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Rapid and sensitive method for the determination of polycyclic aromatic hydrocarbons in soils using pseudo multiple reaction monitoring gas chromatography/tandem mass spectrometry

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ABSTRACT

A method for the rapid determination of 18 polycyclic aromatic hydrocarbons (PAHs) in soil has been established based on a simplified solvent extraction and GC/MS/MS operated in pseudo multiple reaction monitoring mode (PMRM), a technique where the two quadrupoles mass monitor the same *m/z*. The PMRM approach proved superior to the classic single quadrupole technique, with enhanced sensitivity, specificity, and significant reduction in time consuming sample clean-up procedures. Trace level PAHs could be readily confirmed by their retention times and characteristic ions. The limit of quantitation in soil was observed to be 20 ng/g for 16 EPA-priority PAHs and 2 additional PAHs specific to Environment Canada. The developed method was linear over the calibration range 20–4000 ng/g in soil, with observed coefficients of determination of >0.996. Individual PAH recoveries from fortified soil were in the range 58.1 to 110.1%, with a precision between 0.3 and 4.9% RSD. The ruggedness of the method was demonstrated by the success of an inter-lab proficiency test study organized by the Canadian Association for Laboratory Accreditation. The present method was found to be applicable as a rapid, routine screening for PAH contamination in soil, with significant savings in terms of preparation time and solvent usage.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous hydrophobic compounds originating from natural or anthropogenic sources. These compounds are widely distributed in the environment and detected in soils and sediments, mainly due to atmospheric deposition processes [2]. All PAHs in the environment are an ecological and human-health concern. Of the one hundred and twenty-six Environment Protection Agency Priority Pollutants listed by the Clean Water Act, sixteen are PAHs, with seven being known carcinogens [1]. It is recognized that an increase in the relative amount of two to four ring compounds, such as naphthalene, fluoranthene, and phenanthrene, is usually a good indication of the presence of petrogenic hydrocarbons [1]. Larger PAHs such as the 5 and 6-ringed compounds are indicative or pyrogenic sources [3].

The reserves of oil sands bitumen in Northern Alberta, Canada, are estimated at 1.7 trillion barrels, with 173 billion estimated to be economically recoverable. Oil exploration in this region has been intensified over the past 20 years, with production increasing from 100,000 barrels per day to about 1.5 million barrels per day currently [2]. Close monitoring of PAH concentrations in soils and sediment has become critical, and large scale surveillance is being implemented by government agencies. The characterization and knowledge of PAH concentrations in soil and sediments can be instrumental in tracing an oil spill source and enabling remediation efforts. A rapid, sensitive, and robust analytical method for the determination the PAH concentrations in soil is urgently needed [2].

Traditional sample preparation techniques for the determination of PAHs in soil are time consuming and generally require large volumes of toxic solvents, together with multi-step extraction and silica gel or Florisil column clean-up procedures. To address these issues, and as an alternative to the classic Soxhlet solvent extraction methods, various techniques have been developed and used in the analysis of PAHs from soil. Alternative processing includes pressurized liquid extraction or accelerated solvent extraction (PLE or ASE), ultrasonic extraction, supercritical fluid extraction (SFE), and microwave-assisted extraction (MAE) [4–6]. An automated Soxhlet method has recently been developed with corresponding reduction in soil extraction time [7,8]. Despite intensive method development in this area, some of the referenced techniques suffer one or several shortcomings, including low recovery, expensive initial

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investment, frequent equipment malfunction, and lack of robustness or ruggedness. Very recently, a new promising approach of "microextraction" has emerged using MAE combined with solvent bar [9]. While this approach is both "green" and effective, wide application of this method remains to be seen. An elegant approach to the issue would be to take advantage of the modern instrument's enhanced capability of handling less processed sample extracts and use a "dilute and shoot" approach. Perhaps more importantly, simplified sample processing improves method ruggedness, which is critical for routine analysis.

Presently the two most frequently employed techniques to determine PAHs are HPLC with fluorescence, UV, or diode array detection [10,11] and GC with MS detection [1,7,8,10]. The HPLC based methods are usually fast in comparison to the GC/MS methods; however, the disadvantages of the HPLC method are heavy dependence on chromatographic retention time for compound identification and the HPLC methods are typically an order of magnitude lower in sensitivity than GC/MS [12]. In complex matrices, such as soil extract, peak identification based solely on retention time is subject to interference from other components, making trace level PAH contamination difficult to characterize. For this reason, over 15 years the GC/MS technique has become established as the accepted method for PAH determination in the environment [7,8]. Despite numerous improvements to single quadrupole MS instrumentation however, performance cannot match the sensitivity and specificity offered by triple quadrupole MS. As a consequence, an increasing number of peer reviewed publications have applied GC/MS/MS techniques to PAH analysis. However, due to the unique structure stability of the PAH compounds, the traditional Multiple Reaction Monitoring (MRM) approach has been hampered by generally weak fragmentation ion responses for this group of compounds [13–15]. Considering the well-established GC/MS single quadrupole method, the application of the triple quadrupole presently does not provide adequate improvement in sensitivity and specificity to initiate a change from proven procedures. In this regard we challenged this conclusion and successfully applied GC/MS/MS techniques to PAH analysis.

In this paper, we present a rapid analytical method for the analysis of PAHs in soil and sediments, based on a one step, low volume solvent extraction followed by GC/MS/MS in pseudo MRM mode. Long extraction time, large solvent volume consumption, and extensive silica gel column clean-up were eliminated. This was made feasible by the increased sensitivity and specificity achieved by pseudo MRM mode GC/MS/MS. Compelling results will be presented to support the favoring of this pseudo MRM mode GC/MS/MS over that of single quadrupole procedures, even for difficult-to-fragment compounds like PAHs. The present method was validated and applied successfully during an inter-lab proficiency study organized by The Canadian Association for Laboratory Accreditation Inc. (CALA).

2. Material and method

2.1. Reagents and standards

The 18 PAHs analyzed in this study were Acenaphthene (ACE), Acenaphthylene (ACY), Anthracene (ANT), Benzo(a)anthracene (BAN), Benzo(a)pyrene (BAP), Benzo(e)pyrene (BEP), Benzo(b) fluoranthene (BBF), Benzo(g,h,i)perylene (BGP), Benzo(k) fluoranthene (BKF), Chrysene (CRY), Dibenz(a,h)anthracene (DBA), Fluoranthene (FLA), Fluorene (FLU), Indeno(1,2,3-cd)pyrene (IND), Naphthalene (NAP), Perylene (PER), Phenanthrene (PHE) and Pyrene (PYR). A certified standard solution of the 18 PAHs (2000 μg/mL each) was provided by SPEX CertiPrep (Metuchen, NJ). This solution was stored at -20 ± 10 °C in amber glass and had a shelf life of 12 months. An internal standard solution of Naphthalene-d8, Acenaphthene-d10, Phenanthrene-d10, and Perylene-d12 was purchased from Supelco (Oakville, Ontario). This internal standard was employed both in the preparation of calibration standards and in fortifying soil samples for spike recovery.

Calibration standards were prepared in dichloromethane by serial dilution of primary standard to provide final concentrations of 10, 20, 40, 100, 500, 1000, 1500 and 2000 ng/mL. Internal standard at a final concentration of 200 ng/mL was added to all calibration standards.

Disposable centrifuge filter tubes (15 and 50 mL, Polypropylene/Polyethersulfone) were supplied by Pall Corporation (Port Washington, NY). Disposable 50 mL polypropylene centrifuge tubes were purchased from Sarstedt (Numbrecht, Germany). Florisil® adsorbent (60–100 mesh) was from Fisher Scientific (Fairlawn, NJ. USA). OmniSolv solvents dichloromethane (DCM), acetone (ACE), hexane, isopropanol (IPA), acetonitrile (ACN), pesticide grade, were purchased from EM Science (Gibbstown, NJ. USA).

2.2. Sample extraction and clean up

Aliquots of 10 ±0.1 g of air dried free flow homogeneous soil sample were weighed and placed into a 50 mL polypropylene centrifuge tube with screw caps. To the sample, 200 μL of 20 ppm internal standard mixture were added, followed by 5 g of sodium sulphate (pre-dried at 350 °C). The mixture was then hand-shaken to mix sodium sulphate with the soil sample, with occasional spatula use to break any soil lumps to ensure homogeneity. After mixing, 15 mL of dichloromethane was added and the mixture was vortexed briefly. The slurry was further shaken for 10 min at room temperature using a mechanical wrist action shaker. The sample was centrifuged at 5000 rpm (4696 *g*) for 5 min. The supernatant was decanted and retained in a clean 50 mL polypropylene centrifuge tube. The remaining pellet was subjected to a second extraction in 5 mL dichloromethane (breaking up the pellet "cake" with a spatula if necessary), employing only a 5 min shaking time. Supernatant from both extractions were pooled and the volume adjusted to 20 mL with dichloromethane.

An aliquot of the 20 mL extract was transferred to a 15 mL centrifuge filter tube with 0.2 μm filter device. Following centrifugation for 5 min at 5000 rpm (4696 *g*), the filtrate extract was ready for GC/MS/MS analysis. Refer to Fig. 1 for a flowchart of sample extraction steps. For soils contaminated with lube oil, vegetable oil, or animal oil and grease, the filter insert of the centrifuge tube may be pre-packed with approximately 3 *g* of Florisil to improve clean up. These materials may lower analyte recovery and the inclusion of an isotope dilution technique may be required to compensate (Supplementary materials).

2.3. GC-MS analysis

A gas chromatograph (GC) HP 7890A from Agilent Technologies (Palo Alto, CA., USA) equipped with an Agilent 7693B automatic liquid sampler with 10 μL syringe was used for the separation of PAHs. Analysis employed a 1 μL sample injection in pulsed splitless mode (pulsed pressure at 50 psi with the split valve closed for 1 min). All analytes were separated on a Restek Rtx-5MS with Integra-guard column (30 m x 0.25 mm id, 0.25 μm). A 4 mm i.d. single tapered, deactivated inlet liner with glass wool at the bottom (Agilent Technologies) was installed into the injector. The oven temperature program was as follows: initial temperature at 50 °C (hold 2 min), then 6 °C/min to 310 °C, hold for 20 min. The total run time was