Application Brief

Environment

A Rapid Segmented Analysis Method for the Determination of Total Petroleum Hydrocarbons Content from Diesel Products in Water and Soil Samples Using Agilent Intuvo 9000 GC

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Abstract

A rapid segmented analysis method for the determination of total petroleum hydrocarbons (TPHs) content from diesel products in water and soil samples using Agilent Intuvo 9000 GC has been developed. Under these experimental conditions, the curves for C_{10}-C_{14}, C_{15}-C_{28} and C_{29}-C_{36} showed good linearity and the correlation linearity coefficient R^2 was greater than 0.999. The lowest detection limits were 9.9, 29.2 and 23.3 mg/L respectively, with the RSD of repeatability of peak area less than 0.6%. Application of this method to real samples shows advantages over conventional approaches, including fast analysis of less than 3.2 min, while providing high stability and quantitation results consistent with conventional methods. The unique Intuvo Guard Chip design also effectively protects the GC column and reduces downtime for instrument maintenance.

Introduction

In the process of petroleum production, storage, transportation, refining, processing and use, petroleum hydrocarbons may overflow and be discharged due to accidents, abnormal operation and maintenance. The hazard of petroleum pollutants in the environment mainly lies in the harm and impact on human body, water, aquatic organisms and soil. Therefore, the monitoring of total petroleum hydrocarbons pollutants has important practical significance. Petroleum substances have been listed as hazardous wastes in China. The Ministry of Ecology and Environment has issued and implemented a series of technical guidelines for environmental risk assessment and remediation of contaminated sites.[1-4] With the full implementation of these guidelines, the technical requirements for the qualitative and quantitative testing of characteristic pollutants in environment become increasingly rigorous.[2] Internationally, the Total Petroleum Hydrocarbons Criteria Working Group (TPHCWG) of the American Petroleum Institute has studied the classification/segmentation method for petroleum hydrocarbons.[5] The Environmental Protection Agency (EPA), in collaboration with the TPHCWG, has established some practical environmental risk assessment models.

This method involves the analysis of extractable TPH in water and soils. The TPH in soils are extracted with dichloromethane-acetone mixed solution, and the TPH in water are extracted with dichloromethane. The extractable hydrocarbons are divided into three categories: C_{10}-C_{14}, C_{15}-C_{28} and C_{29}-C_{36}. The analysis time of total petroleum hydrocarbons in the diesel products by the existing conventional methods is about 20 min, which can not meet the requirements of high-throughput analysis in commercial laboratories. In this paper, we establish a rapid segmented analysis method for the determination of total petroleum hydrocarbons content from diesel products in water and soil samples. The analysis time is less than 3.2 min. The results show that this method has the advantages of low detection limit, good stability and reduction of necessary maintenance due to column contamination.

Experiment

Reagents and samples

Reference materials: n-Alkane Standards (C_8, C_9, $C_{10,}$ C_{11}, C_{12}, C_{13}, C_{14}, $C_{15,}$ C_{16}, $C_{17,}$ C_{18}, C_{19}, $C_{20,}$ C_{22}, C_{24}, C_{26}, C_{28}, C_{30}, C_{32}, C_{34}, C_{36}, C_{38} and C_{40}) were purchased from Dr. ehrenstorfer GmbH, Germany. The standard solutions at different concentrations were prepared by serial dilution in n-hexane.

Reagents: Dichloromethane, n-Hexane and Acetone are pesticide residue grade reagents which were purchased from Sigma-Aldrich. Anhydrous sodium sulfate: analytical grade, dried at 400 °C for more than 4 hours and cooled down in a dryer. Water and soil samples were routine test samples in the laboratory.

Instruments and equipment

Agilent Intuvo 9000 GC System with FID Detector;
Agilent 7890B GC System with FID Detector;
Water purification system (Millipore, USA);
Agilent OpenLAB CDS Chemstation Version C.01.07

Sample preparation

Water and wastewater samples:

1 L of water sample was transfered into a 2 L separatory funnel, and then extracted with 60 mL of dichloromethane solution for 3 times. Extract was combined and filtered, and concentrated to about 0.5 mL with K-D device. Then the solvent was transform to n-hexane, concentrated to less than 1 mL, then diluted to 1 mL and transfered into the sample vial.

Soil sample:

20.0 g fresh soil samples were weighed, and diatomite was added for dehydration and mixed well. Then extraction was performed by pressurized fluid extraction method, the extraction solvent system was 1:1 acetone-n-hexane.The extraction solution was collected and concentrated to about 0.5 mL, and then diluted to 1 mL (no additional solvent was required).

Instrument conditions:
Intuvo 9000 Gas Chromatograph Conditions

Carrier gas:	high purity helium (purity ≥ 99.999%)
Temperature at the injection port:	300 °C
Injection volume:	1 μL
Injection mode:	splitless injection
Guard Chip temperature:	300 °C
Flow path chip temperature:	350 °C
Chromatographic column:	Agilent J&W DB-5ht non-polar columns (5 m × 0.32 mm × 0.1 μm)
Constant flow:	10.0 mL/min
Heating up procedure:	Initial temperature 40 °C, hold for 0.5 min ramp up to 150 °C at 250 °C/min then ramp up to 300 °C at 100 °C/min finally ramp up to 320 °C at 165 °C/min, hold for 0.6 min
Post-run:	350 °C/min, hold for 1.5 min
FID detector temperature:	300 °C
Hydrogen flow rate:	40 mL/min
Air flow rate:	400 mL/min
Column flow and make-up gas Total flow:	25 mL/min

7890B Gas Chromatograph Conditions

Carrier gas:	high purity helium (purity ≥ 99.999%)
Temperature at the injection port:	300 °C
Injection volume:	1 μL
Injection mode:	splitless injection
Chromatographic column:	Agilent J&W DB-5 capillary column (15 m × 0.25 mm × 0.25 μm)
Constant flow:	1.2 mL/min
Heating up procedure:	Initial temperature 50 °C, hold for 2.25 min ramp up to 200 °C at 30 °C/min then ramp up to 300 °C at 15 °C/min finally ramp up to 320 °C at 25 °C/min, hold for 8 min
FID detector temperature:	300 °C
Hydrogen flow rate:	40 mL/min
Air flow rate:	400 mL/min
Column flow and make-up gas Total flow:	25 mL/min

Results and Discussion

Standard curve of Intuvo 9000 fast method

N-alkane standards were serially diluted to obtain standard solutions at concentrations of 10, 20, 30, 50 and 100 mg/L respectively. The chromatogram obtained by analyzing the standard solution is shown in Figure 1, which shows baseline separation of all compounds and fully meets the requirements of qualitative and quantitative analysis. As shown in Table 1, good linearity was achieved with R^2 greater than 0.999.

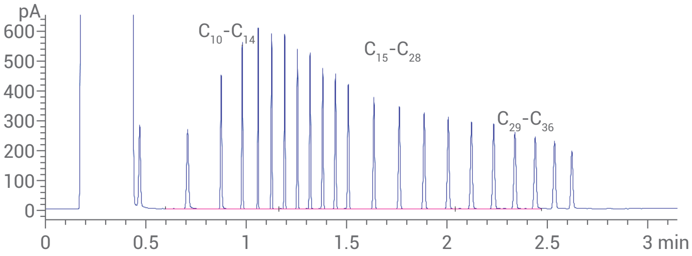

Figure 1. Chromatogram of mixed standard solution containing n-alkane with concentration of 10 mg/L as monostandard

In utilizing the segmentation method, integration from the mid-point of the retention time of C_9 to C_{10} to the mid-point of the retention time of C_{14} to C_{15} provides the total area of C_{10}-C_{14}, integration from the mid-point of the retention time of C_{14} to C_{15} to the mid-point of the retention time of C_{28} to C_{29} provides the total area of C_{15}-C_{28}, and integration from the mid-point of the retention time of C_{28} to C_{29} to the end of the retention time of C_{36} provides the total area of C_{29}-C_{36}.

The n-alkane standard solution with a concentration of 10 mg/L was consecutively injected 7 times, and the detection limit was calculated based on the standard deviation (SD). LOD = 3.143 x SD (when n is equal to 7, t value is 3.143). The results are shown in Table 1.

Table 1. Linear range, linear regression equation, correlation coefficient and detection limit

Compound	Linear regression equation	Linear range	Correlation coefficient	Detection limit (mg/L)
C_{10}-C_{14}	y = 19.57x + 56.4	50-500	0.9997	9.9
C_{15}-C_{28}	y = 19.76x + 107.8	100-1000	0.9998	29.2
C_{29}-C_{36}	y = 19.73x + 31.8	40-400	0.9998	13.3

Repeatability under rapid analytical conditions

In the analysis of total petroleum hydrocarbons in the diesel products, the maximum heating rate of Intuvo 9000 can reach 250 °C/min, which enables the analysis time of the samples to be reduced from 22 min for a conventional 7890 GC method to less than 3.2 min. The n-alkanes standard solution with a concentration of 10 mg/L was consecutively injected and analyzed 7 times using Intuvo 9000, and the results are shown in Table 2. The retention time of n-alkanes shows excellent stability and repeatability, in which C_{10} difference is less than 0.009 min and C_{40} difference is less than 0.003 min. At the same time, the RSD of repeatability of peak area was 0.32% for C_{10}-C_{14}, 0.47% for C_{15}-C_{28} and 0.54% for C_{29}-C_{36}.

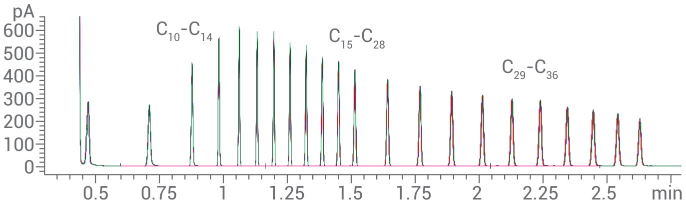

Figure 2. Chromatogram of mixed standard solution containing n-alkanes with concentration of 10 mg/L as monostandard (n = 7)

Assay of real samples

Three representative samples were used to perform 5 replicate injections respectively. As shown in Table 2, the RSD of repeatability of all sample compounds is less than 8.61%. At the same time, the samples were analyzed using the conventional method by 7890B GC, and the results are the values marked with * in Table 2. It can be seen that there is little difference between the results of a conventional method by 7890B GC and a rapid method by Intuvo 9000, both of which can meet the analytical requirements of the laboratory.

In addition, a spiked assay was carried out for real samples. The results showed that the average recovery ratio of water samples was 88% - 102%, and that of soil samples was 80% - 124%.

Table 2. Analysis results of real samples by Intuvo 9000 and 7890B GC (n = 5)

Sample	C_{10}-C_{14}		C_{15}-C_{28}		C_{29}-C_{36}		Total concentration (mg/L)
	Concentration (mg/L)	RSD%	Concentration (mg/L)	RSD%	Concentration (mg/L)	RSD%	
1	19.1 (16.8)*	1.09	131.7 (142.2)*	1.98	167.4 (187.5)*	3.66	318.2 (346.5)*
2	34.0 (28.7)*	1.31	408.6 (379.6)*	0.93	315.0 (339.7)*	8.61	757.6 (748.0)*
3	82.6 (52.7)*	0.65	595.2 (569.2)*	0.76	382.5 (422.1)*	5.2	1060.3 (1044.0)*

Note: the value marked with * is the test result of the conventional method by 7890B GC

Unique Intuvo technology protects the column

The unique guard chip design and inert flow path of the Intuvo 9000 GC can maximize the protection of chromatographic column, effectively reduce maintenance frequency of the system and ensure the stability and reliability of data. After 120 samples were analyzed by the rapid segmented analysis technology, the system was maintained by replacing the liner after every 40 samples analyzed. The standard solution was injected, and the difference in chromatographic peak area was less than 7%. After analyzing 250 samples and replacing the Guard Chip, the chromatographic peak area of the standard solution had no significant change from the initial value. This shows that the Guard Chip can effectively protect the chromatographic column, and the retention time does not shift after the Guard Chip is replaced, which avoids the need to recalibrate after trimming the column and greatly improves the laboratory efficiency.

Conclusions

In this article, we establish a rapid segmented analysis method for the determination of total petroleum hydrocarbons content from diesel products in water and soil samples using the Agilent Intuvo 9000 GC system. The results show that this method has advantages, such as fast analysis and good stability, and the quantitation results are consistent with those of conventional methods using 7890B GC. The unique Intuvo Guard Chip design also effectively protects the GC column and reduces downtime for instrument maintenance.

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Printed in the USA, March 20, 2018
5991-9137EN

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