

# A method for determining the content of petroleum hydrocarbons in soil

Haitian Qin, He Huang\*

Yangtze University, School of Chemistry and Environmental Engineering,  
1 Nanhuan Road, Jingzhou District, Jingzhou City, Hubei Province, China  
He Huang @105367750@qq.com

## Abstract:

In this paper, ultrasonic-centrifugal extraction-infrared petroleum meter is used to determine petroleum hydrocarbons in soil. The optimal conditions of ultrasonic centrifugal extraction of petroleum hydrocarbons from soil were investigated by using simulated soil from the extraction agent, ultrasonic temperature, ultrasonic time, ultrasonic power, centrifugal speed, centrifugal time and other factors. The results showed that using tetrachloroethylene as extraction agent, the extraction efficiency of three times reached 88.34% with ultrasonic temperature of 30°C, ultrasonic time of 10min, ultrasonic power of 180W, centrifugal speed of 4000rpm and centrifugation time of 20min in 1% petroleum-contaminated soil. Under these conditions, the recoveries were 78.97%~96.58% and the relative standard deviations (n=5) of the measured values were 3.82%~12.53%.

**Key words:** Petroleum hydrocarbon; Ultrasonic-centrifugal extraction; Soil; Infrared petroleum meter.

## 1. Introduction

With the increase of petroleum usage, petroleum hydrocarbon polluted soil has been concerned by all circles of society. It is essential to find an efficient and rapid petroleum hydrocarbon detection method in order to accurately understand the oil contaminated soil. Detection of petroleum hydrocarbons in soil with traditional Soxhlet extraction often takes a long time<sup>[1,2]</sup>. In order to save cost and improve efficiency, this paper adopts ultrasonic-centrifugal method to extract petroleum hydrocarbons from soil, and uses infrared petroleum meter to accurately measure the content of petroleum hydrocarbons, and optimates the experimental conditions.

## 2. Experiment

### 2.1 Experimental materials

The soil used in the experiment was simulated petroleum-contaminated soil: the original soil was

collected from the forest on the campus of Yangtze University, and the unpolluted sandy loam with a depth of 20~50cm. The soil was air-dried, screened and reserved. Soil basic properties: water content 0.25%, pH=7.86, organic matter content 1.17%. 1.00000g of petroleum was accurately weighed in a beaker, completely dissolved with petroleum ether (30~60°C), and poured into the above soil to make petroleum-contaminated soil with a pollution concentration of 1%.

Experimental drugs dichloromethane, petroleum ether, anhydrous sodium sulfate are analytical pure, carbon tetrachloride, tetrachloroethylene for infrared spectrum pure, tetrachloroethylene in the petroleum solution standard material purchased from Beijing Shengshipu Chemical Technology Research Institute.

The main experimental instruments are Oil510 infrared spectrometer petroleum measuring instrument (Beijing Huaxia Kechuang),

KQ-300DE numerical control ultrasonic cleaner (Kunshan Ultrasonic Instrument Co., Ltd.), LD-3 electric centrifuge (Jiangsu Jantan Jincheng Guosheng Experimental Instrument Factory), DV215CD electronic balance (sensing capacity 0.01mg, Aohaus Instrument Co., Ltd.). In the experiment, the glass instrument needs to be soaked and washed with chromic acid solution.

## 2.2 Experimental method

### 2.2.1 Selection of extractant

Weighed 1g of contaminated soil into a 50ml centrifuge tube, accurately recorded the soil mass **m** (accurate to 0.01mg), and added an appropriate amount of anhydrous sodium sulfate to remove the moisture in the soil. 5mL of the extractant was added, followed by ultrasonic extraction (30°C, 10min, 300w)-centrifugation (3000rpm, 10min) and then the supernatant was collected in a clean small beaker. The supernatant was combined with the extraction for three times, and the petroleum hydrocarbons in the small beakers were transferred to a 25 mL volumetric flask with tetrachloroethylene. The extraction solution was diluted (**n** times) as needed, and the concentration of **c<sub>1</sub>** was detected with an infrared petroleum meter, and then the content of petroleum hydrocarbons in the soil was determined according to Equation (1). If there are impurities in the extraction solution, it is necessary to use silica adsorption column to purify it<sup>[3]</sup>. Three parallel samples were made for each group of experiments. The extraction agents were selected as tetrachloroethylene, dichloromethane, carbon tetrachloride and petroleum ether to investigate the effects of different extraction agents on recovery.

$$w = \frac{0.025 \times n \times c_1}{1000 \times m} \times 100\% \quad (1)$$

**w**: the content of petroleum hydrocarbons in soil, %;

**n**: the dilution ratio of extraction liquid;

**c<sub>1</sub>**: the concentration detected by the infrared petroleum meter of the diluted extraction solution, mg/L;

**m**: the mass of soil sample, g.

### 2.2.2 Orthogonal experimental design

Ultrasonic-centrifugal extraction is an efficient and rapid extraction method of petroleum pollutants by using the cavitation effect and centrifugal separation effect caused by ultrasound. The power and time of ultrasonic extraction had positive effects on extraction efficiency<sup>[4]</sup>, Centrifugation can separate solid and liquid. Under the extraction conditions, ultrasonic temperature, ultrasonic power, ultrasonic time, centrifugal speed and centrifugal time were selected as test factors, and L<sub>16</sub>(4<sup>5</sup>) was used to design the orthogonal experiment (Table 1).

**Table 1:** Orthogonal experimental design

	A	B	C	D	E
Level 1	20	120	5	1000	5
Level 2	30	180	10	2000	10
Level 3	40	240	15	3000	15
Level 4	50	300	20	4000	20

A:ultrasonic temperature (°C)

B:ultrasonic power (w)

C:ultrasonic time (min)

D:centrifugal speed (rpm)

E:centrifugal time (min)

### 2.2.3 Determination of soil petroleum recovery

Soil samples with petroleum concentration of 0.5%, 1%, 1.5%, 2% and 2.5% were prepared according to the method of soil preparation in 1.1, respectively, and were extracted under the optimal extraction conditions obtained from orthogonal experiment. The content of petroleum hydrocarbons in the soil was detected and calculated with an infrared petroleum meter. The recovery rate is calculated according to Equation (2).

$$\text{Recovery\%} = \frac{w}{w_0} \times 100\% \quad (2)$$

**w**: the content of petroleum hydrocarbons in the soil, %;

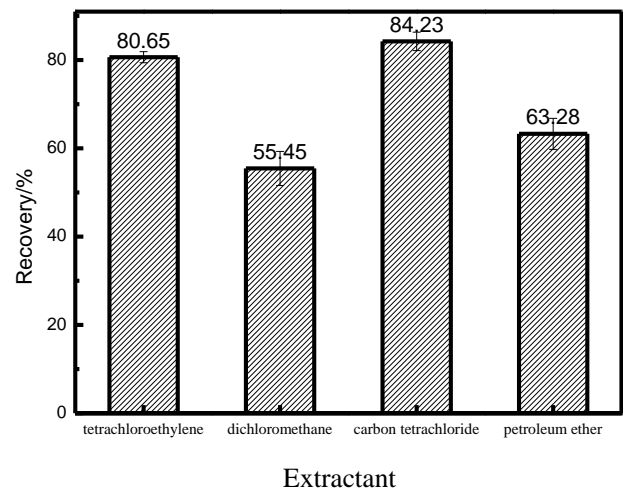
**w<sub>0</sub>**: the content of petroleum hydrocarbons in simulated soil, %.

## 3. Result and discussion

### 3.1 Influence of different extractants on the determination of petroleum hydrocarbons in soil

According to the principle of "similar phase solution" and the extraction agents selected for the detection of petroleum hydrocarbons at home and abroad, four extraction agents including tetrachloroethylene, carbon dichloride, carbon tetrachloride and petroleum ether were selected to extract petroleum hydrocarbons in the soil in the experiment, and Figure 1 was obtained. It can be seen from Figure 1 that the highest detection recovery rate after extraction was carbon tetrachloride (84.23%), while the lowest was carbon dichloride. In Coulon's study, the extraction efficiency could reach 95%~99% by using flared ultrasound, and in this experiment, the maximum extraction efficiency was 88.23% for three times, which may be caused by different ultrasonic forms [4]. The extraction efficiency of petroleum ether was 63.28%. Considering the toxicity of carbon tetrachloride, this experiment uses tetrachloroethylene as extraction agent, because the extraction efficiency of tetrachloroethylene is 80.65%, second only to carbon tetrachloride. The selection of tetrachloroethylene as extraction agent in the experiment can not only reduce the amount of

extraction agent, but also reduce the experimental step of evaporation and concentration, simplify the experimental steps and save the detection time. Therefore, in the subsequent experiments, tetrachloroethylene was used as the extractant.



**Figure 1:** Influence of different extractant on recovery rate

### 3.2 Analysis of orthogonal experiment results

According to orthogonal experimental analysis (Table 2), the extraction influence factors can be obtained: ultrasonic temperature > ultrasonic time > centrifugal time > ultrasonic power > centrifugal speed.

**Table 2** Results of orthogonal experiment

	A	B	C	D	E	Recovery (%)
1	1 (20)	1 (120)	1 (5)	1 (1000)	1 (5)	59.03
2	1 (20)	2 (180)	2 (10)	2 (2000)	2 (10)	75.56
3	1 (20)	3 (240)	3 (15)	3 (3000)	3 (15)	66.87
4	1 (20)	4 (300)	4 (20)	4 (4000)	4 (20)	81.26
5	2 (30)	1 (120)	2 (10)	3 (3000)	4 (20)	88.31
6	2 (30)	2 (180)	1 (5)	4 (4000)	3 (15)	79.04
7	2 (30)	3 (240)	4 (20)	1 (1000)	2 (10)	79.88
8	2 (30)	4 (300)	3 (15)	2 (2000)	1 (5)	85.50
9	3 (40)	1 (120)	3 (15)	4 (4000)	2 (10)	64.62
10	3 (40)	2 (180)	4 (20)	3 (3000)	1 (5)	71.70
11	3 (40)	3 (240)	1 (5)	2 (2000)	4 (20)	62.36
12	3 (40)	4 (300)	2 (10)	1 (1000)	3 (15)	64.97
13	4 (50)	1 (120)	4 (20)	2 (2000)	3 (15)	65.94
14	4 (50)	2 (180)	3 (15)	1 (1000)	4 (20)	74.86
15	4 (50)	3 (240)	2 (10)	4 (4000)	1 (5)	75.89
16	4 (50)	4 (300)	1 (5)	3 (3000)	2 (10)	61.71
k1	70.68	69.48	67.87	69.69	73.03	

k2	83.18	75.29	76.18	72.34	70.44	
k3	65.91	71.25	72.96	72.15	69.21	
k4	69.60	73.36	72.36	75.20	76.70	
Range	17.27	5.81	8.32	5.51	7.49	
Order	A>C>E>B>D					
Choice	A2	B2	C2	D4	E4	
Optimization	A2B2C2D4E4					

The optimal extraction conditions were as follows: ultrasonic temperature of 30°C, ultrasonic power of 180W, ultrasonic time of 10min, centrifugal speed of 4000rpm, and centrifugal time of 20min. Under these conditions, the extraction efficiency of petroleum-contaminated soil with 1% pollution concentration was about 88.34%.

The influences of various factors on extraction effect are as follows:

The effect of ultrasonic temperature on the recovery rate is shown in Figure 2(a): from 20°C to 30°C, the extraction efficiency of petroleum hydrocarbons in the soil increases by about 13%. This is because the viscosity of petroleum decreases with the increase of temperature, and the binding ability of petroleum to the soil also decreases, making it easier for petroleum molecules to break off from the surface of soil particles and enter the extractant. The extraction efficiency decreases when the temperature increases from 30°C to 50°C.

According to the relationship between ultrasonic cavitation and temperature, it can be known that when the temperature is too high, the cavitation is weakened, which is not conducive to the extraction of petroleum. In the experimental study of Zhou Wuju<sup>[5]</sup>, when the temperature was 22-50°C, the extraction efficiency also showed a trend of first rising and then falling, which was relatively stable on the whole. The temperature over 60°C would cause petroleum loss and affect the accuracy of the results.

The influence of ultrasonic power on recovery as shown in figure. 2(b): along with the change of the ascension of the ultrasonic power recovery trend and the trend of temperature elevation was similar, because the power of ascension makes energy increases, can make petroleum hydrocarbon

separated from soil, but high power become more small, can make the soil particle breaking increase soil particles on the adsorption effect of petroleum hydrocarbon, so that the lower the recovery. It was probably the reason that the cavitation bubbles in a greater ultrasonic intensity tended to grow too big to collapse or collapse weakly, which may result in the reduction of cavitation effect<sup>[6]</sup>. Therefore, appropriate ultrasonic power is helpful to improve the recovery rate.

The effect of ultrasonic time on recovery was shown in Figure. 2(c): with the increase of ultrasonic time, extraction efficiency first increased and then decreased. According to the damage of the bonding force of oil and soil by ultrasonic wave, the increase of time helps the petroleum to detach from the soil surface and enter the extractant. However, the energy of ultrasonic wave will not only destroy the binding force of petroleum-soil, but also break the soil particles into finer particles, increase the adsorption capacity of the soil particles to petroleum hydrocarbons<sup>[7]</sup>, and reverse adsorption will be carried out on the released petroleum, thus reducing the extraction efficiency.

The influence of centrifugal speed on recovery is shown in Figure. 2(d): the higher the centrifugal speed, the higher the recovery. The main function of centrifugation is to separate the solid and liquid phases. During the ultrasonic process, petroleum hydrocarbons in the soil were fully mixed with the extractant, and some petroleum hydrocarbons were transferred to the extractant. However, the solution after the ultrasound was very turbid. In order to reduce the detection time, centrifugal method was used to make the solid-liquid two-phase separation quickly. With the increase of centrifugal speed, the

solid-liquid separation is more complete and the recovery rate is also increased.

The effect of centrifugation time on recovery was shown in Figure 2(e): with the increase of centrifugation time, recovery firstly decreased and then increased. The increase of centrifugation time can make the solid-liquid separation more complete,

which should improve the recovery rate. However, this rule is not obvious in the experiment, because various factors in the orthogonal experiment may interact with each other, resulting in a difference between the results and the separate analysis.

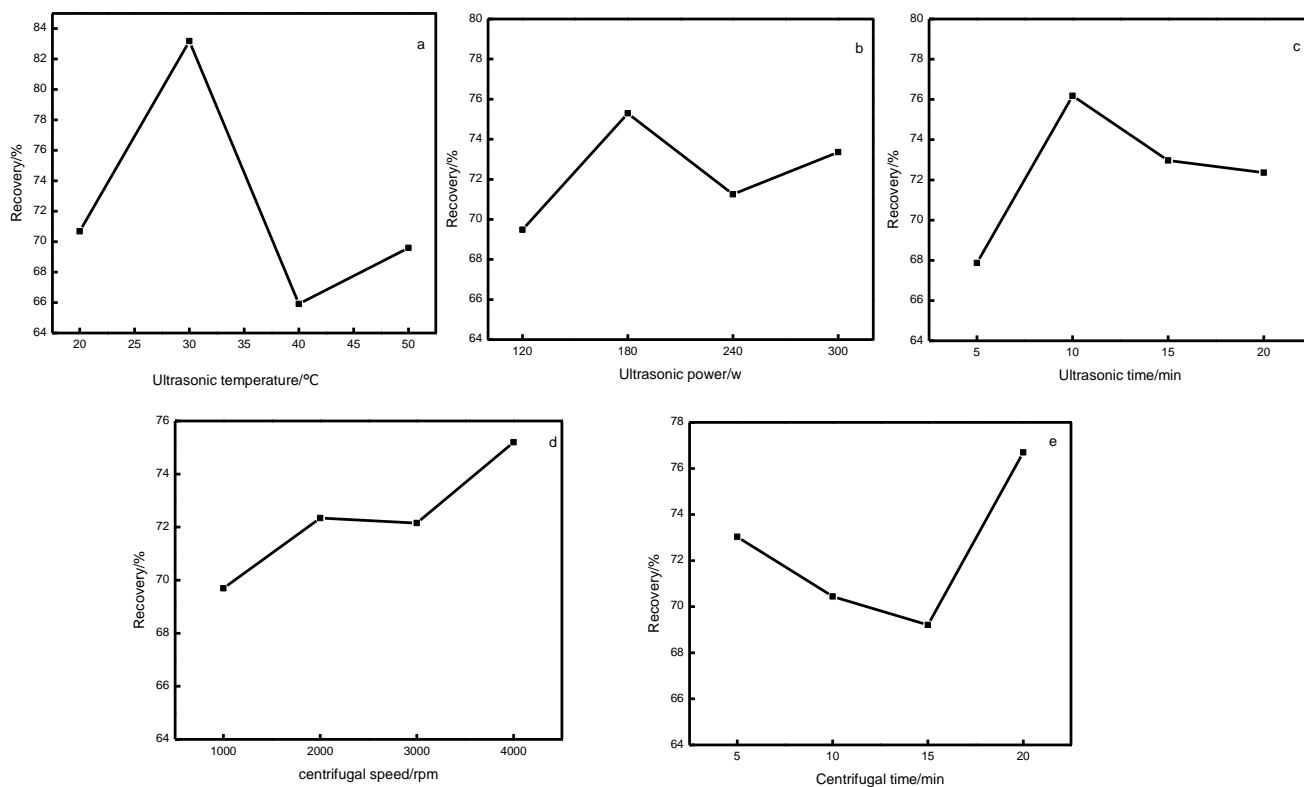


Figure 2: Result of orthogonal experiment

### 3.3 Comparison of extraction effects of soil with different pollution concentrations

In the extraction process, the soil sample with a pollution concentration of 0.5% was nearly colorless in the second extraction, and its chromaticity could not be distinguished by the naked eye in the third extraction, which indicated that the extracted solution contained very little petroleum. As can be seen from Table 3, the recovery rate of petroleum hydrocarbons in the soil reached 96.58% at this concentration. The recovery rate decreased with the increase of pollutant concentration, but the recovery rate was above 78%. When the pollution concentration is 1%, the recovery rate of petroleum hydrocarbons in the soil is about 84.59%, which is decreased compared with 88.34% in the orthogonal

experiment, which may be related to the time of pollution and the degradation of petroleum hydrocarbons in the soil itself. In addition, judging the approximate pollution concentration according to the color depth of the extracted solution, multiple extraction can improve the recovery rate. Therefore, it is necessary to appropriately increase the extraction times according to the color of the extracted solution in the extraction process to make the result more accurate.

Table 3 extraction results of soil with different pollution concentrations(n=5)

Petroleum pollution concentration %	Mean detection concentration %	Recovery %	RSD %



0.5	0.4829	96.58	12.53
1.0	0.8459	84.59	4.39
1.5	1.2133	80.89	9.78
2.0	1.6121	80.61	3.82
2.5	1.9743	78.97	8.24

When extraction times were 5 times, the recovery rate was significantly improved (Table 4). Because according to the Nernst distribution law, the increase of extraction times can effectively improve the extraction efficiency. However, the increase of extraction times requires longer detection time and more detection reagents, so we need to appropriately increase extraction times according to the actual situation.

**Table 4** extraction results of soil with different pollution concentrations(n=5)

Petroleum pollution concentration %	Mean detection concentration %	Recovery %	RSD %
0.5	0.5223	104.46	6.07
1.0	0.9522	95.22	1.42
1.5	1.3505	90.03	2.16
2.0	1.7875	89.38	9.18
2.5	2.1841	87.36	4.74

If this method is used in the actual soil detection, it should be noted that compared with the simulated soil, the actual soil has longer pollution time, stronger binding ability with petroleum hydrocarbons, and more difficult recovery rate<sup>[8]</sup>. Therefore, in the actual detection process, the extraction times should be appropriately increased according to soil properties, petroleum types and pollution concentrations.

#### 4. Conclusion

It is the best choice to use tetrachloroethylene as extraction agent considering toxicity and extraction efficiency when using ultrasonic centrifugal-infrared petroleum measuring instrument to detect the content of petroleum hydrocarbons in soil.

The primary and secondary effects of the factors affecting the extraction of petroleum hydrocarbons in the soil are as follows: ultrasonic temperature >

ultrasonic time > centrifugal time > ultrasonic power > centrifugal speed. The optimal extraction conditions were as follows: ultrasonic temperature of 30°C, ultrasonic power of 180W, ultrasonic time of 10min, centrifugal speed of 4000rpm, centrifugal time of 20min. Under this condition, the soil recovery rate of 1% petroleum content is 88.34%.

Under the optimal extraction conditions, the extraction efficiency of the soil with different pollution concentrations was more than 78%. In the process of extraction, the soil with higher concentration needed to increase the extraction times appropriately to make the results more accurate.

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