

Owlstone At-Line Sampling Module Manual



About this Manual

This user manual contains all the information you will need to initially install and run the at-line sampling module for a Lonestar system. Additional information and updates are available on the owlstonenotech.com website under the support tag.



This symbol is used to highlight a section explaining particularly important safety considerations

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1. Notices

1.1 Copyright

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1.2 Disclaimer

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1.3 Notice of Proper Use of Owlstone Ltd Instruments

The supplied system is in compliance with international regulations. If this system is used in a manner not specified by Owlstone Ltd, the protection provided by the system could be impaired

1.4 Contacting Owlstone

Visit the Owlstone website (www.owlstonenanotech.com) for up to date contact details and service support:

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1.5 Service and Maintenance

No user serviceable parts. Please contact your Owlstone representative for details of the return and repair procedure.

1.6 Recycling and Disposal



This Product has been designed and manufactured with high quality materials and components, which can be recycled and reused.

This product is required to comply with the European Union's Waste Electrical & Electronic Equipment (WEEE) Directive 2002/96/EC so should not be disposed of in normal waste; Dispose of as electric waste or consult Owlstone Ltd for details of our recycling program for this product.

For users outside the European Union consult local authorities for correct disposal or contact Owlstone Ltd.

1.7 Warning labels



This warning label indicates parts of the product that will become hot during use. Please take care.

1.8 CE Declaration of Conformity (DoC)

OWLSTONE Ltd performs complete testing and evaluation of its products to ensure full compliance with applicable domestic and international regulations. When the system is delivered to you, it meets all relevant electromagnetic compatibility (EMC) and safety standards as described in the declaration below.

OWLSTONE Ltd declares under its responsibility that the electronic product AT-LINE SAMPLING MODULE is in conformity with the following standards:

EMC Directive 2004/108/EC

The AT-LINE SAMPLING MODULE system complies with the following standards:

- CR47: 2006 Class A Code of Federal Regulations: pt 15 Subpart B – Radio Frequency Devices – unintentional radiators
- EN61326-1:2006 Electrical equipment for measurement, control and laboratory use – EMC requirements, Group 1, Class B equipment (emission section only)
- EN61326-1:2006 Electrical equipment for measurement, control and laboratory use – EMC requirements, Industrial Location Immunity (immunity section only)
- EN61000-3-2:200 Electromagnetic compatibility (EMC) – part 3-2: Limits – Limits for harmonic current emissions (equipment input current up to and including 16A per phase)
- EN61000-3-3:1995 (+A1/A2) Electromagnetic compatibility (EMC) – Part 3-2: Limits – Limitation of voltage changes, voltage fluctuations and flicker in public low voltage supply systems for equipment with rated current $\leq 16A$ per phase and not subject to conditional connection

Low Voltage Safety Compliance

This device complies with Low Voltage Directive 2006/95/EC.

Changes that you make to your system may void compliance with one or more of these EMC and safety standards. Changes to your system include replacing a part or adding components, options, or peripherals not specifically authorized and qualified by OWLSTONE Ltd. To ensure continued compliance with EMC and safety standards, replacement parts and additional components, options, and peripherals must be ordered from OWLSTONE Ltd or one of its authorized representatives.

FCC Compliance Statement

This equipment has been tested and found to comply with the limits for a Class A digital device, pursuant to Part 15 of the FCC rules. These limits are designed to provide reasonable protection against harmful interference when the equipment is operated in a commercial environment. This equipment generates, uses and can radiate radio frequency energy and, if not installed and used in accordance with the instruction manual, may cause harmful interference to radio communications. Operation of this equipment in a residential area is likely to cause harmful interference, in which case the user will be required to correct the interference at his or her own expense.

1.9 Safety Notice



Caution: Read these operating instructions fully before use and pay particular attention to sections containing this symbol

Always observe the following safety precautions:

- Only connect to an earthed supply socket. **THE MAINS ADAPTOR IS CLASS 1 CONSTRUCTION AND MUST BE EARTHED (GROUNDED)!**
- Ensure the mains outlet is easily reached to disconnect the unit
- Use only the supplied mains adaptor and leads supplied
- The equipment is heavy; use the handle provided to lift and carry the unit
- Always disconnect the equipment from the mains supply before moving
- This equipment is for use in moderate climates only. **NEVER** use the equipment in damp or wet conditions
- Avoid excessive heat, humidity, dust & vibration
- Do not use where the equipment may be subjected to dripping or splashing liquids

1.10 Harmful substances

The AT-LINE SAMPLING MODULE system can be used with a wide range of samples, some of which could be toxic or harmful. On heating these materials, flammable or toxic gases may be released.



The AT-LINE SAMPLING MODULE system is not a fully sealed unit, therefore for this reason **it is essential that the user conduct a risk assessment** for the substances to be used in the AT-LINE SAMPLING MODULE and establish safety protocols to cope with the release of such materials under the normal operation of the unit.

These protocols must include suitable installation (e.g. in a fume cupboard, provision of extraction, etc.) and operational procedures to protect the operator.



Materials with a fire point in excess of 183 °C **must not** be used in the AT-LINE SAMPLING MODULE.

Check chemical compatibility: Materials in the flow path include PTFE, stainless steel, aluminium, silicon, graphite, circuit board and Viton®. Ensure test atmospheres are neither corrosive nor reactive with materials in the flow path. If in doubt please contact an OWLSTONE representative using the contact details provided.

1.11 Installation and Location



The three components together, unpackaged, weigh ~ 12.2 kg; please take care in handling to avoid injury.

Before using the system, ensure that all power cables are intact with no damaged insulation or frays.

Ensure that the LONESTAR instrument and AT-LINE SAMPLING MODULE are placed on a solid, level surface, which is able to support their weight

Only use the OWLSTONE supplied power supply

Ensure cabling is routed behind the system, at bench level, posing no risk of tripping. Ensure all cables are detached from the LONESTAR instrument before attempting to move the unit

The LONESTAR instrument gets warm during operation. Handle with care and ensure there is adequate ventilation around the system

Do not place in space that is poorly ventilated or confined. Allow at least 50cm clearance from walls and free flow of air around the system

Do not place near flammable materials

2. Technical Specification

Table 1 Mains input to heater controller

| Parameter | Specification |
|-------------------------|--------------------|
| Input Voltage | 100–240Vac 47-63Hz |
| Input current | 3.2A |
| Output Voltage: | 24Vdc \pm 2.5% |
| Output current | 5.41A |
| Max Output Power | 130W |

Table 2 Dimensions of At-Line Sampling Module components

| Component | Dimensions / mm | Weight / kg |
|------------------------------|-----------------|-------------|
| Sampling module | 130 x 170 x 200 | 3.8 |
| Pneumatics controller | 105 x 320 x 365 | 3.4 |
| Heater controller | 95 x 320 x 365 | 5.0 |

3. Overview

The At-Line Sampling Module add-on for a Lonestar is made of three sections:

- Sampling module – holds sample bottles to be measured, allows split flows to be set for diluting the headspace sample before feeding it to the Lonestar and provides a particle filter to protect FAIMS chip from blocking or shorting
- Heater controller – sets and controls the temperatures of the sampling module sections and the sample temperature
- Pneumatics box (optional) – brings together regulator, power supplies and air on/off switch

Together this allows the Lonestar system to be used for accurate headspace sampling of discrete samples for a wide range of applications.

3.1. Sampling module

When the sampling module is connected to the Lonestar and in use, it appears as shown in Figure 1 below. The filter heater, heated lid and bottle heater each have a wire already attached to them with a plug that must be connected at the back of the heater control box.

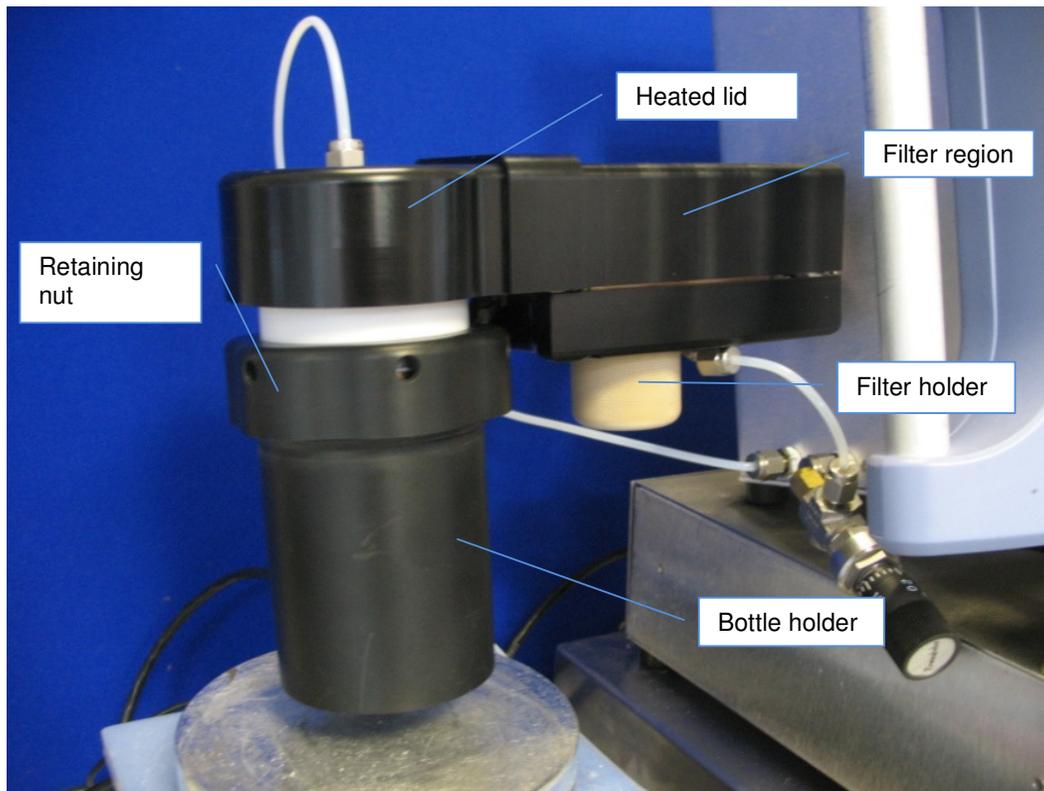


Figure 1 Picture of sampling module

The system is fixed to the Lonestar by a 1/4" inch Swagelok pipe connection and a support screw on the supporting swing arm.

3.2. Heater controller

The connections on the back of the heater control box are shown below.

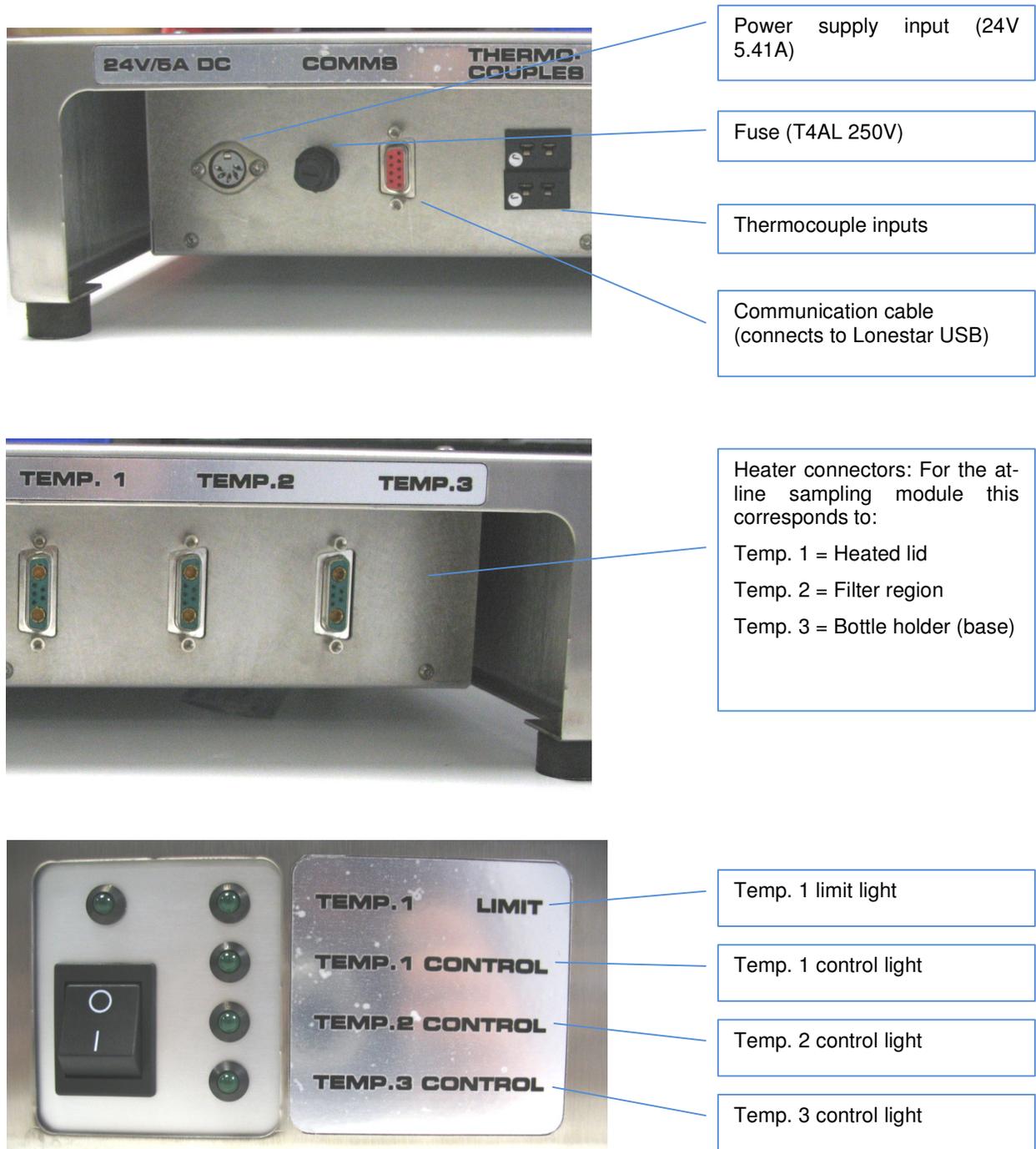


Figure 2 Back (TOP) and front (bottom) of heater control box

If the Temp.1 thermal limit is exceeded then both the Temp 1 limit and control lights will go out and Heater 1 will switch off.

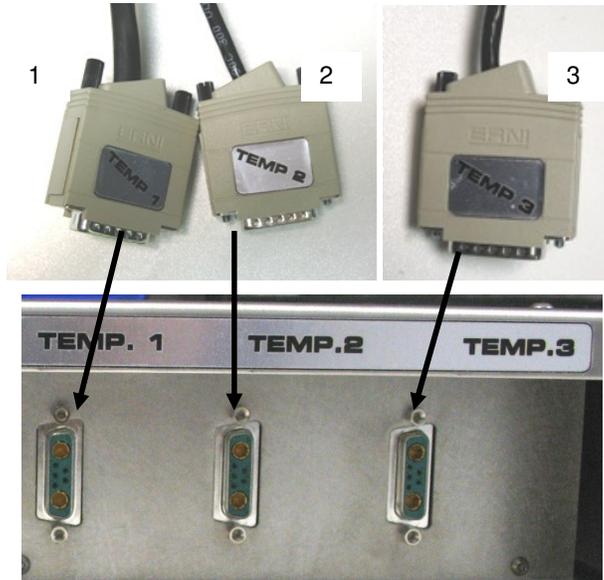
The temp. 1, temp. 2 and temp. 3 control lights are on when the heaters are being brought up to temperature, and flicker on and off when the correct temperature has been reached.

4. Installation

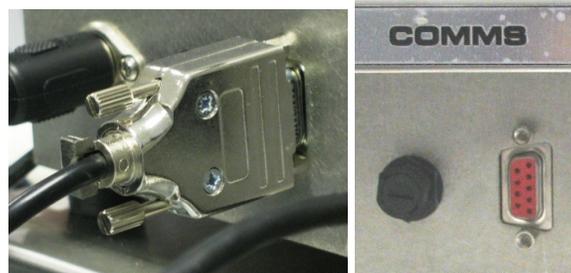
To set up the heater control box, follow these steps:

1. Connect the plugs from the GBH to the correct ports at the back of the heater control box.

The plugs are labelled and *must* be connected in the correct positions.



2. Connect the communication cable to the red port on the heater controller labelled Comms.



3. Insert the other end of the communication cable into one of the USB sockets on the Lonestar.



4. Insert the plug from the power supply into the socket labelled 24 V / 5A DC.



5. Plug in the power supply at the mains and set the power switch to ON. The power light, temp. 1 limit light and all of the control lights come on.
6. When the heated line, heated lid and bottle heater have come up to temperature, the temp. 1, temp. 2 and temp. 3 lights will flicker to show that the temperature is being maintained.
7. If the power and temp. 1 limit lights turn off during operation, this means that the thermal trip has been exceeded and the heaters have been turned off. In this case, turn the heater controller off and contact Owlstone.

5. Operation of sample module

5.1. Sample bottles

A variety of sample bottles can be used. The default bottle is a 120ml trace clean glass bottle. In order to ensure an air tight seal when taking a headspace measurement a 34mm by 4mm o-ring is fitted to the bottle shown by the white arrow in the below picture.



Figure 3: Sample bottle with o-ring

5.2. Mounting a sample

Samples are mounted into the sampling system by inserting the bottle into the bottle holder, pushing it up into the heated lid and spinning the retaining nut until a snug fit is achieved. There is no need to excessively tighten as the sealing is achieved by an o-ring on the neck of the bottle.



Figure 4 Mounting a sample

6. Operation of heater controller

When the heater controller is attached to the sampling module of a Lonestar the controller box will control the temperatures of the three regions of the module within the following ranges:

| | Range | Default |
|----------------------|-------------------|---------|
| Bottle lid | Ambient to 110 °C | 75 °C |
| Filter region | Ambient to 130 °C | 110 °C |
| Bottle holder | Ambient to 60 °C | 35 °C |

The heater controller temperature ranges are modified using the provided software “3-PID configurator”. The boot screen is shown below.

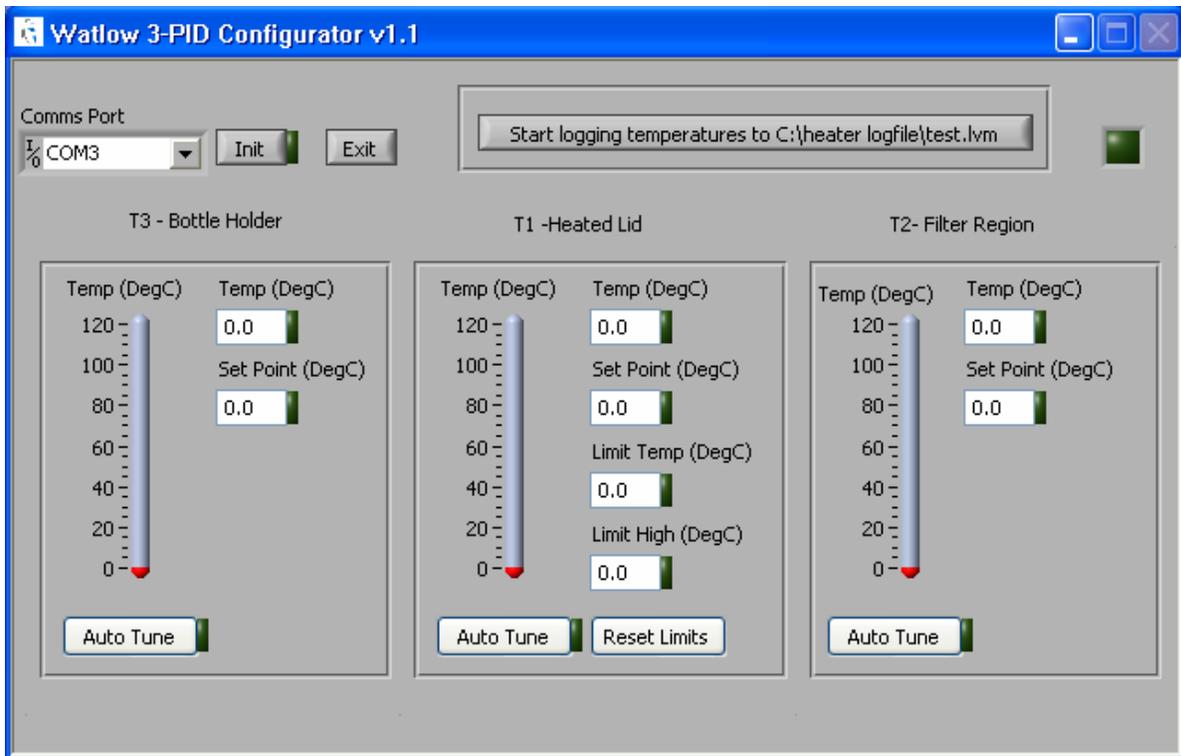


Figure 5 Screen shot of heater controller software

Select the comms port that the heater controller USB cable is plugged into. The default is COM9.

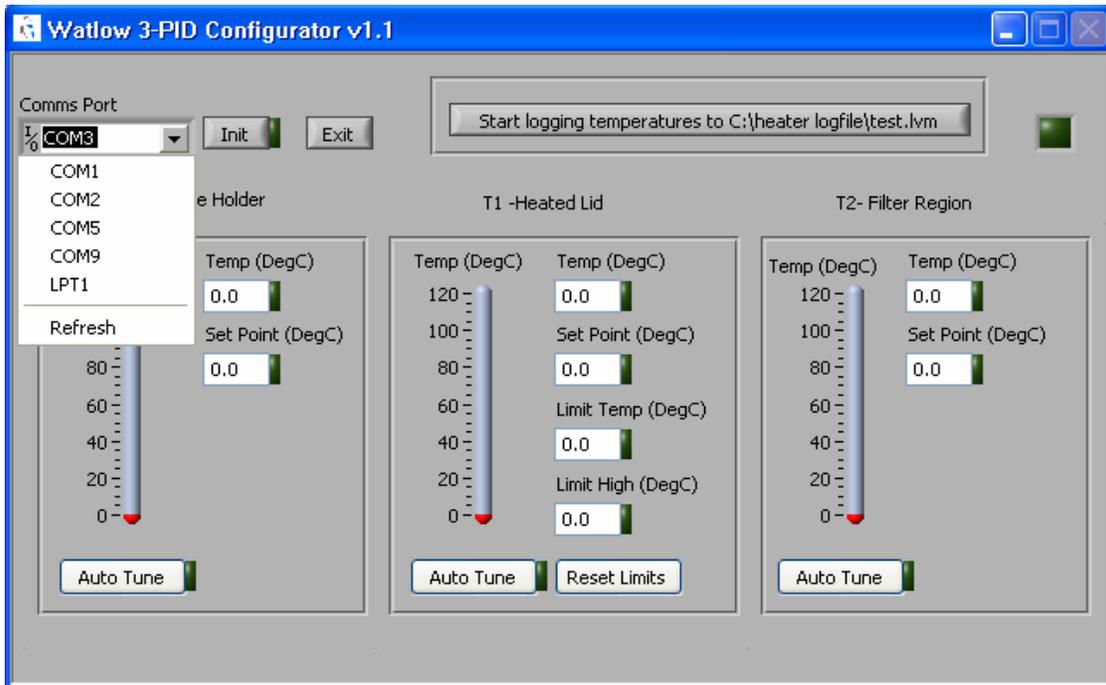


Figure 6 Choosing comms port

Hit the init button and the software will connect to the heater controller and allow monitoring and editing of the temperatures of the heater regions. To change the set points, select the relevant box and type in a new temperature. If you are running a fixed method do not change the settings from those selected in the method setup document as this will invalidate the calibration.

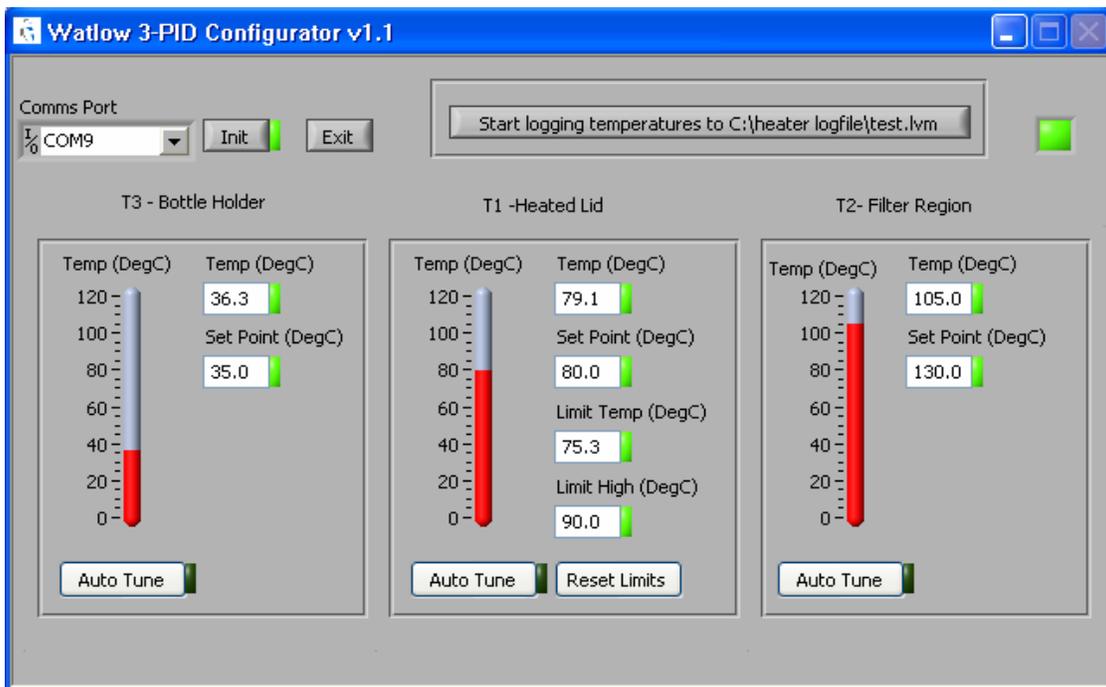


Figure 7 Software communicating with and controlling heaters

7. Maintenance

7.1. Cleaning the At-Line Sampling Module

If required, the insulation on the outside of the At-Line Sampling Module may be cleaned by wiping it with a damp cloth. No solvents should be used on the insulation or inside the sample holder. If further cleaning or decontamination is required, contact Owlstone Ltd. for support.

7.2. Replacing the Dip Tube and Splash Plate

Powder-free nitrile gloves should be worn at all times to avoid contaminating the Lonestar sample flowpath. Set the gas purge to ON in the Lonestar software, wait for 10 seconds and then turn off the gas flow to the Lonestar system. Allow the Lonestar pressure to drop below 0.4bar_g before unscrewing the bottle holder from the heated lid to expose the dip tube.

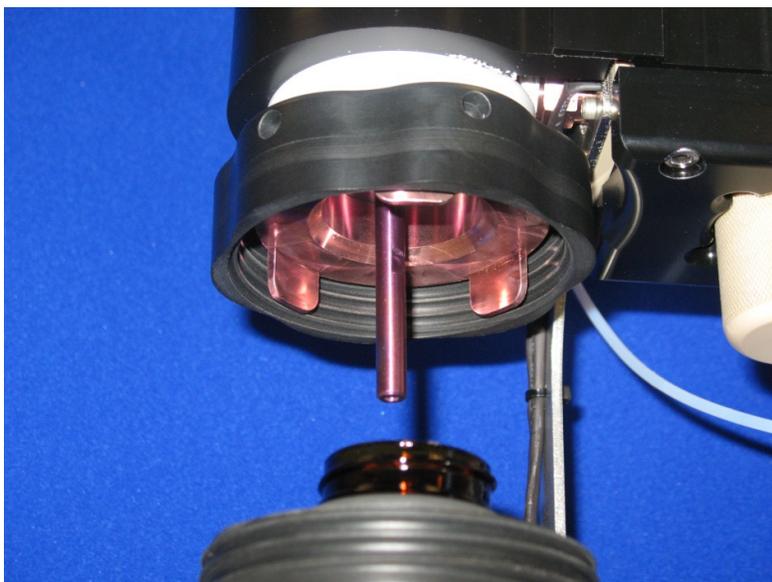


Figure 8 Removing sample holder

Using a 1/4" spanner, undo the dip tube from the heated lid. The splash plate is held captive on the dip tube and will be removed at the same time.

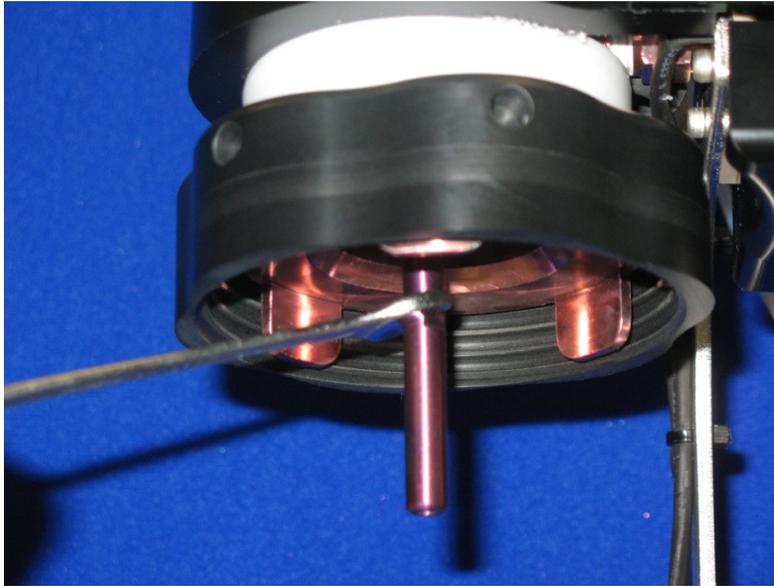


Figure 9 Removing the dip tube

Assemble the splash plate and dip tube by screwing the dip tube through the larger hole in the splash plate.

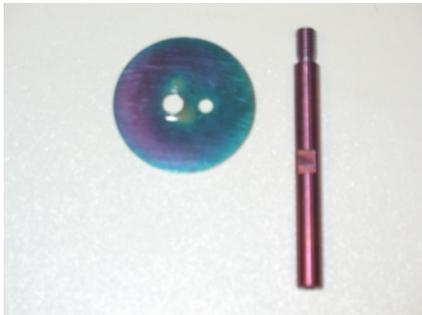


Figure 10 Splash guard and dip tube



Figure 11 Mount splash guard

Slide an Allen key or narrow screwdriver through the smaller hole in the splash plate.

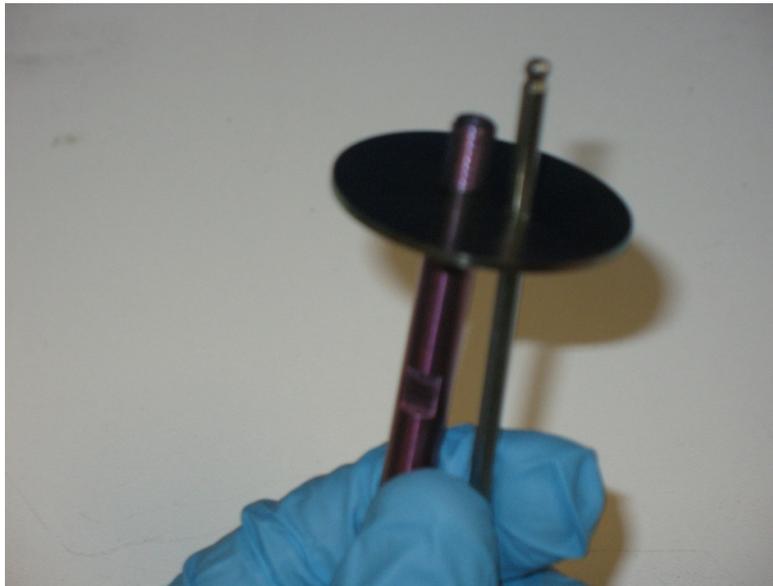


Figure 12 Align dip tube with flowpath exit

Use the Allen key to locate the exit flow path through the heated lid. This also keeps the splash plate horizontal to ensure it passes cleanly into the recess in the heated lid. Locate the screw thread in the heated lid for the dip tube and screw the dip tube into the heated lid.

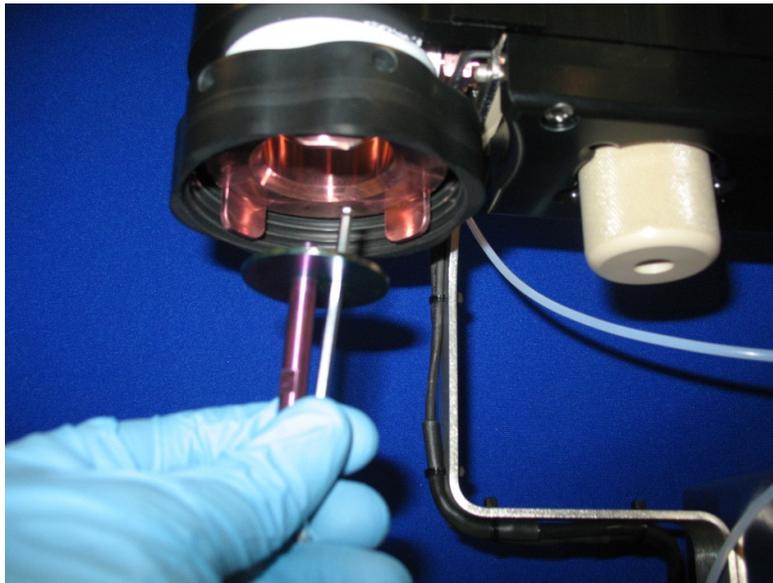


Figure 13 Inserting dip tube

Once the dip tube is snugly tightened into the heated lid, push up against the underside of the splash plate to ensure it is correctly seated in the recess in the heated lid. Tighten the dip tube into the heated lid using a $\frac{1}{4}$ " spanner.

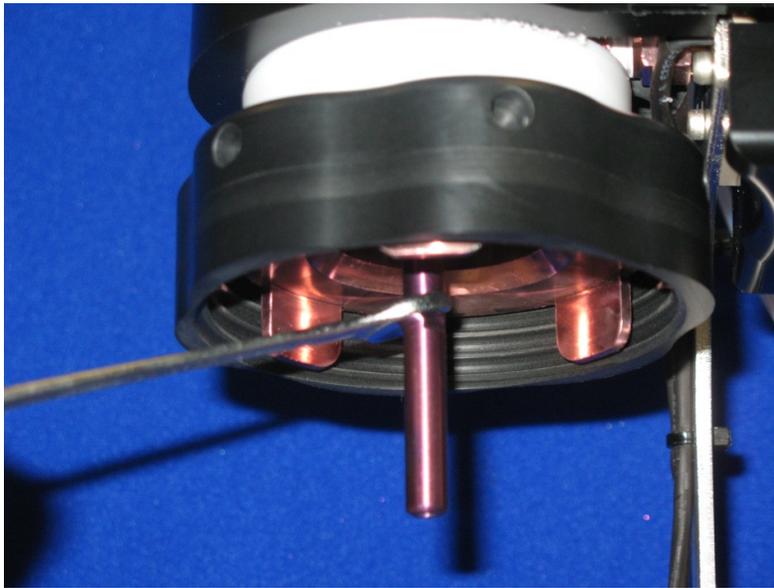


Figure 14 Tighten Dip tube

A blank sample bottle should be placed in the bottle holder and screwed into the heated lid until snug. The carrier gas flow should be restored to the Lonestar system, waiting for the pressure to build before turning the gas purge OFF. Collect a few DF matrices, scanning from 0% to 100% dispersion field to ensure the dip tube and splash plate are not contaminated; this also allows the dip tube and splash plate to reach their operating temperatures, being heated from the heated lid.

7.3. Replacing the filter

Gloves should be worn at all times to avoid contaminating the Lonestar sample flowpath. Turn off the Owlstone heater control box and allow the filter housing to cool. Set the gas purge to ON in the Lonestar software, wait for 10 seconds and then turn off the gas flow to the Lonestar system. Allow the Lonestar pressure to drop below 0.4bar_g before unscrewing the filter from the filter region.

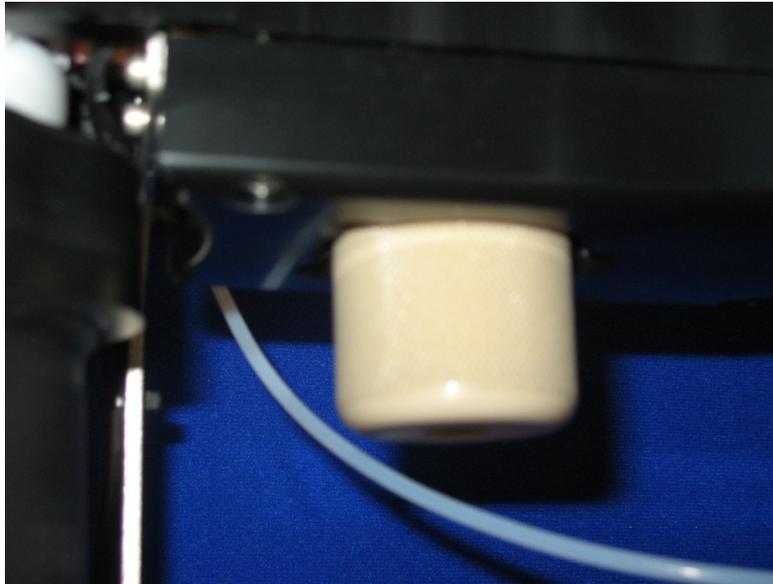


Figure 15 Filter housing

Carefully remove the PTFE seal and coated inner sealing ring from the top of the filter.



Figure 16 Removing the PTFE seal

Remove the top filter plate, the filter and the bottom filter plate, checking to ensure that the filter plates are undamaged. Assemble the filter once more with the bottom filter plate, the new filter, the top filter plate and then the PTFE seal and coated inner sealing ring.



Figure 17 Replacing the filter assembly

Ensure the lower PTFE ring is in good condition, and that the o-ring circles the PTFE sealing ring. If the o-ring does not enclose the PTFE ring, then the filter may leak when re-inserted into the filter region. Replace these parts as required.

Screw the filter into the filter region. The two alignment lugs should be on the left side of the filter when inserting the filter into the filter region to align with the gaps in the filter region insulation.

A blank sample bottle should be placed in the bottle holder and screwed into the heated lid until snug. Turn on the Owlstone heater control box to restore the temperature set points within the bottle holder, heated lid and filter region. The carrier gas flow should be restored to the Lonestar system, waiting for the pressure to build before turning the gas purge OFF. Collect DF matrices, scanning from 0% to 100% dispersion field to determine the cleanliness of the new filter. It is expected for the new filter to be fairly contaminated, requiring several hours to achieve a state of cleanliness before the Lonestar system can be used for sample analysis.

8. At-Line Sampling Module Flow Path

Figure 18 below shows a simplified diagram of the flow path of the At-Line Sampling Module and Lonestar in use.

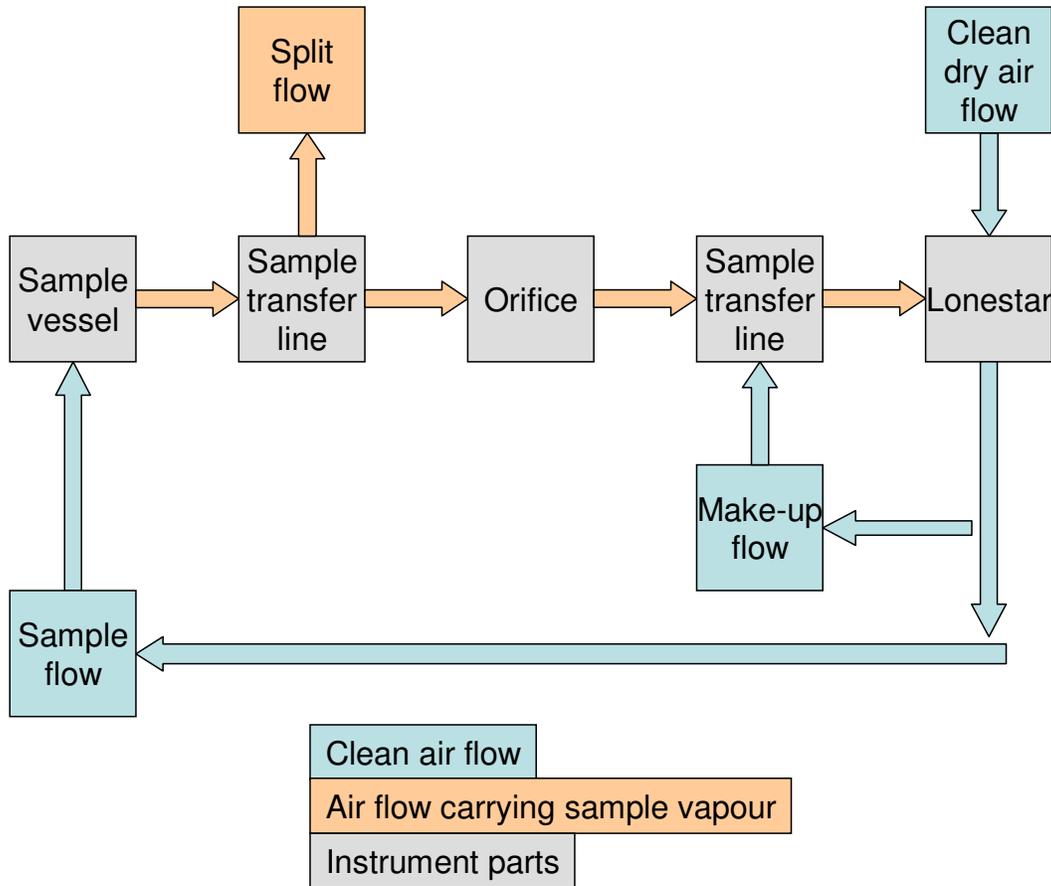


Figure 18 Block diagram of At-Line Sampling Module flow path

There are three heated sections in the At-Line Sampling Module, as described in Table 3 below.

Table 3: Heated sections of At-Line-Sampling Module

| | Section | Suggested initial temperature / °C |
|--------|--|------------------------------------|
| Temp 1 | Sample holder | 30 |
| Temp 2 | Deactivated and heated sample transfer line | 85 |
| Temp 3 | Deactivated and heated particulate filter and sample transfer line | 130 |

The flow path of the At-Line Sampling Module is as follows.

8.1. Sample flow (purge flow)

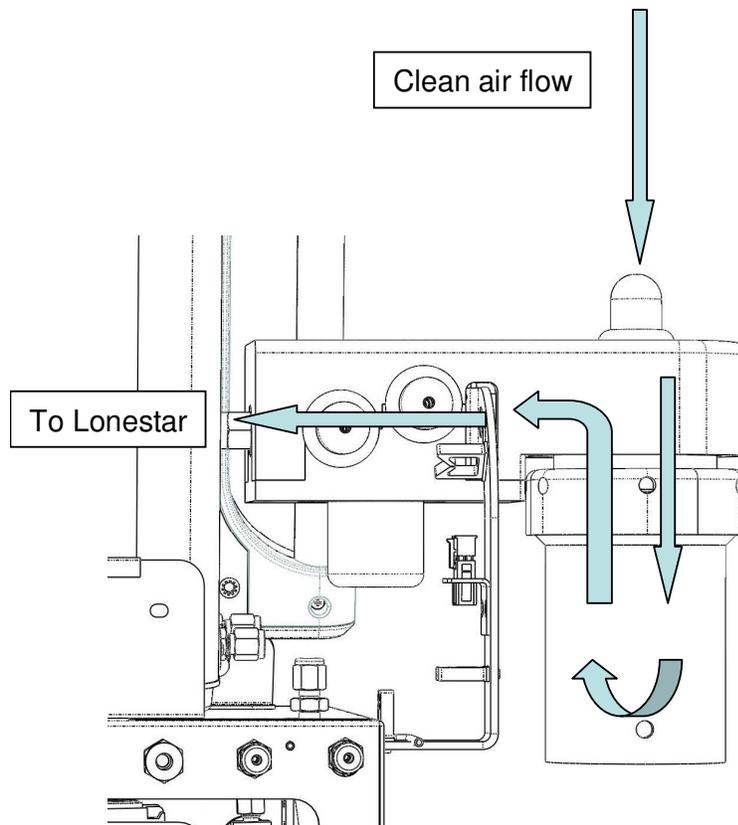


Figure 19: Sample flow path superimposed on rear of the At-Line Sampling Module

- If no split or make-up flows are used (see below), then the sample flow is the total flow through the At-Line Sampling Module and the Lonestar. The pressure of the sample flow is set by adjusting the inlet pressure to the Lonestar, and the flow rate is set by adjusting the needle valve on the exhaust of the Lonestar. The flow rate and pressure at the detector are displayed on the dashboard of the Lonestar software.
- Clean air leaves the Lonestar via the port labelled Clean Air Out. This air has travelled through the Lonestar's integral scrubber and then through a length of PTFE tubing within the body of the Lonestar.
- The sample flow then travels into the At-Line Sampling Module at the left. It flows through the dip tube and into the headspace of the glass sample bottle. Here, the clean, dry air picks up analytes and water vapour from the sample.
- The sample flow then passes along the first heated sample transfer line, through the particulate filter and along the second heated sample transfer line. The flow carries the analytes into the Lonestar detector.
- After passing through the detector, the air flow exits the Lonestar at the port labelled Exhaust.
- **Caution! The exhaust flow should always be vented appropriately. If toxic or harmful compounds are present in the sample, the exhaust flow must be vented into a fume hood.**

The second heated and deactivated sample transfer line has two ports in it, each with an 1/8" Swagelok connector. They may be blanked off or used to split and make up the sample flow as described below.

8.2. Make-up flow

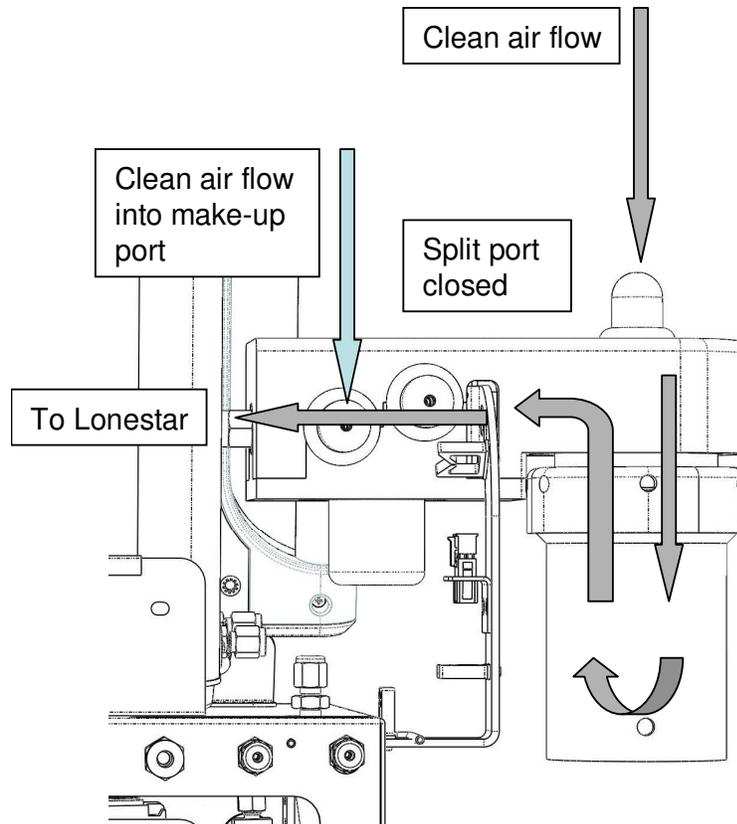


Figure 20: Make-up flow path (blue) superimposed on rear of the At-Line Sampling Module

- The make-up flow is a flow of clean, dry air that has not passed through the headspace of the sample. It is used to supplement the sample flow in the following circumstances:
 - When a split flow is being used;
 - Instead of a split flow, to dilute the sample flow and prevent saturation of the detector;
 - If a flow restriction aperture is in place in the particulate filter block, restricting the rate of the sample flow.
- In all of these cases, the make-up flow is used to bring the total flow through the Lonestar detector to a value that will ensure good operation (1.5-3.0 l/min).
- The make-up flow comes from the Clean Air port on the Lonestar and is split off from the sample flow by means of a Swagelok tee.
- The make-up flow should be connected to the second port in the sample transfer line, after the sample flow has passed through the particulate filter.
- As with the split flow, the make-up flow rate may be controlled by a rotameter or mass flow controller. Alternatively, a flow-restriction aperture may be used (see Apertures section below).
- While running the Lonestar with a make-up flow, the sample flow may also be controlled by a rotameter or mass flow controller inline (before the inlet to the sample bottle). Alternatively, a flow restriction aperture may be installed in the particulate filter block (see Apertures section below).
- Please note that if an aperture is installed in the particulate filter block, the sample flow rate by itself may not be large enough to ensure good operation of the Lonestar detector (1.5-3.0 l/min). To switch back to running the Lonestar without a make-up flow, it will be necessary to remove the aperture from the block.

8.3. Split flow

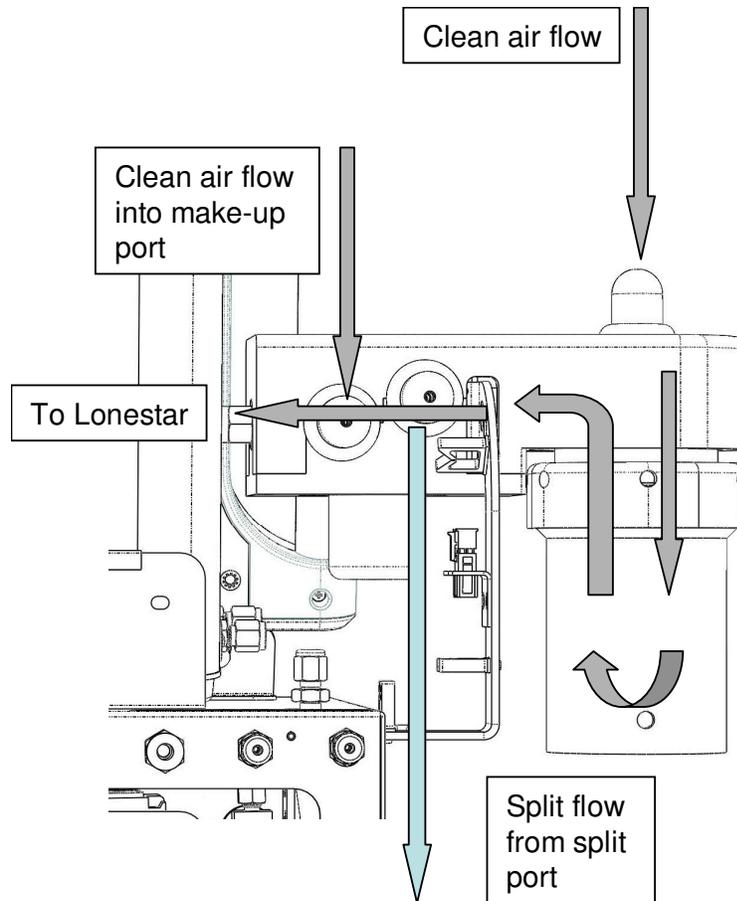


Figure 21: Split flow path (blue) superimposed on rear of the At-Line Sampling Module

- If large amounts of analyte from the sample are saturating the Lonestar detector, it may be useful to split off some of the sample flow and vent it away from the detector.
- It may also be helpful to do this if the humidity of the sample flow is too great and this is suppressing the sensitivity of the Lonestar detector to the desired analytes.
- **Caution! The split flow should always be vented appropriately. If toxic or harmful compounds are present in the sample, the split flow must be vented into a fume hood.**
- The split flow should be taken from the first port in the sample transfer line, before the flow has passed through the particulate filter.
- The flow rate may be controlled by a needle valve, rotameter or mass flow controller. Alternatively, a flow restriction aperture may be inserted into the port (see below).

8.4. Apertures

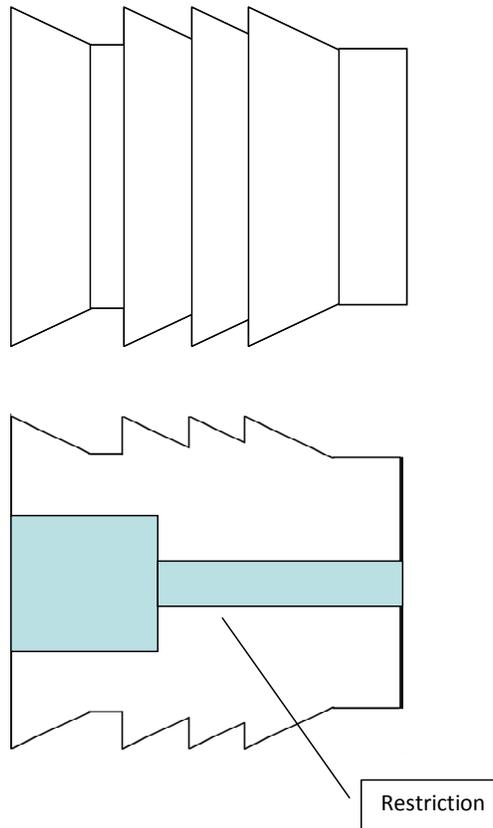


Figure 22: Outer view and cross-section of push-in orifice, showing flow restriction

- The apertures used with the At-Line Sampling Module are 2.5 mm press-in orifices in stainless steel from Lee Co.
- Apertures may be used to control the sample flow, split flow or make-up flow. Putting an aperture in a flow path will set the flow to a constant value as long as the pressure is constant.
- Different sizes of aperture are available, which will restrict the flow by different amounts.
- During method development, controlling the flow rates with a mass flow controller or rotameter may be more convenient, as this allows for greater flexibility. Once a method has been defined, however, using apertures to control the flows gives good repeatability.
- To control the sample flow, an orifice should be inserted into the particulate filter block, as shown in the At-Line Sampling Module Manual.
- To control the split or make-up flow, the orifice should first be pushed into an equal length of 1/8" PTFE tubing and then inserted fully into the relevant port.

8.5. Humidifying the make-up flow

- An increase in humidity is used to increase separation of analyte peaks in the DF matrices produced by the Lonestar.
- One way of doing this is to take the make-up flow from another source, for example an Owlstone Humidity Generator (OHG).
- **Very important:** As the make-up flow enters the At-Line Sampling Module after the particulate filter, it is very important that the air is clean (<0.1 ppm methane) and free of particulates.
- Another way of humidifying the make-up flow is to pass the flow through the headspace of a vessel containing deionised water. See Figure 23 for an illustration of this. The final humidity of the air flow will depend on several factors, including the air flow rate and the temperature of the water.

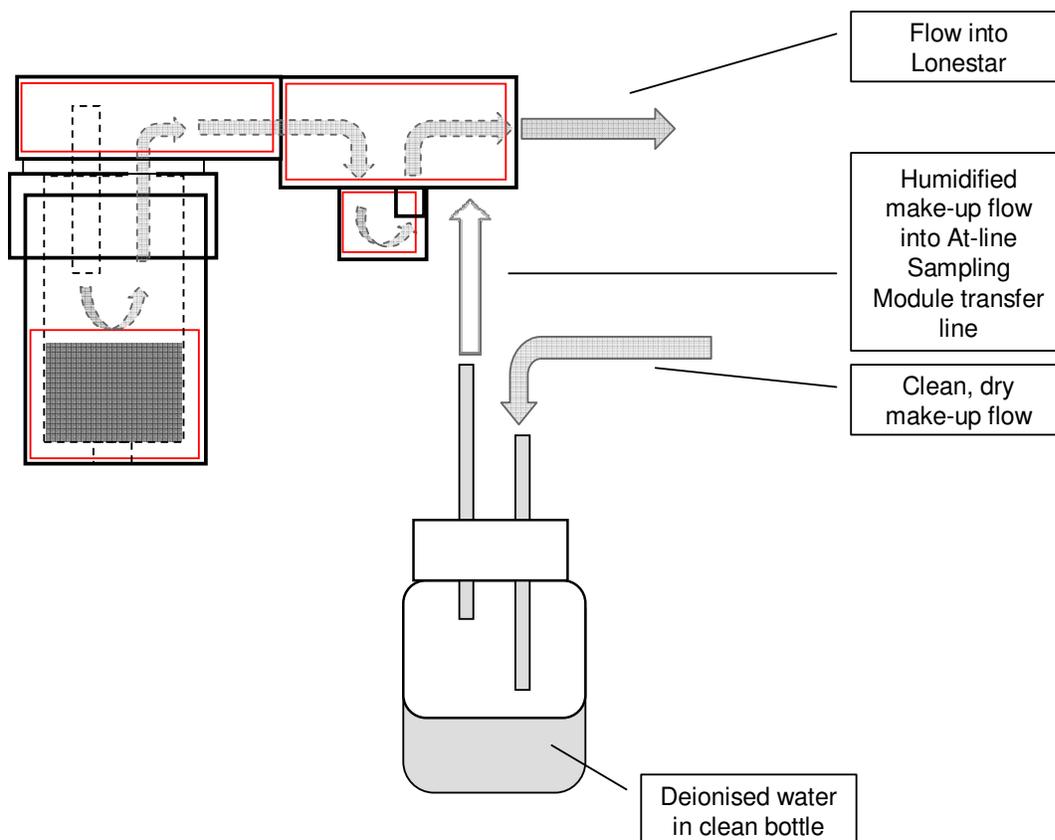


Figure 23: Humidifying make-up flow by passing it through water headspace

9. Theory of Headspace Sampling

9.1. Basics

The Lonestar is a gas phase analyzer. It can be used to analyze liquid and solid substances by headspace sampling, as described here. The At-Line Sampling Module for the Lonestar is designed to make headspace sampling simple and reproducible. Figure 24 shows a cutaway diagram of the sample holder of the At-Line Sampling Module.

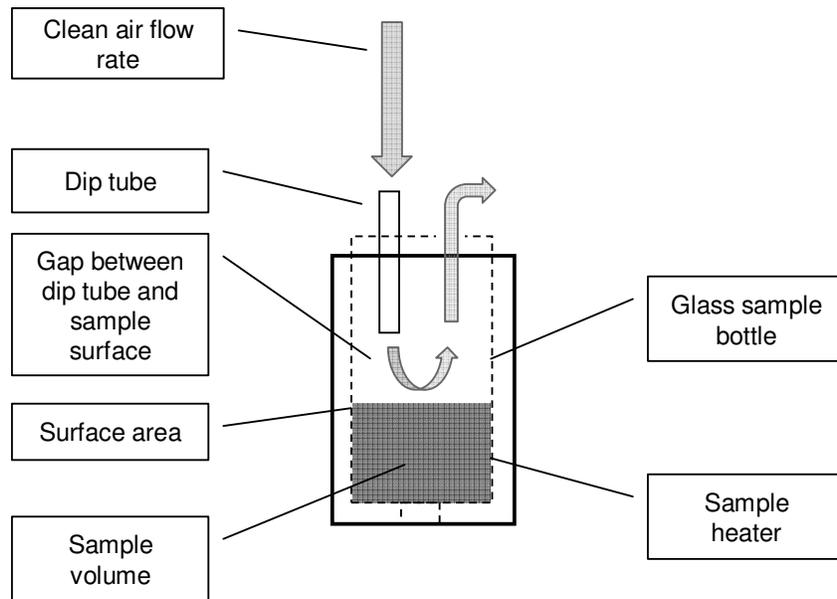


Figure 24: Parameters of the At-Line Sampling Module that affect mass transfer into the headspace

A glass bottle containing the sample is placed in the At-Line Sampling Module and held at a constant temperature. Chemicals from the sample evaporate and move into the headspace of the bottle. A constant flow of clean, dry air is passed through the headspace and then into the Lonestar, sweeping the analytes into the detector.

As can readily be seen, only analytes that move from the sample into the headspace will enter the Lonestar and be detected. This means that the most important work in method development for Lonestar applications focuses on controlling the mass transfer of analytes into the headspace.

There are two types of headspace sampling: static and dynamic. These are described below.

9.2. Static headspace sampling

In static headspace sampling, the sample is left in a closed container until the headspace of the vessel is saturated with analyte vapour. The headspace is then swept into the Lonestar with a purge flow to be analysed.

Figure 25 shows a schematic of static headspace preconcentration, with the factors that influence the final headspace concentration. These are discussed more fully below.

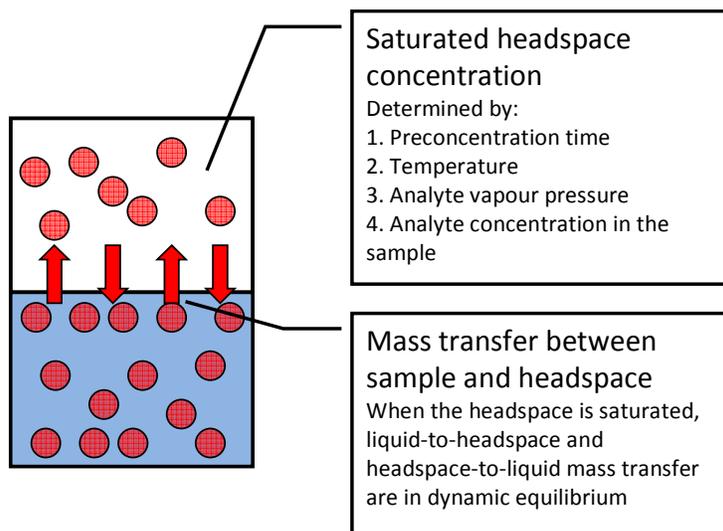


Figure 25: Static headspace sampling

Preconcentration time and volume

The build-up of vapour concentration in the headspace is a time-dependent process and also dependent on analytes vapour pressure and sample concentration and sample temperature. While it is still increasing, the volume of the headspace will be relevant. Once the headspace is saturated, however, the concentration will be the same for any volume.

Sample temperature

The At-Line Sampling Module can heat the sample bottle to a temperature of up to 60 °C, with a tolerance of ± 1 °C. Raising or lowering the sample temperature will increase/decrease the vapour pressure of all analytes leading to increasing /decreasing evaporation rates, and the time it takes to reach saturation, and more importantly it will increase/decrease the saturated concentration. Therefore changing the temperature is a direct way to affect sensitivity of the method and preconcentration timing. It will likely also affect analyte solubility (positively or negatively) and will increase /decrease humidity if the sample is a water solution.

Analyte vapour pressure

More volatile chemicals will evaporate more readily. Volatility of analytes can be compared by checking their vapor pressure: the pressure at which the gas phase of the analyte is in equilibrium with the liquid phase. A higher vapor pressure means higher volatility. The boiling point of a liquid is the temperature at which its vapour pressure is the same as the environmental pressure.

If an analyte with low volatility is not being detected, increasing the sample temperature may help to increase the rate of evaporation.

Calculating the saturated headspace concentration

To calculate the saturated headspace concentration of an analyte, use the following equation:

$$\frac{V_p}{P} \times 10^6 = C$$

where:

- V_p is the vapour pressure of the analyte in mmHg at the sample temperature
- P is the pressure of the container (760 mmHg if at standard atmospheric pressure);
- C is the concentration of the analyte in the headspace, in ppm.

9.3. Dynamic headspace sampling

In dynamic headspace sampling, the headspace of the vessel is continuously swept into the Lonestar by a clean purge flow for analysis. Figure 26 shows a schematic of dynamic headspace sampling in the At-Line Sampling Module. The factors mentioned are discussed in more detail below.

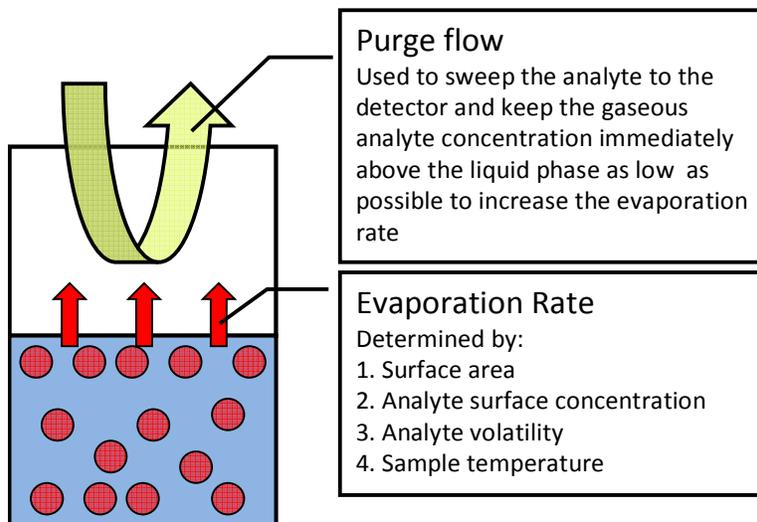


Figure 26: Dynamic headspace sampling

Surface area

As all evaporation occurs at the surface of the sample, the surface area is a major factor in determining the mass transfer rate into the headspace.

Using a wider sample bottle, which produces a larger surface area, may increase the amount of analyte moving into the detector and thus produce larger analyte peaks in the Lonestar DF matrices.

Keeping the surface area constant between samples is very important in ensuring consistent results. For this reason, solid samples should be melted or dissolved before sampling where possible. Alternatively, solids may be introduced in powder form. Sample volumes should be accurately measured and samples should always completely cover the bottom of the sample bottle.

Analyte surface concentration

Mass transfer into the headspace is a function of:

- the difference in concentration of the analyte between the liquid and headspace, at the surface of the liquid
- the concentration gradient between the surface of the liquid and the bulk of the liquid

Transport of analyte molecules from the bulk of the liquid to the surface layer is a diffusion-limited process and can be slow. This can in turn slow down the mass transfer from the surface into the headspace. Magnetic stirrers can be used to homogenize the sample during analysis, which will reduce this problem.

Purge flow rate

The purge flow sweeps analyte vapour from the sample headspace towards the Lonestar analyser. This reduces the concentration of the analyte in the headspace, increasing the rate of analyte mass transfer into the headspace. Thus the flow rate has a significant effect on the mass transfer rate.

A related factor is the distance between the purge flow inlet and the surface of the sample. This is illustrated in Figure 27. When a dip tube is used to reduce the inlet-surface distance, the flow travels through the entire depth of the headspace (A). Without a dip tube, the flow will take the shortest path to the outlet of the sample vessel (B). Analyte vapour from higher up in the headspace is taken to the Lonestar, while vapour from

closer to the surface remains in the vessel. This causes the development of a boundary layer of higher-concentration air above the surface of the sample.

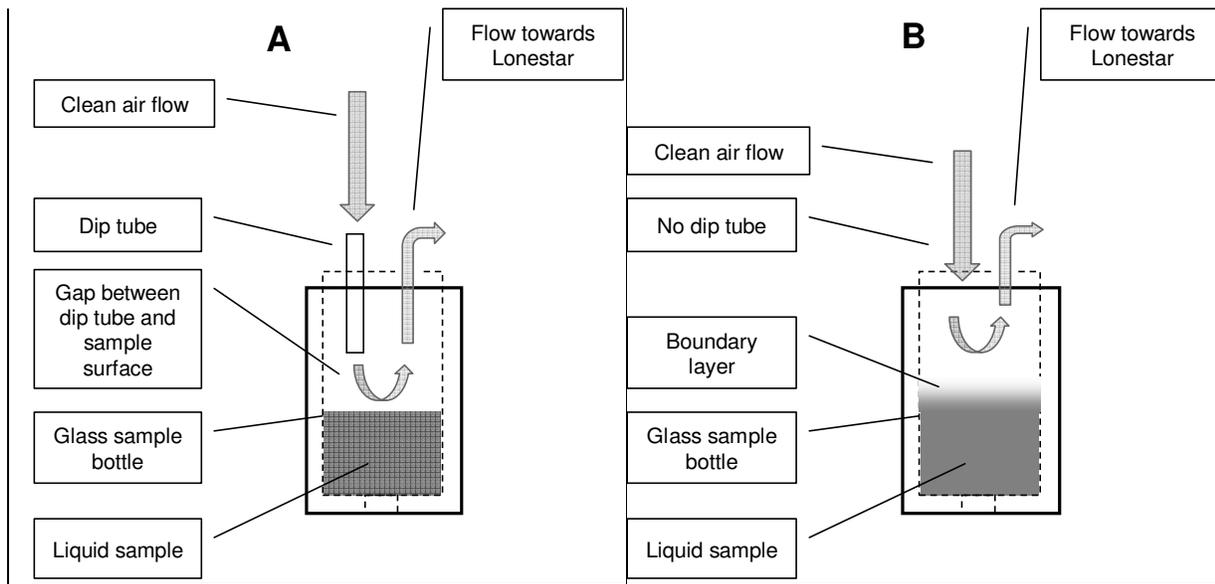


Figure 27: (A) Schematic of sample holder with dip tube in place. (B) Schematic of sample holder without dip tube, showing increased boundary layer

To limit the formation of a boundary layer, either a dip tube or a higher purge flow rate is necessary.

Increasing the purge flow rate will increase its penetration into the sample vessel and increase the rate of headspace replacement for the system.

This value can be calculated as shown:

$$N = \frac{f}{b - s}$$

where:

- *N* is number of headspace replacements per minute
- *f* is the sample flow rate, in ml/min
- *b* is the bottle volume (120 ml for the standard bottles supplied by Owlstone)
- *s* is the sample volume in ml

Calculating the headspace concentration in dynamic sampling

The concentration of the analyte in the headspace may be calculated using the following equation:

$$\frac{MT}{F_{purge}} = C$$

where:

- *MT* is the mass transfer rate in ng / min
- *F_{purge}* is the purge flow rate in ml / min
- *C* is the concentration of the sample flow into the Lonestar, in ng / ml

9.4. Other factors influencing mass transfer into the headspace

The solubility of a chemical measures its propensity to form a homogeneous solution in a solvent by mixing at a molecular level. An analyte will have a different solubility in each solvent.

When analysing solutions with the Lonestar, the solubility of an analyte in the matrix plays a key role in determining its mass transfer into the headspace. The greater the solubility, the less likely the analyte is to leave the sample solution.

Some factors affecting solubility are described below.

Polar vs. nonpolar solvent and solution

In general, polar molecules will have greater solubility in polar solvents (e.g. water, ethanol) than in nonpolar ones (e.g. hexane) and vice versa.

In polar solutions, ionic compounds will dissolve by dissociating into positive and negative ions. The positive ions are attracted to the negative charge on the polar solvent molecules and the negative ions are attracted to the positive charge. Ionic compounds will have very low solubility in nonpolar solvents.

Temperature

The solubility of analytes may increase or decrease with temperature. Solubility profiles for many compounds in water are useful and publicly available.

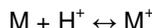
pH

The pH of the solvent can affect the solubility of an analyte that reversibly dissociates in solution, losing a proton, as shown here:



In this case, making the solution more acidic (adding more protons, decreasing the pH) will shift the equilibrium of this process away from the dissociation. More of the analyte will be in the M form and less in the M⁻ form. Only the analyte molecule, M, will evaporate out of the solution, not the ion M⁻, so this will increase mass transfer into the headspace.

In the case of an analyte molecule that tends to pick up a proton and become positively charged, the reverse will apply.



Making the solution more alkaline (adding more OH⁻ ions, increasing the pH) will help here. The extra OH⁻ ions will form H₂O molecules with H⁺ ions, decreasing the amount that are available to form the M⁺ ion. There will be more of the molecular form of the analyte, M, to evaporate and the mass transfer rate will increase.

In the case of amphoteric analytes, which can show either acidic or alkaline behaviour, careful adjustment of the pH level is required to maximise the mass transfer rate into the headspace.

The pK_a value of a chemical is $-\log_{10}(K_a)$, where K_a is the acid dissociation constant of the chemical. This is a reflection of the degree to which the chemical dissociates when in solution. If the pH of the sample solution is equal to the pK_a of the analyte of interest, 50% of the analyte molecules will be dissociated (M⁻ + H⁺) and 50% will be in the molecular form (M). Adjusting the pH of the solution to 2 greater or less than the pK_a of the analyte will be enough to shift towards 100% dissociated or molecular form. Whether the pH should be greater or less than the analyte pK_a depends on the acidity of the analyte, but it is only necessary to examine the pH range pK_a(analyte) ± 2.

Salting

An analyte may be salted out of a solution – that is, made less soluble by adding salt to the solution.

If the solute molecules are nonpolar and have not dissociated, the main forces holding them into the solution are the intermolecular forces between solute molecules and polar water molecules (e.g. hydrogen bonds). The salt dissociates into ions on dissolving. These ions are more attractive to the polar H₂O molecules than

the nonpolar solute molecules, which reduces the intermolecular forces holding them into the solution. The solubility of the analyte, and any other organic/nonpolar molecules, is reduced.

Adding salt to a sample solution can also have the beneficial result of reducing humidity. As above, the extra ions from the salt attract the water molecules in the solution, making them less likely to evaporate out into the headspace. If the Lonestar's sensitivity to an analyte is reduced with higher humidity, adding salt can be very useful.

There are tables available online comparing humidity at various temperatures for saturated solutions of various salts.