures, and then to analyze them one by one [26]. In the current work, we will turn to the chemometric modeling for help; namely, use smart "mathematical separation" instead of the traditional "physical and/or chemical separation" to extract the pure spectra of each PAH from the complex mixed SSTF spectra, and then achieve the rapid and direct analysis of multiple PAHs even in the presence of overlapping peaks and unknown fluorescent interferences.

3.2. Method Development

In this section, we will use the well-known PARAFAC algorithm [27] to resolve the overlapping SSTF spectra of ANT, FLA, and PYR. Figure 4 shows the resolved pure excitation spectra and emission spectra as well as their reference spectra for the three PAHs in the nine calibration samples. As illustrated in Figure 4, although there are serious spectral overlaps of the three PAHs in the excitation and emission modes, the proposed strategy can still extract clear pure excitation and emission spectra for each target PAH from the mixed SSTF spectra. This means that the proposed strategy can indeed use the "mathematical separation" of the PARAFAC algorithm to replace the traditional "physical and/or chemical separation" and achieve the signal separation of each PAH.

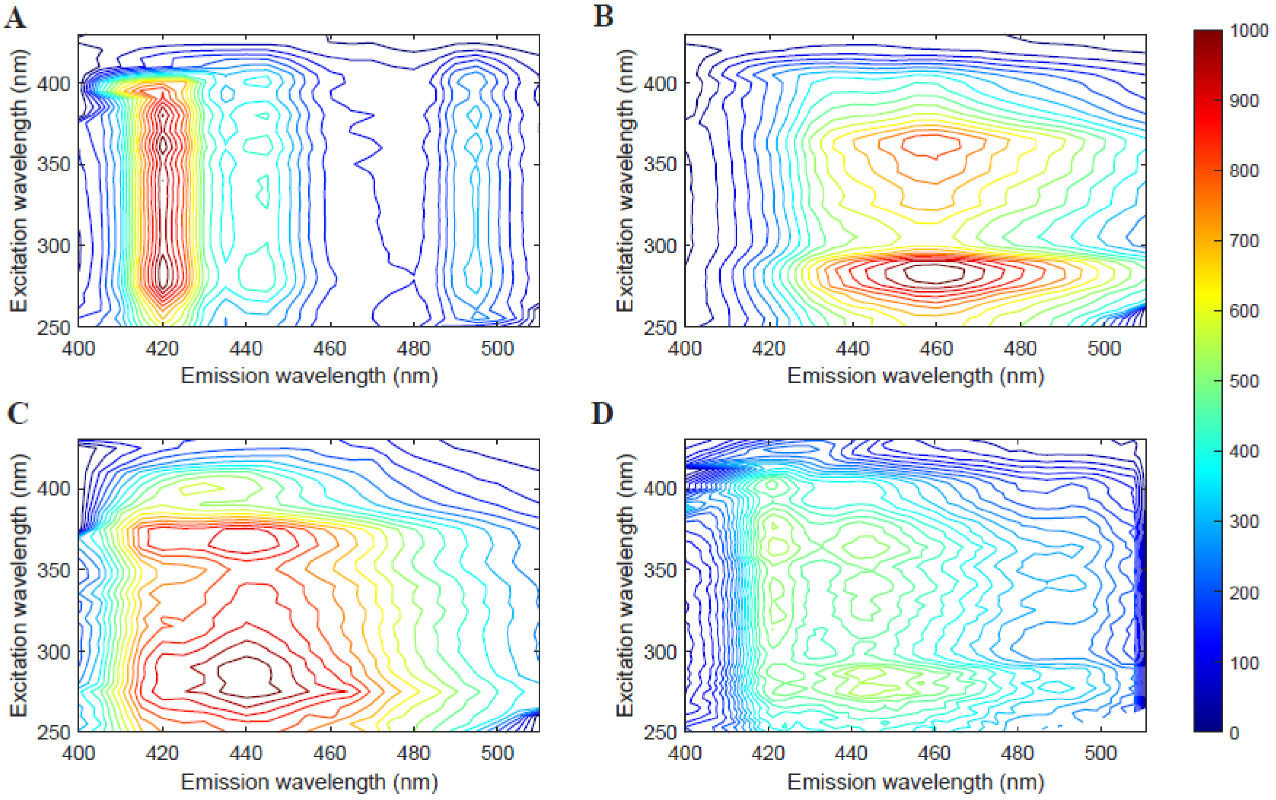

Figure 3. The contour plots of STTF spectra after removing the scattering. (**A**) ANT (10 mg g^{-1}); (**B**) FLA (10 mg g^{-1}); (**C**) PYR (10 mg g^{-1}); (**D**) a mixture of ANT, FLA, and PYR.

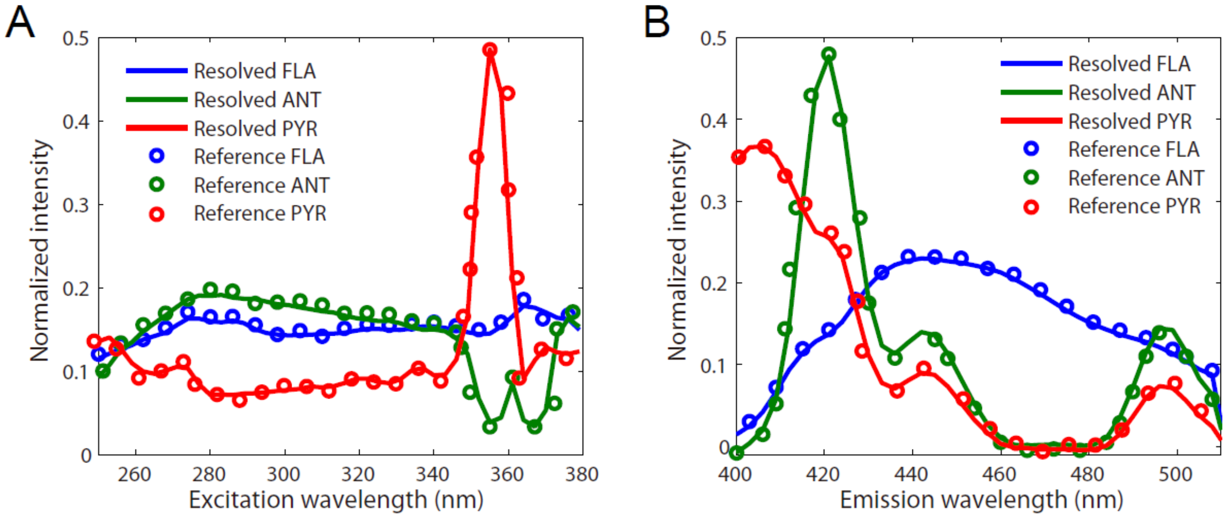

Figure 4. PARAFAC resolved excitation spectra (**A**) and emission spectra (**B**) as well as their reference spectra for the three PAHs in the nine calibration samples.

The calibration models of the three PAHs based on the relative concentrations against the real concentrations in the nine calibration samples are shown in Figure 5 and Table 2. As can be seen, the linearity between the relative concentrations resolved by PARAFAC and the real concentrations are acceptable ($R^2 > 0.96$); these results demonstrate the feasibility of using the SSTF spectroscopy coupled with the PARAFAC algorithm for resolving and quantifying overlapped PAHs. In the following section, the performances of the proposed method on real complex samples (i.e., drill cuttings recycling products) will be further investigated.

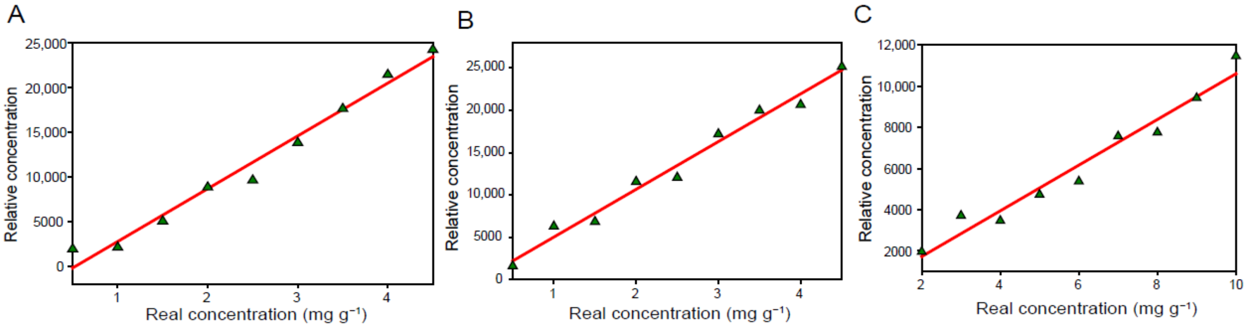

Figure 5. The calibration models of ANT (**A**), FLA (**B**), and PYR (**C**) based on the relative concentrations against the real concentrations in nine calibration samples by least squares regression.

Table 2. The calibration equations and their correlation coefficients for the three PAHs.

Analyte	Calibration Equation	R^2	RMSEC (mg g^{-1})
ANT	$Y = 5918.43X - 3160.37$	0.9785	0.19
FLA	$Y = 5635.00X - 601.08$	0.9811	0.18
PYR	$Y = 1109.05X - 487.40$	0.9607	0.52

3.3. Method Application

As a practical method, we utilized the proposed strategy to quantify the contents of the three PAHs in two kinds of drill cuttings recycling products. The results are summarized in Table 3. As can be seen, some the three PAHs were detected in drill cuttings recycling products. For example, ANT and FLA were detected in pretreated drill cuttings, while only FLA was detected in bricks. As for the remaining target PAHs, they may not be present or may not be detected because of the low sensitivity of the SSTF spectroscopy. In order to prove the accuracy and reliability of the proposed method, the spiked recovery experiments were carried out; the recoveries are listed in Table 3**.** We can see that the average recoveries for the spiked concentration at low levels are a bit worse, while the average recoveries for the spiked concentration at high levels are good. The reason for this phenomenon is that the sensitivity of the SSTF spectroscopy is not high enough. Nevertheless, it has distinct advantages of being simple, fast, green, low-cost, and nondestructive. Given the complexity of the drill cuttings recycling products, the average recoveries of (88.1 ± 19.6)% to (102.7 ± 16.4)% can be considered to be reasonable. Therefore, the SSTF spectroscopy technique has the potential to be used as a preliminary screening approach and allow for a quick survey of PAHs in complex solid samples, thereby giving priority to prompt analysis.

Table 3. Predicted concentration, RMSEP, and spiked recovery of three PHAs in drill cuttings recycling products based on SSTF spectroscopy coupled with the PARAFAC algorithm.

Sample	Analyte	Concentration (mg g^{-1})			Recovery (%)	RMSEP (mg g^{-1})	Average ± SD [b] (%)
		Unspiked	Spiked	Found			
Pretreated drill cuttings	ANT	0.64	1	1.432	79.2	0.26	100.9 ± 19.2
			2	2.952	115.6		
			3	3.874	107.8		
	FLA	1.37	3	4.241	95.7	0.19	102.5 ± 17.6
			2	3.156	89.3		
			1	2.595	122.5		
	PYR	n.d. [a]	3	2.277	75.9	1.04	88.1 ± 19.6
			9	9.963	110.7		
			6	4.656	77.6		

Table 3. *Cont.*

Sample	Analyte	Concentration (mg g^{-1})			Recovery (%)	RMSEP (mg g^{-1})	Average ± SD [b] (%)
		Unspiked	Spiked	Found			
Brick	ANT	n.d.	1	1.215	121.5	0.20	102.7 ± 16.4
			2	1.910	95.5		
			3	2.736	91.2		
	FLA	0.43	3	3.145	90.5	0.27	94.9 ± 18.6
			2	2.736	115.3		
			1	1.219	78.9		
	PYR	n.d.	3	2.529	84.3	0.44	96.0 ± 11.8
			9	8.631	95.9		
			6	6.474	107.9		

[a] not detected; [b] average ± standard deviation.

4. Conclusions

This study has established the capability of SSTF spectroscopy for the rapid and direct determination of three PAHs in drill cuttings recycling products for the first time. The acquired SSTF spectral data were firstly stacked along the sample dimension to construct a three-way data array and then decomposed by the well-known PARAFAC algorithm to extract the pure excitation and emission spectra of each individual PAH, even in the presence of overlapping peaks and unknown interferences. The calibration models based on the relative concentrations resolved by the PARAFAC algorithm against the real concentrations in the calibration samples are good. By applying the proposed strategy to real drill cuttings recycling products, some target PAHs could be detected, and reasonable average spiked recoveries were obtained. In conclusion, the proposed SSTF spectroscopy coupled with chemometrics has the potential to be used as a preliminary screening method for PAHs in drill cuttings recycling products.

Author Contributions: Conceptualization, T.G. and W.C.; methodology, T.G. and W.C.; software, T.G.; validation, Z.L. and X.G.; formal analysis, Z.L. and X.G.; investigation, T.G.; resources, Z.W. and X.L.; data curation, T.G.; writing—original draft preparation, T.G.; writing—review and editing, W.C.; visualization, T.G.; supervision, Z.W., X.L. and W.C.; project administration, Z.W. and X.L.; funding acquisition, W.C. All authors have read and agreed to the published version of the manuscript.

Funding: This study was supported by the Open Project Program of State Key Laboratory of Petroleum Pollution Control (Grant No. PPC2020012), CNPC Research Institute of Safety and Environmental Technology.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Conflicts of Interest: The authors declare no conflict of interest.

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