BAY INSTRUMENTS

Dissolved Gas Analyzer

Operation Guide

with QuikDATA software

for PrismaPlus and HiQuad mass spectrometers

www.bayinstruments.com

Easton, Maryland, USA

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Ver. 1.4.2

Safety Notices

Inlet explosion potential:

The membrane inlet is designed to operate with a liquid nitrogen trap. *DO NOT immerse the trap in liquid nitrogen with the inlet open to air.* This will cause liquid oxygen to collect in the trap. If the inlet is subsequently closed to air (valves closed) and the liquid nitrogen removed, the trapped liquid oxygen will vaporize causing a potentially explosive condition. *Always have the inlet under vacuum when liquid nitrogen is used.*

Operation with furnace:

Always use a liquid nitrogen trap between the membrane inlet and the furnace when operating the membrane with water. In the event of a membrane break, the cryotrap will prevent water from entering the furnace causing steam and an explosion potential and/or damage to the mass spectrometer.

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DGA Set-up and Sampling Guide

This document is a best practices guide to obtaining high precision dissolved gas measurements using the Dissolved Gas Analyzer*.*

Inlet Care

- Cleaning the Inlet: Signal instabilities are often caused by particles adhering to the capillary walls. Clean the inlet periodically (typically prior to each use) by pumping a dilute (~ 2% v/v) liquid soap solution for ca. 5 minutes.

- Do not bend the SS capillary tube sharply. Repetitive bending can cause it to break.

- Do not rotate the capillary at the inlet seals to avoid breaking the seal. Bend it to new angular positions.

- When finished, pump air to remove the water from capillary.

Standard Water

1. Set up the night before analyzing samples or set up with very rapid stirring for ca. 1 hr prior to slowing the stir rate and allowing final equilibration. Use a moistened sponge in the flask neck to provide 100% relative humidity in the flask (this is a condition of the solubility tables).

2. Use ~600ml of DI, saline or filtered site water to provide an optimal surface area to volume ratio for gas exchange. Set the temperature of the water bath to one that is close to the solubility temperature of the samples. Best precision and accuracy is obtained when the solubility of the standard matches that of the samples. Note that the membrane permeability is dependent on salinity, so matching salinity of samples and standard improves precision and accuracy.

3. Stir the standard water at a speed that causes a vortex, but not so rapid that bubbles are formed (approx. 9 o'clock on the stirrer dial). Under this condition the time constant for gas exchange is ca. 10-15 min.

Start-up

1. Turn on computer and open the *QuikDATA* program.

2. Run the peristaltic pump for approximately 1 minute so that water is in the inlet. Stop the pump.

3. Turn on the rough pump and open the valve to the inlet (keep the mass spectrometer primary valve CLOSED at this point).

4. Add liquid nitrogen to the dewar and place it around the U-trap.

5. Allow the inlet vacuum to stabilize for 1-2 minutes (should be <10 mbar).

6. CLOSE the valve to the rough pump. Switch off the rough pump and open the relief valve to bring the roughing line up to atmosphere (prevents pump oil from migrating up the vacuum line).

7. OPEN the mass spectrometer valve slowly while monitoring the chamber pressure. Try to keep the pressure <$2x10^{-5}$ mbar at all times. Eventually, the valve can be spun all the way open and the pressure should stabilize at a pressure < ~$1x10^{-6}$ mbar. If the pressure remains in the high 10^{-6} mbar or 10^{-5} mbar region, it may be due to excess water vapor coming off the inlet fittings. Unless the pressure continues to rise, this is ok but it will take some time for the analyzer to come down to background.

8. Turn on the peristaltic pump. The mass spectrometer pressure will rise to approx. $5x10^{-6}$ mbar for open ion source instruments or $5x10^{-7}$ mbar for closed ion source instruments.

9. For open ion source instruments ONLY: UNPLUG the cable to the QMS pressure sensor (or turn off display unit (SingleGauge), if present). An active sensor causes signal instabilities and high backgrounds.

10. Adjust the pressure plate on the peristaltic pump tubing to maximize flow. To do this, use the adjustment screw to back off the plate pressure until flow stops and then tighten approx. ¼ - ½ turn. Watch the outflow drops while adjusting. Additional adjustment can be done by adjusting flow to maximize the ion current signals of the individual gases.

11. Run the peristaltic pump with both the inlet tube and waste tube in the standard flask access port and allow the signals to stabilize. This may require 1-2 hours depending on the stability desired and amount of initial background gas in the instrument.

12. Test for inlet leaks by recording the signals with the peristaltic pump on. Turn peristaltic pump off and wait 3-4 minutes. Note the 'off' signal. 'Off' signals should be on the order of 0.5% of 'on' signals except within the first couple of hours after startup when they may be higher.

Common leak problems

Two categories of leaks can be distinguished: 1) large leaks that prevent the mass spectrometer from obtaining a pressure <1E-5 mbar and 2) small leaks that influence the background level of gases.

1. *Large leaks* may be (a) 'virtual' (degassing from surfaces) or (b) viscous (flowing through passageways).

    a. High initial pressures are sometimes due to excess water on the inlet surfaces. If the QMS pressure is in the 10^{-5} mbar region, a scan can be run to determine the background gases. Mass 18 (water) may be observed to be >90 of the total gas load (10 times higher than mass 28). This will eventually come down, or its removal can be sped up by heating the inlet fittings.

    b. A viscous leak commonly affects the air gases in proportion. Viscous leaks are most commonly associated with the valve that closes off the rough pump. Try closing it tighter while observing the signals. Old valves may have 'bottomed out' with the Teflon seal being fully deformed and no longer effective. Replacement of the valve stem seal may be required. Large leaks may also be due to a broken epoxy seal on the inlet, a cracked o-ring (from age) in the Ultratorr fitting, or fitting connections not properly sealed.

2. *Small leaks* can be virtual or viscous but of a smaller magnitude whereby the mass spec can attain near base vacuum levels. The easiest way to identify these small leaks is to conduct a 'background test' by monitoring the signals with the peristaltic pump turned off. In practice, the DGA should have N_2 or O_2 signals that are approx. 0.5% or less of the signal with the pump on. With elevated backgrounds, look at the N2:O2 signal ratio. If it is ca. 4, then it is likely to be a viscous leak, most likely associated with a bad seal at the valve to the rough pump. Test this by tightening the valve or turning on the rough pump. Signal deviations indicate incomplete closure. [This is common cause of background problems.] If the N2:O2 signal ratio does not reflect air, is the vacuum gauge turned on? If so, turn it off. Other, less common causes, include a) air behind the membrane, b) cracked O-ring in the Utra-torr fitting (replace O-ring), c) crack in the inlet glass or capillary seal (try a new inlet), or d) fitting or valve leak after conducting a repair.

3. Viscous leaks can often be detected using a He or Ar flow over various fittings while the mass spectrometer is tuned to mass 4 or 40, respectively. You can safely do this *using the Faraday detector* as long as the pressure of the analyzer is below 10^{-4} mbar.

Running Samples

1. Always turn the peristaltic pump off between samples to prevent air from entering the tubing and causing a large pulse of gas in the inlet.

2. Always sip from the bottom of the vessel or vial because air contamination at the surface occurs rapidly. Avoid drawing up particles that may have settled in the bottom of the vial.

3. Adjust, if necessary, the signal amplification to view minor fluctuations. This provides a gauge for instrument performance and signal stability.

4. Standardize frequently for highest precision and accuracy. This can be at intervals of from 15 minutes to an hour, depending on the instrument and its performance. For high precision measurements, drift in the signals and/or ratios can be significant and correction for drift is done during data processing (see *Principals of data analysis* below).

Shut-down

1. SHUT OFF QMS VALVE!!!

2. Remove liquid nitrogen.

3. Pump on air until water stops exiting the tubing, stop pump and release Viton tubing from the rollers.

4. Remove the inlet to minimize humidity build-up in the inlet.

5. Plug in (turn on) QMS vacuum gauge.

6. SAVE your DATA!!!

Operation of DGA Furnace Accessory

Set up

Important note: the glass tube is quartz and although it is strong, it is brittle and subject to cracks at the ends if not carefully handled in the vacuum fittings.

This description pertains to furnace platforms that have a pedestal-mounted valve assembly. Older frame-and-clamp-mounted valves should follow the same general protocol.

1. Place the platform with furnace in position between the mass spectrometer and water bath. *Do not* attach the vacuum hose behind the furnace between the primary and auxiliary valve assemblies, yet. This is best done after attaching the quartz tube to the valve assemblies.

2. Slide the auxiliary valve assembly on the pedestal all the way to the right. Locate the furnace platform so that there is ~1 cm clearance between the Ultra-torr fittings and the quartz tube ends.

3. Remove the knurled nuts, compression rings and o-rings from the two Ultra-torr fittings and place them on each end of the quartz tube.

4. *Carefully* insert the quartz tube in the left-side fitting and gauge the 'play' of the tube with respect to the alignment of the fitting on the right side. (Do not tighten it in the Ultratorr fitting, yet.) You may need to realign the platform to provide a true alignment of the two valve assemblies. Carefully line up the auxiliary valves and test the alignment by sliding the Ultratorr over the quartz tube. Work the alignment so that the quartz tube moves freely inside *both* Ultratorr fittings. Leave 1-2mm clearance and you should hear/feel the tube tap the metal fitting at both ends. Tighten the wing nut on the valve assembly to fix the auxiliary valves in place. Fit the o-ring/nut assembly on the left side and tighten. Recheck the alignment. (The nut should tighten freely. If it doesn't, then there is a slight alignment problem and realignment should be done.) Tighten the o-ring assembly on the right side. If the nut doesn't tighten freely, rework the alignment.

5. With the auxiliary valve assembly tightened securely, attach the vacuum hose between the primary and auxiliary valve assemblies.

Evacuating the copper reduction tube

1. Start with all 4 valves closed. Turn on the roughing pump. Open the roughing valve on the primary valve assembly (left side of furnace).

2. Evaluate the vacuum. It should stabilize at a level within the expected range of the pump (ca. 10 mbar or less). Leak test if necessary.

3. Turn on the furnace and set to 600 C while the vacuum pump is operating on the copper reduction tube. [Never operate the furnace when the reduction tube is at atmospheric pressure as this will oxidize the Cu prematurely.]

4. The pressure will eventually come down to the vacuum level of the rough pump (on the order of 15-30 minutes). After the vacuum has stabilized for 10+ minutes, it is preferred to use the mass spectrometer to further pump down the tube. First, be sure the QMS is OFF. Then close the roughing valve and open the QMS valve while monitoring the vacuum level of the QMS. The QMS vacuum should rise no higher than the low 10^{-4} mbar level. If it is higher, than return to the rough pump for more time. Once you have the tube pumping by the QMS and the pressure is in the low 10^{-5} mbar region, it is ok to turn on the QMS and use it to monitor the progress of the copper 'burn-out'. Adequate base pressure and background signals may require pumping for 1-2 days depending on the condition of the copper.

Operation of the inlet with the furnace

It is assumed that the copper reduction tube is open to (being pumped by) the QMS at this time.

1. Evacuate the membrane inlet by opening the auxiliary valve to the rough pump. [*Do not evacuate the inlet through the copper column*.] Place liquid nitrogen around the inlet cryotrap. It is recommended that an auxiliary U-trap be placed between the QMS and furnace (this lowers the CO_2 and mass 30 outgassing signal). **IMPORTANT:** ***Always use liquid nitrogen on the inlet U-tube trap to prevent water from a burst membrane from entering the hot furnace.***

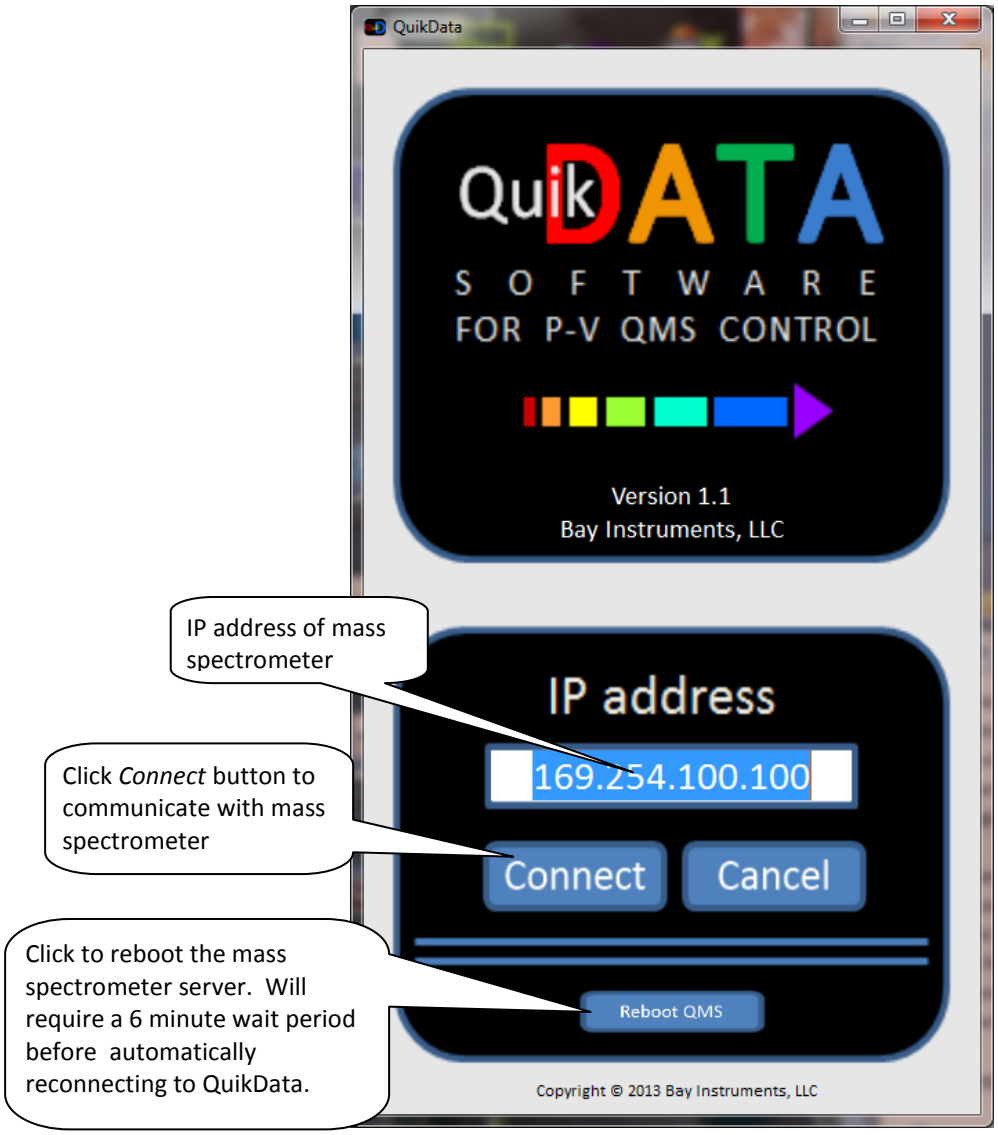
2. In a manner similar to working without the furnace, allow the vacuum to stabilize. Subsequently, close the auxiliary roughing valve and then open the auxiliary valve to the copper reduction tube while you are monitoring the QMS pressure.

QuikDATA Software Guide

The IP of your QMS should be 169.254.100.100

Computer control of the mass spectrometer is through a network cable connection (cross-over cable required) with a WinCE OPC communication server on the mass spectrometer and an OPC client on the laptop or desktop computer. Connection problems may occur if the IP addresses of the computer and mass spectrometer are 'incompatible'. It is recommended that the mass spectrometer use a fixed (not DHCP) address of 169.254.100.100 with subnet mask of 255.255.0.0 with the local computer using IP address 169.254.100.99 with subnet mask of 255.255.0.0 (DHCP is disabled).

Connect Window



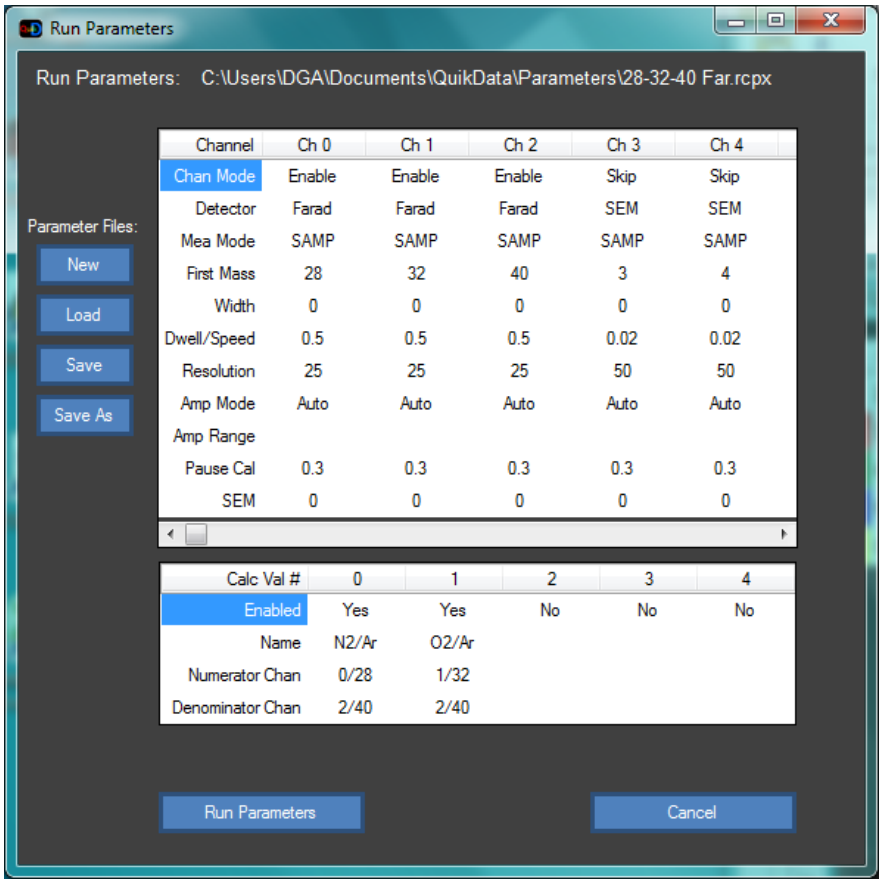
Errors in trying to connect to the mass spectrometer:

1. Confirm using Quadera software that the communication establishes itself using the designated IP addresses. If there are communication problems with Quadera even after rebooting both the computer and mass spectrometer (power off/on) then the IP configuration is incorrect and/or a firewall is active. Turn off all firewalls (some computer vendors add their own firewalls in addition to the Windows firewall). If Quadera halts at 29% loading, it usually indicates a problem with the IP addresses. If Quadera halts at 85% then it usually means that there is a firewall blocking the communication.

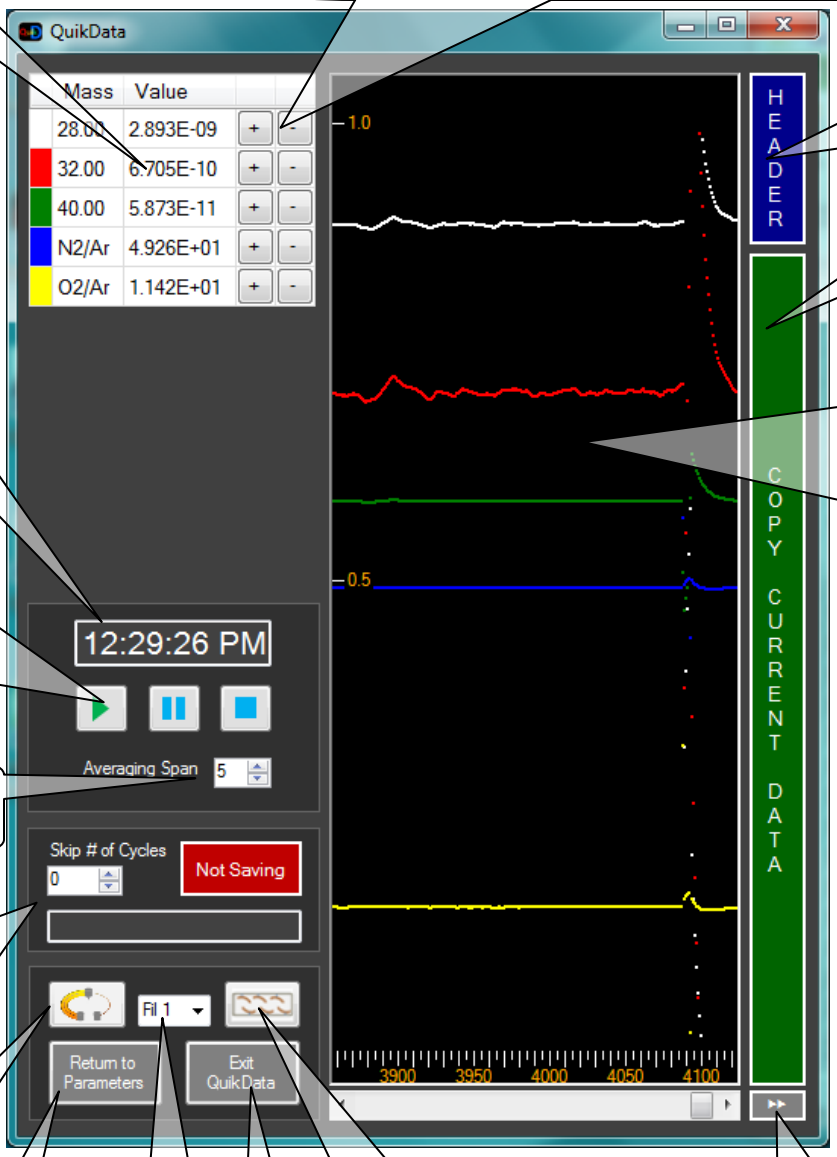
2. "*Exiting, failure to validate instrument registration*" error means that a valid QMGbind file does not reside in the program's home directory. Contact Bay Instruments regarding this error.

Parameters Window

The parameter screen is where the masses and their detection are defined along with calculated ratios. Up to 128 mass channels can be defined along with 5 ratios. Only Sample mode is available in QuikDATA. Refer to Quadera documentation for parameter descriptions.



Data Display Window



Real-time data (ion currents) or data from history when clicking on chart.

[+] [-] Zoom buttons: Three level data zoom by eliminating one or two most significant digits in the mantissa. Exponent is ignored. Example: Mass 28 plots at value 0.893 at present zoom level.

Copies mass and ratio header information to the clipboard.

Copies ion current data to the clipboard.

Time that cycle is completed.

Left button click anywhere on chart to record ion current data from that point in time to the clipboard.

Right button click to interrupt the 6 second hold on the data.

"Play"button to restart cycle. "Pause button to pause data cycle. "Stop" button to halt cycle and clear all data.

Number of points for running averages

Data save panel: All cycles or cycles at intervals (e.g. every 5 cycles) are saved to a cvs file. Initiate and stop using the Saving button.

Filament button: *click* to turn on/off.

Filament select switch.

SEM button: *click* to turn on/off.

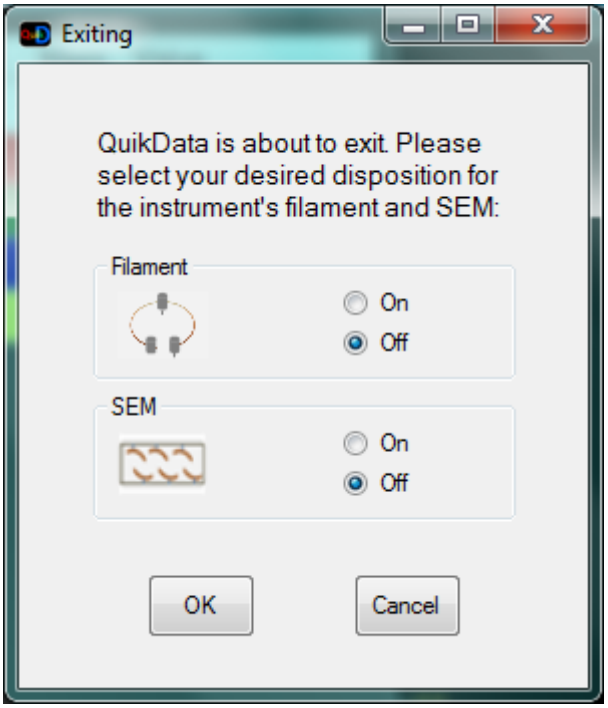
Jump display to current updating data.

Button to return to Parameter window. Will stop run and erase data.

Exits program and asks how to leave Filament and SEM.

Exiting QuikDATA Window

Exiting gives the option of leaving the filament and/or SEM on or off after closing the program.



Principals of Data Analysis

There are a number of ways to covert the ion currents and/or ion current ratios to useful data. Generally, ratios provide higher precision than ion currents of individual gases and many applications allow simple calibration of the measurement ratio (e.g. of N_2/Ar) and conversion of the ratio to a gas concentration (e.g. N_2). Ratios are appropriate when you can assume for your experiment that the denominator gas (Ar typically) is conservative and unchanged. Hence, a calibration factor can be calculated from the ion current ratio of the standard water (R_{mea}) as: Cal = R_{sol}/R_{meas}, where R_{sol} is the ratio of the gases determined from the air saturated solubility of the standard water. Cal is then used to scale the sample measurements to obtain the solubility ratio of the sample. Without losing precision, your spreadsheet can also be set up to calibrate the ion currents of the individual gases using the same method for the ratios, except that you do it on a gas by gas basis. After these calibrations, the gas ratios can be calculated, providing the same result as the first method.

Background correction is commonly done in mass spectrometry. In practice with MIMS and general air gas analysis, subtraction of the background signal (determined by turning off the peristaltic pump for ca. 3-5 minutes) does not impact the data as its effect is usually smaller than the analytical precision of the instrument and there is no effective impact on measuring differences between two samples as is the most common application. However, some gases (e.g. $^{15}N_2$ at mass 30) can have a substantial background and it is necessary to first correct the sample ion current by subtracting the background ion current.

Drift in the instrument signal is usually present at a level that warrants correction. Drift is always more significant early in a run than later and therefore, more standards should be analyzed earlier compared to later. A general rule of thumb is to measure standards at 15 minute intervals until the ion currents or ratios exhibit little change between standards. Subsequently, standards may be run at ~30 minute intervals, and ultimately hourly intervals, assuming the instrument is performing well. Drift correction is accomplished by interpolating the Cal factor as a function of time-of-day using a calculated slope across each interval between two sets of standards. Validation of the assumption of linearity can be done by plotting the Cal factors as a function of time-of-day over the entire analysis run.

Instrument linearity and slope affects accuracy. When tuned correctly and operated in the appropriate pressure range (mid 10^{-6} mbar for open ion sources, mid 10^{-7} mbar for closed ion sources), the instrument is within 0-10% of the expected slope. Calibration of this slope can be accomplished using a second standard bath operated at a temperature of ca. -7 C to +10 C of the primary (inlet) temperature bath (secondary baths set below the temperature of the primary bath will generate supersaturated conditions during measurement and cause outgasing (typically at a delta T of ca. 8-10 C)). A bath sitting next to the peristaltic pump allows direct sampling of the secondary standard. The inlet coil allows the temperature of the secondary standard to equilibrate to the measurement temperature, which *must* remain constant. See section *MIMS Principals and Methods of Calibration* for further calibration discussion.

Troubleshooting Common Signal Instabilities

- ***All gas signals simultaneously exhibit periodic spikes.*** This is caused by gas bubbles in the inlet line. Bubbles may either enter the line at the inlet or formed within the line if it is dirty or if the water is supersaturated. First, check to see if the stirrer is spinning too rapidly and entraining bubbles in the standard water. Reduce the stir speed if necessary. If the problem persists, it is likely that the inlet tubing is dirty (contains particles) or the pressure plate on the peristaltic pump tubing is too tight. To clean/clear the inlet, the following methods can be tried:

    1. Rapidly cycle the direction (forward/reverse) of pumping a number of times.

    2. Pump on a dilute (1-2%) solution of liquid detergent for ca. 5 minutes (don't let the waste go into the standard flask).

    3. Push water forcefully through the inlet using a syringe. *Do this test with the mass spectrometer valve closed.* First, remove the Viton tubing from the peristaltic pump in order to have a free flow path. Then, attach a syringe to the inlet using a needle and tubing connector. Use enough finger pressure to push the syringe water through the inlet until the outlet streams as an attached smooth flow for about 3 cm beyond the capillary. IMPORTANT: excess pressure can cause the membrane to detach from the SS capillary. Also, a particle lodged downstream of the membrane may cause excessive back pressure on the membrane causing the membrane to detach. If there is undue pressure needed to push the syringe water, there may be a particle stuck in the inlet and the following procedure may work.

    4. The peristaltic pump tubing may be worn. You may be able to feel an unevenness in the tubing by pressing and rolling the tubing between your fingers in the area of the rollers. Try switching it end-to-end by slipping it off the tied connections and reattaching in opposite direction.

    5. Insert a thin wire (a high 'E' steel guitar string works well) through the capillary tubing, while being careful not to tear the membrane.

- ***Gas ratios are unstable, more 'chattery' than normal, or shifted from their normal value.*** This usually is a mass spectrometer tuning problem. Peaks should be assessed using the "Tune" program with the peaks displayed with a *Width* of 1 and a *First mass* of 0.5 units below the desired peak (e.g. 39.5 for Ar) and displayed in *linear* mode. Emission current should be 1.0 mA or less and Cathode should be 70V. Adjust *Resolution* so that the peak crosses the margins (i.e. 39.5 and 40.5 for Ar) at approx. 10% of the peak height. Adjust the ion source voltages (Ion Ref, Field Axis, Focus, Extraction) to obtain a 'good looking' peak with high amplitude. To accomplish this, adjust the Field Axis upward until there is an appearance of multiple peaks on the top of the main mass peak. Then lower the Field Axis approximately 20%. Adjust the Focus and Extraction voltages to maximize the peak. Repeat the process starting with the Field Axis until there is a satisfactory peak. The rules of thumb are: 1) err on the side of a lower field axis as signal stability deteriorates at excessively high field axis V, 2) peaks shouldn't be pointy – tune them down to have a little flat area at the top, if possible, and 3) emission current should never be >1 mA as higher currents lead to instabilities.

- ***Approaches to diagnosing instabilities not corrected by methods above:*** It is helpful to first identify the cause as being associated with the mass spectrometer or the inlet. We do this by changing the way gas is inlet into the mass spectrometer. A fused silica capillary (25 micron diameter by ca. 50 cm long) connected to a 3/8" Swagelok adapter can be substituted for the inlet to let air in at the desired rate. If the signals appear smoother (they may not stabilize completely) then the fluctuations are due to the membrane inlet and not the MS. This is by far the most common experience.

- ***Inlet related problems:*** Check/do the following: 1) Try a new membrane inlet. 2) Check the O-ring inside the Ultratorr fitting. 3) Check the secondary (roughing) valve: try closing it tighter – do the signals change? If so then the seal is wearing out. Replace the stem seal. 4) Is there contamination in the inlet fittings/valves? Use a cotton swab or wipe to determine whether there are deposits on the inside of the SS fittings. 5) Do a He (or Ar) leak test by directing He in various parts of the inlet while monitoring the He (mass 4) signal.

Tuning the Mass Spectrometer

Overview

The assumption here is that the instrument will be optimized for high stability and linearity and not high sensitivity. The goal is to set the ion source voltages and currents to settings that 1) produce highly reproducible, smooth peaks, 2) yield highly stable signals through time and 3) minimize pressure-dependent effects on linearity and gas ratios. Tuning is done using Quadera software with gas flow at a pressure near that in general use. Bay Instruments supports several mass spectrometers that have different operational regimes. Use the following table to identify your instrument.

Know your ion source and optimal pressure range

Instrument	*Housing*	*Ion source*	*Preferred operating P*
Prisma or PrismaPlus	CF cross, gauge on top	Open	4-6 E-6 mbar
PrismaPlus	"T" housing, gauge on side	Gas tight	4-6 E-7 mbar
422 or HiQuad	Housing with opposing gauge and inlet flanges	Cross-beam (like open)	4-6 E-6 mbar
HiQuad	Inlet flange axial to housing	Gas tight	4-8 E-7 mbar

A few 'rules' to keep in mind

1. Do not set the emission current above 1 mA. -- Higher emission currents can result in significant drift in the signals as well as shorten the lifetime of the filament. For *gas tight (closed) ion sources*, best linearity is obtained with emission currents ca. 0.3-0.4 mA.

2. Lowering the emission current usually increases linearity and stability and improves ratio consistency across pressures.

3. Do not set the Field Axis voltage too high (not above ca. 6 for PrismaPlus or 15 for 422/HiQuad). -- Excess F.A. may lead to instability.

4. Know your optimum mass spec pressure. -- This depends on the type of ion source. Open ion sources should generally be run in the mid 10^{-6} mbar region and gas-tight ion sources in the mid 10^{-7} mbar region. Linearity and 1:1 proportionality are poorer at higher operating pressures.

5. Old filaments can perform poorly regardless of ion source settings. -- Compare behavior to the other filament.

Target values for key Ion Source parameters Values should not deviate significantly from the following values. (HiQuad and PrismaPlus use negative V for entries.)			
Parameter	*HiQuad/422 QMS*	*Prisma/PrismaPlus open ion source*	*PrismaPlus closed ion source*
Cathode	70 V	70 V	70 V
Emission current	1 mA or less	1 mA or less	0.25-0.4 mA
Field Axis	15 V	5 V	5 V
Resolution	25	50	50

Typical procedure for standard tuning

1. Within the tuning program (Quadstar or Quadera), using Scan-N (raw data output), scan mass 40 (Argon) (First mass=39, width= 2, or First mass = 39.5, width = 1).

2. Keep the Cathode V and Emission mA at the previous setting.

3. Adjust Field Axis (FA) up by small increments until the peak begins to exhibit multiple subpeaks. From that value, decrease FA approx. 20%.

4. Adjust Extract V to maximize peak height.

5. Adjust Focus to maximize peak height.

6. Repeat 4 and 5.

Criteria for good peaks is general 'smoothness' of the peak top. Difficulty in generating a 'smooth' peak may be related to a dirty ion source. This may not be a problem if stability is ok, as assess by steady-state signal statistics.

MIMS Principals and Methods of Calibration

Overview

The relationship between the mass spectrometer signal and the dissolved gas concentration is determined by two general attributes of the instrument, 1) the mass spectrometer response to gas flux and 2) the factors that affect diffusion from the water to the vacuum. The 'ideal' MIMS instrument provides signals that are directly proportional to the dissolved gas concentration. Fick's first law of diffusion (material flux is proportional to the concentration difference across a distance) is commonly cited as the reason MIMS can be used as an analyzer of dissolved gas concentrations. Given that the effective concentration on the vacuum side is effectively zero, the flux is directly related to the concentration in the water on the opposite side of the membrane. MIMS instruments do not always operate in an ideal manner and the following topics provide discussion of evaluating and handling non-ideal behavior.

Fick's 1st law

$$\text{Flux} = -D\frac{\delta C}{\delta x}$$

where D = diffusion coefficient, C = concentration, x = distance.

D is a function of T following an Arrhenius relationship, which is a linear ln-transformed function.

Flux increases with C, T, flow rate (smaller δx).

High precision MIMS measurements are generally valid when the total gas pressure of the sample is close to that of the standard. The physics of gas transport relating to "Knudsen flow" in a MIMS instrument includes a mass-dependent effect that alters the ratio of gases according to √mass(1)/√mass(2), depending on the P at the membrane. Highest accuracy is obtained when the sample and standard total gas pressures in the inlet are similar. Alternatively, if the sample dissolved gas pressure significantly deviates from the gas pressure of the standard, then one can expect a calibration shift in the N_2/Ar ratio.

Do's and don'ts

Important things to remember with explanations below:

- Do run the membrane at a single temperature and flow rate for a given set of analyses.
- Don't do multipoint calibrations by altering the membrane temperature along with the solubility standard.
- Do abide by optimal instrument ion source parameterization and pressures to assure signal linearity and 1:1 proportionality if using single point calibrations.
- Do set the temperature and salinity of the standardization water to values close to those of the samples for best accuracy and precision.

Gas diffusion across the membrane and the calibration factor

The conversion of mass spectrometer ion currents to gas concentration is done using measurement of standards at known solubility. This calibration factor is a function of diffusive flux across the membrane and the mass spectrometer sensitivity to the gas. Calibration factors are often of the form: gas concentration/ion current. Considering only gas flux through the membrane at this stage of the discussion, the signal will be related to ***factors that affect diffusion across the membrane***. These factors include:

- *Temperature* – The diffusion coefficient is temperature dependent with higher fluxes at higher temperatures. It is a log linear relationship, but may appear linear over narrow temperature ranges. Because the calibration factor is temperature dependent, *it is important to keep the temperature constant for all calibrations and sample measurements in a given set of analyses.* In practice, it is convenient to use the same temperature for both the primary solubility standard and the membrane temperature, although this is not a requirement. However, it is a requirement that the membrane temperature, which is set by the water temperature flowing across the membrane, be held constant in order to keep D constant.

- *Flow* – Altering the water flow rate through the membrane tube causes significant changes in the instrument signal. Two principal factors cause this phenomenon. The first is the affect on the diffusive distance (δx in the Fick equation) relating to changes in the laminar and/or turbulent boundary adjacent to the membrane. Even though the δx of the physical membrane may be constant, diffusion also has a component within the water adjacent to the membrane. The second factor has to do with withdrawal of gases from the water as the water flows through the tube. With distance from the upstream point, the gas concentration declines exponentially to the downstream point. The flow rate influences the extent to which there is drawdown in gas concentration (less drawdown at faster flows)and therefore the gas flux increases with flow rate. With highly permeable membranes like silicone, signal levels vary significantly with flow rate. Therefore, calibrations and sample analyses need to be done at a constant flow rate although the chosen flow rate is somewhat arbitrary. A highly stable flow can be repeatable at better than 0.1% signal variation.

- *Salinity* – Salinity influences the water activity and water activity can affect the swelling of silicone membranes. Consequently, there is a salinity effect on the permeation of gases across the membrane. Therefore, if seawater samples were analyzed using DI water for the standard, than there would be an inaccuracy with respect to solubility. In practice for many applications, it is not an absolute requirement for the standard water to be at the same salinity as the sample water *if* the data from the samples will be analyzed on a relative basis (e.g. for time-course changes or inlet vs. outlet concentrations), because it is only the *difference* relative to a constant baseline that is required. However, if the data are to be used for determination of absolute concentration (e.g. to compare to theoretical field solubilities), then the standard water should be at the same salinity as the samples (use of filtered site water would provide highest accuracy).

- *Gas-specific calibration factors* – We do not expect the calibration factors for N_2, O_2 and Ar, for instance, to be similar because the permeability coefficients for the various gases are typically different for most membrane materials. This is the principal reason that measured N_2/Ar ion current ratios are quite different from the expected solubility ratio. This effect is of no concern (as long as the respective permeabilities are constant) since the calibration factor takes this into account. A secondary factor for deviant gas ratios has to do with mass spectrometer sensitivities that differ (slightly) for different gases.

Ion source linearity and 1:1 proportionality

With good control of flow and temperature at the membrane, gas flux across the membrane has a proportional relationship with analyte concentration. Ideally, the gas flux into the ion source should produce a signal that is directly proportional to that flux. Although mass spectrometers are generally noted for their linearity, it is possible to 'drive' the instrument in a way that results in a non-linear response and/or signal change that is not in a 1:1 proportion (i.e. that a doubling in the flux does not result in a doubling of the signal, even though the response may be linear). With single point calibrations, it is necessary to assure

that the instrument is operating in the linear region of the pressure (flux) curve and that the increase in signal is proportional with a relative slope of 1 to the gas flux.

There are several key parameters that need to be optimized to yield the desired response. These include:

- *Pressure in/at the ion source* – Linearity of the ion source is dependent on the gases being in the molecular flow regime, which means that the molecules are so sparse, due to low pressure, that they do not bump into each other – only the walls. Generally, this is at pressures in the 10^{-6} mbar range or lower in mass spectrometers. At higher pressures there is a progressive loss in signal relative to pressure and the pressure-signal relationship is non-linear. Ion source pressures are typically estimated using a pressure gauge that 'sees' the pressure within the mass spectrometer housing. This is a good estimate of the ion source pressure only for those instruments configured with an 'open ion source' (one that 'sees' the gas composition in the housing). Alternatively, instruments with a 'gas tight ion source' use an ion formation chamber that has restricted gas flow out to the chamber and the relevant pressure inside the ion source is ~10 fold greater than the chamber pressure. In both cases it is necessary to establish the relationship between pressure (related directly to gas flux) and signal. The table in the *Tuning the Mass Spectrometer* section provides information for identifying which mass spectrometer you have and the optimal pressure for linearity.

- *Ion source tuning* -- The ion source settings in Pfeiffer Vacuum mass spectrometers can influence the calibration slope. The effects are instrument specific. Generally, if the tuning is done as specified in the Tuning section, than the instrument provides linearity and slopes that are close (within 10%) to the desired 1:1 proportionality. However, there are some important settings that may cause significant deviations from the 1:1 slope. The following are ***two settings to avoid***.

    1. *Prisma/PrismaPlus open ion source*: It has been observed that the calibration slope is very sensitive to the *Extract voltage*. It is important to set that voltage to a value that maximizes the peak (see Tuning section).

    2. *PrismaPlus gas tight ion source*: It has been observed that the calibration slope is very sensitive to the *Emission current.* Emission should be set in the 0.25-0.4 mA region.

Analyzing ^{15}N isotopes in N_2 by MIMS

General Principals

The ^{15}N isotope of nitrogen exists at an abundance of 0.00365 (0.365%) and this value is reflected in the isotopic distribution in N_2 of the atmosphere. Using MIMS, dissolved N_2 isotopic distribution is measured at masses 28, 29, and 30. The relative fractions of these masses is 1.34×10^{-5} for $^{30}N_2$:$^{28}N_2$ and 7.32×10^{-3} for $^{29}N_2$:$^{28}N_2$. Immediately, we see that mass 30 is at a level of ~13 ppm relative to the dominant mass. Consequently, efforts need to be made to 1) precisely resolve the minor component and 2) assure that interferences at mass 30 are minimized and corrected.
In practice, the ion current ratio of mass 29:mass 28 is close to the expected $^{29}N_2$:$^{28}N_2$ ratio when measuring air-equilibrated water. The ion current ratio of mass 30:mass 28, however, is usually elevated relative to the expected 1.34×10^{-5}. Mass 30 contributions from nitric oxide (NO) and trace organic compounds can be a major fraction of the mass 30 peak. Two major factors have been identified: 1) the cold cathode pressure gauge produces products at mass 30 and 2) the mass spectrometer produces NO in the ion source from the reactions of O_2 and N_2 at the hot cathode

(filament). The first interference is eliminated by turning off the pressure gauge. The second interference can be reduced by preventing O_2 from entering the MS using an in-line furnace with hot (600^o C) copper in the gas stream.

Use of furnace accessory

Details of making connections are described elsewhere in the Operations Guide. General setup should include cryotraps on both sides of the furnace. The trap between the inlet and furnace prevents water from entering the heated area in the event of a membrane break. The trap located between the furnace and mass spectrometer eliminates CO_2 that is produced by the heated Cu column.

Optimizing Multiple Ion Detection

Because mass 30 is near trace levels, better sensitivity is obtained using electron multiplier (SEM) detection compared to Faraday detection. It is only necessary to operate the SEM at a voltage that amplifies the signal by ~100, which elevates the ion current of mass 30 from the 10^{-14} amps region to 10^{-12} amps region. Dwell settings of 0.5 s are appropriate for all masses. Alternatively, good precision of the gas ratios can be obtained using Faraday detection if the dwell for mass 30 is set to 2 or 5 seconds.

The following masses are typically measured: 28, 29, 30, 32, 40. Mass 32 (O_2) should be near trace levels with the furnace operating.

Determining calibration factors for masses 28, 29 and 30

There is little interference for masses 28 and 29 and calibration factors should be relatively similar. Calibration factor for mass 28 = N_2 solubility/IC, where IC is the ion current. Calibration factor for mass 29 is 7.27E-3(N_2 solubility)/IC. The factor 7.27E-3 is the amount of mass 29 for atom% normal N_2. Because there is typically an elevated mass 30 background signal in the mass spectrometer, the calibration factor for mass 30 is taken to be the average of the calibrations for masses 28 and 29. The concentration of mass 30 *above background* is determined by (Cal. factor)*(IC_{sample} - $IC_{standard}$).