

**International Atomic Energy Agency**  
**Minutes of a laser group meeting November 2011**

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

This tips and tricks document was produced as an outcome of a Liquid Isotope Analyzer Users Meeting held at the IAEA in November, 2011. The participants identified the most important factors associated with the performance of the instrument to be sample volume, machine stability and syringe longevity. The following proposals are thus recommended. The IAEA has not tested all of these tips and tricks so use/follow them with caution and at your own discretion.

**Running the stable isotope analyzer**

Allow the instrument 2–8 hours start up time to reach a stable temperature (if it is run without this warm up phase, a temperature flag might be issued).

Try running the instrument in continuous mode (24/7); if there is a lack of samples and no urgency wait to fill multiple trays and then run. There is no need for further spectrum readjustment.

After a cold start, make a short test run and adjust the spectrum position. Try to maintain stable room conditions while the instrument is in operation.

Transfer line maintenance: Blow the line regularly with air, clean the injection block often (this is a time costly and tedious procedure), follow manufacturer instructions or even add a diluted base solvent during sonication (for organically rich waters causing coatings on stainless steel).

Optionally, remove the whole transfer line, close the inlets to the instrument, fill a transfer line from the inlet filter side fully with water and sonicate. Blow out air afterwards and allow for several injections to fully evaporate the droplets in the line, watch for the pres–norm change flag before starting a regular run. Run using only deionized water prior to this.

It is advisable to use the configuration save and upload option (after date modification of the text file on PC) and upload via the transfer-files and run-upload options to provide a convenient run preparation (use for operating systems of the Jan. 2010 version or newer). It is advisable to replace the system (replace the hard disk with extra caution) if there are problems with frozen screen or if there is no generation of results; consult with the manufacturer, providing your serial number.

Preferably connect the instrument to the network over Ethernet cable; this should allow the opportunity to observe measurement progression and on-line performance control (it is possible to check real time data and instrument performance). Transferring results onto a USB memory unit may cause damage to the USB memory unit (which can be reformatted).

**2. Room condition (temperature / humidity / vibration)**

Temperature fluctuation is one of the biggest problems for the operation of the instrument and abrupt temperature changes are critical (even within a narrow band of temperatures); check for the rate of temperature change, not the absolute value. Try to keep a constant room

temperature at any reasonable level (adjust your air conditioner according to the ambient temperature, prevent fluctuating performance). The Liquid Water Isotope Analyzer (LWIA) can run up to 50°C according to the manufacturer.

Improving room temperature conditions has been clearly proven to increase proficiency. Try to house your analyzer in a separate room if possible with no windows and no direct sunlight (for example in a utility room or cellar). Try to avoid undertaking other daily laboratory tasks in the same room, especially those involving devices producing heat or movement of people. If this is not possible, analyze overnight, on weekends, or at other times when there is no such activity.

Moderate ventilation of the space is advisable to avoid temperature build-up; heat is produced by LWIA and KNF vacuum pumps. At a minimum, try to find a corner with minimal air drafts and temperature fluctuation for the setup (curtain isolation from the rest of the space in the room might help to avoid big temperature changes).

Try to avoid performing analyses in extremely humid conditions, such as intensive rainy periods and/or during high ambient temperatures. In general, dehumidify the room as much as possible; the dehumidifying function of an air conditioner (AC) can do this (to slow down the use of desiccant, e.g. drierite). In dual mode ACs, divert the condensate drain outside the room to avoid re-evaporation of the condensate. Install AC at the top of the room (where the hottest air collects) allowing the natural mixing of air (cold AC outlet and hot ambient air); do not direct the AC outlet towards the analyzer.

Use a separate table for the analyzer, autosampler and vacuum pump to avoid damage to LWIA and the LC-PAL autosampler (if possible, choose a heavy duty KNF vacuum pump supplied with LWIA v2. This is a square pump version of 9xx KNF series (N920AP.29.18, N920KT.29.18; search for diaphragm vacuum pumps).

UPS/APC (electrical energy backup) can be interfaced for the proper shutdown of the instrument (at least 10 min of operation under 300W consumption is required).

In many cases, an energy backup is only seen as an emergency solution for proper handling; it cannot maintain operation over a blackout of any length.

Allow a limited number of persons to operate the instrument.

### 3. Syringe

The syringe should always be kept in use. The machine should be kept running continuously to prevent the syringe from clogging after a few hours. Waters with high TDS or suspended solids may cause clogging to occur even earlier. During such cases, the operator should replace the syringe according to the 'change syringe procedure' mentioned in the manual. It is advisable to replace the syringe immediately after the end of a run. Removal of a syringe from the blue magnetic block is not difficult; lift up the black needle guide carriage (the part that has the round rings) upward with your left hand (this is even more important when placing the syringe back into the autosampler).

Use lubricants such as deionized water and/or N-Methyl-2-pyrrolidone (NMP, <http://en.wikipedia.org/wiki/Methylpyrrolidone>) to rejuvenate or store used syringes. The safety recommendations for NMP should be followed due to its toxicity (NMP can be ordered from major laboratory suppliers, including Sigma). Clean the syringe manually after using a solvent (like NMP or acetone) to avoid contamination of the cavity and incorrect measurement. If in doubt, check your spectra using LGR freeware for organic contents

(Spectral Contamination Identifier) — access codes for the software download must be requested at LGR.

#### Sonication Procedures

- Sonicate the syringe/needle in the open position (with the piston moved up) so that water can access the needle and make the sonication process efficient.
- If the plunger/piston gets stuck, sonicate for approx. 30 min. After sonication, check that the needle is properly tightened on the syringe. Start sonication in the closed position; move the piston out with care, as needle build-ups are broken by sonication.

Manually handle the syringe with care to prevent the plunger from being damaged. If not in use, store used syringes in deionized water (do not let needles/plungers dry out), keep vertical, with the piston in half position. If stored for weeks, keep syringes in a cold and dark place (such as the refrigerator) to prevent or slow down any microbial and chemical activities.

With care, a syringe can sometimes be used for up to over 20 000 injections, though decision-making should be undertaken with data quality in mind, not syringe fluctuation. A syringe typically should last at least 5000 injections (sample quality dependent).

Up until now, there has been no better alternative for use in LGR DLT-100 laser analyzers than the Hamilton 1.2  $\mu$ L syringe. Attempts are being made to use higher volume syringes or sampling loops. However, there are no clear recommendations for practical use of the higher volume syringes.

#### **4. Standards and calibration**

Water standards are as important as the analyzer itself; take extra care of the standards.

Preferably use in-house standards for daily routine measurements. Obtain these through measurements based on VSMOW, SLAP, GISP–IAEA reference standards, or let your samples be analyzed at a well-recognized laboratory (preferably using mass spectrometry). Optionally, with extra care (under the best conditions: stable temperature, new syringe, clean transfer line, new drierite), analyze your in-house standards using LWIA following the IAEA template for standard analyses. The IAEA half or full template can be used for calibration. Mind the distinctive memory effect when measuring typical samples following SLAP or GISP.

When needed, re-check in-house standards through independent re-measurement using the above explained procedure.

Use one or both of the following options to store in-house standards: (1) an inert metal container under pressure with inert gas (nitrogen, argon) or (2) glass bottles with a ground glass stopper greased with stopper grease; leave no space for ambient vapor (use some inert fillings in glass bottles, such as transparent glass beads).

When using a metal (stainless steel inner coated) container, the upper outlet should be the only outlet used to pump up the water standard (see figure below left); pressure in the vessel is obtained through use of a known inert pressurized gas and is maintained in order to avoid outside contaminants, esp. isotopic contaminants like ambient vapor, from entering the container (use clean vessels and fittings available in the food industry); see Annex 1 for details of the container system. Rusting was observed in the case of sea water storage in some steel containers with a tap at the bottom (see figure below right).

Use glass containers as a backup when the performance of metal containers is in doubt.

Preferably store containers in a dark and cold place to avoid/minimize biochemical processes if the standard is not distilled/properly filtered or treated by other means (sterilization by UV light to treat microbiological contents is preferred when available).

Select in-house water standard bracketing your typical range of isotopic values in your samples. This involves two standards: one heavy and one depleted, with a third standard in the middle of the desired range. Use the cleanest source water available. Preferably use rain, snow, tap or bottled drinking water.

Use lake, river, saline or ground water with caution. Filter samples in any case with a 5  $\mu\text{m}$  filter. Measure physiochemical properties prior to storage and measurement of isotopic content (typically such water will be used as your intermediate standard). Do not use waters with an electrical conductivity of over 200  $\mu\text{S}/\text{cm}$ .

The source of the isotopically depleted water standard should be collected in winter time from high altitude locations.

Alternative sources of depleted water in the tropics include AC condensed water, especially at the end of rain events. Collect regularly in closed bottles with an air vent (to prevent evaporation). Filter such collected water if selected as the standard source, since it is a washout of the atmosphere, including, for example, flying dust.

Alternative sources of enriched water standard include sea water, lake water, any evaporated water (be careful about being off the meteoric water line (GMWL) with the latter; it is not critical but advisable to have the standard close to the GMWL).

Alternatively mix waters and exchange standard candidates globally based on personal contacts.

Buy reference standards from certified laboratories, or from LGR (these are of a limited amount and are expensive). Do not use reference standards like VSMOW, SLAP or GISP for daily routine (they are expensive and there is a limited supply); use them for calibrating in-house standards only.

#### IAEA Isotope Hydrology Laboratory in-house standards

Name	Source	Treatment
STD06	Heidelberg tap water 1999	Deionized
STD08	Vienna tap Water 1999	Deionized
STD09	Greenland Ice Sheet Precipitation	Distilled, Filtered 5 $\mu\text{m}$
STD10	USGS Antarctica	Filtered 5 $\mu\text{m}$
STD11	Monaco Sea water	Distilled, Filtered 5
STD12	Leppersdorf Dead Water	Distilled, Filtered 5 $\mu\text{m}$
STD13	Rest of Greenland water for GISP2	Filtered 5 $\mu\text{m}$



*Recommended (left) and inadequate (right) containers for storage of water standards.*

## **5. Storage of samples and standards during operation**

Smaller glass bottles can be used to store standards for routine operation. Other good alternatives include keeping standards in multiple vials in the refrigerator ready to use, or changing the septa after analysis of the first batch and masking the lid with a Teflon tape. The larger the volume of stored standard, the smaller the risk of isotope exchange and drift.

Fill completely bottles used for standards (e.g. 50 mL), or refill them with glass beads, as with the standard long term storage option, to prevent airhead or local vapor in the bottles. Store prepared samples/standards vials in a refrigerator, ensure lab conditions are temperate prior to measurement, and shake the tray in order to allow the condensate formed on the vial wall to mix with the liquid sample.

There is no evidence of gradual water evaporation from vials below LWIA precision while re-penetrating standards or samples during a run (even over two days with multiple injections). Nevertheless, reuse standard vials during the run with extra caution, especially in a hot climate.

## 6. Drierite

Use drierite up to 1:1 (blue:pink) in the gas purifier, especially during the first use of drierite, when pink effectively clogs the air paths.

Reuse the blue part; optionally recycle the pink part (up to 3–4 times). Drierite blends during the recycling process and loses its drying ability. Handle with caution ([color indicator](#): cobalt chloride —  $\text{CoCl}_2$  is present in the dust and is harmful. [http://en.wikipedia.org/wiki/Cobalt%28II%29\\_chloride](http://en.wikipedia.org/wiki/Cobalt%28II%29_chloride)). Multiple recycling causes an increasing dust fraction (which may be problematic regarding clogging of the inlet filter in the LWIA). Technical data for the regeneration of drierite desiccants are provided on the manufacturer's web page ([https://secure.drierite.com/catalog3/page19b.cfm?p=23&img\\_scale=200](https://secure.drierite.com/catalog3/page19b.cfm?p=23&img_scale=200)).

Purchase drierite containers from the manufacturer (<https://secure.drierite.com/catalog3/page4b.cfm>) or via LGR. Store in dry and preferably cold conditions, no warmer than room temperature.

Silica gel is not the best alternative to use due to its lower performance (it is designed for drying in a closed container, not with flowing air).

Optionally use other 'chromatography type' dessicant such as anhydride (magnesium perchlorate). It has a high performance, but is expensive, not recyclable and harmful (strong oxidant).

Optionally, use inert gas (nitrogen) or dried distributed gas in the laboratory for flushing the cavity following LWIA manufacturer instructions (there is a pressure limitation regarding cavity safety).

## 7. Pollutants in water and memory effects

Organic pollution of water samples (from artificial organic compounds, solvents, driving gases for air containers, organic juices, etc.) results in absorption within the range of chosen water 'isotopologs' spectra (in the LWIA spectrum). When in doubt check the spectral distribution using the LGR freeware *Spectral Contamination Identifier*.

Alternate highly mineralized water such as brines or sea water with deionized water. A proposal to prepare an alternative scheme, including the configuration upload file has been strongly supported by meeting participants (as one injection per sample, considering the vial to vial memory effect correction to be incorporated).

The memory effect depends on the isotope content departure of the preceding injection from the latest injection. In the case of highly depleted water such as, for example, SLAP, a memory effect can be observed within 6–10 injections for  $\square^{18}\text{O}$  and approximately 14 injections for  $\square^2\text{H}$ . In normal cases, up to four injections may show a memory effect higher than LWIA precision. It is advisable to incorporate a memory effect correction option in post-processing schemes (in order to utilize the good performance of initial injections of the samples/standards based on consecutively mixed waters as well).

## 8. Recycling vials and septa

Vials 2 or 1.5 mL (ND8 e.g. [https://ie.vwr.com/app/catalog/Product?article\\_number=548-0018](https://ie.vwr.com/app/catalog/Product?article_number=548-0018)) in size can be used for analyses. There is no obvious reason not to reuse cleaned and (oven or air) dried vials. Recycle with caution when saline or dirty samples have been placed in the vials. Writing on vials using ethanol based markers may change the color of the

cleaning water, thus appearing inside the vial after cleaning. Take off labels (writing or sticker) before washing. Test wax type pens before you use them.

Recycle vials following this proposed procedure: empty out vial contents (shake out, extract using disposable injectors), fill vial fully with deionized water, put in a sonication bath for approx. 30 min. (optionally heated), take out, shake or extract the contents (repeat the filling if desired), dry using air or in a clean oven.

Recycling vial caps is also advisable when economically effective.

### **Replace the vial septa**

Buy septa of the same kind separately.

Red Teflon double sided vial septa (PTFE red/silicone white/PTFE red 45° shore A, e.g. [https://ie.vwr.com/app/catalog/Product?article\\_number=548-0312](https://ie.vwr.com/app/catalog/Product?article_number=548-0312)) or light blue white Teflon one sided septa can be used (Silicone blue transparent/PTFE white 45° shore A, [https://ie.vwr.com/app/catalog/Product?article\\_number=548-0320](https://ie.vwr.com/app/catalog/Product?article_number=548-0320)).

Red septa (more expensive) create less dirt when re-penetrated however softer blue septa are sufficient for less than 20 injections. With extensive use, 'rubber' material will clog the syringe needle.

Septa can be purchased in the screw caps with a central hole as well.

red: [https://ie.vwr.com/app/catalog/Product?article\\_number=548-0022](https://ie.vwr.com/app/catalog/Product?article_number=548-0022)

blue: [https://ie.vwr.com/app/catalog/Product?article\\_number=548-0357](https://ie.vwr.com/app/catalog/Product?article_number=548-0357)

Heater septa: This type is thicker (SGE SEP0089), predrilled (exclusive via LGR only) and can perform at least 800 injections. Cases of safe use (with a maintained vacuum) in the range of 1500–4000 injections have been proven (may cause increased dirt of the septum in the transfer line). Retightening of the septum during or after a run is possible, however replacing it at around 1000 injections is advisable; it is relatively inexpensive.

## **9. Post-processing**

For post-processing, use one of the following options: IAEA calculation scheme or manufacturer software LWIA Post Analysis Tool (ask LGR to provide access to this software free for LWIA users). You can download IAEA templates from [www.iaea.org/water](http://www.iaea.org/water). You may adopt your own scheme, taking extra caution for possible calculation errors.

## **10. Other issues**

What is the effect of re-using vials? Feedback on this issue is required to assess its importance.

How does salt water in a line affect isotope fractionation? When fractionation takes place in a line/injector block, a pres flag is issued.

In the case of saline waters or high (or low) pH waters, what is the effect of diluting a sample prior to analysis? Is there decreasing precision? This is not recommended. (With low pH, clean water, there are no observable problems with isotope identification).

What is the relation between salinity and absolute results? When measuring saline samples, extend the evaporation time in the block.

In case there is a need to modify a run while in operation, must one start all over again? Yes. Use the 'shut down and restart' command, replacing the penetrated vial septa (and maybe the heater septum).

Annex 1. Technical specifications of containers for storage of in-house standards.

No	Description	Swagelok	Parker
1	Male connector	SS-6-TSW-1-4	6FW-316
2	Female cross	SS-4CS	4FX-316
3	Needle valve	SS-1KM4-S4	4M4Z- V4LN-SS
4	Tube adapter	SS-4-HC-A-401	4B2TU4-316
5	Male connector	SS-400-1-4BT	4MTC4N-316
6	Toggle valve	SS-1GS4	4A-V4AQ-SS

For assembly, additionally a conventional manometer (range of 2000 hPa) is needed.

VULCASCOT HandelsgmbH. & Co.KG  
Muthgasse 25  
A-1190 Vienna, Austria  
Tel. +43 (0)1 3694477-0 Fax +43 (0)1 3694477-60  
Vulcascot: <http://www.vulcascot.at>

Webpages of other supply companies:  
Franke: [http://www.franke.com/en/activities/beverage\\_systems/index.html](http://www.franke.com/en/activities/beverage_systems/index.html)  
Swagelok: <http://www.swagelok.com/>  
Parker: <http://www.parker.com>

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