Title: Performance Monitoring Protocol (QA/QC) for GC/MS Systems

A. Introduction

This procedure describes how to maintain, perform, evaluate, and verify instrument performance for acceptable analyses within the Chemistry Unit. It is a combination of work instructions and general protocol. Gas chromatography (GC) and mass spectrometry (MS) instruments must be maintained in such a way as to verify their reproducibility and their reliability. One of the purposes of this procedure is to provide general guidelines for maintenance of gas chromatographs and mass spectrometers. Another purpose is to verify and track reproducibility, quality, accuracy, and reliability of routine instrument operation and data that are generated. Information is available to track instrument performance patterns for troubleshooting purposes. The Agilent systems consist of a gas chromatograph with a single quadrupole mass selective detector (MSD) mass spectrometer, often referred to as a GC/MS. The mass spectrometer has a dedicated electron ionization (EI) source and may be referred to simply as an 'MSD.'

B. Scope

The Chemistry Unit uses analytical instruments to analyze a wide variety of evidence. These instruments must be maintained and evaluated in such a way so that cases can be analyzed in a timely manner and so that scientifically sound data are produced.

All analysts who use the GC/MS instruments within the Chemistry Unit will be responsible for following this procedure. If problems occur with instruments and they can't be resolved in-house then it is the responsibility of analysts to notify a Lead Examiner (or higher) for alternative solutions (i.e., contact service engineer).

C. Principle

Gas chromatograph instruments are essentially comprised of an inlet, a column, and a detector. Mass spectrometers are often referred to as the detector of a GC instrument, hence the MSD term. However, they are also considered separate instruments and thus need specific procedures.

Preventative maintenance involves routine monitoring of performance, adjustment of common parameters, and replacement of consumable items in order to ensure reproducible and uninterrupted operation. Corrective maintenance may be required when poor performance is observed or the instrument fails to operate properly. All performance monitoring protocols are based upon manufacturer's recommendations. Users shall be familiar with the operation of the instrument prior to independent operation.

The maintenance and operating procedures are categorized by how often they shall be performed (Daily, Monthly, and/or As Needed) to ensure the integrity of the system. These terms are approximate time intervals, based on instrument use, and allow for weekends and other periods of

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instrument inactivity. The term 'as needed' refers to maintenance that is to be performed based on system performance or major interruptions in service. If other intervals will be followed, they will be specified in the applicable procedure. The terms 'daily, weekly or monthly' refer to the day, week, or month an instrument is used for casework.

D. **Equipment/Materials/Reagents**

Any materials (such as septa, columns, liners) and all replacement parts should meet the manufacturer's specifications and recommendations for the applicable instrument.

1. General laboratory glassware
2. Gas chromatograph with mass spectral detector (GC/MS)), Agilent (or equivalent)
3. Perfluorotributylamine (PFTBA, FC-43) (Agilent or equivalent)
4. Autosampler – Agilent (or equivalent)
5. GC Column - DB-5(MS), 30 m, 0.25 mm i.d., 0.25 µm film (or equivalent)
6. Carrier Gas - Helium, 99.9% (high purity)
7. Autosample vials – 2 mL GC vials, crimp or screw top, with or without 100-500 µL inserts (or equivalent)
8. Injection port liners (Agilent or equivalent)
9. Injection port septa – standard low-bleed 11 mm or a 'Merlin Microseal' (or equivalent)
10. Syringes – Hamilton 701ASN 10 µL (or equivalent)
11. Hexane (reagent grade or equivalent)
12. Cyclohexane (reagent grade or equivalent)
13. Pentane (reagent grade or equivalent)
14. ASTM 1618 Hydrocarbon Mix (~C8-C20 ; prepared in house or equivalent)

E. **Preparation of Performance Check Solution**

The GC/MS Performance Check Solution is a solution comprised of a homologous series ~C_8-C_{20} n-alkane hydrocarbons in a solvent (e.g., CH_2Cl_2/pentane). This solution should have a concentration of approximately 50 ppm in an appropriate solvent and can be stored at room temperature and, if refrigerated, has a shelf-life of at least three (3) years since its last verification. The Performance Check Solution is used to verify daily operating performance and continued integrity of the GC/MS system. The GC/MS instrument will be evaluated using this performance solution prior to analysis of evidence and is usually done daily.

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The concentrations of analytes within the Performance Check Solution should be:

Analyte	Stock Solution Concentration	Volume of Stock Solution	Volume of Solvent	Final Concentration of Analyte in Mix
C-8 Hydrocarbon	500 µg/mL	1 mL	10 mL	50 µg/mL (50 ppm)
C-10 Hydrocarbon				50 µg/mL (50 ppm)
C-12 Hydrocarbon				50 µg/mL (50 ppm)
C-14 Hydrocarbon				50 µg/mL (50 ppm)
C-16 Hydrocarbon				50 µg/mL (50 ppm)
C-18 Hydrocarbon				50 µg/mL (50 ppm)
C-20 Hydrocarbon				50 µg/mL (50 ppm)

Perflurotributalamine (PFTBA) is a chemical used when the mass spectrometer is tuned. Tuning is the adjustment of parameters (e.g., lens voltages), usually done automatically by the instrument, wherein instrument performance is maximized. While manual tuning can be done, this practice should be used only when necessary.

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F. **GC/MS Maintenance**

Each type and model of instrument may have different, specialized components requiring specific preventative maintenance. While not every step-by-step direction for all of the specific instrumental maintenance procedures will be found within this document, the more common have been listed. All maintenance performed on the instruments shall be recorded within the appropriate binder or file. Some of the procedures that are generic in nature are for reference only.

1. GC Injector

   The injector is the most likely place that unwanted sample residue and analytical artifacts may collect over periods of usage. Regular replacements of the septum and liner will aid in reduction and removal of these undesirable interferences. The intervals for checking and replacement of septa and liners are 'as needed' and occur based on the data from the Performance Check Solution during QA/QC of the instruments. Internal injector parts should not be touched with bare hands. It is recommended that lint-free gloves be worn when needed and that the operator cool heated areas on the instrument prior to any maintenance.

   a. Septum and Liner Replacement

      i. Set the oven to 30 °C.

      ii. Cool the inlet to room temperature and turn off the inlet pressure.

iii. Remove the septum and liner retainer nut. Remove the old septum with tweezers and replace it with a new septum.

iv. Remove the old liner from the injector with tweezers.

v. Place an o-ring on the new liner about 5-7mm from its top end.

vi. Place the liner straight down into the inlet and replace the septum and liner retainer nut.

vii. Restore the instrument conditions.

b. Replacing the Inlet Base Seal

i. Cool the oven to room temperature and then turn off the oven.

ii. Cool the inlet to room temperature and turn off the inlet pressure.

iii. Remove the column from the inlet. Cap the open end of the column with a septum or other suitable material in order to prevent contamination.

iv. Use a wrench to loosen the reducing nut and remove it. Remove the washer and seal inside the reducing nut.

v. Replace the inlet base seal and washer in the reducing nut.

vi. Replace the reducing nut and tighten using a wrench.

vii. Reinstall the column (see further in the procedure).

2. GC Corrective Maintenance

a. Column

Typically, the overall separation performance of a GC column will degrade over time, requiring corrective maintenance. Column maintenance is performed on an 'as needed' basis and is dependent on instrument performance. The column ends should not be touch with bare hands. It is recommended that lint-free gloves be worn when possible and that the operator cool heated areas on the instrument prior to any maintenance.

b. Clipping the column

i. Set inlet and oven to room temperature.

ii. Remove the column from the inlet and remove the column nut from the column.

iii. Place the column nut and a new ferrule on the injector end of the column.

iv. Score the column using a column cutter at six (6) or more inches. The score must be square to ensure a clean break.

v. Break off the column end and inspect (e.g., with a magnifying glass) to ensure there are no burrs or jagged edges.

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vi. Position the column so it extends the required length above the end of the ferrule. Mark the column underneath the column nut with a marker or typewriter correction fluid.

vii. Insert the column into the inlet and slide the nut and ferrule up the column to the inlet base. Finger tighten the column nut and adjust the column position so that the marker or correction fluid mark on the column is even with the bottom of the column nut.

viii. Tighten the column nut an additional ¼ to ½ turn so that the column cannot be pulled out from the fitting.

c. Replacing the column

i. Set inlet and oven to room temperature.

ii. After all heating zones are at room temperature, remove the column from the inlet and detector, and eventually from the gas chromatograph.

iii. Place a capillary column nut and ferrule on the injector end of the replacement column.

iv. Score the column using a column cutter. The score must be square to ensure a clean break.

v. Break off the column end and inspect (e.g., with a magnifying glass) to ensure there are no burrs or jagged edges.

vi. Position the replacement column so it extends the required length above the end of the ferrule. Mark the column underneath the column nut with a marker or typewriter correction fluid.

vii. Insert the column into the inlet and slide the nut and ferrule up the column to the inlet base. Finger tighten the column nut and adjust the column position so that the marker or correction fluid mark on the column is even with the bottom of the column nut.

viii. Tighten the column nut an additional ¼ to ½ turn so that the column cannot be pulled out from the fitting.

ix. Install the column into the transfer line leading to the mass spectrometer.

3. MS Preventative and Corrective Maintenance

Lint-free gloves and appropriate personal protective equipment (PPE) must be worn during the disassembly and reassembly of the mass spectrometer. Appropriate PPE must be worn during pump oil changes. Source performance within the MS can be monitored by use of the performance monitoring solution. Although the preventative maintenance intervals are left to the analyst, minimal time frames are described.

a. Vacuum Pumps

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All MS systems have one or more rough/mechanical pumps. If pumps use oil (some newer ones are oil-free) it is suggested that the pump oil level and clarity be checked periodically and that the oil be changed about every six (6) months (yearly at a maximum). Some systems also have one or more turbo pumps as well. Turbo pumps are very sensitive and vary greatly, even within the same instrument. It is suggested that the oil not be replaced in turbo pumps. For changing the oil in the rough/mechanical pumps:

i. Vent the MS instrument and ensure the pump is off and unplugged.

ii. Allow the pump to cool for at least ten (10) minutes before continuing.

iii. Open the pump vent/fill hole.

iv. Place a sturdy plastic container under the oil drain.

v. Open the oil drain and allow the old oil to empty.

vi. Add 10-20 mL of fresh oil to the pump with the drain open in order to flush the system.

vii. Replace the cover on the oil drain.

viii. Fill the pump with fresh oil until the proper fill level is noted in the level indicator.

ix. Replace the cover on the pump vent/fill hole.

x. Seal, label, and dispose of the used oil appropriately.

xi. Plug in the pump, and ensure it turns on before/when the MS is turned on.

b. Source Bake-out

It should be noted that an occasional overnight baking-out of the MS detector may be useful when elevated baselines and other interferences are observed. The source temperature can be temporarily raised to 250 °C . The transfer line should not be set to a temperature above the limit of the GC column. Refer to specific column documentation for more information.

i. Note the current source temperature.

ii. Set the source temperature to 250°C.

iii. Allow the source to bake-out for several hours.

iv. Return the source temperature to the original setting.

v. Allow the source to cool to the original temperature before operating the instrument.

vi. This process can be repeated keeping the source temperature elevated overnight. However, if problems persist, it is likely that the source and/or analyzer need to be cleaned.

c. Source Cleaning

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The source shall be cleaned on MS systems as needed and based on system performance. The GC/MS systems require the removal of the entire source for cleaning to occur.

i. Vent the MS system and turn off the main power.

ii. Allow the source to cool before continuing.

iii. Open the vacuum manifold.

iv. Disconnect any gas lines or electrical connections to the source.

v. Loosen and/or remove source retaining bolts and clips and remove the source.

vi. Disassemble the source in order to separate the lenses and any surfaces that come in contact with the ionization chamber.

vii. Mix a slurry of aluminum oxide and methanol.

viii. Thoroughly clean the pieces of the source with the slurry. Using a cotton-tipped applicator clean all dark or discolored areas, particularly around holes.
Warning: Only clean metal surfaces.

ix. Place the parts in a beaker containing deionized water and sonicate for at least (1) one minute.

x. Thoroughly rinse the parts with deionized water and then rinse with methanol.

xi. Re-assemble the source. Remember to avoid contaminating source/parts with oils from hands.

xii. Place the source in the manifold and secure.

xiii. Reconnect all gas lines and electrical connections.

xiv. Seal the manifold.

xv. Turn on the main power and pump-down the system. Observe for vacuum leaks.

d. Analyzer Cleaning

Mass Spectrometer systems in the Chemistry Unit employ quadrupole analyzers. In general, these analyzers do not need regular cleaning. A quadrupole is more sensitive to shock and manipulation and should only be cleaned when warranted by poor performance of the mass spectrometer.

i. Vent the MS system and turn off the main power.

ii. Allow the analyzer to cool before continuing.

iii. Open the vacuum manifold.

iv. Disconnect any gas lines or electrical connections to the quadrupole.

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v. Remove the quadrupole from the manifold.

vi. Mix a slurry of aluminum oxide and methanol.

vii. Thoroughly clean the first inch of the inner surfaces of the quadrupole with the slurry. Using a cotton-tipped applicator clean the area of interest along with all dark or discolored areas
Warning: Only clean inner metal surfaces.

viii. Rinse by running water through the inside of the quadrupole for several minutes until all aluminum oxide has been removed.

ix. Thoroughly rinse with methanol and allow quadrupole to dry.

x. Place the quadrupole in the manifold and reconnect any gas lines and electrical connections.

xi. Seal the manifold.

xii. Turn on the main power and pump down the system, observing for vacuum leaks.

e. Filament Replacement

Generally a broken filament results in a total loss of ions rather than degraded system performance. To replace a filament:

i. Vent the MS system and turn off the main power.

ii. Allow the source to cool before continuing.

iii. Open the vacuum manifold.

iv. Disconnect any gas lines or electrical connections to the source.

v. Loosen and/or remove source retaining bolts and clips.

vi. Remove the source.

vii. Disassemble the source in order to expose the filament.

viii. Unplug the old filament and replace it with a new one.

ix. Re-assemble the source.

x. Place the source in the manifold and secure.

xi. Reconnect all gas lines and electrical connections.

xii. Seal the manifold.

xiii. Turn on the main power and pump down the system, observing for vacuum leaks.

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G. **Performance Monitoring**

Performance monitoring is essential not only to ensure the production of quality results but to avoid unnecessary sample loss and to minimize time wasted due to instrument inoperability. The Performance Check Solution is used to assess operating performance, mass assignment accuracy, and continued integrity of the entire GC/MS system.

1. Evaluate the line pressure of the helium supply (carrier gas). The regulator should read 100 p.s.i. or above. If it cannot maintain this pressure do not operate the instrument until the tank has been changed to one which contains more helium gas.
2. Check the Ion Gauge to ensure that there are no significant leaks in the system. Do not use if the pressure is higher than 1 x 10^{-4} torr.
3. Perform a tune of the instrument. Autotune (ATUNE) should be used and the mass spectrometer will optimize its parameters automatically using PFTBA. Evaluate the results using the 'Decision Criteria' section within this procedure. If the results are acceptable then save and print the tune file (ATUNE) when completed. A second autotune may be necessary if the first tune produced questionable results or was unacceptable. If the tune results are still unacceptable after repeating a tune and corrections are unsuccessful then the instrument should be removed from service until corrected and an FSE2 (or higher) is notified.
4. Perform an analysis of the multi-component Performance Check Solution daily using the parameters listed in the 'Instrumental Conditions' section of this protocol. Evaluate the results using the 'Decision Criteria' section of this protocol. If the results are acceptable then print the total ion chromatogram (TIC) and associated spectra and store the printouts within the QC file.
5. If the results are not acceptable then a second sample can be analyzed and evaluated. If the results are still unacceptable and can't be improved then the GC/MS is removed from service, a sign is placed indicating, 'Out of Service' until the problem is corrected, and an FSE2 (or higher) is notified.
6. After the problem has been corrected the instrument in question must be checked and shown to pass evaluation before being returned to service.
7. If environmental conditions are such that optimum performance of the instruments is questionable then testing should be suspended.

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H. Instrumental Parameters

The following instrument parameters should be used for monitoring instrument performance. Values within this section can be changed, if necessary, but will be documented and should be approved.

GC Oven:

Initial Temp	40 °C	Inj. Vol.	1.0 µL
Initial Time	2.0 min.	Mode	Splitless
Ramp	10 °C/min.	Inlet Temp.	250 °C
Final Temp	300°C	Total Flow	55 mL/min
Hold Time	12.5 min.	Septum Purge	4 mL/min
Equil. Time	0.1 min.		

GC Inlet/Injector:

GC Column:

Type	HP-5MS (or equivalent	Mode	Constant Flow
Length	30 m	Init. Flow	1 mL/min
Diameter	0.25 mm	Ave. Linear Velocity	36 cm/sec
Film Thickness	0.25 µm	Carrier Gas	Helium (He)

Mass Spectrometer:

Transfer Line	300 °C
Source	230 °C
Quadrupole	150 °C
Low Mass	40
High Mass	400

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I. Decision Criteria

1. Tune

   Evaluate MS performance using the criteria below. The results can be compared to tune results from previous tunes to indicate trends in instrument performance. Significant voltage increases

or changes in the isotope ratios may indicate the need to initiate corrective maintenance procedures. The following are typical ATUNE values for the MSD:

PFTBA Tune	Mass +/- 0.4 for m/z 69, 219, 502
Peak Width	0.45 – 0.65
Relative Abundance	69 greater than 50% 219 greater than 30% 502 greater than 1%

2. Performance Check Solution

   Verify the results of the Performance Check Solution:

   a. In order for the instrument to be considered in good operating condition all components should generate well-resolved Gaussian-shaped peaks with baseline separation.

   b. A signal-to-noise ratio (SNR) of 3:1 will be the minimum response necessary to consider a chromatographic response a 'peak.' The SNR can be calculated using area or height values.

   c. There should be no extraneous peaks within the total ion chromatogram (TIC) greater than 5% of the height of the tallest peak in the Performance Check Solution.

   d. The retention times of the components within the Performance Check Solution will not deviate by +/- 3% when compared to the previous analysis of the performance standard solution.

   e. The mass assignments from the mass spectra of the components within the Performance Check Solution must compare favorably to known spectra and to previously analyzed spectra.

J. **Safety**

Appropriate personal protective equipment and engineering controls (e.g., hoods) will be utilized whenever handling potentially hazardous materials. At a minimum this should entail gloves, a laboratory coat, and safety glasses. Many instrument components are held at temperatures of 250°C and higher. Precautions need to be taken to prevent the contact of skin with heated surfaces and areas.

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Revision #	Revision History
2	Title change (from "GC and MS performance check" to "Performance Evaluation and Maintenance for GC/MS" in order to incorporate both the maintenance procedure (CH SOP-04) with the performance evaluation procedure (CH SOP-03). Merged information from CH SOP-04 into this procedure and added information within many of the sections of that document. Made slight grammatical modifications. Changed 'section' to 'Unit' where necessary. Updated the purpose section. Added a scope and a principle section. Analytical procedure updated. Removed the requirement of instruments being password protected. Expanded the procedure section. Added a decision criteria section. Added a safety section. Added a 'Revised History' section to the document.
3	Inserted title header within document. Overall format change throughout entire document ; Renamed 'Purpose' to 'Introduction' ; Moved 'Responsibility' section into 'Scope' section ; updated 'Equipment' section to include purchased ASTM solution, solvents, and other changes ; added section describing preparation of Performance Check Solution ; removed 'twice weekly verbiage' and better defined daily, weekly, monthly terms ; Clarified what to do if problems with evaluation ; Changed title of Instrumental Parameter section and updated certain values ; Updated decision criteria and safety sections.

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