



GC/MS ANALYSIS

OF

PETROLEUM HYDROCARBONS

IN WATER

BY EQUILIBRIUM HEADSPACE



Standard Operating Procedure

1.1.

SOP #13 Rev. # 2

1.0 Introduction

This Hapsite GC/MS method is used to determine Petroleum Hydrocarbons in water.

2.0 Summary of the Method

This method is designed for the rapid determination of Petroleum Hydrocarbons in the field. It has been developed to produce definitive results in less than an hour.

Samples are collected in 45ml VOA vials. A 50ml syringe is used to take 20ml of sample into a separate 40ml screw cap VOA vial. The vial is then sealed with a PTFE coated septum. Internal standards and surrogates are added to the sample prior to equilibration. The vials are then placed in a heated chamber, maintained at 60°C, and allowed to equilibrate for 20 minutes. The sample is transferred using a nitrogen carrier gas, displacing the gas phase in the vial through a heated transfer line into a gas sampling loop. The contents of the sample loop are then injected onto the GC column. Detection of the analytes is performed using the ion chromatogram produced by the mass spectrometer.

3.0 Safety

Safety is of utmost importance during all projects. On-site safety procedures established by the client will be adhered to at all time. It is the responsibility of KDA personnel to ensure they are aware of all safety procedures and hazards they may encounter on-site.

Proper personal protective equipment (PPE) including safety glasses, hard hats and steel-toed shoes will be worn when working directly at the sampling location.

In addition to site specific and general field safety procedures, KDA personnel must adhere to standard safe laboratory practices. This includes:

- Maintenance and availability of Material Safety Data Sheets (MSDS)
- Use of appropriate PPE during the handling and preparation of standards
- Safe high pressure cylinder handling practices

Note: All hazardous, neat materials stored on-site must have a copy of the MSDS maintained on-site as well. This does not include working standards and standard mixtures.



4.0 Equipment and Supplies

4.1 Instrumentation

Inficon HAPSITE portable GC/MS
Supelco SPB 1, 30m x .32mmid x 1.0 μ film column
HAPSITE Headspace sampling accessory
Peripherals (Computer, Printer, Consumables, etc.)

4.2 Materials

Syringes: - 50ml, Teflon Luer Lock gastight
 - 10ul, 25ul, 100ul gastight
Vials: - 40ml with PTFE septa
 - 1ml micro-reaction with Mini-inert valves
 - 2ml with PTFE septa

4.3 Gases

Carrier: Nitrogen 99.999% purity (for portable mode Inficon # 930-430)
Mass Calibration: Internal Standard 1 Inficon # 930-431 (50ppmv) Bromopentafluorobenzene,
(100ppmv) 1,3,5-Tris (Trifluoromethylbenzene)

5.0 Reagents and Standards

5.1 Reagents - Methanol - HPLC Quality - Organic Free Water

5.2 Standards

- Internal Standards/Surrogates (500ug/ml)
 - Pentafluorobenzene, 4-Bromofluorobenzene,
1,4-Difluorobenzene-d₄, Toluene-d₈, Bromofluorobenzene
Chlorobenzene-d₅

Note - Individual compound quantification is performed on each analysis. Therefore, internal standards are present for reference. For TPHg, the internal standards are subtracted from the total chromatogram but not used for quantification.

- Stock standards are purchased from a commercial vendor.



6.0 Instrument Parameters

6.1 GC Conditions

Column Temp.	60° C Initial
Head Pressure	104 pa
Inlet Temp.	60° C
Probe Temp.	40° C
Valve Temp.	60° C
Run Time	15 Min.
Equilibration Temp.	60° C

6.2 MS Conditions

Scans/Sec.	1.04 scans/sec.
Getter PumpTemp.	400 - 480° C
Scan Range	42 - 300 amu

7.0 QA/QC Procedures

7.1 Initial Calibration

The initial calibration will contain a minimum of 3 levels. The low level must be no more than 5 times the reporting limit. The highest level should encompass the linear range of the instrument or the highest concentration of the samples expected. The typical calibration range is from 5ug/L to 5000ug/L. Acceptance criteria for the initial calibration are 30% relative standard deviation (%RSD).

Corrective action for the initial calibration is to investigate the outlying level and reanalyze that level. If the problem is not corrected, it may be necessary to remake the standard or correct the tune with the instrument and reanalyze all levels.

7.2 Continuing Calibration Verification

The continuing calibration standard is analyzed each day before the analysis of any samples. The acceptance criteria for the Continuing Calibration are $\pm 30\%$ Difference compared to the Initial Calibration.

Corrective action for the Continuing Calibration is to reanalyze the standard. If it continues not meet criteria, remake the standard from the stock and reanalyze. If criteria are still not met, repeat the Initial Calibration.



7.3 Method Blank

The method blank should be analyzed after the continuing calibration and before any samples. A blank should also be analyzed after any sample with concentrations exceeding the calibration range by 10%. The blank acceptance criteria are no detections above the reporting limit.

Corrective action for the method blank is to reanalyze the blank. If the system is still not clean, take actions to remove the contaminants and reanalyze the blank. The blank must be clean before proceeding unless agreed upon with the client.

7.4 Duplicates

Duplicate analyses should be performed on a frequency of 30% of the total samples. The sample chosen to duplicate should contain concentrations of targets if possible. The acceptance criteria are 30% relative percent difference (% RPD).

Corrective action for the duplicate is to reanalyze the sample. If criteria are still not met, results must be flagged.

7.5 GC/MS Manufacturer Tune Verification

The Hapsite GC/MS tune must be verified every 12 hours or at the beginning of each day. The Hapsite automatically tunes every 12 hours to manufacturer specifications.

7.6 Internal Standards

Internal standards are injected with every sample. Internal standards will be referenced in the calibration, and used to calculate concentrations. The areas for these compounds will be determined from the daily calibration verification. Acceptance criteria for these are 70 to 130% Recovery.

8.0 Reporting Limits

The reporting limits will be defined as half the concentration of the low point of the three point calibration. This will be the lowest point reported. Sample concentrations below the reporting limit, but above the detection limit will not be reported.



11.0 Procedure

- 11.1 Sample preparation - Fill 40ml VOA vial with 20ml of sample to be analyzed. Cap the vial with a PTFE coated septa and cap insert. Inject 2ul of 500ug/ml of internal standard/surrogate solution through the needle port in the septum cap. To minimize loss of volatiles while filling the vial, it is important to minimize sample turbulence and the length of time the sample is exposed to atmosphere.

When injecting the sample with the standard, tilt the vial so that the standard is injected into the water.

- 11.2 Sample Equilibration - Place the samples to be analyzed into the Headspace sampler. Allow each sample to equilibrate for a minimum of 20 minutes.
- 11.3 Sampling - Pierce the septum of the sample to be analyzed with the Headspace needle assembly. Press the start run button.

12.0 Equations

12.1 Relative % Difference

$$\% RPD = \frac{Samp_1 - Samp_2}{\frac{(Samp_1 + Samp_2)}{2}} \times 100$$

12.2 Relative Standard Deviation

$$\% RSD = \frac{STDev}{Avg} \times 100$$

12.3 Percent Difference

$$\% D = \frac{AvgRRF - DailyRRF}{AvgRRF} \times 100$$

12.4 Method Detection Limit

$$MDL = STDev \times 3.14$$



14.0 References

1. U.S. EPA Method 3810 Headspace
2. U.S. EPA Method 5021 Volatile Organic Compounds in Soil and other solid Matrices Using Equilibrium Headspace Analysis
3. U. S. EPA Method 8260B
4. Determination of Gaseous Organic Compounds by Direct Interface Gas Chromatography-Mass Spectrometry - May 28, 1997 Laura L. Kiner Ph.D. & James W. Peeler, Emission Monitoring Inc.
5. Quantitative Trace Analysis of VOC's in Air, Water and Soil by Equilibrium Headspace Gas Chromatography, Bruno Kolb, Perkin-Elmer Corp.