

# International Atomic Energy Agency

## Minutes of a Laser group meeting December 2009

### Summary of presentations and discussions on the operation of laser-based isotope analyzers

This tips and tricks sheet describes various, typically undocumented, approaches and lessons learned that users of the LGR DT-100 have found useful in operating, maintaining, and troubleshooting their instruments. It contains assorted information that can help users keep their instruments running and produce better analyses. This tips and tricks sheet was initially produced as an outcome of an LGR DT-100 Users Meeting held at the IAEA in December, 2009. The IAEA has not tested all of these tips and tricks, so use them with caution and at your own discretion.

#### 1. Syringe storage, cleaning, and replacement

The most expensive consumable for laser absorption analyzers are syringes and bad syringes will not produce good data. Examples are given below on how to keep syringes running longer, how to rejuvenate bad syringes (as long as they don't have a bent needle), and a few other syringe related tips.

Autosampler syringes usually fail after 1-3 weeks of use even if you include DI water rinses at the end of a run. However, the following techniques have been used to keep syringes functional for longer and make syringes functional again.

#### **Jacobus Pretorius' method to keep syringes functioning during periods where the instrument is not being used.**

Many people have found that after the instrument sets even for a few days that a perfectly functional autosampler syringe no longer works properly when the instrument is restarted. To store a used but functional syringe remove it from the autosampler and soak it in a tray of DI water until it is needed again. Loosen the needle nut slightly and pull the plunger to make sure some water gets inside the syringe barrel. Make sure not to bend the plunger or needle.

#### **Andrew Schauer's Cleaning Method (posted on Isogeochem, 5.10.09)**

This approach is a way that bad syringes can be rejuvenated for additional analyses. First, program the following as methods in your PAL autosampler:

Method 1:

- 1) rinse 10 times with reagent grade acetone using a reasonably SLOW plunger motion
- 2) rinse 10 times with reagent grade methanol or ethanol (they both have worked...even the alcohol mix has worked), again, with a very slow plunger motion



Water  
Resources  
Programme

3) rinse 10 times with DI water (we use 18 M ohm, but DI should be fine), then follow up with method 2.

Method 2:

4) in a separate PAL method, we then do 300 actuations of the plunger with the syringe in DI water, here again, with SLOW plunger motion

After doing 1 through 4 , it takes 2-3 injections for the H<sub>2</sub>O<sub>cm\_3</sub> to return to  $3.2 \times 10^{16}$  but then it usually stays there. In addition to this process, we do #4 (above) if the instrument has sat idle for more than a few hours and we start and end each run with a vial of 18 M ohm water. Note, all of this assumes the rest of the instrument is functioning properly (pump, new septum, fresh reagents, etc, etc).

**A caution about this method and alcohol in general.** Be aware that with laser absorption, samples containing alcohol can produce erroneous results because alcohol absorption peaks are similar to those of water. Make sure syringes are well rinsed after cleaning with alcohol (see caution later in this document for more information).

#### **Paul Eby's Method (posted on Isogeochem 9.10.09)**

Here is a simpler method that has also been used to rejuvenate syringes. Use phosphoric acid (any acid, presumably) for rejuvenating syringes that seize up with brown crud after many water injections.

Some users are having success using the solvent 1-methyl-2-pyrrolidinone for lubricating and extending the life of the syringes. We have just started testing it ourselves, dead syringes seem to come back to life and it seems to give more stable injected volumes when the syringe is lubricated with this stuff. (Tip from Martin Sanda).

#### **Syringe Replacement**

Some users like to install syringes directly instead of removing the blue plate from the autosampler.

#### **Syringe Quality**

Users have noted that some batches of the syringes used in the autosampler appear to have sub-par quality. Users have observed syringes generating black "material or stuff" and some do not have smooth plunger action right out of the box. If you install a new syringe and don't get good results don't be afraid to try another new one.

## **2. Autosampler control panel gets scrambled and doesn't work.**

Here is an approach from LGR/PAL that may help if the autosampler control goes haywire.

First, try reimaging the autoloader. If this doesn't work, try the sleep mode trick and then reimage.

### Reimaging the Autoloader

1. Turn off the autoloader.
2. Connect a computer to the autoloader using the provided autoloader Serial Cable.
3. Insert the provided CD from the PAL manual into the computer.
4. Copy the program labelled “paload.exe” in the directory “\Loader\” from the CD onto the computer hard drive.
5. Run the program “paload.exe”.
6. Depress “Update”
7. Depress “Browse”
8. Select the file “092506.sss” in the directory “\Loader\BACKUP\” on the CD (note you will probably need to get this file from LGR, as it is not usually on the CD. A version of the file may also be available through the IAEA Water Resources Programme website).
9. Depress “Update”
10. The autoloader firmware will take about 5 minutes to be replaced.
11. Depress “StartPal” to start the autoloader.
12. Disconnect the autoloader from the computer.

### Install the LGR Software

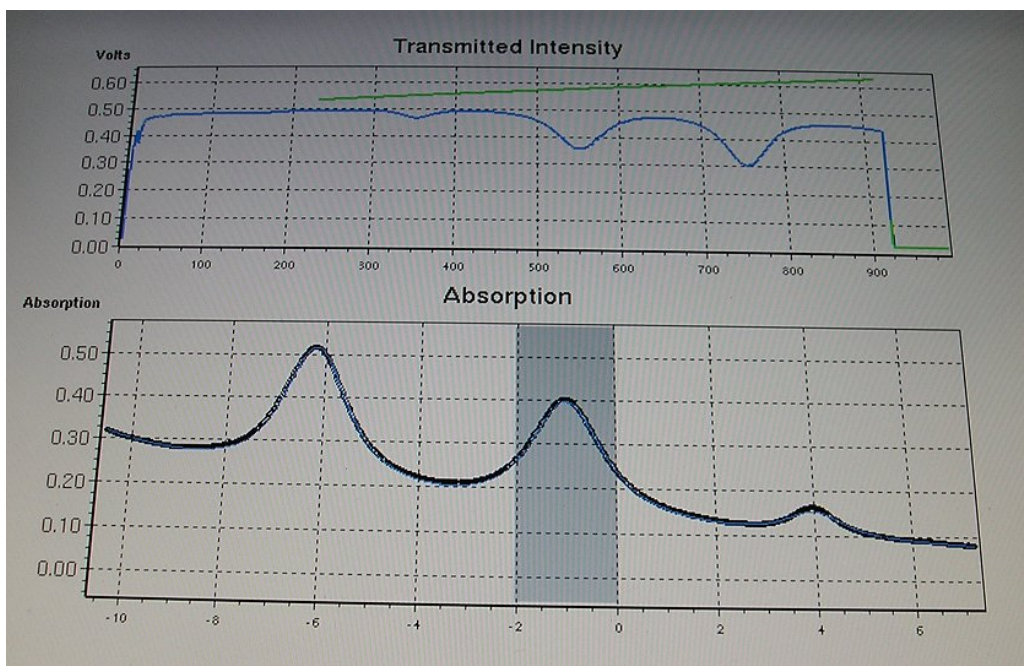
- Turn Auto Loader ‘ON’. The switch is located on the back of the power supply.
- Wait until the arm goes home.
- Attach the RS232 cable from the back of the auto loader to the back of the computer. These are the commands to follow:
  - Insert the provided PAL CD into the computer.
  - Copy the program labelled “paload.exe” in the directory “\Loader\” from the CD onto the computer hard drive.
  - Run the program “paload.exe”.
  - Double click – “PAL Loader” Icon
  - Click ‘update’
  - Click ‘browse’
  - Select ‘092506.SSS’ program, then click ‘Open’ (note: this file is not included on the PAL disk and should be preloaded on the computer. It is available from LGR. A version of the file may also be available through the IAEA Water Resources programme website).
  - Click ‘update’
  - Wait for ≈5 minutes while the program loads. When the message, “Update of target memory succeeded” comes, loading was successful.
  - Click ‘close’
  - Click ‘Start Pal’ – this command will activate the auto loader.

- Click 'Exit'
- Remove RS232 cable from computer. Reattach RS232 cable to the LGR.
- Relocate the injection port, tray holder, and sample trays as indicated in the LWIA Users Manual or IAEA procedure.
- Set the syringe over-injection to 10 %.
- Check the change syringe position and change if necessary.
- The autoloader should now be functioning properly and ready to use.

**The Sleep Mode trick:** If you can't reimage the autosampler, you may try this approach which can trick the autosampler into accepting the new software. If you turn the unit on, then off for about 1 or 2 seconds, and back on again, it will freeze up in "sleep mode". It may take a couple of tries. The trick is to switch it off just as it starts booting up and back on again after just a moment. You can tell it's in the sleep mode because it just sits and does nothing even though powered up, usually with a garbled display. The software can then be reimaged

### 3. Troubleshooting Leaks, Vacuum Pump, and Drierite Problems

Leaks or pressure change problems can occur through failure/problems with the vacuum pump or with the internal valves of the laser system. The image below shows the effect of leaks on the absorption spectrum. Note that the spectrum is tilted down to the right instead of in its normal flat baseline condition.



(source: M. Sanda)

If leaks are suspected the following procedure from LGR can be used to test the system.

- (1) Initiate septum change.
- 2) When instrument says ready for new septum, remove the transfer line and filter assembly from the back of the laser and immediately cap the inlet port with the Swagelok cap that was supplied with the instrument.
- 3) Click septum change complete.
- 4) Remove the drierite connection from the back of the laser. Note that this is to assure that there is some water (ambient air moisture) in the sample so that you can see the relevant absorption spectrum. Otherwise, you would be measuring dry air and there would be very little absorption, and you would be unable to see the (hopefully) flat baseline.
- 5) Run a couple of “injections”. Even though no water vapor will be introduced through the transfer line, the instrument will still run. The flush cavity procedure will introduce ambient air moisture into the cavity as a “sample” via the Drierite inlet port (make sure the Drierite cartridge is removed).
- 6) Examine the spectrum from each run. If the system doesn’t leak you will see a flat baseline as opposed to the tilted one shown in the image above. If the system leaks you will have to discuss how to proceed with LGR. If it is flat, you can reconnect and proceed with analyses.
- 7) If you see a flat baseline after performing steps 1-6, but have a tilted baseline with a fully connected setup (i.e. with the transfer line attached), examine the tightness of the septum and all the inlet port connections, Also look carefully for cuts or breaks in the transfer line tubing near the Swagelok ferrules on each end of the transfer line.

Leaks are also indicated by condensation of water in the transfer line tubing near the filter because of higher pressure (non-ideal vacuum conditions allowing recondensation of water droplets). Additional heating of the tubing will not help the laser unit performance/quality or solve the leak problem!

**Testing pump efficiency.** If you suspect that the vacuum pump is not doing a good job flushing the system, the following procedure can be used.

1. Place a DI water vial and an empty vial in positions 1 and 2 in the autosampler tray.
2. Make a scheme to alternate injections between the DI water vial and then the empty vial. Run each vial three times.
3. You should see a significant decrease in the water amount when the empty vial is run if the pump is working properly.

### **Testing Drierite Efficiency**

- 1.) Follow steps 1-5 of the leak check procedure above (no Drierite attached and a capped transfer line inlet port) and note the water amounts measured during the injections.
- 2) Reconnect the transfer line and Drierite lines to the laser.
- 3) Run a couple of injections of an empty vial on the autosampler tray.
- 4) Note the water amounts measured during the injections
- 5) The Drierite is ok if you see an order of magnitude (or more) lower water amount than what you saw when the Drierite was disconnected. If not, your Drierite is likely not working as well as it should be.

### **4. General Tips**

#### **Operating Conditions**

- An uninterruptible power supply system or an alternative clean power source is highly recommended. The instrument and autosampler should be protected from power surges.
- It is generally better to keep the system powered on even if you are not going to use it for a few days. If you know that you will not be using it for a week or more then it is a good idea to turn the system off. If the instrument is cold, turn it on and let it warm up for a day or two if possible before starting analyses.
- Some users have had difficulties in obtaining consistent results when temperatures are over 32°C. A stable temperature environment will also help with consistency of results. If air conditioners and heaters are used, make sure they do not blow directly on the instrument.

**Starting a New Run.** When starting a new run it is best to run a few dummy samples to let the instrument equilibrate. You can also check that your spectrum looks good and that you have proper water amounts. Some users run an extensive set of dummies before starting a run of samples.

**Using the Load Configuration Option.** If you are running a version 1 system (V1), do not use the load configuration buttons on the screen. Just do inputs manually.

**Lock Up Problems.** Lock ups of the LGR do happen and often the instrument will not let you abort the run. If this occurs you will have no choice but to turn the power switch off and then on again. You will likely lose the data from the run. You can sometimes download the data file from a locked up run using the Ethernet connection before you switch off the power.

**Memory Effects.** For typical hydrological samples the five or six injection approach used by many laboratories appears to be sufficient to remove significant memory effects. However, it is important to review the individual injection results for your samples to verify that memory effects have been sufficiently eliminated because sometimes they pop up unexpectedly. In cases where samples with strongly contrasting isotope compositions are run one after the other, memory effects can sometimes significantly impact the results of the second sample. For example, if a very negative sample is placed in the autosampler tray before a normal or positive sample, extended memory effects can occur that will affect the results of the normal or positive sample. When running very positive or very negative samples you may want to put a dummy afterwards to allow the memory effect to dissipate before running a sample with a strongly contrasting isotope composition. Alternatively, you may need to run many more injections to be sure that the memory effect has been removed.

### Important Caution about Alcohol, Toluene, and Other Organic Solvents

Laser absorption systems have been shown to produce erroneous stable isotope values for samples containing alcohol. Reports on ISOGEOCHEM also indicate toluene is a problem and other organic solvents may cause problems as well. Alcohol absorption of the laser light occurs at a similar wavelength as water, which causes the bias in stable isotope values. Brand et al. (2009, RCMS, 23) and Singleton et al. (2009, EGU abstract) discuss the alcohol problem. After cleaning syringes make sure that they are well rinsed of any alcohol before running samples. Also be aware that if your samples contain alcohol or toluene (say from a contaminated site), your standards may look fine, but the sample values can be off significantly. If alcohol or solvents are of potential concern, it would be wise to have a few splits run on an IRMS system to verify you are getting correct numbers from your LGR or Picarro.

### **Autosampler Septum Issues**

- **Version 2 LGR System.** If you are running the new V2 LGR system (the fast system with the big heater and pump) remember that the autosampler septa are different from the older LGR systems and are not interchangeable.

- **Bent Needles and Predrilling.** Some users recommend doing the predrilling procedure five to ten minutes after the new septum is installed instead of directly after installation. This allows time for the septum to heat up and may reduce the risk of bent needles. When doing the “late” predrilling make sure that you have not yet clicked “septum changed” on the LGR screen, otherwise air will be introduced into the evacuated system when you punch the septum.

## Dessicant/Drierite Issues

**Alternatives to Drierite.** In case Drierite cannot be obtained, silica gel can be used instead. Magnesium perchlorate (commonly known as one-time dessicant) also works, but it is a strong oxidant, cannot be regenerated, and it is costly.

**Regenerating Drierite.** Spread the granules in a layer about one granule deep and heat for 2 hours at 200°C. After regeneration, Drierite loses its hue, becoming pale blue. This will not affect how well it removes water. It is the activated gypsum (inside the grains) which is doing the drying job. Regenerate only the used up (pink) Drierite when the cartridge is 1/2 to 2/3rds pink. Store the blue Drierite in a closed jar while the pink Drierite is being regenerated. Cool the regenerated Drierite in a closed container and keep it sealed when not in use (e.g., in the original Drierite jar). Be careful about the high temperatures when you remove it from the oven! (see also <http://www.drierite.com>)

**Vacuum Pump.** It is recommended that you don't change the tubing length from the vacuum pump. The pump can be placed on an independent platform to reduce vibration effects. V2 pumps vibrate a lot.

**Saline Samples.** If you are running saline samples, clean the transfer line, ferrule (septum support), and heater area with DI water often to remove salts. Salts can accumulate above the transfer line, so cleaning the septum/heater area is a good idea.

**Standards.** The standards supplied from LGR are only for initial testing of the instrument. They are not intended for daily use or for calibrating your internal standards. Run VSMOW2, GISP, and SLAP2 (available through the IAEA) to calibrate your own internal standards. It is recommended to make your own internal standards. The IAEA is currently drafting a procedure on how to make and store your internal standards.

### Autosampler Vials, Septa, and Consumables:

- **Alternative vial septa.** Some users have had success with vial septa with only one layer of Teflon instead of the normal two layers which reduces the amount of Teflon entering the transfer line.

- Manufacturing defects at the top of vial mouths and septa do occur, so be aware when filling vials to discard any bad ones.

An alternative source for vials and caps including small volume vials can be found through Alltech/Grace Davison (<http://www.discoverysciences.com/>). Some users like their low volume (100 µl) glass vials for small sample sizes (Cat. No. 9482). You can also use their standard 2 mL vials with cap and septa (e.g., Cat. No. 980611)

An additional source of LC Pal compatible products can be found at <http://www.la-pha-pack.com/en/produkte/>

#### **5. Links to more laser based stable isotope analyzer info**

For additional or new information about laser absorption systems the following can be consulted:

- IAEA Water Resources Programme web page (<http://www.iaea.org/water/>)
- Isogeochem ([isogeochem@list.uvm.edu](mailto:isogeochem@list.uvm.edu))
- Isotope Hydrology Forum (special section on laser absorption systems) [www.isotope-hydrology.net](http://www.isotope-hydrology.net)