Title: Quality Assurance / Quality Control (QA/QC) for the Gas Chromatography / Mass Spectrometry (GC/MS) Instrument

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 MS or 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 the FSE 2 (or higher) for alternative solutions (e.g., 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. Analysts 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 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. Vacuum pump oil (compatible grade)
5. Alumnium oxide (or compatible source cleaning powder/product)
6. Autosampler (Agilent or equivalent)
7. GC column - DB-5(MS), 30 m, 0.25 mm i.d., 0.25 µm film (or equivalent)
8. Carrier gas - helium, 99.9% (high purity) (or equivalent)
9. Autosampler vials – 2 mL GC vials, crimp or screw top, with or without 100-500 µL inserts (or equivalent)
10. Injection port liners (Agilent or equivalent)
11. Injection port septa – standard low-bleed 11 mm (or equivalent)
12. Injection port gold seals (Agilent or equivalent)
13. Column nuts and ferrules (Agilent or equivalent)
14. Syringes – Hamilton 701ASN 10 µL (or equivalent)
15. Ethyl acetate (syringe wash solvent) (reagent grade or equivalent)
16. Chloroform (syringe wash solvent) (reagent grade or equivalent)
17. Hexane (reagent grade or equivalent)
18. Acetone (reagent grade or equivalent)
19. Pentane (reagent grade or equivalent)
20. ASTM E1618 test mixture (or equivalent)

E. **Preparation of the ASTM E1618 Test Mixture**

The ASTM E1618 test mixture is a solution comprised of a homologous series of ~C_8-C_{20} (even numbered) n-alkane hydrocarbons and several aromatic hydrocarbons in a solvent (e.g., CH_2Cl_2/pentane) and shall be stored according to manufacture specfications. The following diluted

preparation of the ASTM E1618 test mixture is used to verify daily operating performance and continued integrity of the GC/MS system:

Add 1mL of stock ASTM 1618 Hydrocarbon Mix into a 10 mL volumetric flask, bring to a final volume with pentane, and mix. Solution is stable for 1 year or until earliest manufacturer's expiration date, whichever is sooner.

F. **GC/MS Maintenance**

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

   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.

   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 Gold 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.

      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 gold seal and washer in the reducing nut.

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

      vii. Reinstall the column.

2. GC Corrective Maintenance.
   a. 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 to ensure there are no burrs or jagged edges.
      vi. Position the column so it extends the required length (3-5mm) above the end of the ferrule.
      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.
      viii. Tighten the column nut an additional ¼ to ½ turn so that the column cannot be pulled out from the fitting.
   b. Replacing the column
      i. Set inlet and oven to room temperature. Set the MSD to vent using instrument program.
      ii. After instrument has completed the vent cycle, power down GC then MSD. Remove column.
      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 to ensure there are no burrs or jagged edges.
      vi. Position the replacement column so it extends the required length (3-5mm) above the end of the ferrule.
      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.
      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. Column should be minimally visible from end of transfer line on MSD side.
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

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 yearly (or sooner). 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 Cleaning

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 chamber.

iv. Disconnect any appropriate 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. Place parts in a beaker with methanol and sonicate for at least (1) one minute.

xi. Additional sonication steps using acetone followed by hexane may be performed as needed.

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

xiii. Place the source in the vacuum chamber and secure.

xiv. Reconnect all lines and electrical connections.

xv. Seal the vacuum chamber.

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

c. 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 chamber.

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

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

vi. Remove the source.

vii. Remove the old filament and replace it with a new one.

viii. Place the source in the vacuum chamber and secure.

ix. Reconnect all lines and electrical connections.

x. Seal the vacuum chamber.

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

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 ASTM

E1618 test mixture is used to assess operating performance and continued integrity of the entire GC/MS system.

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 troubleshooting instrument.

1. Evaluate the tank pressure of the helium supply (carrier gas). The tank pressure gauge must read 100 psi or above. Change the tank prior to analysis if the tank contains 100 psi or less. The regulator should be adjusted so that the gauge for the pressure to the instrument reads ~60 psi.
2. Perform a tune of the instrument. Autotune (ATUNE or ETUNE) 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 or ETUNE) 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.
3. Perform a daily analysis of the ASTM E1618 test mixture 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 store the printouts within the QC file.
4. If the results are not acceptable then a second sample can be analyzed and evaluated. If the results are still unacceptable, and cannot be improved upon, then the GC/MS will be removed from service and tagged with a sign indicating 'Out of Service' until the problem is corrected. The FSE2 (or higher) will be notified of the issue.
5. After the problem has been corrected the instrument in question must be checked and shown to pass evaluation before being returned to service.
6. If environmental conditions are such that optimum performance of the instruments is questionable then testing should be suspended.

Instrumental Parameters

The following instrument parameters are typically used for monitoring instrument performance. Values within this section may be changed, but any changes will be documented within the applicable method.

GC Oven:

Initial Temp.:	40 °C
Initial Time.:	2.0 min.

GC Inlet/Injector:

Injection Vol.:	1.0 µL
Mode:	Splitless

Ramp:	10 °C/min.		Inlet Temp.:	250 °C
Final Temp.:	300 °C		Septum Purge:	3 mL/min
Hold Time:	5 min.			
Equil. Time:	0.5 min.			

GC Column:

Type:	HP-5MS (or equivalent)		Mode:	Constant Flow
Length:	30 m		Flow:	0.9 mL/min
Diameter:	0.25 mm		Avg. Linear Velocity:	~34 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

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 TUNE values for the MSD:

PFTBA Tune:	Mass +/- 0.2 for m/z 69, 219, 502
Peak Width (Pw50):	0.45 – 0.65
Relative Abundance:	69 = 100%, 219 > 40%, 502 > 2%
Air/Water Check:	N_2 < 10%, O_2 < 10%, H_2O < 20%

2. ASTM E1618 Test Mixture:

   Verify the results of the ASTM E1618 test mixture:

   a. In order for the instrument to be considered in good operating condition, all components of the test mixture (excluding n-hexane) should generate well-resolved, Gaussian-shaped, peaks with baseline separation. Note: n-hexane falls within the typical solvent delay, however, the ASTM E1618 standard only calls for n-octane to be the lowest n-alkane mixture component.

   b. There should be no extraneous peaks within the total ion chromatogram (TIC) greater than 5% of the height of the tallest peak amongst the components of the test mixture.

   c. The retention times of the components of the test mixture will not deviate by +/- 3% when compared to the previous analysis of the test mixture.

   d. The mass assignments from the mass spectra of the components of the test mixture 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.