Headspace GC/MS Performance Monitoring and Maintenance

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Headspace GC/MS Performance Monitoring and Maintenance

1 Introduction

This document addresses the performance monitoring and maintenance of the Agilent GC/MS System with a headspace autosampler. The system consists of a Gas Chromatograph (GC), headspace autosampler, and a single quadrupole Mass Selective Detector (MSD) Mass Spectrometer (MS). The system may also be equipped with additional detectors, such as a Flame Ionization Detector (FID) or Nitrogen Phosphorus Detector (NPD). A headspace autosampler is a device used to sample the gas phase volatile analytes within a sealed vial. This sampling is transferred to a GC inlet and onto a column where the components are separated and sent to a detector. Definitions and guidelines are outlined in IOSS-701.

2 Scope

This document applies to personnel using the associated instrument(s)/equipment in the following disciplines/subdisciplines: General Chemistry, Explosives Chemistry, Fire Debris, and Seized Drugs.

3 Equipment

- Instrumentation
  - Agilent 7890 or 8890 Gas Chromatograph, Agilent 5975 or 5977 MSD with EI Source, FID (if equipped), NPD (if equipped), and Chemstation/MassHunter Software (or equivalent)
  - Gerstel MPS2, CTC PAL, or MPS Robotic automated sampler, accessories, and Gerstel Master/Gerstel Maestro Software (or equivalent)
- Materials
  - Agilent DB-624 GC column, 30 m, 0.25 mm i.d., 1.4 µm film (or equivalent) (MSD)
  - Restek RT-QS-Bond GC column, 30 m, 0.32 mm i.d., 10 µm film (or equivalent) (NPD)
  - Restek RTX-BAC-2 GC column, 30 m, 0.32 mm i.d., 1.2 µm film (or equivalent) (FID)
  - Helium, 99.99% (high purity)
  - Nitrogen (high purity)
  - Hydrogen gas (high purity)
  - Compressed air
  - Perfluorotributylamine (PFTBA, FC-43) (Agilent or equivalent)

Redacted

- Deionized Water, 18 MΩ·cm (Milli-Q or equivalent)
- Potassium cyanide (Reagent Grade)
- Sodium hydroxide (Reagent Grade)
- ~5 N (20% w/v) Sodium Hydroxide (NaOH)
  To a 100-mL beaker or Erlenmeyer flask, add 60 mL water and 20 g sodium hydroxide. Mix well to dissolve and bring to volume with deionized water. Store in a Nalgene container at room temperature. Stable for 1 year.
- Acetonitrile (HPLC Grade)
- 5 N Sulfuric Acid (H_2SO_4) (Reagent Grade)
- Low-bleed 11 mm injection port septa (Agilent or equivalent)
- 4 mm split-splitless tapered injection port liners and o-rings (Restek or equivalent)
- 2.5 mL headspace and 1 mL liquid syringes (Gerstel or equivalent)
- General laboratory supplies

4 STANDARDS AND CONTROLS

The testmix is used to assess daily operating performance and continued integrity of the system. It will be analyzed and evaluated prior to the analysis of evidence.

- Testmix (General Chemistry) for HS-MSD
  Refer to the analyte-specific procedure for unique samples (e.g., GHB, cyanide) for the preparation of the positive control, which will be used as the testmix. For general volatiles analysis, prepare the testmix by adding 500 mL of deionized water into a 1000-mL volumetric flask. Add 0.1 mL each of ethanol and isopropanol. Add 0.01 mL of chloroform. Bring to the mark with deionized water. Store refrigerated in glass or plastic. Stable for at least one year, verified with each use. Transfer 0.5 mL of the solution into a 10-mL headspace vial. Alternatively, transfer 1.0 mL of the solution into a 20-mL headspace vial.

- Testmix (Explosives Chemistry, Fire Debris) for HS-MSD
  The volatiles test mix is a 0.01% (0.1 µL/mL) solution of Redacted in 18.2 MΩ deionized water. Prepare the testmix by adding 50 mL of deionized water into a 100-mL volumetric flask. Add 0.01 mL each of Redacted Bring to the mark with deionized water. Store refrigerated in a tightly sealed container. Stable for two years. This preparation may be appropriately scaled.

  Refer to the analyte-specific procedure for unique samples, Redacted for the preparation of the positive control, which will be used as the testmix.
  The PFTBA tuning solution is used for tuning the mass spectrometer and verifying mass calibration. It is supplied by the instrument manufacturer and does not expire. It is stored in a glass container attached to the MSD.

- Testmix for HS-NPD

- Cyanide Stock Standard (0.2 mg/mL)
  Prepared by adding 50 mg of potassium cyanide to a 100-mL volumetric flask containing 2 mL of ~5 N NaOH. Dilute to volume with deionized water and mix thoroughly. Store at room temperature in a tightly sealed glass or plastic container. Stable for at least 1 year, verified with each use.

- 0.08% Acetonitrile (v/v) (Internal Standard)
  Add 80 µL acetonitrile to about 90 mL deionized water in a 100-mL volumetric flask. Dilute to volume with deionized water and mix thoroughly. Store at room temperature in a tightly sealed glass or plastic container. Stable for at least one year, verified with each use.

- Aqueous Positive Control (10 µg/mL cyanide)
  Prepared by adding 5 mL of the Cyanide Stock Standard into to a 100-mL volumetric flask. Dilute to volume with deionized water and mix thoroughly. Stable for at least one year, verified with each use.

- Performance Verification Sample
  Measure 0.5 mL of the Aqueous Positive Control (10 µg/mL cyanide) and 25 µL of 0.08% acetonitrile (Internal Standard) into a 10-mL headspace vial and cap. Using a 2.5 cc syringe, inject 0.5 mL of 5 N H_2SO_4 into the vial and thoroughly vortex the sample to uniformly distribute the acid. Wipe any residual H_2SO_4 from the septum and/or cap. Allow the sample to equilibrate at room temperature for 30 minutes.

- Testmix for FID
  Add 500 mL deionized water to a 1000-mL volumetric flask. Add 0.1 mL each methanol, ethanol, isopropanol, and acetone. Bring to the mark with deionized water and mix well. Store refrigerated in glass or plastic. Stable for at least one year, verified with each use.

  Transfer 0.5 mL of the testmix solution to a 10 mL headspace vial. Alternatively, transfer 1.0 mL of the testmix solution to a 20 mL headspace vial. Stable for at least one year, verified with each use.

- PFTBA Tuning Solution (MSD)
  The PFTBA tuning solution is used for tuning the mass spectrometer and verifying mass calibration. It is supplied by the instrument manufacturer and does not expire. It is stored in a glass container attached to the MSD.

5 PROCEDURE

5.1 Daily Checks – HS-MSD

The following steps will be performed daily. Enter the appropriate information in the instrument log.

A. Record the remaining disk space on the hard drive. Verify that the hard disk has at least 100 MB of free disk space. Do not use if less than 100 MB remain.
B. Record the line pressure of the building helium supply (carrier gas). The regulator should read 70 p.s.i. or above. If it cannot maintain this pressure, contact appropriate instrument support personnel. If the instrument is supplied by a gas cylinder, record the tank pressure. Change the tank if less than 100 p.s.i. is remaining.
C. Check the Ion Gauge to ensure that there are no significant leaks in the system. Do not use if the pressure is higher than 6×10^{-5} torr.
D. Perform a tune of the instrument. If Autotune (ATUNE) is selected, the mass spectrometer will tune itself using PFTBA. Evaluate the results using the 'Acceptance Criteria' section. If the results are acceptable, save and print the tune file (ATUNE) when completed.
E. Refer to the analyte-specific technical procedure (e.g., GHB, cyanide, TATP) for the appropriate procedure, instrumental conditions, and acceptance criteria for performing an analysis of the testmix. For general volatiles analysis perform a HS-MSD analysis of the applicable Testmix prior to the analysis of evidence. Open the appropriate testmix instrument method and verify the parameters. Analyze the appropriate testmix and evaluate the results using the 'Acceptance Criteria'.
F. If all requirements are within specification, prepare the documentation as outlined in IOSS-701. If any requirements fail, contact appropriate instrument support personnel.

5.2 Daily Checks – HS-NPD

The following steps will be performed daily. Enter the appropriate information in the instrument log.

A. Record the remaining disk space on the hard drive. Verify that the hard disk has at least 100 MB of free disk space. Do not use if less than 100 MB remain.
B. Record the line pressure of the building nitrogen supply (carrier gas). The regulator should read 50 p.s.i. or above. If it cannot maintain this pressure, contact appropriate instrument support personnel. If the instrument is supplied by a gas cylinder, record the tank pressure. Change the tank if less than 100 p.s.i. is remaining.
C. Ensure that the NPD is operational using the front panel controls of the GC.
D. Ensure that autosampler is injecting into the appropriate GC inlet.
E. Analyze the HS-NPD Performance Verification Sample and evaluate the results using the 'Acceptance Criteria'. Alternatively, refer to the analyte-specific technical procedure for unique samples (e.g., azide) for the appropriate procedure, instrumental conditions, and acceptance criteria for performing an analysis of an applicable positive control.
F. If all requirements are within specification, prepare the documentation as outlined in IOSS-701. If any requirements fail, contact appropriate instrument support personnel.

5.3 Daily Checks – HS-FID

The following steps will be performed daily. Enter the appropriate information in the instrument log.

A. Record the remaining disk space on the hard drive. Verify that the hard disk has at least 100 MB of free disk space. Do not use if less than 100 MB remain.
B. Record the line pressure of the building nitrogen supply (carrier gas). The regulator should read 50 p.s.i. or above. If it cannot maintain this pressure, contact appropriate instrument support personnel. If the instrument is supplied by a gas cylinder, record the tank pressure. Change the tank if less than 100 p.s.i. is remaining.
C. Ensure that the FID flame is lit.
D. Ensure that the autosampler is injecting into the appropriate GC inlet.
E. Analyze the HS-FID Volatiles Testmix and evaluate the results using the 'Acceptance Criteria'.
F. If all requirements are within specification, prepare the documentation as outlined in IOSS-701. If any requirements fail, contact appropriate instrument support personnel.

5.4 As Needed Maintenance/Checks

The following steps are to be performed as needed. Enter the information in the appropriate instrument log to indicate completion. Refer to IOSS-701 for more information on instrument maintenance and documentation.

A. Replace the GC split vent trap(s).
B. Check the overall column performance. Clip the inlet side of the GC column(s) if needed.
C. Check the MSD calibrant level. Fill if needed.
D. Check the MSD filaments and overall MSD performance. Replace blown filaments and clean source if needed.
E. Replace the septum in the GC injection port(s).
F. Replace the liner and o-ring within the GC injection port(s).
G. Replace the gold seal within the GC injection port(s).
H. Check the GC syringe in the autosampler. Replace if needed.
I. Check the water level in the hydrogen generator. Fill with 18 MΩ·cm deionized water if needed.
J. Check the internal bungee cords in the autosampler (if applicable). Replace if needed.
K. Check the FID jet (if applicable). Clean or replace if needed.
L. Check the NPD bead (if applicable). Replace if needed.

6 INSTRUMENTAL CONDITIONS

6.1 HS-MSD (General Chemistry) Testmix Parameters

6.1.1 Headspace Autosampler

Incubation Temperature:	80°C
Incubation Time:	10.0 min
Agitator Speed:	300 rpm
Agitation Timing:	10 sec on, 1 sec off
Syringe Temperature:	90°C
Sample Fill Volume:	1.0 mL
Sample Fill Rate:	1.0 mL/sec
Sample Fill Strokes:	5
Sample Injection Speed:	1.0 mL/sec
Syringe Flush Time:	1.0 min

6.1.2 Gas Chromatograph

Oven	
Initial Temperature:	50°C
Initial Time:	3.0 min
Ramp:	10°C/min
Final Temperature:	250°C
Hold Time:	5.0 min
Run Time:	28.0 min
Equilibration Time:	0 min
Inlet/Injector	
Inlet Temperature:	150°C
Mode:	Split
Split Ratio:	10:1
Flow Mode:	Constant flow
Pressure:	6.5 psi
Carrier Gas:	Helium
Column	
Type:	DB-624
Length:	30 m
Diameter:	0.25 mm
Film Thickness:	1.4 µm

6.1.3 Mass Spectrometer

Ionization Mode:	Electron impact (EI)
Scan Mode:	Full Scan
Scan Range:	27-400 m/z
Relative Voltage:	106 V
Transfer Line Temp:	260°C
Quad Temperature:	250°C
Source Temp:	230°C
Solvent Delay:	1.75 min

6.2 HS-MSD (Explosives Chemistry, Fire Debris) Testmix Parameters

6.2.1 Headspace Autosampler

Incubation Temperature:	80°C
Incubation Time:	5.0 min
Agitator Speed:	300 rpm
Agitation Timing:	10 sec on, 1 sec off
Syringe Temperature:	90°C
Sample Fill Volume:	1.0 mL
Sample Fill Rate:	1.0 mL/sec
Sample Fill Strokes:	5
Sample Injection Speed:	1.0 mL/sec
Syringe Flush Time:	4.0 min

6.2.2 Gas Chromatograph

Oven	
Initial Temperature:	40°C
Initial Time:	4.0 min
Ramp:	10°C/min
Final Temperature:	120°C
Ramp 2:	30°C/min
Final Temperature 2:	250°C
Run Time:	16 min minimum
Equilibration Time:	0.25 min
Inlet/Injector	
Inlet Temperature:	150°C
Mode:	Split
Split Ratio:	10:1
Flow Mode:	Constant flow
Pressure:	5.3 psi
Nominal Initial Flow:	3.7 mL/min
Carrier Gas:	Helium
Column	
Type:	DB-624
Length:	30 m
Diameter:	0.25 mm
Film Thickness:	1.4 µm

6.2.3 Mass Spectrometer

Ionization Mode:	Electron impact (EI)
Scan Mode:	Full Scan
Scan Range:	29-400 m/z
Relative Voltage:	106 V
Transfer Line Temp:	260°C
Quad Temperature:	150°C
Source Temp:	230°C
Solvent Delay:	2.0 min

6.3 HS-NPD Testmix Parameters

6.3.1 Headspace Autosampler

Syringe:	2.5 mL headspace
Syringe Flush Time:	4.0 min
Syringe Temperature:	55°C
Incubation Temperature:	45°C
Incubation Time:	5.0 min
Agitator Speed:	250 rpm
Agitation Timing:	10 sec on, 1 sec off
Sample Fill Volume:	1.0 mL
Sample Fill Rate:	500 µL/sec
Sample Fill Strokes:	5
Sample Injection Speed:	1.0 mL/sec
Injection Penetration:	40 mm
Injection Volume:	250 µL

6.3.2 Gas Chromatograph

Oven	
Initial Temperature:	110°C
Initial Time:	0 min
Ramp:	4°C/min
Final Temperature:	130°C
Hold Time:	5 min
Run Time:	10 min
Equilibration Time:	0.2 min
Inlet/Injector	
Inlet Temperature:	150°C
Mode:	Purged
Flow Mode:	Constant Flow
Carrier Gas:	Nitrogen
Column	
Type:	RT-QS-Bond
Length:	30 m
Diameter:	0.32 mm
Film Thickness:	10 µm

6.3.3 Detector Parameters (NPD)

Temperature:	250°C
Offset:	20
Equilibration Time:	0.01 min
Air Flow:	60 mL/min
Transfer Line Temp:	260°C
Hydrogen Flow:	3.0 mL/min
Electrometer:	ON

6.4 HS-FID Testmix Parameters

6.4.1 Headspace Autosampler

Syringe:	2.5 mL headspace
Syringe Flush Time:	2.0 min
Syringe Temperature:	70°C
Incubation Temperature:	60°C
Incubation Time:	30.0 min
Agitator Speed:	250 rpm
Agitation Timing:	10 sec on, 1 sec off
Sample Fill Volume:	500 µL
Sample Fill Rate:	500 µL/sec
Sample Fill Strokes:	5
Sample Injection Speed:	500 µL/sec

6.4.2 Gas Chromatograph

Oven	
Temperature:	40°C
Isothermal Run Time:	6.0 min
Equilibration Time:	0.2 min
Inlet/Injector	
Inlet Temperature:	200°C
Mode:	Split
Split Ratio:	1:1
Flow Mode:	Constant Pressure
Pressure:	10.2 psi
Carrier Gas:	Helium
Column	
Type:	RTX BAC-2
Length:	30 m
Diameter:	0.32 mm
Film Thickness:	1.2 µm

7 ACCEPTANCE CRITERIA

7.1 MSD Tune

Verify the results of the tune. Compare the results of the tune to previous tune results. Significant voltage increases or changes in the isotope ratios indicate the need to initiate corrective maintenance procedures. The following are typical ATUNE values for the MSD:

A. PFTBA tune:
   - m/z ±0.4 for m/z 69, 219, and 502

B. Peak width:
   - 0.45-0.65

C. Relative abundance:
   - 69 greater than 50%
   - 219 greater than 50%

- 502 greater than 1%
- 18 and 28 (water & nitrogen) each 5% or below

7.2 HS-MSD Testmix

Verify the results of the Testmix.

A. In order for the instrument to be considered in good operating condition, all testmix components should generate well-resolved, Gaussian-shaped peaks with baseline separation
B. A SNR of 3:1 will be the minimum response necessary to consider a response a peak.
C. There should be no significant extraneous peaks in the chromatogram.
D. The retention times of each component should be similar to previous analyses (unless GC maintenance has been performed, such as column clipping or replacement).
E. Check for the correct mass assignments for the mass spectra. In order for the MS to be considered in good operating condition, the correct mass assignments for each of the analytes in the appropriate testmix should be present. The following ions at m/z should be present:

General Chemistry

- ethanol (31, 45, 29)
- isopropanol (45, 43, 29)
- chloroform (47, 83, 85)

Explosives Chemistry, Fire Debris

Redacted

7.3 HS-NPD Testmix

Verify the results of the Testmix. The peaks of both cyanide and acetonitrile (or the alternate positive control) should show good chromatographic fidelity, with reasonable peak shape, width, and resolution. Peak areas should compare favorably to previous analyses of the performance standard. The retention times of each component should be similar to previous analyses (unless GC maintenance has been performed, such as column clipping or replacement).

7.4 HS-FID Testmix

Verify the results of the Testmix. The peaks of all four analytes should show good chromatographic fidelity, with reasonable peak shape, width, and resolution. Peak areas should compare favorably to previous analyses of the performance standard. The retention times of each component should be similar to previous analyses (unless GC maintenance has been performed, such as column clipping or replacement).

8 LIMITATIONS

Only properly trained personnel will perform duties involved in the operation, maintenance, or troubleshooting of this instrument.

9 SAFETY

Many instrument components are held at temperatures of 250°C and higher. Precautions should be taken to prevent the contact of skin with heated surfaces and areas.

10 REVISION HISTORY

Revision	Issued	Changes
09	09/15/2022	Revised to match new format requirements. Section 5- Added annual maintenance and expanded as-needed maintenance.
10	08/01/2024	Section 6.2.2 – Added second oven ramp, adjusted run time, added nominal initial flow. Section 7.2, E – Added isopropanol.
11	02/18/2025	TOC – Removed Toxicology Section 2 – Removed Toxicology Section 5.4 – Moved Yearly Criteria to As Needed, removed section 5.4, renumbered section 5.5 to 5.4. Section 7.2, E – Removed Toxicology