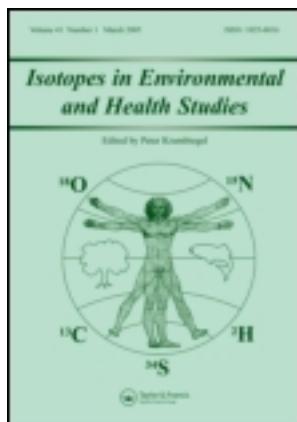


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Quality assurance and quality control in light stable isotope laboratories: A case study of Rio Grande, Texas, water samples[†]

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New isotope laboratories can achieve the goal of reporting the same isotopic composition within analytical uncertainty for the same material analysed decades apart by (1) writing their own acceptance testing procedures and putting them into their mass spectrometric or laser-based isotope-ratio equipment procurement contract, (2) requiring a manufacturer to demonstrate acceptable performance using all sample ports provided with the instrumentation, (3) for each medium to be analysed, prepare two local reference materials substantially different in isotopic composition to encompass the range in isotopic composition expected in the laboratory and calibrated them with isotopic reference materials available from the International Atomic Energy Agency (IAEA) or the US National Institute of Standards and Technology (NIST), (4) using the optimum storage containers (for water samples, sealing in glass ampoules that are sterilised after sealing is satisfactory), (5) interspersing among sample unknowns local laboratory isotopic reference materials daily (internationally distributed isotopic reference materials can be ordered at three-year intervals, and can be used for elemental analyser analyses and other analyses that consume less than 1 mg of material) – this process applies to H, C, N, O, and S isotope ratios, (6) calculating isotopic compositions of unknowns by normalising isotopic data to that of local reference materials, which have been calibrated to internationally distributed isotopic reference materials, (7) reporting results on scales normalised to internationally distributed isotopic reference materials (where they are available) and providing to sample submitters the isotopic compositions of internationally distributed isotopic reference materials of the same substance had they been analysed with unknowns, (8) providing an audit trail in the laboratory for analytical results – this trail commonly will be in electronic format and might include a laboratory information management system, (9) making at regular intervals a complete backup of laboratory analytical data (both of samples logged into the laboratory and of mass spectrometric analyses), being sure to store one copy of this backup offsite, and (10) participating in interlaboratory comparison exercises sponsored by the IAEA and other agencies at regular intervals.

Keywords: carbon-13; hydrogen-2; IAEA; isotope measurement methods and equipment; mass spectrometry; nitrogen-15; oxygen-18; reference materials; sulphur-34; Texas; water; procurement

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1. Introduction

In a new stable isotope-ratio laboratory, pursuit of quality assurance and quality control in hydrogen, carbon, nitrogen, oxygen, and sulphur isotope-ratio measurements requires careful planning and attention to detail. The process begins prior to selection of equipment for the laboratory, and it continues daily for as long as the laboratory generates isotopic data.

2. Equipment procurement fundamentals

Critical to obtaining good analytical results is procuring high quality mass spectrometers, sample introduction systems, and laser-based isotope-measurement instrumentation. New laboratories often make critical mistakes in their analytical equipment procurement (including procurement of inappropriate instruments). There are various fundamentals for procurement including:

- (1) Do not accept manufacturer's acceptance testing procedures. Write your own acceptance testing procedures and put them into your equipment procurement contract. Be sure to put these procedures in your solicitation or request for proposal at the beginning of the procurement process. Failure to carry out these steps is one of the major mistakes laboratories make in equipment procurement.
- (2) If the instrument has 96 ports, require the manufacturer to analyse the same sample in all 96 ports during performance acceptance to demonstrate that the precision specified in the contract is achieved. This procedure will enable the purchaser to test instrument drift; low drift commonly is critical to achieving satisfactory analytical results.
- (3) Require a minimum one-year warranty on all instrumentation. Commonly, the standard warranty for purchase of a peripheral device without purchase of a mass spectrometer is 90 days. A warranty period of one year minimum is needed for all instrumentation because it can take six–eight months experience to identify a defect in a device.
- (4) Determine between-sample memory during the acceptance procedure by analysing materials that differ in isotopic composition by at least twice that expected for routine samples. For example, analyse water sequentially having the following $\delta^2\text{H}$ values: -400 , -400 , -400 , $+500$, $+500$, and $+500$ ‰ relative to VSMOW (Vienna Standard Mean Ocean Water). For $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, and $\delta^{34}\text{S}$ analyses in organic materials with elemental analysers, use of USGS40 and USGS41 L-glutamic acid, IAEA-S-2 and IAEA-S-3 silver sulphide are useful.
- (5) It is important for you to make sure that the contract specifies that the mass spectrometer source does not turn off when the mass spectrometer computer is rebooted or replaced with a backup computer. This feature can be important in the isotopic analysis of some gases, such as oxygen, because stabilisation often takes hours. If a software glitch requires the computer to be rebooted and the filament turns off, substantial time can be lost.

3. Rio Grande case study

A customer request to the US Geological Survey for validation of the quality of isotopic analyses produced by its stable isotope laboratory in Reston (RSIL), Virginia, serves to illustrate factors that should be considered to achieve good quality control and quality assurance for isotope samples.

3.1. Laboratory equipment

Stable hydrogen isotope-ratio analyses are performed in the RSIL using H₂-H₂O equilibration with a platinum catalyst and automated isotopic analysis [1,2]. Not mentioned by Coplen *et al.* [1] is that water from samples condenses in the manifold during equilibration and must be removed daily. It can be removed by replacing sample vessels with solid plugs and evacuating the manifold for at least 2 h prior to loading new unknown and reference waters. Because of the substantial isotopic fractionation between H₂ and H₂O, the $\delta^2\text{H}$ of H₂ equilibrated with common meteoric water samples is about 700 ‰ relative to VSMOW reference water. A reference gas of about -700 ‰ relative to VSMOW should be used to minimise the analytical uncertainty for both dual-inlet and continuous flow measurements [1]. With such an isotopic reference gas, uncertainty in hydrogen gas measurements of 1 ‰ should lead to an uncertainty of 1 ‰ in the water being analysed. Compressed tank hydrogen with an isotopic composition of -700 ‰ relative to VSMOW is commonly available when regular grade hydrogen is obtained from companies that do not use electrolysis for hydrogen production. When electrolysis is used, the isotopic composition commonly is closer to that of the water used for the electrolysis. Values of -200 to -300 ‰ are common. Such hydrogen can be used for the analysis of water using zinc reduction, uranium reduction, and chromium reduction.

To increase the long-term precision of isotopic analyses in dual-inlet mass spectrometry, the amount of H₂ gas in the reference bellows or piston is maximised to eliminate the daily filling of the reference bellows or piston with reference gas. The gas pressure in the bellows or piston (which has a volume of about 600 cc in the RSIL) is increased to about 1/3 atmosphere, and the crimp in the capillary is adjusted to provide the same flow rate as that of the sample capillary, which is of the order of 1 pmol s⁻¹. In this manner, a reference gas can last 750–1500 h and daily drifts in reference gas isotopic composition are minimised. If there is an isotopic fractionation between the two capillaries, it remains constant and cancels out in isotopic composition calculations.

Oxygen isotope-ratio analyses are performed using the CO₂-H₂O equilibration technique of Epstein and Mayeda [3] using an automated 48-port equilibration device with a double focusing dual-inlet CO₂ isotope-ratio mass spectrometer [4]. As described above for the hydrogen mass spectrometer, the pressure (and amount) of the gas in the reference gas piston is loaded into substantially higher than that of the sample piston in order to minimise addition of aliquots of reference gas and to improve long-term precision.

To minimise sample handling errors, unknown waters and laboratory reference waters are loaded onto paper templates, which are generated by a Laboratory Information Management System (LIMS) for Light Stable Isotopes [5,6]. This strategy of interspersing references among unknown samples for normalisation is called the principle of identical treatment by Werner and Brand [7]. The reference waters are of two types. One is local surface water (Potomac River water with $\delta^2\text{H}$ of about -63 ‰ and $\delta^{18}\text{O}$ of about -6.5 ‰ relative to VSMOW) and has a relatively equatorial isotopic composition. For hydrogen isotopic analysis, nine deionised Potomac River waters are analysed with each batch of 60 waters. To prepare this reference water, 50 litres of homogenised water in a clean plastic trash can was loaded into 250-ml glass bottles having plastic conical insert caps. It is critical that during use of these bottles that they not be allowed to drop below 80 ‰ full (200 ml of water), because the amount of water vapour that can be lost when the cap is removed is sufficiently high that the isotopic composition of the liquid water is measurable increased in ²H and ¹⁸O over time with daily opening of the bottles. When 30 ml has been used from each of nine bottles, the water from one of the nine is decanted into the other eight bottles to fill them. Because there are now only eight bottles, a new bottle is obtained from stock to make a total of nine reference waters again.

The second reference water is Antarctic meltwater, which is strongly depleted in ²H and ¹⁸O (approximately -398 ‰ and -50 ‰, respectively, relative to VSMOW). One litre of Antarctic

meltwater is available to laboratories annually by contacting the author. This water was kindly provided by the US National Science Foundation's Office of Polar Programs. Fifty litres of water was sealed in 7000 10-ml glass ampoules with an automatic ampoule-filling machine. Seven millilitres of water was loaded into each of the ampoules. After sealing, each ampoule is inverted and sterilised in a 5 litre steriliser or autoclave at a temperature of 110 °C for 30 min. Because the ampoules are inverted, any ampoule that was not sealed tight will empty itself by expelling its contents through the leak. Sterilisation will also prevent algae from forming in reference waters. Algae have formed in some of the containers of VSMOW reference water stored in the US but does not appear to affect stable hydrogen or oxygen isotopic composition [8]. Storing samples in the dark should minimise algae formation in case sterilisation is not performed. In the event that a laboratory does not have access to an automatic ampoule-filling machine, ampoules can be loaded by hand using a Repipet® dispenser and a manual three-burner ampoule sealer, often used for oceanographic sealing of glass ampoules. Once prepared, each reference water is calibrated to the VSMOW-SLAP reference water scale using fresh ampoules of VSMOW2 and SLAP2 obtained from the International Atomic Energy Agency (IAEA) or the US National Institute of Standards and Technology (NIST). One glass ampoule is opened daily for normalising stable hydrogen isotope-ratio scales. For oxygen isotopic analysis, five deionised Potomac River waters and two Antarctic meltwaters (from one ampoule) are analysed with each batch of 48 waters. With this strategy, a laboratory can be assured that the isotopic composition of reference waters remains constant over time.

3.2. *The quality-assurance strategy*

Consider that a customer has sent the following email message to the RSIL (this is an actual email received by the RSIL):

Dear Isotope Lab,

Please have the attached isotope values verified. These data are approximately 2.5X greater than the signature found historically.

Site ID: 08377200; Site Name: Rio Grande at Fosters Ranch; Collection Date: 22 July 2003 11:20 a.m.; Our Lab ID: W-78875; $\delta^2\text{H}$ value: -86.7‰ ; $\delta^{18}\text{O}$ value: -11.9‰ .

Thank you,
Stephanie

When a request for verification of isotopic data is made, there are a number of items that should be checked. These items include:

- checking the mouth of a glass sample container for cracks that could allow leaks;
- checking the cap of the sample container to ensure it seals correctly;
- checking the label to ensure that the container is not mislabelled;
- checking that the isotopic results are within expectations based on geography, hydrology, geology, or biology; and
- checking the analytical results for compliance with measured values of reference samples and reproducibility.

Lacking an explanation, the sample may need to be reanalysed or an archived sample, if available, may need to be requested from the sample submitter and analysed.

Common laboratory policy dictates that samples be retained for six months from the date results are reported to the sample submitter. In this manner, if samples are needed for reanalysis, they will be available. In the case of Stephanie's sample above, her request was made within six months of

data reporting, and her sample was available for reanalysis. A check of the glass bottle indicated that the mouth of the glass container was not chipped or cracked.

Glass bottles with plastic conical insert caps are preferred over other bottle types for stable hydrogen and oxygen isotope-ratio samples. Plastic sample bottles may be suitable for collection of samples in rough terrain, but samples should be transferred to glass bottles as soon as convenient, especially if they will be archived prior to sample analysis. In the case of Stephanie's sample above, the cap was found to seal correctly.

During the laboratory login procedure, it is possible for samples to be confused with incorrect labels being affixed to bottles. In the case of Stephanie's sample, it was found that the container was not mislabelled by RSIL personnel.

The majority of stable hydrogen and oxygen isotope-ratio samples plot near the global meteoric water line [9] (Figure 1). If a sample were inadvertently mixed up with another during isotopic analysis, the delta values typically might not fall on the global meteoric water line. The $\delta^2\text{H}$ value of -86.7‰ and $\delta^{18}\text{O}$ value of -11.9‰ of Stephanie's sample plot on this line; thus, there is no suggestion of analytical error.

The sample in question is a surface-water sample from the Rio Grande in Texas. One can next check to determine if the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values are as expected for this site. Kendall and Coplen [10] determined $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values at 390 sites of the US Geological Survey's National Stream Quality Accounting Network (NASQAN). A plot of the mean weighted $\delta^2\text{H}$ values throughout the 48 contiguous states is shown in Figure 2. Results indicate that the $\delta^2\text{H}$ value of mean weighted Rio Grande (site 08377200) is between -40‰ and -20‰ . The value of -86.7‰ appears to be far too depleted in ^2H . From past laboratory records a profile over time of the stable hydrogen isotopic composition of Rio Grande (site 08377200) surface water can be compiled. These data (Figure 3) indicate that the value of -86.7‰ appears to be very unusual. An evaluation of the analytical methods and data is needed.

A laboratory information management system (LIMS) can provide an easy audit trail to past analyses of unknowns and reference samples. A review of the RSIL LIMS database indicated that on the day the first aliquot of water sample W-78875 was analysed for hydrogen isotopic composition, nine deionised Potomac River reference waters were analysed. The first analysis of the day was ignored, and a standard deviation of 0.69‰ was achieved. Two aliquots of Antarctic reference water yielded $\delta^2\text{H}$ values of -388.23‰ and -388.92‰ . Thus, the laboratory reference waters used for normalisation of isotopic data have good agreement. A query of LIMS for all

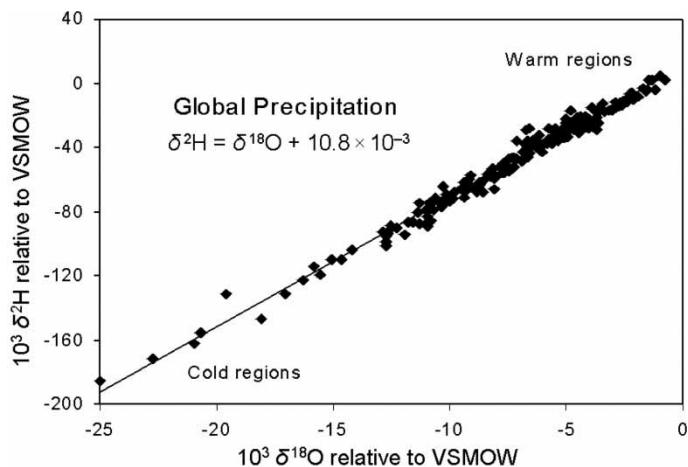


Figure 1. Global meteoric water line of Rozanski *et al.* [9].

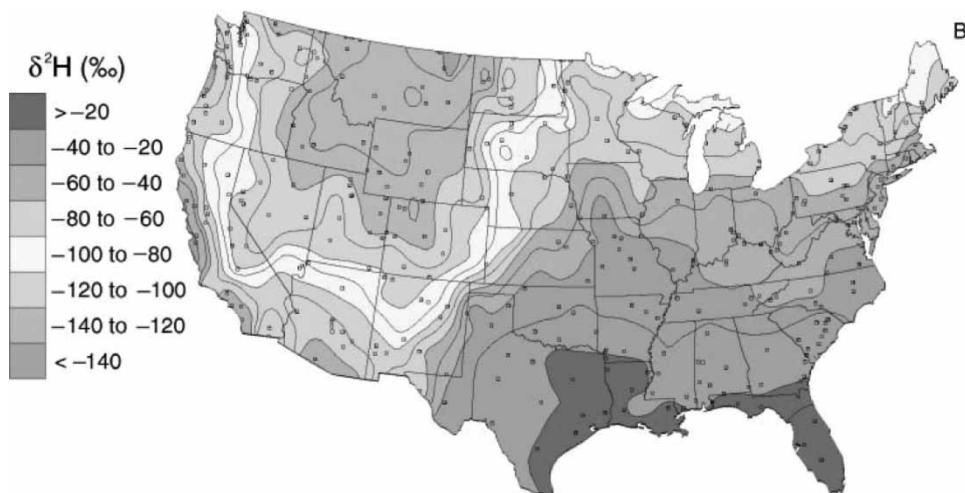


Figure 2. Discharge-weighted mean $\delta^2\text{H}$ of NASQAN and benchmark samples [10]. Location of site 08377200 is shown by the solid black circle. Smaller solid black circles are locations of surface-water sites.

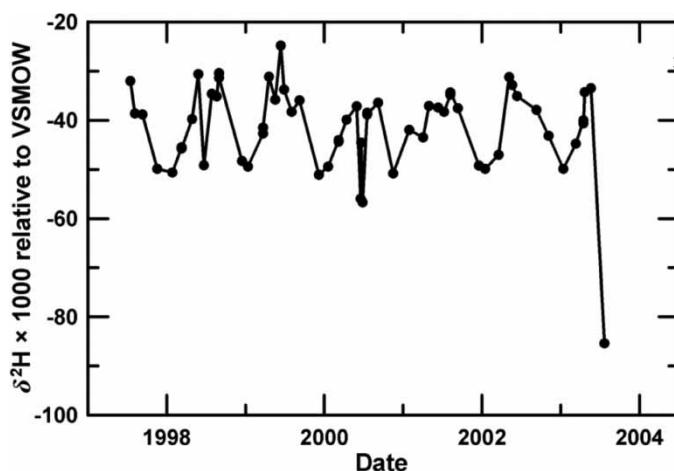


Figure 3. Variation in $\delta^2\text{H}$ over time of water collected from USGS surface-water site 08377200, Rio Grande at Foster Ranch.

the hydrogen isotopic analyses of W-78875 yields $\delta^2\text{H}$ values of -86.4 , -88.1 , and -85.5 ‰ over a span of 13 days. A similar query for the $\delta^{18}\text{O}$ values of W-78875 yielded -11.93 and -11.87 ‰ for analyses seven days apart. Thus, there appears to be no analytical problems with $\delta^{18}\text{O}$ measurements.

All of the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ queries were completed in a total time of less than 4 min with LIMS for Light Stable Isotopes. This timely completion demonstrates the value of a good LIMS. Although it may take one–two weeks to set up a LIMS, long-term benefits to a laboratory's quality assurance and quality control are substantial. An additional benefit of using an LIMS is that it is easy to follow recommendations of the International Union of Pure and Applied Chemistry and report results on scales normalised to internationally distributed isotopic reference materials (where they are available) and provide to sample submitters the isotopic compositions of internationally distributed isotopic reference materials of the same substance had they been analysed with unknowns [11].

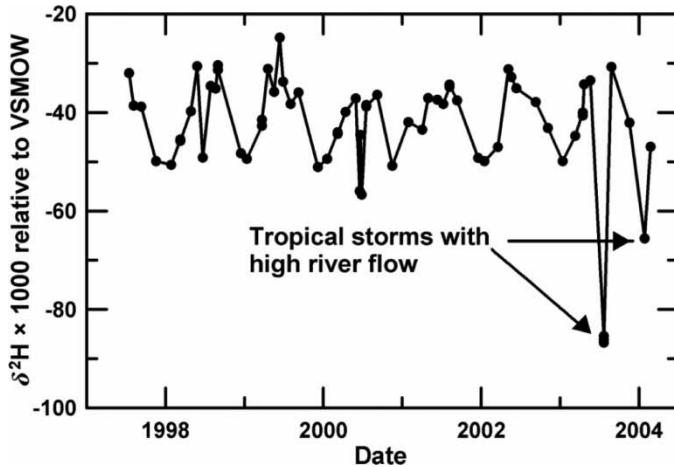


Figure 4. Variation in $\delta^2\text{H}$ of water from site 08377200, Rio Grande at Foster Ranch, between late 1997 and early 2004.

Had W-78875 been analysed only once for stable hydrogen and oxygen isotopic composition, it would be appropriate to re-analyse it for both isotope ratios. Because replicate analyses had already been performed, it was necessary to obtain a duplicate sample from the archive of the sample submitter. In this case, an archived sample was available in Denver, Colorado, at the National Water Quality Laboratory of the US Geological Survey. Stable hydrogen and oxygen isotopic analyses of the archived sample yielded the same $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values within analytical uncertainty. Therefore, an email was sent to Stephanie indicating that the archived sample had the same surprising $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values, and the email recommended that she needed to look for a hydrological, chemical, or other explanation.

When the sample arrived, it was noted that it was muddy. A review of the river level indicated that the water level was high on the day the sample was collected. Further detective work indicated that the high river flow correlated with a large tropical storm that had come ashore. A subsequent plot in mid-2004 including additional data from the Rio Grande at Fosters Ranch shows another tropical storm two–three months later (Figure 4). These results agree with observations of Gedzelman and Lawrence [12], who demonstrated that tropical storms have low $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values. The $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of Stephanie's sample now can be explained hydrologically.

4. Summary

In a new light stable isotope-ratio laboratory, pursuit of quality assurance and quality control in $\delta^2\text{H}$, $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, $\delta^{18}\text{O}$, and $\delta^{34}\text{S}$ measurements requires careful planning and attention to detail. The process begins prior to selection of equipment for the laboratory, and it continues daily for as long as the laboratory generates isotopic data. The aim of the stable isotope-ratio laboratory is to be able to analyse a sample today and analyse another aliquot of the same sample in 10 years and report the same isotopic compositions within experimental uncertainty. The process requires the laboratory to:

- (1) Identify, procure, and perform proper acceptance testing of equipment for stable isotope-ratio determinations, being careful never to accept a manufacturer's acceptance testing procedures. Write your own testing procedures and include them into your equipment procurement contract. Be sure to put these procedures in the solicitation. Make sure the warranty is at least one year because some problems are slow to materialise.

- (2) Obtain large quantities of local isotopic reference materials spanning isotope scales of interest and calibrate them with internationally distributed isotopic reference materials obtained from IAEA or NIST. For analysis of small amounts of material, such as less than a milligram of EA analyses, it is suggested that rather than producing 'local' isotopic reference materials, that users rely on international isotopic reference materials, which can be ordered at three-year intervals.
- (3) Bottle these local isotopic reference materials in containers that inhibit or minimise change in isotopic composition over time, such as glass sealed ampoules for water.
- (4) Obtain appropriate carrier gases and isotopic reference gases for any continuous flow isotope-ratio measurements.
- (5) Obtain and analyse materials greatly different in isotopic composition to quantify between-sample memory and determine algorithms to account for this between-sample memory.
- (6) Daily analyse unknowns and intersperse local isotopic reference materials with substantially different isotopic compositions among the unknowns – this analysis and interspersation applies to $\delta^2\text{H}$, $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, $\delta^{18}\text{O}$, and $\delta^{34}\text{S}$ measurements. For analysing carbonates, two isotopically different carbonates should be analysed with unknowns. For elemental analyser C and N in organic samples, NBS 22 oil, USGS40 glutamic acid, and USGS41 glutamic acids are good choices.
- (7) Calculate the isotopic compositions of unknowns by normalising isotopic data to that determined from the local reference materials.
- (8) Report results on scales normalised to internationally distributed isotopic reference materials and provide to sample submitters the isotopic compositions of internationally distributed isotopic reference materials of the same substance had they been analysed with unknowns.
- (9) Set up an LIMS that can provide an audit trail in the laboratory for analytical results.
- (10) At regular intervals make a complete backup of laboratory analytical data, both of samples logged into the laboratory and of mass spectrometric analyses. Be sure to store one copy of this backup offsite.
- (11) At regular intervals, laboratory personnel can benefit by participating in inter-laboratory comparison exercises sponsored by the IAEA and other agencies.

Adoption of these recommendations can help laboratories achieve the goal of reporting the same isotopic composition (within analytical uncertainty) for the same material decades apart.

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