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Algorithmic study of total petroleum hydrocarbons in contaminated soil by three-dimensional excitation-emission matrix fluorescence spectroscopy

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Abstract: Assessment of Total Petroleum Hydrocarbons (TPHs) from contaminated soils demands reliable measurement to analyze the types and contents of mixed petroleum hydrocarbons in soils. Three-dimensional excitation-emission matrix (3DEEM) fluorescence spectroscopy has been demonstrated as a powerful technology for rapidly analyzing mixed petroleum hydrocarbons by identifying its abundant spectral information. However, detection precision in soil still demands improvement. This study investigates the correction methods of 3DEEM fluorescence spectra to correct the complicated matrix and scattering effects of soils. To improve the analytical accuracy, parallel factor analysis (PARAFAC) and the Alternating Trilinear Decomposition method (ATLD) were used to qualitatively and quantitatively analyze mixed petroleum contaminated soils. The methods were used to assess three commonly observed petroleum hydrocarbons: machine oil, lubricating oil, and diesel oil. Compared with the results of PARAFAC, the average recoveries of ATLD increased from 85% to 95%, implying that ATLD can effectively distinguish between similar fluorescence spectra and is more effective in the detection of the components and total content of petroleum in soil. This work can have applications of risk assessment and remediation techniques.

Key words: 3DEEM fluorescence spectroscopy; mixed petroleum hydrocarbons in soils; parallel factor method; alternating trilinear decomposition method; total petroleum hydrocarbons

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土壤石油烃总量三维荧光光谱定量分析方法研究

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摘要:混合石油烃污染土壤中准确的种类识别和含量检测有助于土壤石油烃污染总量的检测。石油烃是多种化合物的混合,而三维激发发射荧光光谱技术含有大量的荧光光谱信息,故被用于快速定性和定量检测土壤石油烃污染,但该技术仍面临着石油烃组分的准确识别以及土壤背景干扰引起的定量分析问题。本文研究了土壤石油烃污染物的三维荧光光谱复杂基质和散射效应校正方法,最大程度地保留了光谱信息。为了提高土壤石油烃定性识别和含量检测精度,本文以机油、润滑油和柴油为例,采用平行因子和交替三线性分解法对不同类型混合土壤石油烃污染进行定性和定量分析。实验结果表明,与平行因子法对土壤混合石油烃污染的检测结果相比,交替三线性分解法将土壤混合石油烃污染的平均回收率由85%提高至95%,说明交替三线性分解法能更好地分离相似荧光光谱,对土壤中石油成分和总含量的检测更有效,其可为土壤石油烃污染风险评估提供快速检测方法。

关键词:三维荧光光谱;土壤混合石油烃;平行因子法;交替三线性分解;总石油烃

中图分类号:O433.4:X833

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1 Introduction

Due to the rapid development of industry, the use of petroleum has increased enormously. Many types of petroleum are transported by the same pipeline, or used in industrial estates jointly, etc, which directly leads to the mixed petroleum hydrocarbons pollution in surrounding soils^[1-2]. Petroleum has become one of the main sources of soil pollution, since these compounds can cause the disruption of surrounding ecosystems very quickly and influence the health of humans and animals through the bioaccumulation of the food chain, and they are difficult to be degraded by organism^[3]. Therefore reducing the total concentration of petroleum is important, and the most crucial task is to qualitative and quantitative analyze the pollutants accurately^[4].

At present, traditional analysis methods in petroleum hydrocarbon detection are high performance liquid chromatography^[5], gas chromatography^[6] and UV spectrophotometry^[7], etc. However, the inherent limitation of these techniques is requiring sample preparation^[8]. Fluorescence spectroscopy de-

tection methods have been powerful analytical techniques for organics for their attributes of high sensitivity, rapid and multi-component analysis with very little sample preparation, which meet the needs of real-time online monitoring and have been widely concerned by researchers^[9-10]. For petroleum are the mixed organic compounds by various polycyclic aromatic hydrocarbons and alkanes with abundant fluorescent groups, the fluorescence spectra are the superposition of fluorescent groups. Based on the excitation spectrum and emission spectrum, 3DEEM fluorescence spectroscopy technique has been used for the analysis of multi-component mixtures by its advantages of abundant information, remarkable characteristics and good selectivity^[11-12].

Many researchers have focused on the research of petroleum hydrocarbons by 3DEEM fluorescence spectroscopy. Lemke M^[13] *et al.* used synchronous fluorescence technique to analyze the types and contents of organic pollutants in asphalt. Sinski J.F^[14] *et al.* analyzed the red-shifted phenomena of fluorescence spectral peaks in weathered petroleum. Ferretto N^[15] *et al.* utilized PARAFAC combined with 3DEEM fluorescence spectroscopy tech-

nique to analyze the types and contents of Polycyclic Aromatic Hydrocarbons (PAHs) and pesticides in aquatic environments.

However, different from the free suspension state of petroleum hydrocarbons in water, the inorganic nitrogen and phosphorus in soils can react with petroleum, which can change the chemical structures of petroleum hydrocarbons, considering the complicated matrixes of soils simultaneously, it is of great significance to researching an accurate analysis method of petroleum hydrocarbons in soils based on 3DEEM fluorescence spectroscopy^[16-17]. Christensen J H^[18] *et al.* applied PARAFAC to verify the fluorescence signal of naphthalene, phenanthrene and fluorine in petroleum. Yang Liu^[19] *et al.* utilized fluorescence regional integration combined with an analytic hierarchy process to identify and quantify the main types of organic matter. Shurong Zhang^[20] *et al.* applied ATLD to analyze the fluorescence spectra with complex mixture and severe spectra overlap, determining the spectra of corresponding individual components.

In this paper, the main purpose of this work is to evaluate the potential of accurate qualitative and quantitative analysis of mixed petroleum in soils and estimate the total content of petroleum hydrocarbons by 3DEEM fluorescence spectroscopy technique on the use of PARAFAC and ATLD. For this purpose, the methods of fluorescence spectra correction were investigated.

2 Experimental methods

A 3DEEM fluorescence spectrometer (Hitachi, HITACHI F-7000) was used for fluorescence detection. For F-7000 was designed to detect transmission fluorescence spectra and suitable for liquid, to get the fluorescence spectra of petroleum hydrocarbons in soils, the soil powder was packed into a plastic cube which has the same size of the sample container of F-7000, the surface of the soil sample was smooth and at a 45 degree angle with the xenon light source, which ensured that the soil sample was full contacted with the light source and we could detect the fluorescence spectra of solid.

The base soils in this experiment were collected from a farmland and measured by chromatography to choose the one without petroleum hydrocarbons. They were dried, grinded and sieved through 100-mesh to remove roots for reserve. Three commonly observed petroleum hydrocarbons (machine oil, 5w-40 lubricating oil and 0# diesel oil) were selected to represent the petroleum pollutants. 64 soil samples labeled 1# to 64# were prepared in the laboratory, and the contents of petroleum hydrocarbons configured are listed in Table 1.

3 Results and discussion

In this experiment, the width of the excitation slit and emission slit of the instrument were both adjusted to 5 nm, the corresponding spectral resolution was 2 nm. The integral time was fixed at 0.5 s, and the voltage of the photomultiplier tube was set to 600 V. The range of fluorescence excitation wavelength was from 200 nm to 400 nm, and the

Tab. 1 Contents of mixed petroleum in the configured soil samples(%)

(a) The soil samples with the mixture of two types of petroleum

calibration set	Machine oil	lubricating oil	Test set	Machine oil	lubricating oil
1#	0.11	0.21	17#	0.42	0.41
2#	0.32	0.50	18#	0.61	0.72
3#	0.51	0.52	19#	1.00	1.02
4#	0.52	0.21	20#	0.41	0.23
5#	0.22	0.79	21#	0.64	0.43
6#	0.83	0.52	22#	1.02	5.03

续表 1

(a) The soil samples with the mixture of two types of petroleum

calibration set	Machine oil	lubricating oil	Test set	Machine oil	lubricating oil
7#	0.82	1.54	23#	2.01	0.52
8#	1.33	2.60	24#	1.50	1.12
9#	1.51	1.12	25#	1.01	10.2
10#	3.14	5.81	26#	2.12	2.41
11#	5.02	4.08	27#	2.52	4.11
12#	3.44	4.47	28#	4.23	3.52
13#	6.78	2.10	29#	6.54	1.12
14#	2.93	5.52	30#	4.61	1.72
15#	7.82	4.22	31#	7.32	2.23
16#	4.13	7.88	32#	8.11	1.12

(b) The soil samples with the mixture of three types of petroleum

calibration set	Machine oil	lubricating oil	Diesel oil	Test set	Machine oil	lubricating oil	Diesel oil
33#	0.10	0.11	0.13	49#	0.42	0.44	0.43
34#	0.22	0.21	0.24	50#	0.71	0.51	0.62
35#	0.52	0.54	0.49	51#	0.63	0.48	0.32
36#	0.21	0.12	0.54	52#	0.22	1.31	0.42
37#	0.52	0.51	0.11	53#	0.43	1.83	0.62
38#	0.72	0.64	0.72	54#	0.51	1.02	8.01
39#	1.12	4.23	0.84	55#	1.04	8.00	0.52
40#	0.82	0.24	0.49	56#	1.02	1.01	1.01
41#	3.02	4.45	1.03	57#	1.51	0.78	1.18
42#	0.51	5.22	1.47	58#	2.42	5.19	2.11
43#	4.94	0.79	2.33	59#	4.21	1.31	1.51
44#	3.04	3.0	2.45	60#	4.41	2.98	0.64
45#	1.10	1.8	4.41	61#	2.13	0.84	5.20
46#	4.12	2.0	3.30	62#	2.04	0.82	6.41
47#	1.04	0.8	5.51	63#	2.81	0.54	6.05
48#	2.14	1.12	6.70	64#	8.01	0.51	1.03

step length was 2 nm. Meanwhile, the emission wavelength range was set from 200 nm to 500 nm, and the step length was 2 nm.

3.1 Spectral pretreatment

Fig.1 (a) (color online) and Fig.1 (b) (color online) depict the soil fluorescence spectra of diesel oil and the pure soil fluorescence spectra obtained from the experimental scanning, one can observe from Fig.1 (a) that the fluorescence peak of diesel

oil is significantly influenced by the soil organic matter, Rayleigh scattering, Raman scattering, etc. This affects the measurement accuracy of petroleum hydrocarbon. In order to eliminate the influence of the soil background effect and scattered light, background correction method and Eemscat function method were used in the pretreatment of the 3DEEM fluorescence spectra. Fig.1 (c) (color online) and Fig.1 (d) (color online) show the fluor-

escence spectra of diesel oil after background correction and scatter correction. It is clarified that fluorescence spectral information of diesel oil can

be better highlighted after background correction and scatter correction.

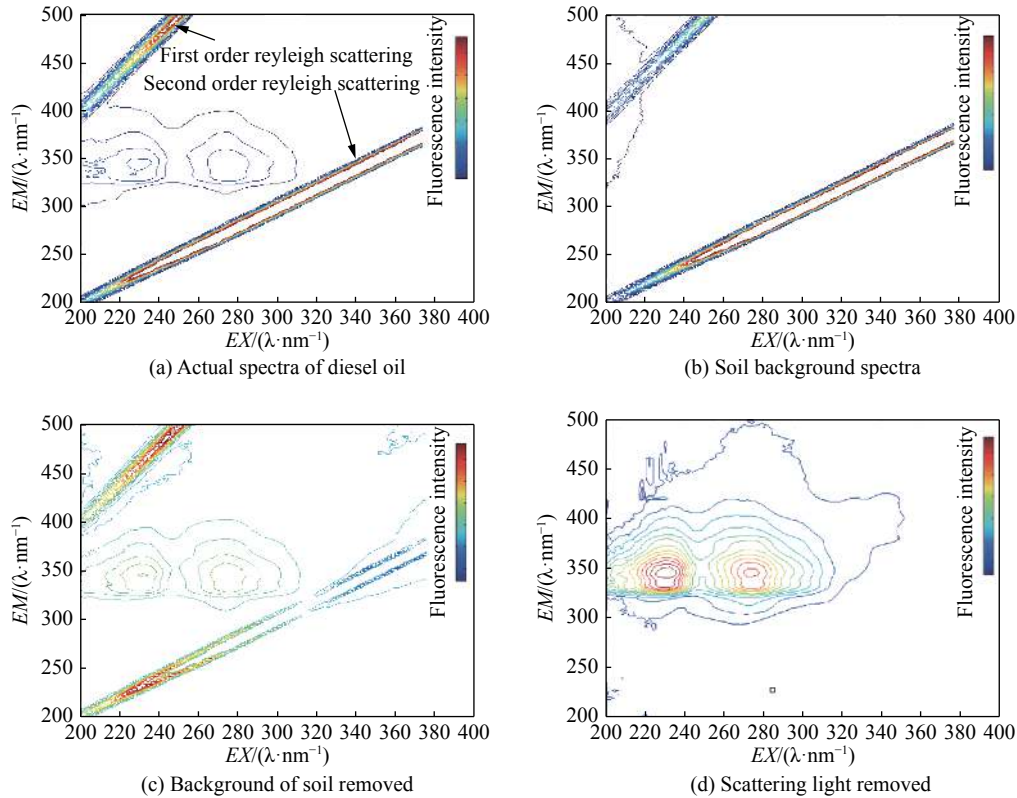


Fig. 1 The 3DEEM fluorescence spectral pretreatment of diesel oil in soil.

The matrixes of soil samples are too complicated, it is difficult to ensure that the soil background signals in each trial are completely consistent, just as shown in Fig.1 (d), after the spectral pretreatment of diesel oil, there are a lot of spectral background noises in the fluorescence spectra. Therefore, weighted mean filter was adopted to eliminate the random noise spread on the 3DEEM fluorescence spectra. Fig.2 (color online) shows the fluorescence spectra of the three pure petroleum hydrocarbons before and after smooth filtering.

As shown in Fig.2, compared with the original spectra, the smooth filter can efficiently preserve the

spectral information and eliminate noise error. Since each type of petroleum is a mixture of various fluorescent substances in a certain proportion, their fluorescence spectra are the spectral superposition of all the fluorescent substances, and their specific components form their own unique characteristics of fluorescence spectra. The coordinates of peak positions in three petroleum hydrocarbons are shown in Table.2. Fig.2 and Table.2 indicate that different types of petroleum hydrocarbon have different fluorescence peak positions and intensities, which can be used as the basis of identification.

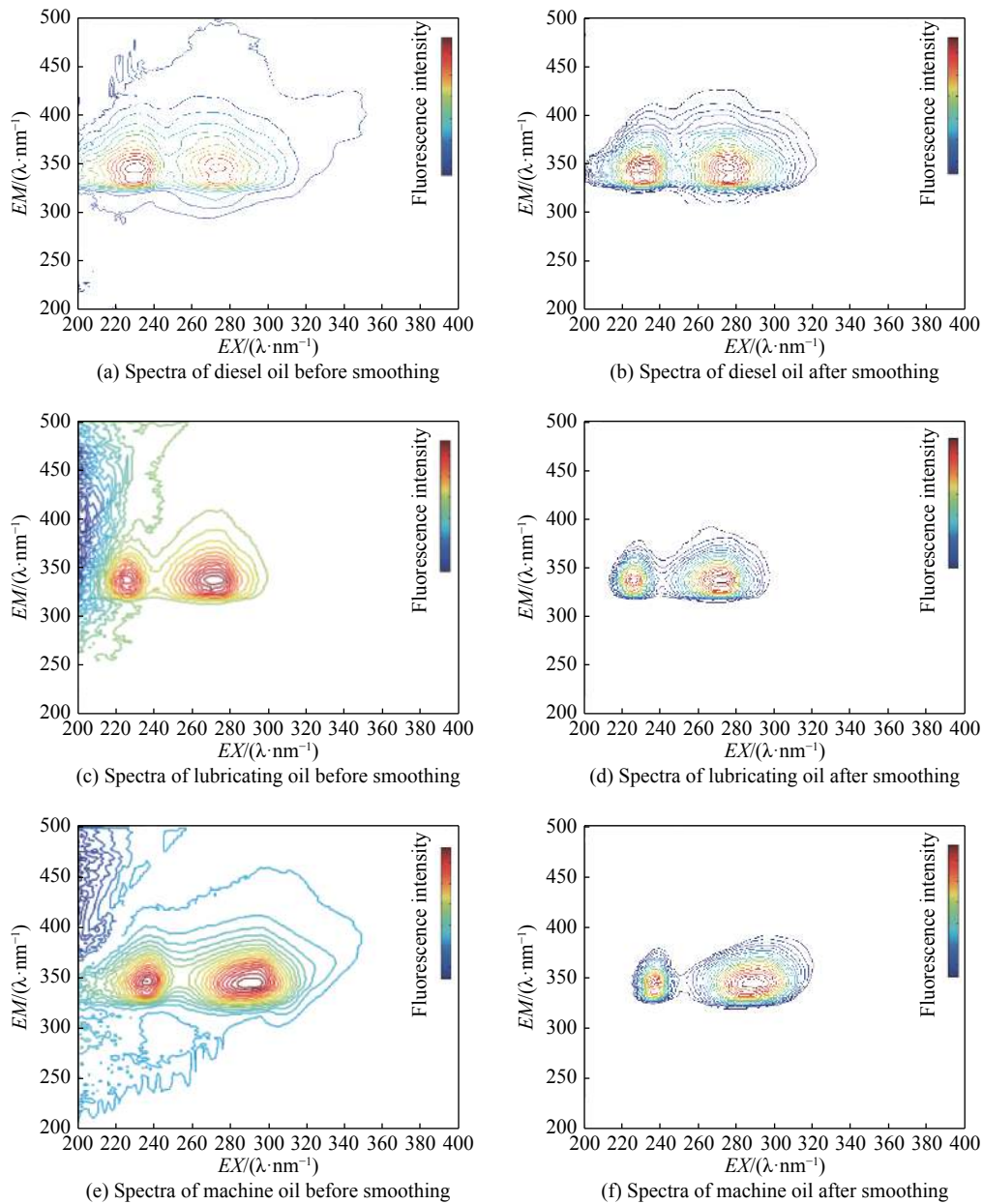


Fig. 2 The typical fluorescence spectra of three kinds of pure petroleum in soils

Tab. 2 The coordinates of peak positions in three petroleum hydrocarbons

Types	Left area (EX, EM)	Right area (EX, EM)
Diesel oil	(232,334)	(288,334)
Lubricating oil	(236,336)	(290,348)
Machine oil	(238,346)	(270,372)

Fig.3 (color online) depicts the 3DEEM fluorescence spectra of mixed oil in soil, where only few differences at the central peak positions were observed. Fig.3 (b) was the fluorescence spectra of two

petroleum mixtures and Fig.3 (d) was the fluorescence spectra of three petroleum mixtures, they are extremely consistent. It is clarified that the difference at the central peak positions of various petroleum hydrocarbons in soils was not significant, resulting the 3DEEM fluorescence spectra of mixed petroleum hydrocarbons remain similar. Therefore, it is necessary to identify and quantify the 3DEEM fluorescence spectra of mixed petroleum hydrocarbons in soils by using effective algorithms.

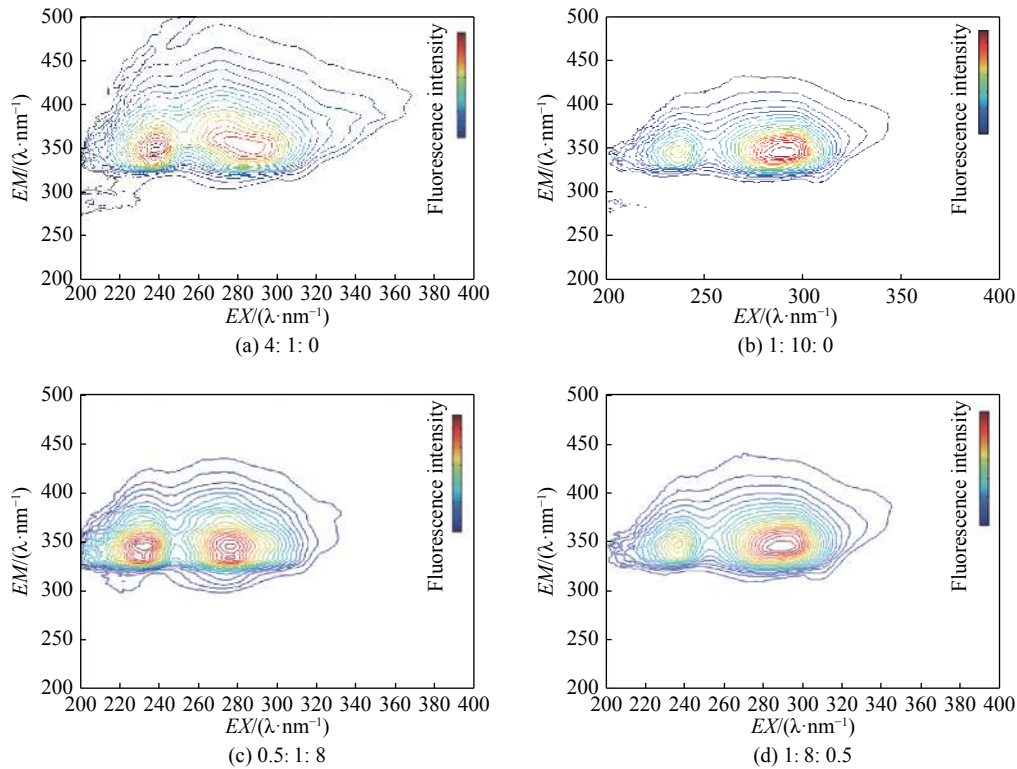


Fig. 3 3DEEM fluorescence spectra of mixed oil in soil (Machine oil:Lubricating oil:Diesel oil)

3.2 Parallel factor analysis

PARAFAC (Parallel factor analysis) is a dimensional decomposition analysis which was used for analyzing 3DEEM or multidimensional data. For 3DEEM fluorescence spectra, it is a trilinear analysis. In the experiments of 3DEEM fluorescence, assuming that I is the number of excitation wavelength, J is the number of emission wavelength, K is number of samples, then a 3DEEM data matrix of size $I \times J \times K$ can be obtained. The measured fluorescence intensity χ has a relationship with the contents of petroleum hydrocarbons in samples, the trilinear model can be expressed as in Eq.1.

$$\chi_{ijk} = \sum_{n=1}^N a_{in} b_{jn} c_{kn} + e_{ijk} \quad i=1,2,\dots,I; j=1,2,\dots,J; k=1,2,\dots,K, \quad (1)$$

where χ_{ijk} is the element of matrix \mathbf{X} , N is the types of petroleum hydrocarbons, a_{in} is the element of excitation spectral data matrix \mathbf{A} , b_{jn} is the element of emission spectral data matrix \mathbf{B} , c_{kn} is the element of concentration matrix \mathbf{C} , e_{ijk} is the element of residual matrix. In this paper, the rule of minimum SSR (Residual Sum of Squares) was used to gain the op-

timum PARAFAC model. Equation 2 shows the expression.

$$\text{SSR} = \sum_{i=1}^I \sum_{j=1}^J \sum_{k=1}^K e_{ijk}^2. \quad (2)$$

CORCONDIA was used to estimate the number of factors in PARAFAC, which is very sensitive to the number of factors. Equation 3 shows the expression.

$$c = 100 \times \left[1 - \frac{\sum_{i=1}^F \sum_{j=1}^F \sum_{k=1}^F (g_{ijk} - t_{ijk})^2}{\sum_{i=1}^F \sum_{j=1}^F \sum_{k=1}^F t_{ijk}^2} \right], \quad (3)$$

where F is the number of factors, g_{ijk} is the element of least squares fitting matrix \mathbf{G} , t_{ijk} is the element of hyperdiagonal matrix \mathbf{T} , when the chosen number of factors is less than or equal to the true number, c is roughly equal to 1, otherwise it is approximately equal to 0.

For mixtures of two petroleum hydrocarbons, the soil samples labeled 1#~16# were chosen as the calibration set and the remaining samples were chosen for the test set. As shown in Fig.4 (color online), the core consistency coefficient is 98.56%

when the number of factors was set to 2, which is close to 100%, and the core consistency coefficient is 63.82% when the number of factors was set to 3,

which is also greater than 60%, then the optimal number of factors was set as 2.

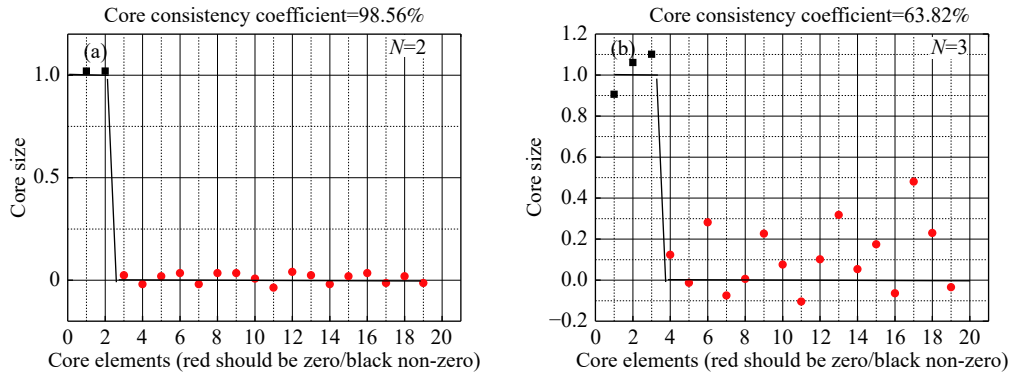


Fig. 4 The core consistency diagnosis results for mixtures of two petroleum hydrocarbons. (a) $N = 2$; (b) $N = 3$

In order to avoid the meaningless of negative value, the non-negative limit was added in the calculation of the three matrixes in the program running process. Fig.5 (color online) shows the typical emission spectra and excitation spectra which were decomposed by PARAFAC, where the emission spectra and excitation spectra obtained by decomposition not be that different from the pure petroleum spectra at the same concentration, proving that

PARAFAC can recover and distinguish the spectra of the components. The calculation curve was established by the concentration scores of target analyst and the corresponding real contents in the calibration set, and Table 3 shows the results of predicted contents using PARAFAC, and recovery rate was used to estimate the accuracy of the quantitative method. Equation 4 shows the expression.

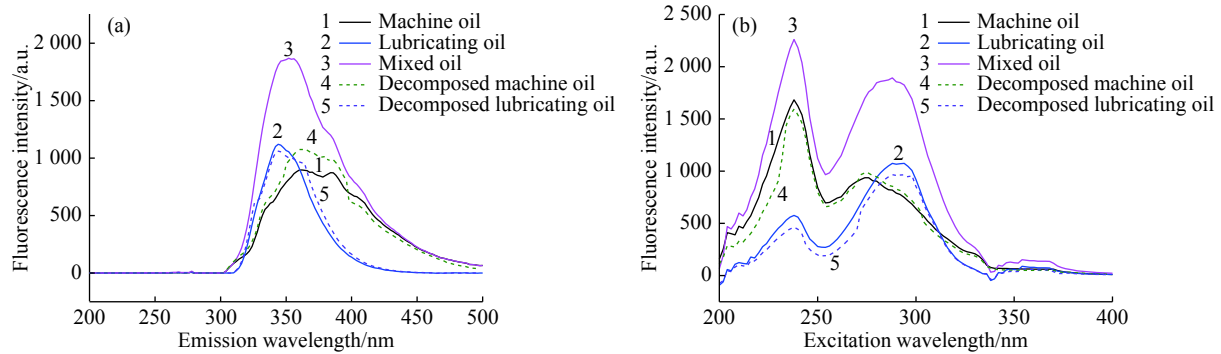


Fig. 5 Classifying the mixture of two petroleum hydrocarbons by PARAFAC. (a) Classification of emission spectra; (b) classification of excitation spectra

Tab. 3 The predicted results of two types of petroleum mixture using PARAFAC

Sample	Predicted(%)			Recoveries(%)		
	Machine oil	Lubricating oil	TPHs	Machine oil	Lubricating oil	TPHs
17#	0.35	0.35	0.70	82.38	85.85	84.10
18#	0.52	0.60	1.12	85.74	83.61	84.59
19#	0.87	0.98	1.85	87.00	96.08	91.58
20#	0.34	0.19	0.53	83.90	83.91	83.91
21#	0.54	0.42	0.96	84.06	96.88	89.21

22#	0.82	4.41	5.23	80.00	87.59	86.31
23#	1.82	0.54	2.36	90.30	103.77	93.07
24#	1.26	0.90	2.16	84.00	80.71	82.60
25#	0.92	9.29	10.21	91.29	91.08	91.10
26#	1.70	1.84	3.54	80.38	76.35	78.23
27#	2.24	3.08	5.32	88.97	74.94	80.27
28#	3.11	3.04	6.15	73.52	86.42	79.38
29#	6.09	1.05	7.14	93.12	94.11	93.26
30#	4.13	1.49	5.62	89.61	86.86	88.86
31#	6.11	1.80	7.91	83.50	80.54	82.81
32#	6.75	0.93	7.68	83.24	83.39	83.26
Average recoveries (%)				85.06±4.80	87.01±7.52	85.78±4.70

$$\text{Recovery rate} = \frac{\text{Predicted value}}{\text{Actual value}} \times 100\%. \quad (4)$$

For mixtures of three petroleum hydrocarbons, the soil samples labeled 33#~48# were chosen as the calibration set and the remaining samples were chosen for the test set. As shown in Fig.6 (color on-

line), the core consistency coefficient is 97.05% when the number of factors was set to 3, and the core consistency coefficient is 53.75% when the number of factors was set to 4, then the optimal number of factors was 3.

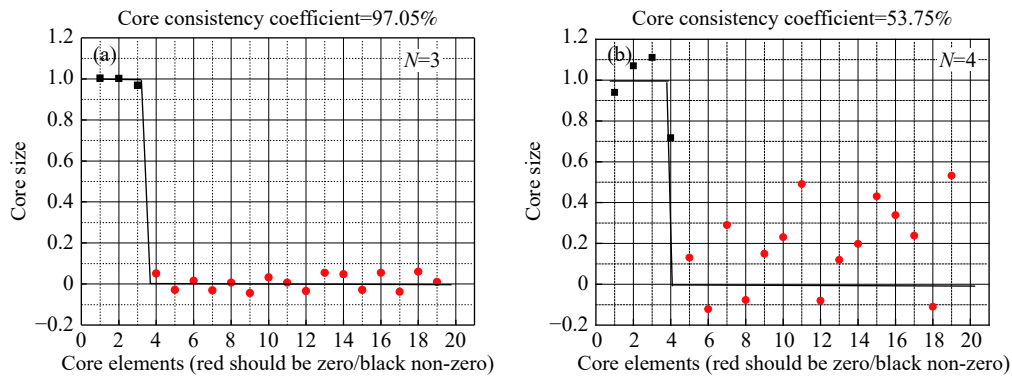


Fig. 6 The core consistency diagnosis results for mixtures of three petroleum hydrocarbons. (a) $N = 3$; (b) $N = 4$

Fig. 7 shows the typical emission spectra and excitation spectra which were decomposed by PARAFAC, where the emission spectra and excitation spectra obtained by decomposition can correspond

with the pure petroleum spectra at the same concentration. Table 4 shows the results of predicted contents using PARAFAC.

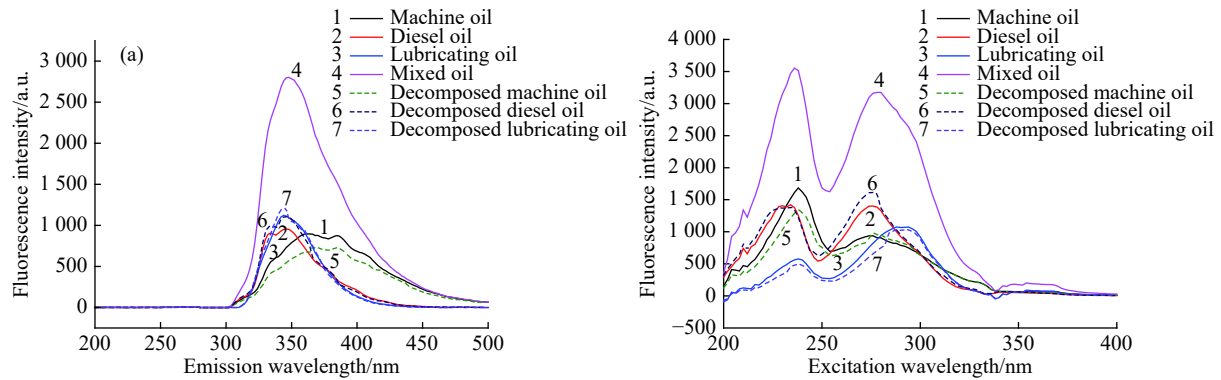


Fig. 7 Classifying the mixture of three petroleum hydrocarbons by PARAFAC. (a) Classification of emission spectra; (b) classification of excitation spectra

Tab. 4 The predicted results of three types of petroleum mixture using PARAFAC

Sample	Predicted(%)				Recoveries(%)			
	Machine oil	Lubricating oil	Diesel oil	TPHs	Machine oil	Lubricating oil	Diesel oil	TPHs
49#	0.35	0.42	0.38	1.151	83.81	95.45	88.14	89.22
50#	0.58	0.49	0.53	1.61	81.83	96.86	86.13	87.45
51#	0.53	0.42	0.26	1.21	83.97	86.67	81.25	84.27
52#	0.21	1.12	0.35	1.67	93.64	85.34	82.38	85.64
53#	0.37	1.56	0.48	2.41	85.12	85.36	78.06	83.75
54#	0.47	0.86	6.92	8.24	91.18	83.92	86.37	86.36
55#	0.99	6.50	0.45	7.94	95.00	81.25	87.31	83.08
56#	0.85	0.74	0.88	2.47	83.73	72.87	87.23	81.28
57#	1.65	0.71	0.94	3.29	108.94	90.51	79.63	94.83
58#	1.97	4.44	1.95	8.36	81.26	85.53	92.54	85.99
59#	3.50	1.01	1.51	6.02	83.16	77.33	100.00	85.69
60#	4.23	2.12	0.57	6.92	96.00	71.14	88.76	86.20
61#	1.55	0.76	4.78	7.09	72.72	90.24	92.00	86.79
62#	1.70	0.83	5.40	7.94	83.43	101.59	84.32	85.65
63#	2.53	0.49	4.97	7.99	90.18	90.30	82.09	84.98
64#	6.70	0.40	0.81	7.91	83.61	78.43	78.64	82.80
Average recoveries (%)					87.35±8.03	85.80±8.14	85.92±5.60	85.87±2.97

As shown in Table 3 and Table 4, all the average recoveries are lower than 90%, it could be because of machine oil and lubricating oil belonging to a larger category of petroleum, it has been discussed earlier that machine oil and lubricating oil have the similar fluorescence spectra in soils, which weaken the ability of identification and quantitation of PARAFAC. In order to improving the measure-

ment accuracy, a precise calibration model was required to establish to qualitatively and quantitatively analyze the mixed petroleum in unknown samples.

3.3 Alternating trilinear algorithm

ATLD (Alternating trilinear algorithm) is a potential learning algorithm which was adopted to decompose 3DEEM matrix basing on Moore-Penrose generalized inverse calculation through singular

value decomposition and alternating iteration using alternating least squares. Comparing with PARAFAC, the convergence speed of ATLD is quick, and it is not sensitive to the number of factors estimation, giving full play to the advantages of second-order correction. The load matrices could be expressed as in Eq.5.

$$\begin{aligned} \mathbf{a}_i^T &= \text{diag}(\mathbf{B}^+ \mathbf{X}_{i.} (\mathbf{C}^T)^+) \quad i = 1, 2, \dots, I \\ \mathbf{b}_j^T &= \text{diag}(\mathbf{C}^+ \mathbf{X}_{.j} (\mathbf{A}^T)^+) \quad j = 1, 2, \dots, J, \\ \mathbf{c}_k^T &= \text{diag}(\mathbf{A}^+ \mathbf{X}_{..k} (\mathbf{B}^T)^+) \quad k = 1, 2, \dots, K \end{aligned} \quad (5)$$

where + expresses Moore-Penrose generalized inverse, and the objective function of ATLD is the sum squares of residual matrix elements, which can be posed as in Eq.6.

$$\sigma = \sum_{i=1}^I \sum_{j=1}^J \sum_{k=1}^K \left(x_{ijk} - \sum_{n=1}^N a_{in} b_{jn} c_{kn} \right)^2, \quad (6)$$

where x_{ijk} is the element of 3DEEM data matrix, and

the convergence criterion in the iterative solution can be posed as Eq.7.

$$\left| \frac{\sigma^m - \sigma^{m-1}}{\sigma^{m-1}} \right| \leq \varepsilon. \quad (7)$$

Fig. 8 (color online) depicts the typical emission spectra and excitation spectra which were decomposed by ATLD, which shows a good consistent with the real emission spectra and excitation spectra at the same concentration. Table 5 and Table 6 show the predicted results using ATLD for the mixtures of petroleum. As shown in Table 5 and Table 6, all the average recoveries for the components and the total petroleum hydrocarbons are all above 95% and the results imply that the qualitative and quantitative accuracy for mixed petroleum in soils can be obviously improved by ATLD. Then the ATLD is more effective for rapid petroleum measurement in soils with sever effects of soil background fluorescence.

Tab. 5 The predicted results of two types of petroleum mixtures using ATLD

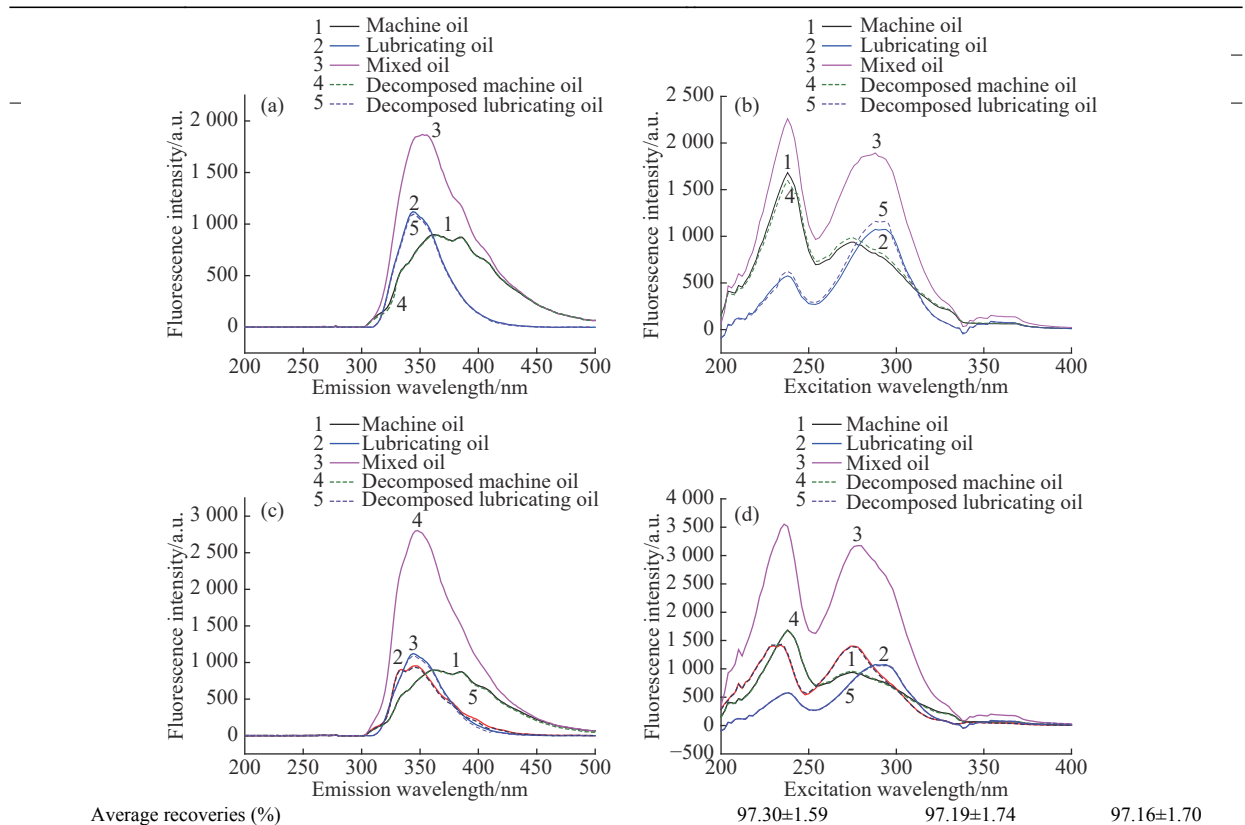


Fig. 8 Classifying the mixtures of petroleum hydrocarbons by ATLD. (a) Classification of emission spectra and (b) classification of excitation spectra for the mixture of two; (c) classification of emission spectra and (d) classification of excitation spectra for the mixture of three

4 Conclusions

In summary, this study focuses on the qualitative and quantitative analysis for mixed petroleum in soils, estimating the total content of petroleum hydrocarbons in soils. Background correction method, Eemscat function method and weighted mean filtering algorithm were combined to correct the complicated soil background spectra and scattering spectra. PARAFAC and ATLD were applied for the qualitative and quantitative analysis of mixed petroleum in soils. The results demonstrate that the measurement accuracy of recoveries should be improved because the machine oil and lubricating oil belong to a larger category of petroleum and have the simi-

lar fluorescence spectra. Compared with the results of PARAFAC, the measurement recovery accuracy of ATLD were increased from 85% to 95%, implying that ATLD can distinguish the similar fluorescence spectra well and be more effective in the components and total contents detection of petroleum in soils by its advantage of second-order correction. These results gained through this experiment make it possible for the application of 3DEEM fluorescence spectroscopy technique to fast and accurate analyze the types of components and their contents of mixed petroleum in soils with complicated fluorescence background. This study can lead to the appropriate application of risk assessments and remediation techniques.

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Sample	Machine oil	Lubricating oil	Diesel oil	TPHs	Machine oil	Lubricating oil	Diesel oil	TPHs
49#	0.39	0.41	0.41	1.151	92.86	93.18	93.35	93.80
50#	0.69	0.46	0.59	1.61	97.18	90.20	95.16	94.57
51#	0.68	0.46	0.59	1.61	97.18	90.20	95.16	94.41
52#	0.39	0.41	0.41	1.151	92.86	93.18	93.35	93.80
53#	0.39	0.41	0.41	1.151	92.86	93.18	93.35	93.80
54#	0.49	0.98	7.89	8.24	96.08	96.08	98.50	98.11
55#	0.99	7.49	0.51	7.94	95.19	93.62	98.08	94.04
56#	1.00	0.08	0.99	2.47	99.02	97.03	98.02	98.03
57#	1.00	0.08	0.99	2.47	99.02	97.03	98.02	98.03
58#	1.00	0.08	0.99	2.47	99.02	97.03	98.02	98.03

续表 646(9): 1438-1445.

Sample	Method	Accuracy (%)	Precision (%)	Recovery (%)	Limit of Detection (LOD)	Limit of Quantification (LOQ)
DENG W, QING X D, CHEN D, <i>et al.</i>	Chemometrics-assisted three-dimensional fluorescence	95.25	94.66	99.34	6.02	96.02
[12] XU J L, WANG J, WANG C, <i>et al.</i>	Effective oxidation of crude oil in soils by consuming less hydroxyl radical with target iron	93.65	96.98	92.19	6.92	94.77
[13] LEMKE M, FERNÁNDEZ-TRUJILLO R, LÖHMANNSRÖBENC H G.	In-situ LIF analysis of biological and petroleum-based hydraulic oils on soil	98.12	94.05	98.27	5.11	97.80
[14] HINSKI J F, COMPTON B S, PERKINS B S, <i>et al.</i>	Utilizing three-dimensional fluorescence's red shift cascade effect to monitor mycobacterium PRY-1 degradation of aged-petroleum	96.00	96.08	96.12	6.49	96.02
[15] FERRETTO N, TEDETTI M, GUIGUE C, <i>et al.</i>	Identification and quantification of known polycyclic aromatic hydrocarbons and pesticides in complex mixtures using fluorescence excitation-emission matrices and parallel factor analysis	95.34±2.00	95.19±2.05	95.84±2.50	4.13	95.82±1.58
[16] YIN J, LIU J Z, CHEN T, <i>et al.</i>	Influence of melanoidins on acidogenic fermentation of food waste to produce volatility fatty acids	96.00	96.08	96.12	6.49	96.02
[17] MA ZH F, YANG Y, LIAN X Y, <i>et al.</i>	Identification of nitrate sources in groundwater using a stable isotope and 3DEEM in a landfill in Northeast China	96.00	96.08	96.12	6.49	96.02
[18] CHRISTENSEN J H, HANSEN A B, MORTENSEN J, <i>et al.</i>	Characterization and matching of oil samples using fluorescence spectroscopy and parallel factor analysis	96.00	96.08	96.12	6.49	96.02
[19] LIU Y, WANG T T, YANG J.	Evaluating the quality of mine water using hierarchical fuzzy theory and fluorescence regional integration	96.00	96.08	96.12	6.49	96.02
[20] ZHANG SH R, WU H L, CHEN Y, <i>et al.</i>	An investigation on hydrogen bonding between 3-methylindole and ethanol using trilinear decomposition of fluorescence excitation-emission matrices	96.00	96.08	96.12	6.49	96.02