

STANDARD OPERATING PROCEDURE FOR
GAS ANALYSIS BY MICRO GAS CHROMATOGRAPHS
(HP Series P200H and MTI P200 GC)

1. Disclaimer:

This standard operating procedure has been prepared for use by the Ground Water Ecosystems Restoration Division of the U.S. Environmental Protection Agency and may not be specifically applicable to the activities of other organizations. **THIS IS NOT AN OFFICIAL EPA APPROVED METHOD.** This document has not been through the Agency's peer review process or ORD clearance process.

2. Purpose: (Scope and Application)

This method describes the setup and use of a HP Series P200H and a MTI P200 gas chromatograph, hereafter referred to collectively as micro gas chromatographs (micro GCs). This method is applicable to the analysis for gases in the headspace above water samples to determine the concentration of gases dissolved in the water and for whole gas samples. The actual sample preparation and method of calculation of gas concentration in the liquid is not within the scope of this method and can be found in RSKSOP-175. This method describes the use of a micro gas chromatograph (GC) which can analyze the gases in a fraction of the time it takes on a conventional GC.

This method can analyze the following gases, with quantitation levels in parentheses: methane (10 ppm to 100,000 ppm), ethane (10 to 10,000 ppm), ethylene (10 to 10,000 ppm), acetylene (10 to 10,000 ppm), propane (10 to 10,000 ppm), butane (10 to 10,000 ppm), carbon dioxide (100 to 10,000 ppm). This list is not meant to be all inclusive.

Actual GC analysis time is 80 seconds. The rate at which samples can be analyzed will depend on various factors, but a fair estimate is about 15 samples per hour. Each micro GC is equipped with dual TCD detectors. Column temperature may be independently controlled to allow simultaneous use of both columns within a micro GC. When an injection is made the sample is split between the two columns and detected by the two detectors to produce a side A and a side B signal.

This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatography and in the interpretation of chromatograms.

3. Method Summary:

The sample is introduced into the Micro GC via a built-in vacuum pump in the GC, which draws a sample into the sample loops/injectors. Samples are injected and split onto two different capillary columns and detected by two independent thermal conductivity detectors.

4. Reagents:

A multi-level calibration curve is developed for each gas. The following nominal gas concentrations* are used:

Methane: 10 ppm, 100 ppm, 1000 ppm, 10,000 ppm, 100,000 ppm
Ethylene: 10 ppm, 100 ppm, 1000 ppm, 10,000 ppm
Ethane: 10 ppm 100 ppm, 1000 ppm, 10,000 ppm
Acetylene: 10 ppm, 100 ppm, 1000 ppm, 10,000 ppm
Propane: 10 ppm, 100 ppm, 1000 ppm, 10,000 ppm
Butane: 10 ppm, 100 ppm, 1000 ppm, 10,000 ppm
Carbon Dioxide: 100 ppm, 1000 ppm, 10,000 ppm

*See the gas standard bottles for the actual concentrations.

Gas standards are received in either size 6AL cylinders from BOC standard gases (Edison, New Jersey), or size 3AL cylinders from Air Liquide standard gases (LaPorte, Texas)

High purity helium

5. Equipment/Apparatus:

MTI P200 Gas Chromatograph equipped with a 10 meter MS-5A capillary column and a 8 meter Poraplot U capillary column. The GC is interfaced to a Dell laptop computer with EZChrom Software.

HP Series P200H GC Chromatograph equipped with a 10-meter Alumina Oxide capillary column and an 8-meter Poraplot U capillary column. The GC is interfaced to a Dell laptop computer with EZChrom Software.

Glaspak syringe, stopcock

6. Health and Safety Precautions:

There are no additional precautions which need to be taken other than those in keeping with standard laboratory practices.

When using the small gas cylinders be sure to stabilize them with a suitable support (such as the wooden box holder) so they will remain upright and not tip over when they are being used.

7. Interferences:

Any non-target gases which elute within the retention time windows of the gases of interest, will be erroneously reported as the analyte. This is true of any chromatographic procedure with nonspecific detection. Air is detected by the detectors but is separated from the analytes of interest.

8. Procedure:

GC Operation:

The user needs to have a working knowledge of the micro GCs and EZChrom software. Users without this knowledge will not be able to produce reliable, defensible results.

Begin operation of the MTI GC by first turning on the computer, followed by the GC power. Start the EZChrom software, then follow 1-8 below:

Begin operation of the HP Series P200H GC by first turning on the computer, then turning the GC off then on to establish communication between the GC and the computer. Start the EZChrom software, then follow 1-8 below:

1. At the EZChrom Main Menu bar, click on "**Instrument**".
2. Click on the "**Send the Current Method**".
3. Click on "**Instrument**".
4. Click on "**Status**". With this window the GC temperature and baseline mV may be monitored. When the baseline has stabilized it is ready to use. This takes about 10-15 minutes.
5. Exit Status and click on the "**Start**" button on the menu bar.
6. At the Run window, enter a file name for the sample or standard. Select "Save", "DIF Save" and "Extended". Puncture the vial septum with the ground glass syringe, Luer lock and needle attachment. Draw out 2mL of sample from the headspace. Close the

Luer lock and remove the needle from the septum. Remove the needle from the Luer lock and place the syringe with the Luer lock in the injection port of GC. Open the Luer lock.

7. Click on the “start” button on the run window to begin GC analysis.
8. After 80 seconds the GC run will be complete. Manually record the sample results in a lab notebook. Results will be either in ppm or percent (%). Refer to RSKSOP-175² for calculating dissolved gas concentrations to partial pressure.

GC Conditions:

Side A on MTI P200: 10 meter MS-5A (molecular sieve)
Side A on HP Series P200H: 10 meter Alumina Oxide
Side B on both: 8 meter Poraplot U

For both micro GCs:

	<u>A</u>	<u>B</u>
Column Temperature, °C	100	45
Run Time, seconds	80	80
Sample Time, seconds	15	15
Inject Time, milliseconds	40	40
Detector Sensitivity	Low	High
Detector Autozero	On	On
Pressure, psi	31.2	27.6
Typical Baseline, mV	70	170

Component Retention Times (seconds):

Components	<u>A</u>	<u>B</u>
methane (both GCs)	22.0	22.0
Carbon Dioxide (both GCs)	*	37.4
ethylene (both GCs)	*	47.2
ethane (both GCs)	*	45.8
acetylene (both GCs)	*	76.3
propane (P200H)	27.3	*
butane (P200H)	47.2	*

*These gases are not analyzed with this column under these conditions.

Timed Events for both micro GCs (seconds):

Side A:

<u>Event</u>	<u>Time</u>	<u>Value</u>
INTG off	0.00	40.0
SLPSEN	0.00	100.0
FINE SLPSEN	0.00	5.00
PKWD	0.00	3.00

Side B:

<u>Event</u>	<u>Time</u>	<u>Value</u>
INTG off	0.00	17.0
SLPSEN	0.00	100.0
FINE SLPSEN	0.00	35.0
PKVVD	0.00	0.20
TAN	19.13	20.55
PKWD	29.72	1.61
PKWD	31.23	1.77
PKWD	36.06	2.98

Propane and butane are quantified on side A of the HP Series P200H micro GC. All other gases are analyzed and quantified on side B of both micro GCs. Side A of the MTI P200 is currently not being used.

Calibration may be stable for up to a month, and recalibration should not be necessary as long as the criteria are met as stated in section 9. If there are problems with the calibration of the micro GC, it might help to bake it out at 180°C for 24-36 hours and recheck the calibration before recalibrating the instrument. To bakeout the instrument, click on method on the menu bar, then click open, and then bakeout.met, click on instrument on the menu bar and send the current method. This will start the instrument bakeout. To check if the instrument is baking out, click on instrument on the menu bar and then click on status. If recalibration is necessary, the standards need to be analyzed three times each and an average taken of the three analyses to be used in the calibration curve. An acceptable calibration curve will have a correlation coefficient >0.995.

Refer to the MTI User Manual for instructions on how to set-up the calibration curves for both micro GCs¹. The software will report the concentration based on peak response.

Each sample that is analyzed needs to have a unique filename. The software does not allow the operator to change the directory for data storage; therefore, to avoid confusion caused by having potentially hundreds of filenames in a directory, it would be prudent to save all data to a floppy disk at the end of the day in a unique directory, which can be referenced in the lab notebook. After saving all data to the floppy disk, the directory on the hard disk can be purged to prevent

the buildup of hundreds of filenames, and the potential problem of writing over old files. Data as stored on floppy disks are archived to CD according to the appropriate EPA Records Schedule.

9. QA/QC:

Initial Checks:

Prior to starting analysis, at least one calibration standard for each gas should be analyzed to check the initial calibration. The analyzed values from the run should be within 15% of the expected value. Also, helium should be analyzed to determine if there are any background concentrations of the analytes. The background concentrations should be at or below the method detection limit (MDL). If these conditions are met, then analysis may proceed.

Continuing Calibration Check Standards:

The data quality objective for the continuing calibration check (CCC) standards is 85-115% accuracy for standards analyzed on the micro GC. CCCs should be analyzed before a sample set is analyzed, after every 10 samples and at the end of the sample set.

Blanks:

A helium blank should be analyzed first, before any set of standards, and last after all samples and standards have been analyzed. All target analyte concentrations should be at or below the MDL. For dissolved gas analysis, a laboratory reagent blank comprised of RO water is prepared in exactly the same manner as samples and should be analyzed before starting analysis of any samples containing water. It is not necessary to analyze this blank for gas samples. This blank is used to determine if background analyte concentrations or interferences are present in the analytical system and procedure associated with water samples.

Field or trip blanks when provided, are prepared and analyzed in exactly the same way as samples. The presence of target analytes in the field or trip blanks should be noted in the analytical report as long as the helium and water blanks meet their data quality objective (DQO), no corrective action for the field or trip blanks is required.

Duplicates:

Sample duplicates should be analyzed to check for sampling precision. A laboratory duplicate should be analyzed for every 10 samples in the batch. The DQO for the precision of lab duplicates is a relative percent difference (RPD) of ≤ 20 .

Second Source:

Second source (SS) gas standards from sources different from calibration standard suppliers should be analyzed within the sample queue. A SS standard for each target analyte should be analyzed with each sample set.

Alternatively, standards from the same supplier as the calibration standards supplier may be used, but the SS standards must have different lot numbers. The DQO for SS standards is a measured concentration within 15% of the expected value.

If SS criteria are not met in verifying the calibration of the GC, all calibration standards of the gas in question need to be analyzed to determine if all levels no longer meet the data quality objective. If they do not, then the GC should be recalibrated.

These MDLs are for both micro GCs.

MDL Calculation Micro GC 12-14-04 Units = ppm

Analyte	#1	#2	#3	#4	#5	#6	#7	Average	Standard Deviation	M.D.L.
Methane	10.6	10.5	10.5	10.4	10.2	10.6	10.4	10.5	0.141	0.424
Ethylene	10.0	10.3	10.2	10.3	10.2	10.3	10.7	10.3	0.192	0.575
Ethane	10.9	10.7	10.5	10.7	11.0	11.2	9.70	10.7	0.499	1.496
Acetylene	11.4	11.3	11.7	9.43	11.2	10.7	11.8	11.1	0.799	2.40
Propane	9.49	9.43	9.43	9.35	9.31	9.38	9.28	9.38	0.0750	0.225
Butane	9.80	9.58	9.72	9.52	9.38	9.38	9.41	9.54	0.170	0.509
Carbon Dioxide	93.43	94.27	96.91	96.44	98.42	100.69	103.37	97.65	3.508	10.525

The method detection limit (MDL) for each calibration is determined from seven runs of the lowest calibration standard.

The MDL is calculated using the following formula:

$$MDL = S * t(n-1, 1-\alpha = 0.99)$$

where S = the standard deviation of the replicate analysis

$$T(n-1, 1-\alpha = 0.99) = \text{Student's } t \text{ value for the 99\%}$$

Confidence level with n-1 degrees of freedom

n = number of replicates.

Table 1. QC operations, frequency, control limits and description of corrective actions.

Operation Check	Frequency	Control Limits	Corrective Action
Method Blank	Before any series of standards	at or below MDL	Repeat blank analysis until objective met or obtain adequate quality blank water or gas
Continuing Calibration Check	First, last and every 10 samples	85-115% of true value	Check calibration equipment function. Reanalyze affected samples
Duplicate Sample	After every 10 samples	≤20 RPD	Reanalyze samples. Flag data if Objective remains unmet.
Second Source QC Standard	After first CCC standard analysis	85-115%	Check calibration equipment function. If DQO remains unmet, determine cause. Recalibrate.

10. Calculations:

The DQO for lab duplicates is calculated according to the following equation:

$$RPD = \frac{[\text{Sample Concentration (ppmv)} - \text{Duplicate Concentration (ppmv)}] * 100}{[(\text{Sample Concentration (ppmv)} + \text{Duplicate Concentration (ppmv)}) / 2]}$$

Calculations for dissolved gas samples are described in RSKSOP-175². The EZChrom software will calculate the concentrations based on their responses in single phase gas samples.

11. Miscellaneous Notes:

The carrier gas (helium) should be left on at all times. Power to the HP Series P200H Gas Chromatograph should be left on at all times. If it is turned off for more than 24 hours and then turned back on, the baseline may be flat. If this occurs, the unit will need to be baked out at 180°C for 24-36 hours for the peaks to return. The MTI Micro GC does not need to be left on all

the time.

It is necessary to close all icons for other programs or utilities on the computer used to operate the GC prior to analyzing samples. If this is not done, it is possible that data may be lost due to communication errors between the computer and GC.

Make sure that the GC conditions are correct. A change in carrier pressure can change response on the detectors.

If there is a problem with “ghost” peaks or baseline upsets during a run, the column(s) may be baked out at for an hour or longer if necessary. It is desirable to perform a bake out after running samples which contain very high levels (>100,000 ppm) of volatile organics.

12. References:

- (1) MTI (Microsensor Technology Inc) P200 Micro Gas Chromatograph user’s manual and HP (Hewlett Packard) P Series P200H Micro GC user’s manual.
- (2) RSKSOP-175: Sample Preparation and Calculations for Dissolved Gas Analysis in Water Samples Using a GC Headspace Equilibration Technique.