

Title: High Resolution GC / Low Resolution MS Analysis		Copy No: ##
SOP No.: 5.01/5.2/S	Effective Date: October 11, 2013	Location: ###

QSM Approval: _____

High Resolution GC / Low Resolution MS Analysis

1. Introduction

High Resolution Gas Chromatography (HRGC) coupled to Low Resolution Mass Spectrometry (LRMS) is the analytical tool used for the determination of semi-volatile and volatile compounds such as PAH, C1-C4-alkylated PAH, PCB, CB, HCB, CP, OCS, VOCs, SPAH, MPAH, Chlorinated Parafins and DBD/DBF. Proper maintenance and calibration is instrumental in the delivery of high quality data. The following procedures apply to all seven benchtop GC/MS systems in the instrumental analysis labs (lab 171, 154/155).

2. System Calibration

- 2.1 Prior to sample analysis a daily calibration standard is analyzed to verify system performance and calibration (verification check). The results obtained from the standard run are verified for discrepancies in RRF, RT, sensitivity, peak shape and resolution.
- 2.2 Once the daily calibration standard has been analyzed and found to meet the performance criteria set as described in the applicable method, samples are loaded onto the autosampler for analysis.
- 2.3 A verification check is performed after every 5 to 10 samples injected to monitor the system as a minimum requirement.

3. System Operation and Maintenance

3.1 Gas Chromatograph Operation

- 3.1.1 When not in use the gas chromatograph (GC) is maintained on standby with an oven temperature between 30 and 90°C.
- 3.1.2 Effluent gas streams from the detector are vented to an exhaust arm or through a carbon filter to remove potentially toxic emissions.
- 3.1.3 Gas cylinders are replaced when the pressure in the tank falls below 200 psi. Shut off regulator valve to avoid letting air into the system. Cool the oven, injector, and GC/MS interface before changing the carrier gas cylinder.
- 3.1.4 Gas Line Traps
Replace oxygen, hydrocarbon, or combination traps after 3-4 tank replacements. Record the tank replacement date on the trap, in the GC/MS

Title: High Resolution GC / Low Resolution MS Analysis		Copy No: ##
SOP No.: 5.01/5.2/S	Effective Date: October 11, 2013	Location: ###

injection logbook, and in the instrument logbook. Traps are changed using the following procedure:

- 3.1.4.1 Cool the injector, oven and GC/MS interface below 100°C. Set the gas source supply pressure to 10-15 psi.
- 3.1.4.2 Change the trap at the gas source by connecting the gas source tubing to the INLET end of the trap. Do not open the plug on the OUTLET end while performing this procedure.
- 3.1.4.3 Wait for 3 minutes to stabilize the gas pressure inside the new trap.
- 3.1.4.4 Increase the gas source pressure to 60 psi, open the OUTLET fitting, and purge the trap for 3 minutes.
- 3.1.4.5 Adjust the gas source pressure to normal operating level. Connect the OUTLET fitting of the trap to the instrument tubing.
- 3.1.4.6 If using the Agilent Renewable Gas Purifier System or Gas Clean Filter System replace the filter cartridge when either the moisture or oxygen indicator change colour indicating contamination. Follow the instructions provided with the replacement cartridge.

3.1.5 Analytical Column

- 3.1.5.1 For cool-on-column injectors, the analytical column is connected to a non-coated open tubular fused silica column of up to 10 m in length used as a retention gap (often referred to as pre-column). For split/splitless injectors a retention gap is optional.
- 3.1.5.2 The retention gap is cut when required as indicated by the chromatogram of the daily calibration standard (i.e. peak tailing, low sensitivity, poor resolution). Check the pre-column for black deposits or small cuts. Usually removing 0.3 m of pre-column is adequate to eliminate the problem. When less than 0.5 m remains replace the pre-column.
- 3.1.5.3 If cutting the pre-column does not remedy the problem then the analytical column may be affected. Cut back the analytical column by about 1 meter. If the problem persists the analytical column may need to be changed. The expected lifespan of any given capillary column is 6 months to 2 years depending upon the quantity of samples analyzed, sample matrix and system performance.

3.2 Cool On-column and Split/Splitless Injector

- 3.2.1 A 5 - 10 µL, 26 gauge (for cool on-column)/ 23 gauge (for split/splitless), approx. 4.3 cm tapered syringe is used for sample injection.
- 3.2.2 Make sure that the syringe is aligned with the injection port otherwise the needle may bend or break.
- 3.2.3 The plunger should be checked regularly to ensure that it moves freely in the barrel. If the plunger sticks, rinse with solvents to correct the problem or change plunger or the whole syringe assembly.

Title: High Resolution GC / Low Resolution MS Analysis		Copy No: ##
SOP No.: 5.01/5.2/S	Effective Date: October 11, 2013	Location: ###

- 3.2.4 The injector vent flow is maintained between 15 to 20 mL/min for automated injection. Column head-pressure is set according to the column length and internal diameter, and the method used. Any drop in head-pressure or vent flow rate may be indicative of a septum leak or other leak.
- 3.2.5 Change septa when a leak is suspected and record in the injection logbook. Septa require changing typically once a month for on-column and once a week for split/splitless injectors or for manual injections.
- 3.2.6 The injector is maintained at the same temperature as that of the starting temperature of the GC run or oven temperature + 3°C when oven tracking is used for cool on-column injections. The inlet temperature for split/splitless injections is set to just above the highest boiling point of the solutes (+20°C) The starting oven temperature for a given method should be about 10-25°C below the boiling point of the solvent used to ensure concentration at the head of the column.

3.3 Carrier Gas

- 3.3.1 Helium U.H.P is used as carrier gas unless otherwise specified. Oxygen, hydrocarbon, or combination traps are placed in-line with each carrier gas source. Traps are changed after 3-4 gas tank replacements or as required.

3.4 Autosampler

- 3.4.1 Samples are loaded onto the numbered sample tray in the same order as recorded in the injection logbook. The robot arm picks up samples one at a time in ascending order for analysis following the sequence entered in the acquisition method.
- 3.4.2 Prior to injection, the syringe must be solvent rinsed. The solvent rinse vials on the injection tray are filled regularly (one with toluene, the other with iso-octane or other solvents as required). Waste vials are also in place and kept clean by emptying and rinsing once every two weeks or as required.
- 3.4.3 A cooling bath may be used to keep samples cool and avoid evaporation.
- 3.4.4 Monitor the system until the first injection is made to ensure proper functioning.

3.5 Sample Analysis

- 3.5.1 Record all samples to be analyzed in the appropriate injection logbook along with pertinent information (i.e. sample ID, dilution, method used, sample acquisition number, analyst, tracking sheet #, batch# and project ID). After data acquisition, process raw data using the appropriate data interpretation method.
- 3.5.2 See appendix 1 for guidance on the naming of files and methods.

Title: High Resolution GC / Low Resolution MS Analysis		Copy No: ##
SOP No.: 5.01/5.2/S	Effective Date: October 11, 2013	Location: ###

3.6 MS Source

- 3.6.1 The source is cleaned when EM voltage reaches 2500-2700 (maximum level is 3000) or as required.
- 3.6.2 Check rough pump oil level routinely for leakage or contamination.
- 3.6.3 Refill the rough pump with oil every 6 months or when oil level falls below the mark.
- 3.6.4 To clean the source follow the manufacturers recommendations as described in the appropriate maintenance manuals, videos and/or CD-ROM.
- 3.6.5 If using an oil free dry rough pump replace the diaphragm as required.

4. Mass Selective Detector Tuning

Proper operation and calibration of the mass spectrometer is critical in the delivery of valid data. MSD tuning must be performed routinely to monitor system performance and optimize the mass spectrometer for analyte detection.

4.1 Leak Checks and Corrective Actions

Leak checks must be performed on the MSD prior to tuning the system at least once a week. The following procedures are followed to best judge if leaks are present in the system and what corrective actions need to be taken:

- 4.1.1 Leak checks are performed by opening the PFTBA valve to allow tuning compound into the ion source and then monitoring the 28/69 (air leak check) and the 18/69 (water leak check) percentages. Both percentages should be less than 5%.
- 4.1.2 If leak check percentages are greater than 5%:
 - 4.1.2.1 Check tightness of seal most recently opened
 - 4.1.2.2 Check seals for tightness at the gas cylinder, cylinder traps, injector, injector pre-column nut, pre-column/analytical column union nut, interface nut, vent valve O-ring, calibration valve, front and rear end plate O-ring (on MSD), diffusion pump co-seal and/or baffle adapter O-ring, turbomolecular pump O-ring
 - 4.1.2.3 Consult instrument manuals for further information
 - 4.1.2.4 Consult laboratory supervisor
 - 4.1.2.5 Contact Agilent's Technical Support line (1-800-227-9770) or Agilent's on-line Technical Support.
- 4.1.3 The responsible analyst reviews the leak check reports and files reports in the appropriate log for future reference.

4.2 Automatic Tuning

Title: High Resolution GC / Low Resolution MS Analysis		Copy No: ##
SOP No.: 5.01/5.2/S	Effective Date: October 11, 2013	Location: ###

- 4.2.1 The system tuning parameters are verified at least weekly when samples are being analyzed to monitor system performance. The system is tuned using the reference compound perfluorotributylamine (PFTBA).
- 4.2.2 A manual or automated tune may be performed to optimize the system. The following interpretation of the tune report applies to all MSDs (Agilent).

4.3 Interpretation of the Tune Report

Any one of the following results in the tune report may indicate the need for maintenance procedures such as source cleaning:

- 4.3.1 An increase in electron multiplier voltage;
- 4.3.2 A decrease in lens offset &/or an increase in ion focus voltage;
- 4.3.3 Peak width outside of the range 0.4 to 0.65 amu;
- 4.3.4 Mass assignment outside of a 0.2 amu window around m/z 69.0, 219.0, and 502.0;
- 4.3.5 The relative abundances of tune masses are outside of the following limits:

<u>Mass</u>	<u>Rel Abund</u>
69.0	100%
219.0	>20%
502.0	>0.5%

Note: relative abundance will vary depending on the system used.

- 4.3.6 The ratio of the isotope masses to the tune masses are outside of the following limits:

<u>Isotope mass</u>	<u>MSDs</u>
70.0	0.54 - 1.6%
220.0	3.2 - 5.4%
503.0	7.9 - 12.3%

4.4 Tune Reports

- 4.4.1 All tune reports are reviewed by the responsible analyst. Tune reports are filed in the appropriate log for future reference.
- 4.4.2 After performing a tune that meets the acceptable criteria, additional tuning may be performed to optimize sensitivity for a particular application.

4.5 MS Maintenance

If the tune report indicates significant changes in system performance (as listed in sections 4.3.3 to 4.3.6, Interpretation of the Tune Report) then corrective action

Title: High Resolution GC / Low Resolution MS Analysis		Copy No: ##
SOP No.: 5.01/5.2/S	Effective Date: October 11, 2013	Location: ###

must be taken. The corrective actions necessary may include any one of the following:

- 4.5.1 Elimination of leaks in the system
- 4.5.2 Replacement of filament
- 4.5.3 Cleaning of ion source/replacing heavily oxidized and/or bent/broken source parts
- 4.5.4 Replacement of the electron multiplier
- 4.5.5 Cleaning of quadrupoles
- 4.5.6 Service call
- 4.5.7 Sections 4.3.1 & 4.3.2 (Interpretation of the Tune Report) indicate gradual deterioration of the ion source caused by routine usage and time and do not always necessitate corrective action. These items should however be closely monitored and any significant changes investigated further.

4.6 Calibration

- 4.6.1 Whenever there are changes incurred in the tuning electron multiplier voltage (increase or decrease) the analyst must re-calibrate the system for each group of target analytes monitored prior to further analysis. Recalibration using the daily calibration standard as a minimal requirement.
- 4.6.2 If the resulting voltage for a given acquisition method is modified to compensate for the change in tune voltage (the resulting EM voltage is equal to the previous tune voltage) then recalibration is not necessary.

5. Corrective/Preventative Action

- 5.1 A record of all maintenance performed on the systems is kept in the corresponding maintenance logbooks at each workstation and includes but is not limited to the following: maintenance checklists, software installation/upgrades, hardware upgrades, consumable replacement and service calls.
- 5.2 Agilent Technologies provides a very comprehensive website with product and service information, applications, support assistance and troubleshooting guidance for their instruments and products. This website should be consulted regularly to keep informed of potential problem areas, new products/services and improvements to existing systems or products (www.chem.agilent.com).
- 5.3 Corrective measures are conducted as described within the SOP. If the problem cannot be resolved consult the appropriate manuals for further instructions and/or the Supervisor.
- 5.4 If problems persist contact Agilent Technologies Customer Support Services: Agilent's Technical Support line (1-800-227-9770) or Agilent's on-line Technical Support (http://www.chem.agilent.com/scripts/cag_techsupport.asp).
- 5.5 The supervisor or designate must approve all on-site service required.

Title: High Resolution GC / Low Resolution MS Analysis		Copy No: ##
SOP No.: 5.01/5.2/S	Effective Date: October 11, 2013	Location: ###

6. Data Backup and Storage

The following procedure ensures the consistent storage of all sample data generated by the GC/MS instruments and provides easy retrieval and access of data. This procedure applies to data generated by all Agilent GC/MS systems operated in the laboratory.

- 6.1 A backup of the data from each MSD is performed on the first working day of each month, to its Home Drive on the network Server.
- 6.2 The data from each instrument is stored on its hard drive (D: drive or E: drive) under the folders Data, Methods, Results and Sequence. Under each of these four folders are directories created at the start of each month with names based on the month and year (MMYY) where the data from each month is stored. Copy the Data, Methods, Results and Sequence folders from the D:drive or E-drive to the home drive; if prompted to overwrite files click "yes to all".
- 6.3 Each MSD is backed up to DVD. The backup is performed on the LABRR0171DAHARN computer located in lab171 using the LAB171 account. Using Roxio Easy Media Creator 7 Basic Edition, format a DVD-R and name it as the current month and year (MMYY). Create a folder for each MSD and copy the Data, Methods, Results and Sequence directories from the D drive of each MSD to the corresponding folder on the DVD. Eject the DVD and choose the option so that the disk cannot be written to again. Label the disk with the name given during formatting and store in the locked cabinet in 171b.
- 6.4 When the backup to both the home drive and to DVD are complete, delete the directories from three months ago leaving two months of data.
- 6.5 The D drive or E-drive from each MSD is also backed up on a nightly basis using Agilent OpenLab Electronic Content Manager.

7. References

HP 5890 Series II Gas Chromatograph	
Operating Manual	Part No. 05890-90260
Reference Manual	Part No. 05890-90270
Site Prep/Installation Manual	Part No. 05890-90280
Tutorial	Part No. 05890-90290
Programmable Cool On-Column Inlet Manual	Part No. 05890-90300
HP 5972A Mass Selective Detector	
Hardware Manual	Part No. 05972-90001
HP 5972A & HP 6890 Series Mass Selective Detector	
Hardware Manual	Part No. 05972-90026
HP 6890 Series Gas Chromatograph	
Operating Manual Volume 1. General Information	Part No. G1530-90440
Operating Manual Volume 2. Inlets	Part No. G1530-90450

Title: High Resolution GC / Low Resolution MS Analysis		Copy No: ##
SOP No.: 5.01/5.2/S	Effective Date: October 11, 2013	Location: ###

HP 5973 Mass Selective Detector	
Hardware Manual	Part No. G1099-90001
Reference Collection (3 CDs) Rev. C.00.00	
HP Automatic Liquid Sampler	
Operating Manual	Part No. G1513-90100
Sampling Techniques Handbook	Part No. G2612-90120
HP G1034C MS ChemStation Software	
MS ChemStation User's Guide	Part No. G1034-90043
Maintaining your GC/MS System	Part No. 5988-3960EN

8. Revisions

- October 2005: Section1: insert SPAH, MPAH and Gasoline as additional analytes and add another MSD (7)
 Section 3.1.4: add the instrument logbook, some formatting
 Section3.1.5: specify "for cool-on-column injectors" as well as minor text changes to clarify procedures
 Section 4.1: Specify leak checks "at least once a week" and clarify procedure "by opening PFTBA valve...."
 Section 4.5: correct references within Section 4.3.3.
 Section 6.4: add 'sequences' to list of files to store
 Section 6.5: Remove reference to ETC08; Remove information to backup which is included in Section 6.2
- October 2009: Lead Reviewers: Jennifer Verner and David Harnish
 Section 1: removed MSD-1, 3 and 4, added MSD-8, 9, 10
 Section 3.4.2 Removed "two" and changed bottles to vials
 Deleted old section 6, added new section 6.
- September 2011: Lead Reviewer: David Harnish
 Add references to MSD11
 Section 3.2.6 add reference to oven tracking of injector temperature
 Updated header and footer, and approval authority
 Archived old revisions history from Sept. 1995 to Nov. 2003
- September 2013 Lead Reviewer: David Harnish
 Removed reference to specific MSDs in sections 1 and 6.
 Added lab numbers (171, 154/155), section 1
 Section 3.6.5 added section on oil free rough pumps.
 Added section 3.1.4.6 re Agilent Renewable Gas Purifier and Gas Clean Filter Systems
 Added reference to replacing diaphragm in section 3.6.5

Title: High Resolution GC / Low Resolution MS Analysis		Copy No: ##
SOP No.: 5.01/5.2/S	Effective Date: October 11, 2013	Location: ###

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Approved by: Mylaine Tardif
Title: Coordinator, Analysis and Air Quality Section

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Title: High Resolution GC / Low Resolution MS Analysis		Copy No: ##
SOP No.: 5.01/5.1/S	Effective Date: September 23, 2011	Location: ###

Appendix 1
Nomenclature of Methods and Files Used on the Agilent Chemstation MSDs

Table 1: Nomenclature of Acquisition Methods for Sample Analyses

Analysis Type	Abbreviation	MSD #	Version (A to Z)	Year (yy)	Extension	Complete name	Example
Polyaromatic hydrocarbons	PAH	#(5-6-7-8-9-10)	letter	yy	.m	PAH(MSD#)(Version)(yy).m	PAH4A01.m
Hexachlorobenzene, pentachlorophenol, octachlorostyrene	HPO	#(5-6-7-8-9-10)	letter	yy	.m	HPO(MSD#)(Version)(yy).m	HPO4A01.m
Dibenzo-p-dioxin/dibenzofuran	DBDF	#(5-6-7-8-9-10)	letter	yy	.m	DBDF(MSD#)(Version)(yy).m	DBDF4A01.m
Sulfur containing PAH	SPAH	#(5-6-7-8-9-10)	letter	yy	.m	SPAH(MSD#)(Version)(yy).m	SPAH4A01.m
Total polychlorinated biphenyls Standard Analysis	PCBST	#(5-6-7-8-9-10)	letter	yy	.m	PCBST.m *	
Total polychlorinated biphenyls Sample Analysis	PCBSA	#(5-6-7-8-9-10)	letter	yy	.m	PCBSA.m *	
WHO PCB	PCBC	#(5-6-7-8-9-10)	letter	yy	.m	PCBC(MSD#)(Version)(yy).m	PCBC4A01.m
Gasoline	GAS	#(5-6-7-8-9-10)	letter	yy	.m	GAS(MSD#)(Version)(yy).m	GAS4A01.m
Ozone-depleting substances	ODS	#(5-6-7-8-9-10)	letter	yy	.m	ODS(MSD#)(Version)(yy).m	ODS4A01.m
Method Development	MD	#(5-6-7-8-9-10)	letter	yy	.m	Assign name as required (maintain records in instrument logbook)	

Title: High Resolution GC / Low Resolution MS Analysis		Copy No: ##
SOP No.: 5.01/5.1/S	Effective Date: September 23, 2011	Location: ###

Table 2: Nomenclature of Acquisition Methods for QA/QC Analyses

Method description	Abbreviation	Injection Vol.	Analyte Group Abbreviation	MSD #	Specification	Extension (1,3,4 or5)	Complete name	Example
Column Bleed test	BL	NA	PAH,HPO,CB, PCB,CP,SPAH, DBDF	#		.m	BL(AnalyteGroup)(MSD#).m	
Calibration Curve	CU	NA	PAH,HPO,CB, PCB,CP,SPAH DBDF	#	H(high level) L(low level)	.m	CU(AnalyteGroup)(MSD#)(letter).m	
Full Scan	FS	NA	PAH,HPO,CB, PCB,CP,SPAH DBDF	#		.m	FS(AnalyteGroup)(MSD#).m	
Detection Limit	DL	## (see table 3)	PAH,HPO,CB, PCB,CP,SPAH DBDF	#		.m	**DL(##)(AnalyteGroup)(MSD#).m	

NA = not applicable

Table 3: Injection volume

Volume Injected	Number Assigned (##)
0,5 uL	05
1,0 uL	10
1.5 uL	15
2.0 uL	20
2.5 uL	25

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Page:
11 of 12

Title: High Resolution GC / Low Resolution MS Analysis		Copy No: ##
SOP No.: 5.01/5.1/S	Effective Date: September 23, 2011	Location: ###

Table 4: Nomenclature of Agilent Chemstation Files

Data file name	MSD(MSD#)####.d	example: MSD50001.d
Result file name	MSD(MSD#)####.crt	example: MSD50001.crt
*Sequence name	(First letter of last name of analyst)(MSD#)(dd/mm/yy).s	example: B4300701.s

* Sequence files are identified by the analyst who sets up the sequence. If an analyst runs more than one sequence on the same instrument in a day then he/she uses a second letter which uniquely identifies them. Records of letters assigned are maintained to avoid duplication. See file called "letterassignment". New analysts chose a letter corresponding to the first letter of their last name unless the letter is already used.

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