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DETERMINATION OF POLYCYCLIC AROMATIC HYDROCARBONS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY USING SELECTED ION MONITORING

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Abstract: *Polycyclic aromatic hydrocarbons and their alkylated homologues are quantitatively determined using a gas chromatography/mass spectrometry by selected ion monitoring mode.*

Keywords: *PAHs, GC/MS, SIM, RRF*

INTRODUCTION

Polynuclear aromatic hydrocarbons (PAHs) are important environmental pollutants, for many of them are known or suspect to be carcinogens. In environmental studies, the extent of PAH contamination as a group is often quantified by the concentrations of 16 of the representative PAH species, which are included in the list of priority pollutants as defined by USEPA [1]. Many analytical techniques have been developed in the past years for the determination of these 16 PAH species, and among them two of the most widely practiced ones are HPLC-Fluorescence [2] and GC/MS [3]. HPLC with fluorescence detection (HPLC-FLD) cannot be used for the detailed analysis of individual alkylated PAHs. Gas chromatography with mass spectrometry (GC-MS) is presently the preferred analytical technique for the analysis of both parent and alkylated PAHs [4]. As is often the case in environmental analysis, effective sample preparation and cleanup holds the key of success for the analysis of trace PAHs.

A gas chromatograph/mass spectrometer (GC/MS) in selected ion mode (SIM) coupled to a capillary column is used to resolve, detect and quantify polycyclic aromatic hydrocarbons (PAH) in solids at parts per billion levels. Samples are injected into a temperature-programmed GC/MS, operated in split-free mode. The capillary column is a DB-5MS (30 m x 0.25 mm ID and 0.25 mm film thickness). The mass spectrometer is capable of scanning from 50 to 500 AMU every second or less and uses 70 electron volts energy in electron impact ionization mode. The data acquisition system continuously acquires and stores all data analyses [5-6].

APPARATUS AND MATERIALS

Equipment

Gas chromatograph, split/split-free injection port and electronic pressure control. Autosampler CombiPal, capable of making 1 µL injections.

Capillary column, Agilent Technologies DB-5MS (30 m x 0.25 mm ID and 0.25 mm film thickness).

Mass spectrometer, capable of scanning from 50 to 500 AMU, utilizing 70 electron volts of energy in impact ionization mode. Data acquisition system, ThermoElectron-Finnigan Technologies Xcalibur, capable of continuous acquisition and storage of all data during analysis.

Micropipettes, calibrated, 1% accuracy, disposable tips.

REAGENTS AND STANDARDS

Dichloromethane (pesticide grade), Helium (99.999% purity).

Internal and Surrogate Standard Solution

The standard solutions is made from aliquots of mixture (Z-014J-PAK; M-525—SS-PAK; M-8310-SS-PAK, AccuStandard, Inc., USA) or pure compounds and diluted with dichloromethane to a final concentration of 0.25 mg/mL. The standards solution includes naphtalene-d8, acenaphthene-d10, phenantrene-d10, pyrene –d10, crysene-d12 and perylene-d12. The internal standard compounds are resolved from, but elute in close proximity to the analytes of interest. The internal standard solution is added to all samples and quality control samples just prior to instrument analysis. Internal standards are used to calculate relative response factors and specific analyte concentrations based on retention time.

MATRIX SPIKING SOLUTION

Certified solutions containing 2 to 6-ring PAH compounds are purchased from commercial vendors (Benz(a)pyrene, Chrysene, 1-Methylnaphthalene, 2-Methyl-naphthalene, Phenanthrene, Pyrene; Cat.M-610-MS-PAK, AccuStandard, Inc., USA) and diluted with dichloromethane to prepare the matrix spiking solution. The matrix spiking solution is diluted and is added to all matrix spike samples.

CALIBRATION SOLUTION

Calibrations solutions (16EPA PAHs and their 34 individual Alkyl PAHs components, AccuStandard, Inc. or Sigma-Aldrich)) are prepared at 5 concentrations ranging from approximately 0.05 to 1 μg/mL (see Table 1) by diluting commercially available certified solutions containing analytes of interest.

RETENTION INDEX SOLUTIONS

The mid-level calibration standard, (containing analytes at approximately 0.50 μg/mL), is used as a retention index solution to determine the retention times of unsubstituted compounds and certain substituted compounds. Individual alkyl standards are used as a retention index solution for the determination of retention times for the remaining alkyl homologues. The retention index solutions are also used to evaluate instrument drift over time.

Quantitative Determination of PAHs by GC/MS-SIM.

Mass Spectrometer Tuning

Prior to calibration, the MS is auto-tuned to perfluorotributylamine (PFTBA) using criteria established by the instrument manufacturer.

Initial Calibration

Prepare calibration standards at a minimum of seven concentration levels for each parameter (Naphthalene, 2-Methyl-naphthalene, 1,3-Dimethylnaphthalene, Acenaphthylene, Acenaphthene, Fluorene, Dibenzothiophene, Phenanthrene, Anthracene, 4-Methyldibenzothiophene, 1-Methylphenan-threne, 3,6-Dimethylphenanthrene, Fluoranthene, Pyrene, 2-Methylfluoranthene, 1-Methylpyrene, Benz[a]Anthracene, Chrysene, 9-Methylbenz[a]Anthracene, 6,8-Dimethylbenz[a]Anthracene, Benzo[b]fluo-ranthene, Benzo[k]fluoranthene, Benzo[a]Pyrene, Perylene, 9-Methylbenzo-[a]pyrene, 7,10-Dimethylbenzo[a]pyrene, Indeno(1,2,3-cd)pyrene, Benz[g,h,i]perylene, Dibenz[a,h]Anthracene) of interest by adding volumes of one or more stock standards to a volumetric flask and diluting to volume with dichloromethane. The following calibration levels are used 0.010, 0.020, 0.050, 0.100, 0.200, 0.500 and 1.000 μg/L for the PAH components. A 7-point relative response factor (RRF) calibration curve is established for

analytes of interest prior to the analysis of samples and quality control samples.

A RRF is determined, for each analyte, for each calibration level using the following equation 1:

$$RRF = \frac{\text{Astd} \times \text{Amount(IS)}}{\text{Ais} \times \text{Amount(S)}} \quad (1)$$

Where:
Astd – peak area of the standard;
Amount(S) – amount of standard, ng;
Amount(IS) – amount of internal standard added to the sample and standard solutions, ng:
Ais – peak area of the internal standard.

Table 1. Quantitation Ion and RRF for target analytes.

Analyte	Quantitation Ion, m/z	Reference to Internal Standard and Surrogate	RRF
Naphthalene	128	Naphthalene-d8	1.22
C1-Naphthalenes	142	Naphthalene-d8	1.36
C2-Naphthalenes	156	Acenaphthene-d10	1.34
C3-Naphthalenes	170	Acenaphthene-d10	1.22
C4-Naphthalenes	184	Acenaphthene-d10	1.22
Acenaphthylene	152	Acenaphthene-d10	1.61
Acenaphthene	153	Acenaphthene-d10	1.15
Fluorene	166	Acenaphthene-d10	1.28
Dibenzothiophene	184	Phenanthrene-d10	1.18
C1-Dibenzothiophenes	198	Phenanthrene-d10	0.86
C2-Dibenzothiophenes	212	Phenanthrene-d10	1.18
C3-Dibenzothiophenes	226	Phenanthrene-d10	1.18
Phenanthrene	178	Phenanthrene-d10	1.21
Anthracene	178	Phenanthrene-d10	1.12
C1-178 PAHs	192	Phenanthrene-d10	0.63
C2-178 PAHs	206	Phenanthrene-d10	0.95
C3-178 PAHs	220	Phenanthrene-d10	1.21
Fluoranthene	202	Pyrene-d10	1.04
Pyrene	202	Pyrene-d10	1.14
C1-202 PAHs	216	Pyrene-d10	0.68
C2--202 PAHs	230	Pyrene-d10	1.14
C3--202 PAHs	244	Pyrene-d10	1.14
Benz[a]anthracene	228	Chrysene-d12	0.99
Chrysene	228	Chrysene-d12	1.33
C1-228 PAHs	242	Chrysene-d12	1.16
C2-228 PAHs	256	Chrysene-d12	1.16
Benzo[b]fluoranthene	252	Perylene-d12	1.53
Benzo[k]fluoranthene	252	Perylene-d12	1.65
Benzo[a]Pyrene	252	Perylene-d12	1.32
Perylene	252	Perylene-d12	1.08
C1-252 PAHs	266	Perylene-d12	1.39
C2-252 PAHs	280	Perylene-d12	1.39
Indeno(1,2,3-cd)pyrene	276	Perylene-d12	1.26
Benz[g,h,i]perylene	276	Perylene-d12	1.63
C1-276 PAHs	290	Perylene-d12	1.45
C2-276 PAHs	304	Perylene-d12	1.45

Dibenz[a,h]Anthracene	278	Perylene-d12	1.56

The response factors determined for each calibration level are averaged to produce a mean relative response factor (RRFi) for each analyte (Table 1). The percent relative standard deviation (%RSD) for the 7 response factors must be less than or equal to 25%, for each analyte.

CONTINUING CALIBRATION

A mid-level calibration standard is analyzed at the beginning and end of each analytical set or every 20 samples (whichever is more frequent). The daily relative response factor for each compound is compared to the mean relative response factor from the initial calibration curve and the average relative percent difference (RPD) of all analytes must be less than 25%. If the calibration check does not meet this criterion then the initial seven point calibration is repeated.

GC/MS-SIM ANALYSIS

The initial calibration of the GC/MS must meet the previously described criteria prior to sample analysis. Samples are analyzed in analytical sets that consist of standards, samples and quality control samples. Quality control samples are method blanks, laboratory duplicates, blank spikes, matrix spikes and standard reference materials. The type and number of quality control samples depend upon client requests and material availability.

Thermo-Electron GC/MS Trace DSQ System equipped with a CombiPal Auto Sampler was used for analysis. Chromatographic separation of 2-6 ring PAHs was accomplished on a DB-5MS capillary column (30 m×0.32 mm I.D., 0.25 mm film thickness). Helium was the carrier gas and a flow-rate of 1.2 mL/min was used for column elution. Sample injection was carried out in the splitless mode with an injection volume of 1 μL. The GC oven temperature was programmed first from 40ºC (hold 1 min), 40ºC to 120ºC at a rate of 15ºC/min, then to 256ºC at a rate of 6º/min (hold 5.0 min), and then to 300ºC at a rate of 6º/min finally held constant for 5 min. The temperatures of the injection port and the interface to the MS system were set at 300ºC and 300ºC, respectively. Peak quantification was carried out in Selected Ion Monitoring (SIM) mode. MS Ion source temperature at 250ºC. Software – Thermo-Electron-Finnegan Technologies Xcalibur 1.4SR1, capable of continuous acquisition and storage of all data during analysis. For identifications of components used 4 segments (in the each segments present 12 ions), for each segments scan time equal to 1.39s and dwell time 0.1 sec per ion.

The effluent from the GC capillary column is routed directly into the ion source of the MS. The MS is operated in the selected ion monitoring mode (SIM) using appropriate windows to include the quantitation and confirmation masses for the PAHs listed in Table 1.

ANALYTE IDENTIFICATION

The extracted ion current profiles of the primary m/z and the confirmatory ion for each analyte must meet the following criteria:

- The characteristic masses of each analyte of interest must be in the same scan or within one scan of each other. The retention time must fall within ±5 seconds of the retention time of the authentic compound or alkyl homologue grouping determined by the analysis of the daily calibration check.
- The alkylated PAH homologue groupings (e.g. C4-naphthalene) appear as a group of

isomers. The pattern of each group and the retention time window for the group is established by the analysis of a reference oil standard. Each group of alkylated homologues is integrated in its entirety and the total area response is used to determine the concentration of the entire group.

- The relative peak areas of the primary mass ion, compared to the confirmation or secondary mass ion, must fall within ±30 percent of the relative intensities of these masses in a reference mass spectrum (Table 1). The reference mass spectrum is obtained from the continuing calibration solution or the reference oil standard for the parent compounds and alkylated homologues, respectively. In some instances, a compound that does not meet secondary ion confirmation criteria may still be determined to be present in a sample after close inspection of the data by a qualified mass spectrometrist.

QUANTITATION CALCULATIONS

Sample analyte concentrations are calculated based on the concentration and response of the internal standard compounds (Table 1). The equations 1 are used to calculate the RRF of each analyte relative to the concentration and area of the internal standard in the initial calibration. Response factors for same alkyl homologues are presumed equal to the average response factor of the respective unsubstituted (parent) compound.

The concentration of PAHs components in the wet soil sample, C_w is calculated from the following equation 2:

$$Cw = \frac{\text{As} \times \text{Amount(IS)} \times \text{DF}}{\text{Ais} \times \text{RRF} \times \text{Msample}} \qquad (2)$$

Where:
Cw - Concentration of compound of interest in the wet sample, ng/g;
As – peak area of the compound of interest;
Ais – peak area of the corresponding internal standard;
Amount(IS) – the amount of internal standard added to the sample, blank, calibration satandard solution and QC samples, ng;
DF – dilution factor;
RRF – the response factor; and
Msamp – mass of wet sample taken for extraction, g.
To convert the result to a dry matter basis, the following equation-3 is used:

$$Cd = Cw \times \frac{100}{DM} \qquad (3)$$

Where:
Cd – concentration of compound of interest in the dry sample *(*ng/g for PAHs compounds);
Cw - concentration of compound of interest in the wet sample (ng/g for PAHs compounds);
DM – the percent dried weight of the sample.

The concentration of PAHs components in the water sample, C is calculated from the following equation 4:

$$C = \frac{\text{As} \times \text{Amount(IS)} \times \text{DF}}{\text{Ais} \times \text{RRF} \times \text{Vsample}} \qquad (4)$$

Where:
C- Concentration of compound of interest in the water sample, ng/L;
Vsample-volume of sample, L.

QUALITY CONTROL

The initial calibration must pass established criteria before sample analysis can begin. All continuing calibration checks must pass established criteria for analysis to continue. An acceptable method blank analysis may not contain more than two target analytes at concentrations three times greater than the MDL. This criterion does not apply if the analytes detected in the method blank are not detected in the associated samples or if the sample analyte concentrations are 10 times greater than the blank analyte concentrations.

If the method blank exceeds these criteria then the analytical procedure is not in control. The source of the contamination must be investigated, and corrective measures taken and documented before further sample analysis occur.

All samples and quality control samples are spiked with deuterated PAH standards compounds prior to extraction. The deuterated compounds evaluate sample matrix effects and analytical efficiencies associated with sample preparation and analysis. The recovery of deuterated surrogate compounds is monitored in each sample and quality control sample. The laboratory will take corrective action if the average surrogate recovery, with the exception of perylene-d12, is less than 40% or greater than 140%. The following corrective action will be taken if the above criteria are not met:

Calibration checks solution. If relative percent difference (RPD) of any analyte within a calibration check standard varies from the predicted response by more than 25%, a new calibration curve must be prepared for that analyte -per 20 samples

Laboratory Blank -per 20 samples. The criteria less than MDL or less than 30 % of minimal values of sample.

Quality Control Samples (Certified Reference Material (CRM), Laboratory Fortified Blank (LFB) or Matrix Spike (MS), depend from lab QC program)- at least per 20 samples. The recovery criteria equal to 40%-140 %.

Sample duplicates (laboratory or field, depend from project)- at least per 20 samples. The % RPD of duplicate samples must not exceed 50%.

Accuracy of the applied method was regularly verified by participation in the WEPALs quarterly SETOC and LGC ring tests.

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İON SEÇİMİ MONİTORİNQİ ÜSULUNDAN İSTİFADƏ ETMƏKLƏ POLİTSİKLİK AROMATİK KARBOHİDROGENLƏRİN GAZ XROMATOGRAFİYA / KÜTLƏ-SPEKTROMETRİK TƏYİNİ

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Məqalə politsiklik aromatic karbohidrogenlər və onların alkilli birləşmələrinin gas xromatografiya / kütlə-spektrometriya cihazında ion seçimi monitorinqi üsulu ilə təyinindən bəhs edir.
Açar sözlər: *PAHs, GC/MS, SIM, RRF*

ГАЗОХРОМАТО-МАСС-СПЕКТРОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ ПОЛИЦИКЛИЧЕСКИХ АРОМАТИЧЕСКИХ УГЛЕВОДОРОДОВ В РЕЖИМЕ СЕЛЕКТИВНОГО МОНИТОРИНГА ИОНОВ

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Статья посвящена газохромато/масс-спектрометрическому определению полициклических ароматических углеводородов с использованием метода селективного мониторинга ионов.
Ключевые слова: *PAHs, GC/MS, SIM, RRF.*

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