



Development, optimization, validation and application of faster gas chromatography – flame ionization detector method for the analysis of total petroleum hydrocarbons in contaminated soils



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ABSTRACT

This paper presents an important new approach to improving the timeliness of Total Petroleum Hydrocarbon (TPH) analysis in the soil by Gas Chromatography – Flame Ionization Detector (GC-FID) using the CCME Canada-Wide Standard reference method. The Canada-Wide Standard (CWS) method is used for the analysis of petroleum hydrocarbon compounds across Canada. However, inter-laboratory application of this method for the analysis of TPH in the soil has often shown considerable variability in the results. This could be due, in part, to the different gas chromatography (GC) conditions, other steps involved in the method, as well as the soil properties. In addition, there are differences in the interpretation of the GC results, which impacts the determination of the effectiveness of remediation at hydrocarbon-contaminated sites. In this work, multivariate experimental design approach was used to develop and validate the analytical method for a faster quantitative analysis of TPH in (contaminated) soil. A fractional factorial design (FFD) was used to screen six factors to identify the most significant factors impacting the analysis. These factors included: injection volume (μL), injection temperature ($^{\circ}\text{C}$), oven program ($^{\circ}\text{C}/\text{min}$), detector temperature ($^{\circ}\text{C}$), carrier gas flow rate (mL/min) and solvent ratio (v/v hexane/dichloromethane). The most important factors (carrier gas flow rate and oven program) were then optimized using a central composite response surface design. Robustness testing and validation of model compares favourably with the experimental results with percentage difference of 2.78% for the analysis time. This research successfully reduced the method's standard analytical time from 20 to 8 min with all the carbon fractions eluting. The method was successfully applied for fast TPH analysis of Bunker C oil contaminated soil. A reduced analytical time would offer many benefits including an improved laboratory reporting times, and overall improved clean up efficiency. The method was successfully applied for the analysis of TPH of Bunker C oil in contaminated soil.

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1. Introduction

In the past, there was no standard method for the analysis of total petroleum hydrocarbon (TPH) in the soil in Canada, leading to differing analytical methods and regulations in different jurisdictions. Methods used for the analysis of TPH in the soils typically varied across commercial laboratories. This did not only make it difficult to compare analytical results, but may also caused over and/or under estimation of contaminated sites under remediation, as well as affected the effectiveness of remediation services and

technologies. The need to develop a harmonized methodology for analysis of petroleum hydrocarbon compounds (across Canada) became necessary to remove these uncertainties. Turle et al. [1] reviewed the Canadian Council of Ministers of Environment (CCME)'s Analytical Method Technical Advisory Group's (AMTAG) process in developing the reference method for the Canada-Wide Standard (CWS) for Petroleum Hydrocarbons (PHC) in Soil – Tier 1 Method (CCME-CWS method) [2]. This methodology is designed for the assessment and remediation of contaminated sites, and requires that four petroleum fractions be determined analytically by a combination of extraction and Gas Chromatography (GC). The fractions are based on molecular weight. The first fraction, F1, includes hexane to decane ($\text{C}_6\text{--}\text{C}_{10}$); the second fraction, F2, includes decane to cyclohexane ($\text{C}_{10}\text{--}\text{C}_{16}$). The third fraction,

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F3, includes cyclohexane to tetratriacontane (C_{16} – C_{34}), and the fourth fraction, F4, from tetratriacontane to pentacotane (C_{34} – C_{50}), respectively. Gravimetric heavy hydrocarbon (F4G) is defined as the extremely heavy carbon fraction (above C_{50}) and determined (by gravimetric and not chromatographic analysis) only if the chromatogram of the F4 (C_{34} to C_{50}) hydrocarbon fractions fail to return to baseline at or above C_{50} .

The limitations in the published method became apparent in our research related developing a model on soil remediation. In the course of analyzing soils contaminated with Bunker C oil using the CCME method, and following the sample preparation procedures stated in the published method, most of the carbon fractions were not eluting in the chromatogram. The sampling period of 20 min specified in the method was also perceived to be too long. The researchers had an inkling that this variability in the chromatographic output in which most of the carbon fractions were not eluting may be due to the GC chromatographic conditions as well as use of inappropriate solvents. Although other factors such as errors during sample preparation and extraction, interferences from natural organic content of the soil, and from soil amendment procedures [2] may also lead to variability in hydrocarbon analysis in the soil. Other studies in the past have reported disparities in published analytical methods. Saari et al. [4] did an inter-laboratory comparison of TPH analysis using the International Organization for Standardization (ISO) and European Committee for Standardization (CEN) standards, and reported wide discrepancies in methodology and results. Similar studies attributed these kind of differences (in analytical methods) to GC calibration [5,6]. Therefore, these discrepancies are not unexpected [4].

The gas chromatography (GC) is perhaps the most robust analytical instrument for analyzing volatile compounds such as TPH. The ability to couple highly sensitive detectors such as the flame ionization detector (FID) and mass spectrometry (MS) makes it a choice for highly sensitive petroleum analysis. The FID detects ions produced during the combustion of compounds (separated by gas chromatography) in a H_2 /air flame. The FID response depends on the number of ions produced by a compound. Since this varies considerably between compound classes, FID response factors vary correspondingly [7,8]. The ability of a chromatographic method to successfully separate, identify and quantify species is determined by many factors [9]. The identification of these significant operating factors can be facilitated by multivariate statistical methods and result in better overall methodologies.

Multivariate experimental designs are a statistical methodology which allows for systematic variation of multiple factors within one experimental design, and the use of the results to create mathematical models for the experimental. Using these models, the optimum conditions (factors) of a process are determined, interactions between, and the most important factors into that process are revealed [10]. This statistical approach is particularly useful in quantitative analysis when several experimental factors have to be optimized. It is especially more important in regulatory or forensic research such as pharmaceutical active ingredient screening, environmental contaminant analysis, and criminal investigations, as these methods require not only fast analysis but also reliable analytical results. They also ensure the efficient use of time and resources provide information about the physio-chemical properties of the system, and allow for prediction of responses based on experimentation. In addition, there are robust and reliable statistical tools (software) to aid in the design and model fitting [9]. The most commonly used multivariate designs are the fractional factorial and full factorial designs, and the more complex response surface designs such as the Central Composite, Box-Behnken, Doehlert and mixture designs.

A large number of applications of multivariate approaches for optimization of different chromatographic analytical methods

have been reported in the literature, in applications such as High Performance Liquid Chromatography (HPLC) [1,2], GC – Mass Spectrometry (GC-MS) [3,4], GC-FID [11,12], Capillary Electrophoresis - UV detection (CE-UV) [13], and Micellar Electro-kinetic Chromatography (MEKC) [14,15].

The objective of this study was to use multivariate experimental design approach to optimize and validate the CCME Canada Wide Standard method for total petroleum hydrocarbon analysis in the soil, for a more reliable total petroleum hydrocarbon analysis. The specific objective was to determine the optimum GC operational settings and conditions for a more reliable TPH analysis with this method.

The work is divided into four sequential phases. The first phase involved the screening experiments (Section 3.1), designed to identify the experimental factors that were most important, and which factors do not significantly affect the experimental results. Fractional factorial (FFD) design was used to screen six (6) factors, namely - injection volume (μ L), injection temperature ($^{\circ}$ C), oven program ramp up ($^{\circ}$ C/min), detector temperature ($^{\circ}$ C), carrier gas flow rate (mL/min) and solvent ratio (v/v hexane/dichloromethane). In the second phase (Section 3.2), optimization experiments were conducted in which the significant factors identified from the screening experiments were optimized using a Central Composite Response Surface Design (CCD). In the third phase (Section 3.3), optimized conditions were tested for robustness and the developed model was validated by calibrating the GC system with a hydrocarbon standard using the optimized GC settings. The fourth and final phase (Section 3.4) involved application of the optimized experimental conditions for the analysis of real hydrocarbon (Bunker C oil) sample extracted (via soxhlet method) from contaminated soil.

2. Materials and method

2.1. Chemicals and reagents

The hydrocarbon standard used for calibration was a Supelco 1000 μ g/mL of hydrocarbon mix in Cyclohexane (Sigma-Aldrich, Canada) and contained a mixture of decane (C_{10}), hexadecane (C_{16}), tetracontane (C_{34}) and pentacontane (C_{50}) in cyclohexane (F2 to F4 fractions). Other reagents used included hexane, acetone, and methanol (Fisher Scientific, Canada), dichloromethane (ACP Chemical Company, Canada), anhydrous sodium sulfate, and the silica gel (Sigma-Aldrich, Canada). All the solvents were ACS reagents/certified.

The Bunker C contaminated soil used to validate the method was obtained from an old mining site which has been contaminated for over three decades. The contaminated site was discovered during the reconstruction phase of the abandoned mine site, and investigation showed that the oil leaked from a storage tank. Upon analysis, the soil texture was found to be made up of 10.7% silt, 40.5% sand, 7.2% clay, and 41.6% coarse-grained sediments respectively. The bulk density was 1.4 g/cm^3 , moisture content 11% and the pH was 7.85. Soxhlet extraction method was used to extract the oil from the soil following the procedure outlined in the CCME reference method [2].

2.2. GC-FID instrumentation

The TPH analyses were performed on an Agilent Technology gas chromatography system 7890A, equipped with an Auto Sampler 7693 (Agilent Technology), and an FID. Data were acquired and processed using Agilent OpenLAB Chromatography Data System (CDS) Chemstation Edition for integrated peak areas, peak heights, and elution and analysis times. The GC used a MXT[®]-1 Columns

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