



The development of a method for the qualitative and quantitative determination of petroleum hydrocarbon components using thin-layer chromatography with flame ionization detection

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ABSTRACT

An analytical scheme to determine groups of petroleum hydrocarbon compounds in crude oil was developed and used for the qualitative and quantitative characterization of crude oil samples from the Shengli oilfield, the second largest oilfield in China. Crude oil samples were fractionated and analyzed by thin-layer chromatography with flame ionization detection (TLC-FID). Relative standard deviation (RSD) values for retention time, peak height and half peak width were less than 5.2% for all classes of compounds, based on nine independent replicates. The crude oil light fraction was further analyzed by GC-MS and the majority of identified compounds were methyl- or hydro-derivatives of long-chain hydrocarbons and aromatic compounds. The external standard method used in the present study can lower detection limits of petroleum hydrocarbon compound classes to 20.0 mg L⁻¹, and the crude oil concentration in the range of 30 and 35,000 mg L⁻¹ has a high linear correlation ($r^2 > 0.97$, $P < 0.05$) with peak area. A comparison between elution chromatography (EC) and TLC-FID regarding the recovery of petroleum hydrocarbon compounds was carried out with aged crude oil contaminated soils of 50, 80, 200 and 300 mg g⁻¹. The tested TLC-FID method showed a 10% higher recovery for total extractable materials than the reference EC method. The calibration factor was fraction-dependent and varied with the recovery rate of TLC/EC. Regarding the tested extraction procedures, accelerated solvent extraction (ASE) had a higher extraction efficiency for crude oil contaminated soils than Soxhlet and ultrasonic extractions.

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1. Introduction

Petroleum is a complex mixture of hydrocarbon and non-hydrocarbons, including a wide range of nitrogen-, sulfur-, oxygen- and chlorine-compounds, which exhibit various physical and chemical properties. There is an increasing worldwide concern of environmental problems by accidental crude oil spills and by the improper discharge and disposal of oily waste and vast amounts of oil sludge. Recent research focusing on the fate of petroleum in aqueous, sediment and soil matrix requires that the analytical methods can provide sufficient information for the evaluation and remediation of petroleum polluted sites. There is however no single approach that can rapidly, reliably and simultaneously characterize crude oil fractions and specific classes of compounds and individual compounds in each fraction. Many standard methods (e.g. ASTM D2007, D4124) had been developed for characterizing the heavy oil fractions [1,2], but the gravimetric quantification

of typical fractions proved inadequate [3,4]. Spectroscopic techniques such as infrared (IR), ultraviolet (UV), X-ray fluorescence (XRF) proved useful for specific research purposes but are so far insufficient for the determination of total petroleum hydrocarbons (TPH) [5,6]. Recently, fingerprinting analysis of preferentially compositional patterns has been developed using advanced techniques such as (i) chromatography-mass spectrometry (GC-MS), (ii) high performance liquid chromatography-electrospray ionization mass spectrometry (HPLC-MS), (iii) isotope dilution mass spectrometry (IDMS), (iv) nuclear magnetic resonance (NMR) and (v) electrospray ionization mass spectrometry (ESI-MS) [7–11]. In addition to the development of the techniques and instruments, the quantum calculation of the chemical structure and electronic parameters was also applied on aromatic compounds, resins, and asphaltenes on the basis of ¹H and ¹³C NMR [12]. Coupling fractionation by TLC and quantification using with flame ionization detection (FID), the TLC-FID method developed in the 1970s showed to offer several advantages: (i) simultaneous fractionation crude oil into saturated, aromatic and polar classes, (ii) applicability for the determination of heavy fractions with high boiling points, (iii) low cost, simple instrument requirements and procedure saving. Therefore, TLC

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method rapidly became extensively applied for analysis of drugs, crude oils, coal-derived liquids [13–15], and miscellaneous environmental samples [16–19].

Recently, the TLC-FID method has been substantially improved. Barman showed that a sample loading as low as 5–10 μg was optimal regarding signal-to-noise ratio [3]. Karlsen and Larter [20], and Cebolla et al. [21] investigated the effect of scan speed on the FID response, and found that the FID response decreased when increasing the scanning speed. Kamiński et al. [22] put forward an optimization of TLC-FID procedure for the analysis of classes of hydrocarbon compounds. Based on a quantum chemical for TLC-FID analysis, Du et al. [23] studied the relationship between several characteristic parameters (e.g. half peak width, peak height, area-to-height ratio) and oil species. As shown in these recent papers, the effect of sample matrix on the analysis of petroleum hydrocarbons was a commonly encountered problem, and varied depending on the nature of matrix and analyte [24]. Fuhr et al. [25] expanded the applicability of TLC-FID method and used it to compare the bitumen fractionation for crude oil samples from different sources. The major disadvantages of TLC-FID method were that it was unable to identify the individual petroleum compounds and the quantification of petroleum fractions had a low accuracy and a low sensitivity through area normalization or empirical equations [26]. To decrease the quantification uncertainty of TLC-FID, calibration through absolute or internal method was extensively studied [14,21,24].

The objectives of this paper were: (i) to compare the extraction efficiency of ASE, Soxhlet and ultrasonic extraction, (ii) to validate the TLC separations of crude oil into classes of compounds using the reference materials obtained from column elution chromatography, (iii) to identify specific compounds in the light fraction of crude oil using GC-MS, (iv) to evaluate the calibration factor depending on a mathematic model used for both elution chromatography (EC) and TLC methods.

2. Experimental

2.1. Chemicals and reagents

Analytical grade reagents were used in this study. Trichloromethane (THM), methanol, n-hexane, dichloromethane (DCM), petroleum ether were obtained from SCRC Co., Ltd. (Beijing, China); anhydrous sodium sulfate, pesticide residue grade silica gel (0.149–0.177 mm), alkali aluminum oxide (0.074–0.149 mm) and Florisil (0.150–0.250 mm) were purchased from Sigma-Aldrich Co., Ltd.

2.2. Crude oil samples and soil samples

The crude oil sample (Table 1) used in this study was obtained from Gudong Oil Production Plant at the Shengli Oil Field located in Shandong province, China. The crude oil was dehydrated by precipitation. 50 g of crude oil was then dissolved in THM and centrifuged at 15,000 r min^{-1} for 20 min and the supernatant was diluted to yield a final concentration of 50,000 mg L^{-1} and stored at 4 °C. This solution has been used as standard stock solution in all experiments.

The crude oil contaminated soils were sampled from a 12,000 m^2 abandoned sludge deposit originating from oil storage tanks in Gudong Oil Production Plant, which has been simply deposited in the open air for the past 20 years. 3000 g surface samples (0–25 cm depth), representing a visible range of hydrocarbon contaminations levels were collected at different sites, and the primary soils sampled at sufficient distance from the polluted area served as controls. The soil is a loamy sand with the following particle size distribu-

Table 1

Characteristics of the crude oil sampled from the Shengli Oil Field.

Crude oil parameters	Value
API	16.2
Gravity (20 °C, g cm^{-3})	0.955
Viscosity (50 °C, $\text{mm}^2 \text{S}^{-1}$)	333.7
Aggregation point (°C)	2
Wax content (m%)	26.2
Resin (m%)	14.8
Asphaltum (m%)	2.9
Residue carbon (m%)	7.4
Nitrogen (m%)	0.43
Sulfur (m%)	2.1
Distillation results (m%)	
<200 °C	9.5
<300 °C	14.3
<350 °C	21.0
<400 °C	27.4
<500 °C	48.2

Source: Research Institute of Petroleum Processing (RIPP). It was classified as the low sulfur naphthenic base crude oil, and the specific data for distillation fractions (200–350, 350–500, >500 °C) were not shown.

tion: sand (0.02–2 mm) 87.7%, fine silt (0.002–0.02 mm) 2.6%, and clay (<0.002 mm) 9.7%. The soil pH, soil bulk density and total cation exchange capacity (CEC) was 8.1, 3.32 kg dm^{-3} and 6.1 cmol kg^{-1} , respectively. The contents of As, Hg, Cu, Cd, Cr, Zn, Ni, and Pb in the contaminated soils were 4.0, 0.097, 27.5, 0.047, 55.8, 52.0, 22.2 and 53.8 mg kg^{-1} , respectively. Test soil samples were air-dried at room temperature, sieved through a 2-mm mesh and frozen at –20 °C.

2.3. Soil extraction and chromatographic conditions

2.3.1. Solvent extraction

The extraction efficiencies of ASE, Soxhlet extraction and ultrasonic extraction were determined using spiked soils at total extractable material (TEM) levels of 0.5, 0.8, 1.0, 2.0, 5.0, 8.0, 20.0, 35.0 mg g^{-1} . To obtain the soil batch, the primary soil was artificially shaken with spiking solutions prepared by mixing the calculated amounts of crude oil and petroleum ether. The soil samples were then dried at room temperature and kept for 2 weeks to equilibrate before experiments. Briefly, the three tested extraction methods used the following protocols: (i) ASE extraction: 10 g of soil was extracted with 60 ml of THM using three extraction cycles, applying 1500 psi at 150 °C (ASE300, Dionex, USA); (ii) Soxhlet extraction: 10 g of soil was extracted using 100 mL of THM for 24 h in a Soxhlet extraction apparatus (KBL, Beijing, China), placed in a water-bath at 80 °C (SY11, YIDAXK, Beijing, China); (iii) ultrasonic extraction: 10 g of soil was placed in a 50 mL glass vial and extracted with 30 mL of THM for 30 min, using an ultrasonic instrument (SK8200, CANY, Shanghai, China) at 70 °C and 70% of power (Max 59 kHz); extracts of three cycles were incorporated.

2.3.2. TLC-FID procedure

A TLC device (MK-6S, Tokyo, Japan) equipped with FID detector was used to test the TLC-FID method. The S-III chromarod (MKI, Tokyo, Japan) used in this study was 15.2 cm long and 1.0 mm in diameter and was coated with a layer of silica gel (5 μm particle size). During experiments the chromarod was spotted with 1 μL of extract, and subsequently was developed with the following program: n-hexane (30 min), 50% (v/v) hexane-DCM (20 min) and 95% (v/v) DCM-methanol (5 min). The chromarod was dried at 40 °C for 2 min after each development. For the TLC-FID method, a scan rate of 40 s/scan was used. Air and hydrogen flows were 2000 mL min^{-1} and 160 mL min^{-1} , respectively.

2.3.3. Elution chromatography

A glass chromatographic column (30 cm × 1.5 cm) was pre-packed with 7 g silica gel (activated at 200 °C for 13 h), 7 g alkali aluminum oxide (activated at 400 °C for 20 h), 5 g Florisil (activated at 130 °C for 20 h) and 1 g anhydrous sodium sulfate (activated at 400 °C for 4 h). The column was pre-eluted with 50 mL n-hexane, and the elution flow was adjusted to 2 mL min⁻¹. The TEM of aged crude oil contaminated soils was determined gravimetrically: the soil extract was transferred into a pre-weighted flask and air-dried in an incubator at 40 °C for 12 h and the flask containing the residue was subsequently weighted. The mass difference of the pre-weighted flask and the flask containing the residue was defined as the TEM value. After the TEM determination, the air-dried extract was re-dissolved in 10 mL n-hexane, and the remaining precipitate at the bottom of the flask was air-dried for asphaltene assessment. The re-dissolved n-hexane solution was injected onto the prepared chromatographic column and eluted as follows: 100 mL n-hexane for saturated compounds, 100 mL 50% (v/v) n-hexane–DCM for aromatic compounds, and 100 mL 50% (v/v) methanol–DCM for resins.

2.3.4. Light fractions analysis with GC–MS

Obtained by the EC procedure, described above, the light fraction containing saturated compounds and aromatic compounds was eluted with 50% v/v n-hexane–DCM. About 1 µL of elution was analyzed on GC–MS (7890A–5975C, Agilent, USA) in a splitless mode. A DB-5MS capillary column was used for gas chromatographic separation (30 m × 0.25 mm I.D., 0.25 µm film thickness; J&W Scientific, Folsom, CA, USA). Helium was used as the carrier gas at the constant flow rate of 1.3 mL min⁻¹. The oven temperature program was as follows: 70 °C held for 2 min, then increased to 160 °C at 5 °C min⁻¹ (and maintained for 5 min), followed by an increase of 3 °C min⁻¹ to 250 °C (held for 5 min), finally reached to 310 °C at 10 °C min⁻¹ and maintained for 5 min. The temperature of the mass transfer line, injector and EI source was set at 280, 250 and 230 °C, respectively. The analysis was completed using the scan mode of 50–500 m/z.

2.4. Analytical method for petroleum hydrocarbons

Crude oil solutions of 200, 800, 2000, 3500, 10,000, 14,000, 16,000 and 35,000 mg L⁻¹ were prepared through dilution of the 50,000 mg L⁻¹ standard stock solution with THM. Calibration curves were constructed by plotting the peak areas against the concentration values. Each calibration curve contained 8 points with three replicates for each point, and regression analysis was carried out using one-way ANOVA followed by Duncan's multiple comparisons test (*p* < 0.05). The repeatability of TLC-FID analysis for petroleum hydrocarbon classes of compounds was determined using the crude oil solution of 5000 mg L⁻¹ with nine repetitions. Retention time, peak height and half peak width values were used to assess the separation of crude oil fractions. In this study, the

signal-to-noise ratio of TLC-FID analysis was kept in the range of 1–100 and the repeatability was acceptable as the RSD was not higher than 25%.

The method detection limit (MDL) was determined analyzing stock solution dilutions with stepwise decreasing crude oil concentrations until a 3:1 signal-to-noise ratio was reached [27]. The limit of quantification (LOQ) was defined as the minimum concentration of analyzed substance with acceptable repeatability and accuracy, which was the lowest calibration level of the calibration curve.

3. Results and discussion

3.1. Comparison of extraction method for petroleum hydrocarbons

The extraction step was critical for the analysis of crude oil contaminated soils and aging had a strong effect on extractable hydrocarbons in solid matrix. Petroleum hydrocarbons in weathered and aged contaminated soils were often observed to decline with time, probably due to volatilization, degradation and/or irreversible incorporation into the solid matrix [28]. Therefore, a comparison the efficiencies of different extraction methods may be a prerequisite for a reliable analysis of crude oil contaminated soils. Soxhlet extraction had been widely accepted as the standard procedure to assess the extraction efficiency of other methods. However, due to the disadvantage of complicated procedures and a high solvents demand for the Soxhlet extraction, alternatives were developed such as ASE and ultrasonic extraction. In this study, the spiked soils at crude oil levels from 0.5 to 35.0 mg g⁻¹ had been used and each test was performed with six replicates. Fig. 1 showed a linear plot of the predicted values against the observed values. Statistic regression analysis of the linear plot was represented by the equation: $y = 0.29 + 0.98x$ (coefficient $r^2 = 0.996$; and standard deviation $SD = 1.08$), with the confidence interval between 95 and 105%. Comparison of the tested extraction method indicated that ASE was comparable to both Soxhlet and ultrasonic extraction. As shown in Table 2, Soxhlet and ultrasonic extraction had lower extraction efficiency when the initial crude oil concentrations were below 5.0 mg g⁻¹. The recovery rates of Soxhlet and ultrasonic methods fluctuated between 70 and 90%, while ASE had a more stable recovery rate in the range of 90–106%. This result was consistent with previous research data [29].

3.2. Chromatographic qualitative analysis of petroleum hydrocarbons

Fossil fuel samples were fractionated by TLC according to their mobility and solubility. The complexity of the composition of crude oil resulted in a great variation of the partition of petroleum compounds on chromarods, and each peak observed in TLC-FID contained many individual compounds. According to TLC-FID stud-

Table 2
Recovery of the ASE, Soxhlet and ultrasonic extraction for crude oil spiked contaminated soils.

Soil sample (mean ± SE ^a) (g kg ⁻¹)	ASE recovery (%)		Soxhlet recovery (%)		Ultrasonic recovery (%)	
	Average	RSD ^b	Average	RSD ^b	Average	RSD ^b
0.5 ± 0.11	97.88	3.94	74.18	17.90	58.82	9.44
0.8 ± 0.06	100.16	5.32	85.80	8.34	77.99	8.66
1.0 ± 0.19	91.12	6.09	78.21	9.67	76.22	14.84
2.0 ± 0.48	90.08	5.25	82.05	5.28	79.73	6.54
5.0 ± 0.85	95.08	4.87	90.78	6.52	76.63	12.70
8.0 ± 0.60	106.26	6.11	92.72	3.91	83.06	6.67
20.0 ± 2.13	103.09	5.07	93.40	6.07	90.36	7.02
35.0 ± 1.41	98.14	5.07	91.47	7.14	88.16	6.05

Each soil sample was determined with 6 duplicates (*n* = 6).

^a SE represents standard error of per concentration level.

^b RSD represents means of per concentration level.

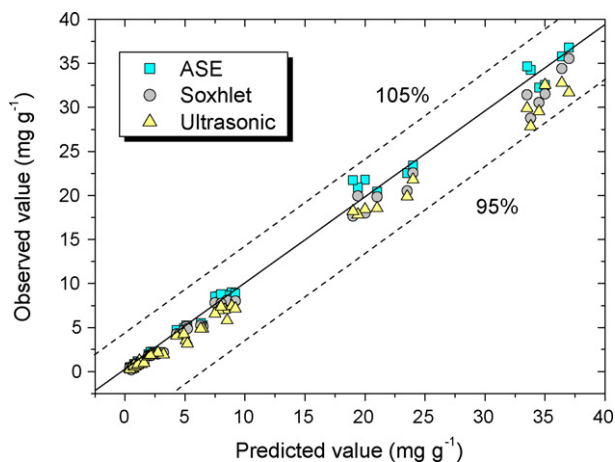


Fig. 1. Influence of extraction procedures (ASE, Soxhlet extraction and ultrasonic extraction) on TEM determination; the spiked soils used at crude oil concentrations from 0.5 to 35.0 mg g⁻¹; the linear regression of predicted and observed values represented by the equation: $y = 0.29 + 0.98x$.

ies on Athabasca bitumen, NIST 1582 and creosote, used as a reference [30], the crude oil fractions in Fig. 3 were identified as n-alkanes (Na), cycloparaffins (Cy), aromatics (Ar), resins (Re) and asphaltenes (As), which were subsequently confirmed by reference materials isolated through EC method. As can be seen from Fig. 3, there were apparent differences of chromatogram between the elution fractions and the raw crude oil, especially for resins and asphaltenes, suggesting that the incomplete separations or desorption of crude oil may generally occur using EC method [3]. In this study, the retention times of Na, Cy, Ar, Re and As were 0.104 ± 0.008 , 0.154 ± 0.008 , 0.236 ± 0.004 , 0.308 ± 0.006 and 0.385 ± 0.004 (mean \pm SE), and the peak heights were 35.6 ± 1.0 , 21.4 ± 1.1 , 45.5 ± 2.3 , 54.1 ± 5.2 and 22.8 ± 1.5 , respectively. Compared with the typical TLC separations [30,31], the appearance of the cycloparaffins peak as shown in Fig. 2, can be partially attributed to the different petroleum compositions and the different TLC development schemes. As shown in Fig. 2, the peak height and half peak width in the 9 replicates were highly reproducible and their RSD values ranged from 5 to 10%. The peak resolution for n-alkanes and cycloparaffins was 0.67, indicating the incomplete separation of n-alkanes and cycloparaffins peaks. This may be caused by the similarity in chemical properties of both classes of compounds, a low selectivity of the used developing solvents and the limited length of the used chromarods. The percentage of Na, Cy, Ar, Re and As to TEM was 23.5, 15.0, 21.6, 25.1% and 14.8% (w/w); the large proportion of As and Re in crude oil may result in an increase of the specific gravity and immobility of the used crude oil samples.

In order to get a more detailed insight of the chemical composition of crude oil fractions that were identified by TLC method,

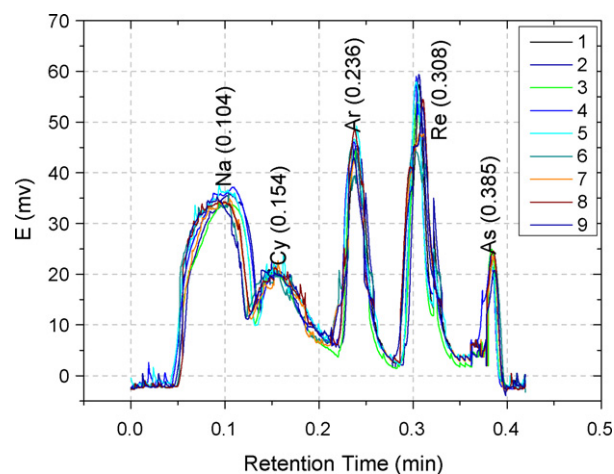


Fig. 2. Identification and reproducibility of petroleum fractions in TLC-FID using a stock solution of 5000 mg L⁻¹ on 9 tracks (1–9 stands for the experiment number).

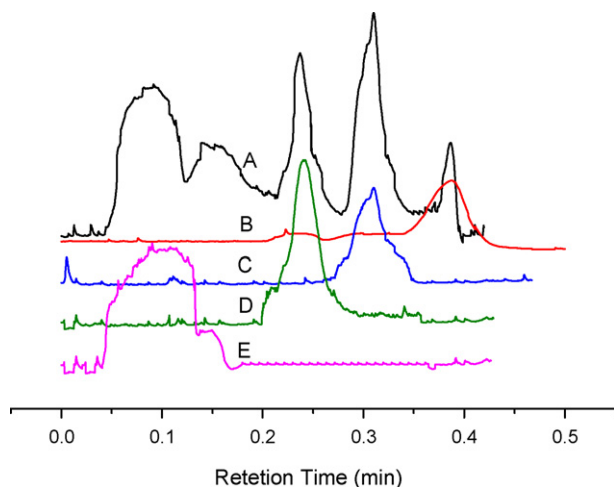


Fig. 3. Verification of the TLC-FID separations of crude oil with reference materials isolated through column elution chromatography (A stands for the raw crude oil solution of 5000 mg L⁻¹; B–E stands for the elution fraction of asphaltenes, resins, aromatics and saturates, respectively).

GC–MS fingerprinting was used to provide a profile of the light fraction isolated from crude oil by EC method. As shown in Fig. 4, the following classes of chemical compounds could be identified by GC–MS analysis: paraffins, 2–3 rings aromatics, 4–6 rings aromatics and biomarkers, and among which the prominent was the two latter components. In Table 3, matching the mass spectra to the NIST 05 library (Agilent, USA), the majority of the 31 identified

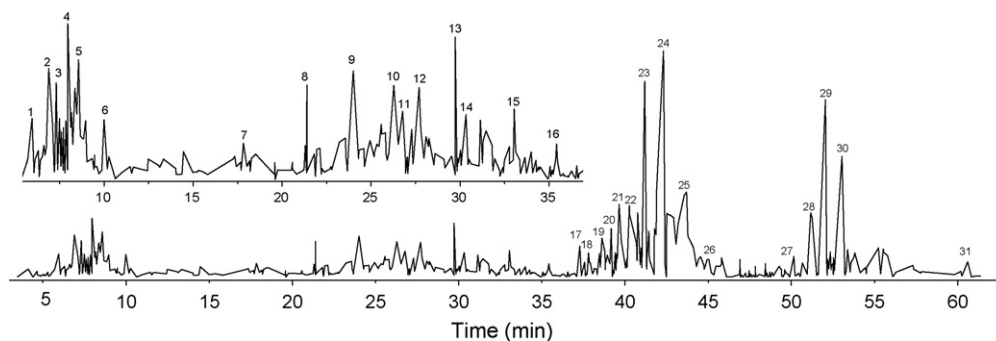


Fig. 4. GC–MS full-scan of the light fractions of saturated compounds and aromatic compounds isolated from crude oil, the identified compounds matching NIST 05 mass library with probability $\geq 70\%$ (peak numbers correspond with numbers in Table 3).

Table 3
Compounds of petroleum hydrocarbons identified by GC-MS.

No.	Compound
1	1-Methyl-4-(1-methylethylidene)-cyclohexane
2	cis,cis-1,6-Dimethylspiro[4,5]decane
3	Bicyclo[2,2,1]heptane,2,2,3-trimethyl
4	1-Pentadecyne
5	1-Methylbicyclo[3,2,1]octane
6	(+)-(2)-Longipinane
7	1,2,3,6b,7,8,9,10,10a,10b-Decahydro-fluoranthene
8	4-(4-Ethylcyclohexyl)-1-pentyl-cyclohexene
9	Octacosahydro-9,9'-biphenathrene
10	3-Methyl-6,7-benzoisoquinoline
11	1,4-Dimethyl-anthracene
12	Decahydro-1,6-dimethyl-4(1-methylethyl)-naphthalene
13	5-Butyl-6-hexyloctahydro-1H-indene
14	2-Butyl-5-hexyloctahydro-1H-indene
15	1,2,3,4,7,12-Hexahydro-benz[a]anthracene
16	9-1-Butyl-anthracene
17	9-Butyltetradecahydro-anthracene
18	(5,Alpha,13,alpha)-D-homoandrostane
19	5,Alpha-cholest-22-ene
20	Benz[a]anthracene
21	Triphenylene
22	Chrysene
23	Androstane
24	Baccharane
25	1,3-Dimethyl-pyrene
26	Cholestane
27	Perylene
28	23,28-Bisnor-17,alpha,(H)-hopane
29	4-Iodo-N-[2,4,6-trimethyl-phenyl]-benzamide
30	28-Nor-17,beta,(H)-hopane
31	2-(4-Chlorophenyl)benzothiazole

The first matching hits derived from the NIST 05 library were given with the match value and probability over 850 and 70%.

individual compounds were the methyl- or hydro-derivatives of long-chain hydrocarbons or aromatics; this finding corresponded to earlier research results [32].

3.3. Chromatographic quantitative analysis of petroleum hydrocarbons

In earlier research [3,14,33], TLC quantification was based on the assumption that the peak area can be linearized with the mass

of the analyte. As shown in Fig. 5, the five fractions of crude oil showed a linear relationship between peak area and concentration with coefficients $r^2 > 0.97$, but each regression coefficient was numerically different. In this study, we found that the LOQ for the TEM and petroleum fractions were in the range of 200–35,000 and 30–8000 mg L⁻¹, respectively. Although there has been a difference between TEM and TPH for polar fraction, the observed MDL value of 20.0 mg L⁻¹ for TEM determined by TLC-FID (Fig. 5), can be compared to a value of 1.4 mg L⁻¹ of TPH determined by GC-FID [34]. Therefore, the TLC-FID method may have the potential application in soil remediation practice because the current cleanup threshold is 10,000 mg L⁻¹ (USA, 609-633-7413) or 5000 mg L⁻¹ (Netherlands, RIVM 601501021) (after unit conversion from mg g⁻¹ to mg L⁻¹).

3.4. Comparison of TLC/FID and EC methods

The tested TLC-FID method, showing a rapid screening of classes, is analogous to EC method that was widely accepted by the petroleum chemical industry. The EC method is solvent- and labor-intensive, but can be used as the reference method to assess more practical alternative screening techniques. As shown in Fig. 6, comparison experiments had been done using aged contaminated soils at TEM levels of 50, 80, 200, 300 mg g⁻¹. It can be seen that a similar distribution of petroleum fractions was observed for EC and TLC-FID method; more than 60% of TEM was constituted by the fractions of saturates and aromatics. For these classes of compounds, the two methods of TLC-FID and EC showed a good repeatability with an average RSD value of 1.21% and 2.23%, respectively. However, the recovery of TEM, saturates and asphaltene using EC method was about 11%, 7 and 10% lower than that when using the TLC-FID method; this can be explained by assuming a higher volatility of saturated compounds or a stronger adsorption of asphaltene to packed materials in EC method.

Research papers indicated that when mixtures contain unknown compounds, the calibration became less straightforward [21,33]. Furthermore, chromatographic responses, matrix-induced effects and linear regression slopes of compounds in different detection systems varied greatly [24]. Therefore, a calibration step is usually necessary. As shown in Figs. 2 and 4, the TLC-FID and GC-MS fingerprinting indicated the chemical complexity of crude

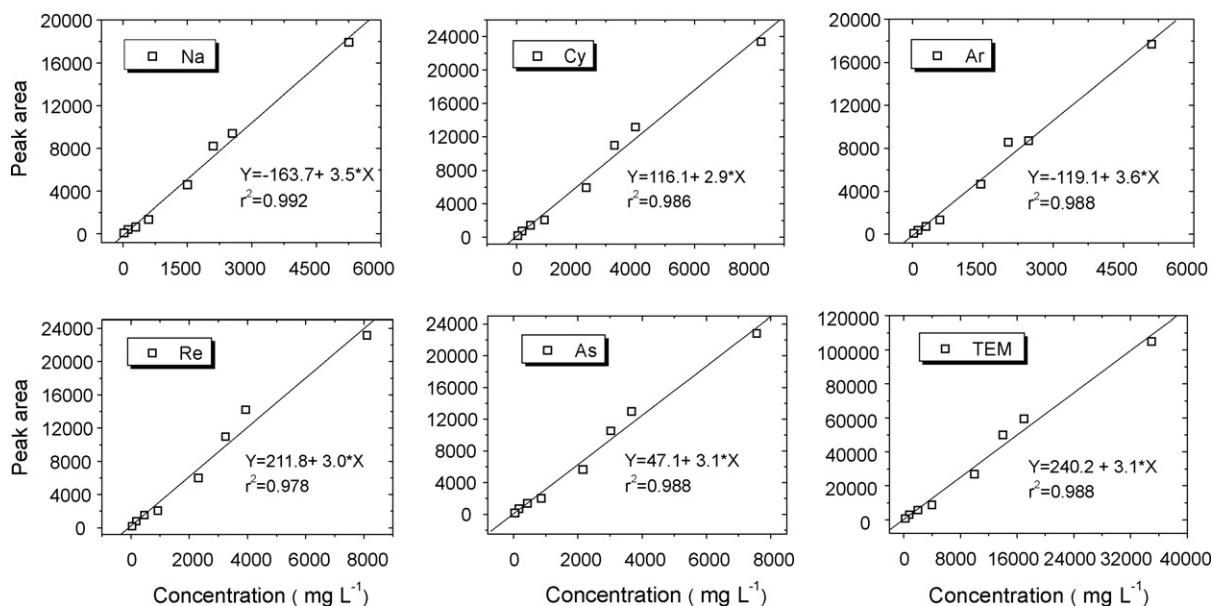


Fig. 5. Quantification standard curves of TEM and component classes with crude oil solutions at the concentration levels ranged from 200 to 35,000 mg L⁻¹.

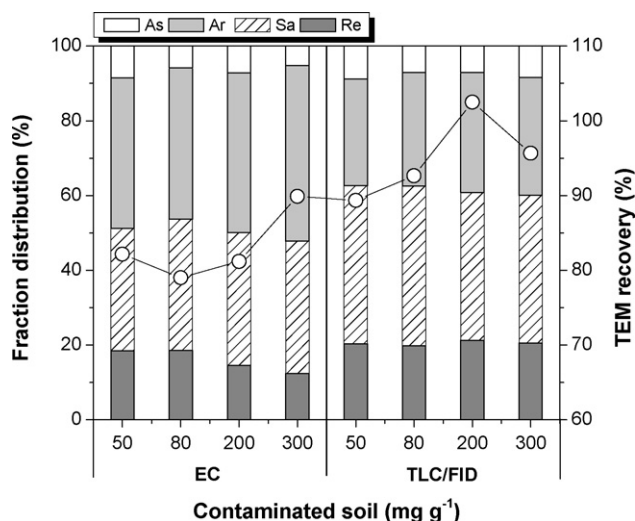


Fig. 6. Comparison of tested TLC and EC method for the determination of aged and weathered contaminated soils with the TEM levels of 50, 80, 200, 300 mg g⁻¹.

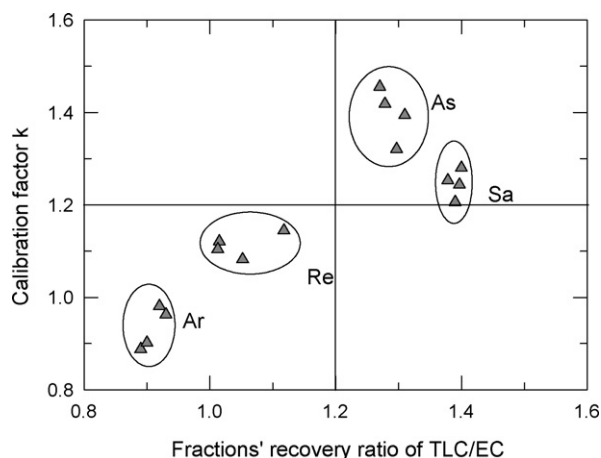


Fig. 7. Relationship between the calibration factor and recovery ratio of TLC/EC based on the analytical data of aged contaminated soils with the TEM levels of 50, 80, 200, 300 mg g⁻¹.

oil. A mathematic model based on the quantification of EC method has been proposed for the calibration of TLC-FID method as follows [23]:

$$m_i = f_i(A_i + \Delta A_i) + b \quad (1)$$

$$m_i = m EC_i\% \quad (2)$$

$$\Delta A_i = \Delta A EC_i\% \quad (3)$$

$$\Delta A = A_0 - A' \quad (4)$$

f_i : calibration factor;

A_0 , A' : integrated TLC areas with and without solvent development;

ΔA : difference between A_0 and A' ;

ΔA_i : area difference of each fraction;

m , m_i : mass of the tested sample and its each fraction;

$EC_i\%$: content of each fraction determined by EC;

b_i : regression constant.

As shown in Fig. 7, the calibration factor appeared to be species-dependent and varied with the recovery ratio of TLC/EC: $Ar < Re < Sa < As$. The values varied between 0.8–1.0, 1.0–1.2, 1.2–1.3

and 1.3–1.5, respectively. This result was consistent with the literature results reported by Yang et al. [35]. However, due to the lower EC recovery for hydrocarbon classes of compounds, the calibration model based on EC method may consequently overestimate the calibration factors of Ar, Re and As. Therefore, before TLC-FID method was adopted for the quantitative determination of different crude oil fractions, appropriate calibration factors seemed to be needed.

4. Conclusion

- (1) ASE had a higher extraction recovery rate and a better repeatability for the analysis of petroleum contaminated soils than Soxhlet and ultrasonic extraction.
- (2) The quantification of TEM and crude oil fractions by TLC-FID was applicable in practice using the external standard method. The LOQ of TEM varied between 200 and 35,000 mg L⁻¹ and the MDL was 20.0 mg L⁻¹.
- (3) The TLC separations of saturates, aromatics, resins and asphaltenes were verified with the reference materials isolated through EC method, and the majority of the light fraction was identified by GC-MS as the methyl- or hydro-derivatives of the long-chain hydrocarbons and aromatics.
- (4) Comparing the analysis of aged crude oil contaminated soils, TLC-FID method proved to be an alternative of the EC method. The calibration factor was species-dependent and varied with the recovery ratio of TLC/EC.

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