

ATTACHMENT 1

TECHNICAL MEMORANDUM: NEIL STURCHIO, Ph.D.

Date: November 7, 2004

To: Project Team

From: Neil C. Sturchio

Subject: Recommendations for Stable Isotope Study to Determine Source(s) of Perchlorate in Off-Facility Groundwater in the Vicinity of the Jet Propulsion Laboratory

Objective

This technical memorandum recommends specific isotopic (and other) measurements of groundwaters for the purpose of fulfilling the objectives stated in the RI Addendum Work Plan (Battelle, 2004) as follows: “(1) to evaluate the downgradient (southern) extent of chemicals that originate from the JPL facility, and (2) to better understand the occurrence of perchlorate distribution in the vicinity of the Sunset Reservoir area.” The RI Addendum Work Plan (Battelle, 2004) was used for site-specific background information, augmented with additional information obtained from the Battelle Technical Memorandum (October 22, 2004) and from the October 25, 2004 meeting held at the Battelle Office in Columbus, OH, for preparation of this memorandum. Additional references are cited.

Outline of Strategy

The recommended strategy for this study is to pursue the most direct lines of evidence that can be used to identify the source(s) of perchlorate in the study area. There are three approaches. The first and most direct approach is to obtain stable isotope ratio measurements for perchlorate extracted from groundwater. This is the most powerful method for perchlorate source identification. The second approach is to obtain additional isotopic measurements for the groundwater, i.e., hydrogen ($\delta^2\text{H}$) and oxygen ($\delta^{18}\text{O}$) isotope ratios, as well as measurements that will constrain groundwater age, including tritium/helium-3 ($^3\text{H}/^3\text{He}$) ratios, and chlorofluorocarbons (CFCs) and sulfur hexafluoride (SF_6) concentrations, which can be used for water source identification and for evaluation of groundwater mixing and travel time. Both of these first two approaches provide information that is crucial for testing hypothetical scenarios for the source(s) and subsurface transport rates and pathways of perchlorate in the study area. A third approach, primarily for the purpose of tracing the maximum extent of the JPL contaminant plume, is to measure to distribution of co-contaminants such as CCl_4 , Sr, or other trace substances known to be present in the plume. Both chemical and isotopic measurements would be part of the third approach.

Approach #1: Isotopic Composition of Perchlorate

There are three important questions that can be addressed directly using stable isotope ratio measurements of perchlorate extracted from groundwaters in the study area: (1) Is there any evidence for the presence of natural perchlorate that may have been derived from past application of Chilean nitrate-derived fertilizers? (2) Is perchlorate from the Colorado River

water, imported by the Metropolitan Water District (MWD) and mixed with local meteoric water in the aquifer, isotopically distinct from JPL-derived perchlorate? (3) Is perchlorate undergoing natural attenuation by microbial reduction in the aquifer?

Recent work has shown that there are significant differences in the stable chlorine (Cl) and oxygen (O) isotope ratios of perchlorate from different sources (Cl isotopes - Ader et al., 2001; O isotopes - Bao and Gu, 2004; both Cl and O isotopes - Sturchio et al., 2004). The work presented by Bao and Gu (2004) and Sturchio et al. (2004) demonstrated that trace amounts of perchlorate can be extracted from different matrices, including Chilean nitrate evaporites and groundwaters, for accurate and precise isotopic analyses. These extractions were done with highly perchlorate-selective bifunctional anion exchange resins using methods developed by B. Gu and colleagues at Oak Ridge National Laboratory. In addition, microcosm experiments performed independently by two groups used pure cultures of perchlorate-reducing microbes to determine the Cl kinetic isotope effect of microbial perchlorate reduction. Both groups found Cl kinetic isotope effects of ~15‰, whereby residual perchlorate was strongly enriched in ^{37}Cl (Sturchio et al., 2003; Coleman et al., 2003). No data have yet been reported for the oxygen kinetic isotope effect accompanying microbial perchlorate reduction, although it is expected to be large.

Chlorine isotope ratios: $\delta^{37}\text{Cl}$ – Chlorine has two stable isotopes, ^{35}Cl and ^{37}Cl , that occur naturally in the ratio of ~3:1. $^{37}\text{Cl}/^{35}\text{Cl}$ ratios are normally reported in terms of per mil deviation relative to Standard Mean Ocean Chloride ($\delta^{37}\text{Cl}_{\text{SMOC}}$). The range of reported $\delta^{37}\text{Cl}$ values for *anthropogenic* perchlorate (including NaClO_4 , $\text{NaClO}_4 \cdot \text{H}_2\text{O}$, KClO_4 , RbClO_4 , and CsClO_4 reagents) is -3.1 to +2.3 ‰ (Ader et al., 2001; Sturchio et al., 2004). This range is based on the analysis of only 10 separate reagents. The range of reported $\delta^{37}\text{Cl}$ values for *natural* perchlorate is -14.5 to -11.8 ‰ (Sturchio et al., 2004), and is based on only 4 analyses of Atacama (Chile) nitrate evaporites and fertilizer derived therefrom. With the caveat that there are not yet many data and the picture may change, we have observed that $\delta^{37}\text{Cl}$ values of natural perchlorate are 10-15‰ *lower* than those of anthropogenic perchlorate.

Oxygen isotope ratios: $\delta^{18}\text{O}$ - Oxygen has three stable isotopes, ^{16}O , ^{17}O , and ^{18}O , which occur in the ratio ~2000:4:1. These three isotopes are normally fractionated by mass-dependent processes so that the information obtained by measuring $^{17}\text{O}/^{16}\text{O}$ is identical to that obtained by measuring $^{18}\text{O}/^{16}\text{O}$, therefore only the $^{18}\text{O}/^{16}\text{O}$ ratio is normally measured and is expressed in per mil deviation from the $^{18}\text{O}/^{16}\text{O}$ ratio of Vienna-Standard Mean Ocean Water ($\delta^{18}\text{O}_{\text{V-SMOW}}$). For *anthropogenic* perchlorate (compounds listed above), the range of $\delta^{18}\text{O}$ values is -24.7 to -16.1‰, whereas the range of $\delta^{18}\text{O}$ values for *natural* perchlorate is -9.3 to -4.2‰ (Bao and Gu, 2004; Sturchio et al., 2004). In contrast to the Cl isotope ratios, $\delta^{18}\text{O}$ values of natural perchlorate are 10-15‰ *higher* than those of anthropogenic perchlorate.

A comparison of the distinct $\delta^{37}\text{Cl}$ and $\delta^{18}\text{O}$ values for anthropogenic and natural perchlorates is shown in Figure 1. Also shown in Figure 1 are data for perchlorate extracted from a sample of groundwater from Edwards Air Force Base, indicating that it has an anthropogenic source. Based on the data shown in Figure 1, it can be assumed that perchlorate having a $\delta^{37}\text{Cl}$ value greater than -5‰ is dominantly anthropogenic, whereas perchlorate having a $\delta^{37}\text{Cl}$ value less than -10‰ is dominantly natural. Likewise, perchlorate having a $\delta^{18}\text{O}$ value less than -15‰ is dominantly

anthropogenic, whereas perchlorate having a $\delta^{18}\text{O}$ value greater than -10% is dominantly natural. Within the field of anthropogenic perchlorate, there may be a fairly wide range of both $\delta^{37}\text{Cl}$ and $\delta^{18}\text{O}$ values, possibly allowing JPL-derived perchlorate to be distinguished from other anthropogenic perchlorate, e.g. that brought in with Colorado River water by the Metropolitan Water District (MWD). Not shown in Figure 1 are preliminary $\delta^{37}\text{Cl}$ values obtained for perchlorate from groundwater on the Kerr-McGee facility at Henderson, NV ($+0.9\%$) and for water from the Las Vegas Wash ($+0.4\%$) that feeds Lake Mead and the Colorado River. These values are indistinguishable within the $\pm 0.3\%$ uncertainty of the measurement. The Kerr-McGee facility has manufactured and released perchlorate since the 1950s and is believed to have been a major contributor of perchlorate to the Colorado River.

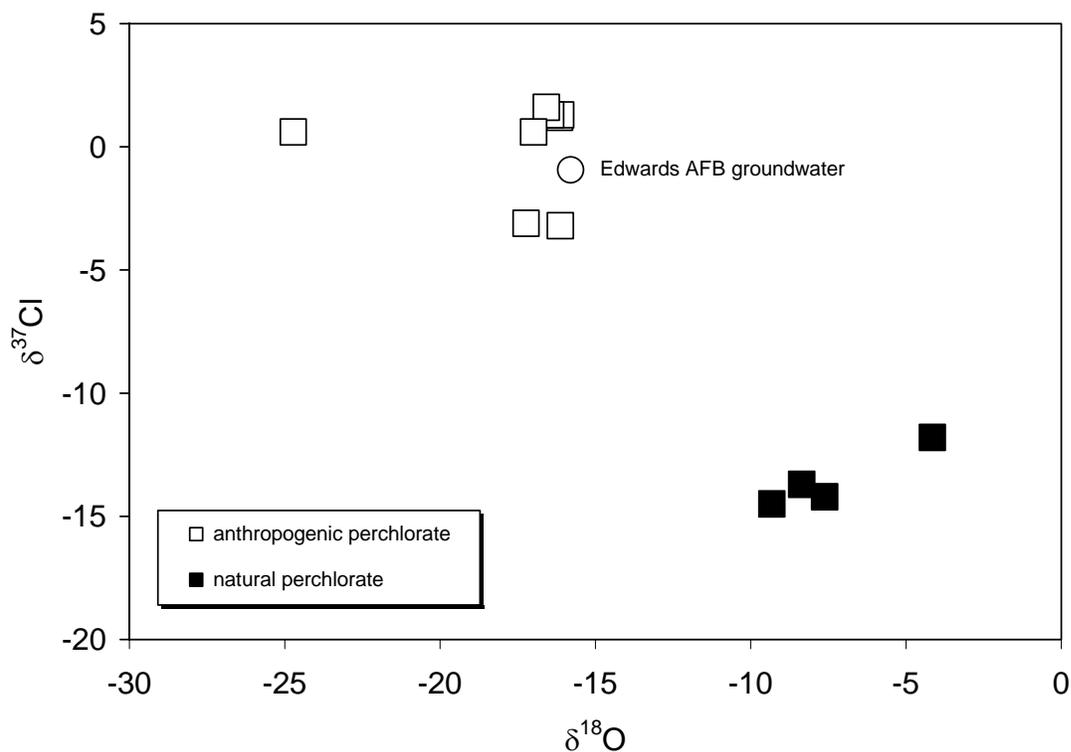


Figure 1. Diagram showing $\delta^{37}\text{Cl}$ vs. $\delta^{18}\text{O}$ values for anthropogenic and natural perchlorate samples, compared with a sample of perchlorate extracted from groundwater at Edwards Air Force Base.

Oxygen isotope ratios: $\Delta^{17}\text{O}$ - In addition to measuring the $^{18}\text{O}/^{16}\text{O}$ ratio of perchlorate, the $^{17}\text{O}/^{16}\text{O}$ ratio provides an especially diagnostic indication of natural perchlorate. This is because of the discovery that natural perchlorate has a large excess of ^{17}O relative to that expected from oxygen having normal terrestrial mass-dependent fractionation in which $\delta^{17}\text{O} \approx 0.52 \times \delta^{18}\text{O}$ (Bao and Gu, 2004). The reason for this ^{17}O -excess is that the natural perchlorate is produced in the atmosphere by reaction of ozone (O_3) with volatile chlorine (e.g., HCl). Natural perchlorate thus inherits its ^{17}O -excess from atmospheric O_3 , which is known to have a large ^{17}O -excess (Thiemens, 1999). Bao and Gu (2004) demonstrated that anthropogenic perchlorate does not have a measurable ^{17}O -excess, whereas natural perchlorate has a large measurable ^{17}O -excess

[expressed as $\Delta^{17}\text{O} \approx \delta^{17}\text{O} - (0.52 \times \delta^{18}\text{O})$], ranging from $\Delta^{17}\text{O} = +4.2$ to $+9.6\%$. The relationship of the $\delta^{17}\text{O}$ values to the $\delta^{18}\text{O}$ values of natural and anthropogenic perchlorates is shown in Figure 2 (from Bao and Gu, 2004).

The presence of a measurable ^{17}O -excess in perchlorate extracted from groundwater in the study area would indicate the presence of natural perchlorate, which we anticipate to be isotopically distinct from JPL-derived perchlorate with respect to all three isotopic parameters being discussed here – $\Delta^{17}\text{O}$, $\delta^{18}\text{O}$, and $\delta^{37}\text{Cl}$. The most likely source of natural perchlorate may be fertilizer derived from Chilean nitrate evaporite deposits. Such fertilizer was once widely applied in citrus orchards throughout California. It is important to note that a small percentage of admixed natural perchlorate (e.g. $\sim 5\%$ or more) could be distinguished in a sample that is dominantly anthropogenic – any significant deviation from $\Delta^{17}\text{O} = 0$ signifies the presence of some natural perchlorate.

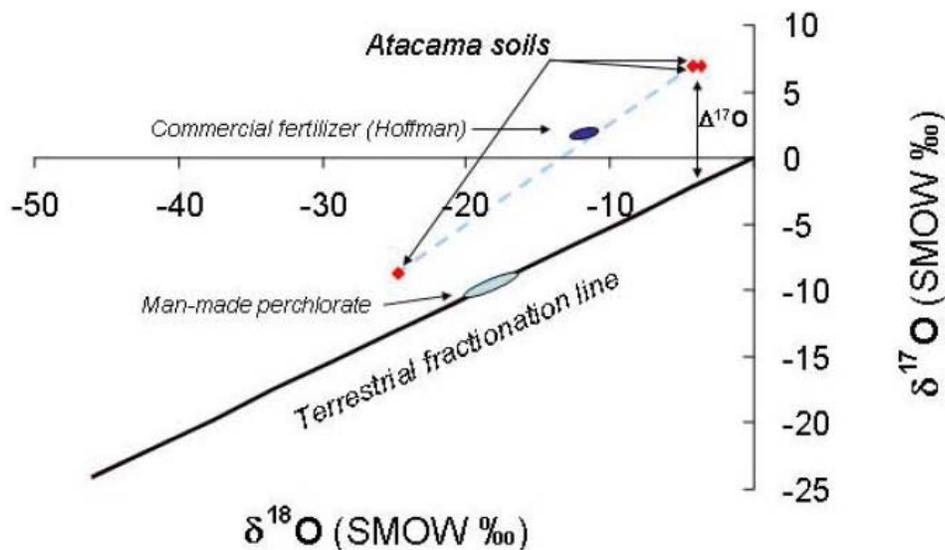


Figure 2. Diagram showing $\delta^{17}\text{O}$ vs. $\delta^{18}\text{O}$ values of man-made (anthropogenic) and natural perchlorate (Atacama “soils” and Hoffman fertilizer), from Bao and Gu (2004).

Identification of natural attenuation from perchlorate isotopic compositions - The Cl kinetic isotope effect of natural attenuation of perchlorate by microbial reduction is sufficiently large ($\sim 15\%$) that reduction of 4% or more perchlorate can be identified by a resolvable ($+0.61\%$) shift in $\delta^{37}\text{Cl}$ value of the residual. Although the concomitant O kinetic isotope effect has not yet been reported for microbial perchlorate reduction, it might be expected to have a similar or perhaps larger magnitude than the Cl kinetic isotope effect. If the two effects are assumed to be identical, then the trajectory of hypothetical residual perchlorate in Figure 1 would move toward the upper right along a line with a slope of 1. After 50% reduction, the residual perchlorate would be enriched in ^{37}Cl and ^{18}O by 10.4%; after 80% reduction, by 24.1%; after 90% reduction, by 34.5%, and after 99% reduction, by 69%! If natural attenuation is progressive along a flow path, then δ values of samples collected along the flow path would define a linear

array in Figure 1. The $\Delta^{17}\text{O}$ value of residual perchlorate is not affected by microbial reduction, however, because kinetic isotope effects are mass-dependent.

Approach #2: Isotopic Composition and Age of Water

In the event that perchlorate isotopic compositions are not sufficiently diagnostic of perchlorate sources in the study area, then additional lines of evidence must be sought to meet the objectives of the study. The next most direct line of evidence regarding perchlorate source lies with the source of the water containing the perchlorate, and the age of that water.

Hydrogen and oxygen stable isotopic compositions of groundwater reflect the isotopic composition of the recharge water. Tritium, a radioactive isotope of hydrogen (^3H), has a half-life of 12.4 years, and its activity relative to its stable decay product ^3He can indicate the age of the groundwater. Measurements of certain trace gas concentrations (CFCs and SF_6) are also useful for age determination of young (≤ 50 year) groundwaters.

In the study area, three types of water have been identified based on major ion compositions: Type 1 (Ca- HCO_3 type water, believed to represent recent recharge of precipitation falling on the San Gabriel Mountains); Type 2 (Na- HCO_3 type water, found in deeper portions of the aquifer, having similar TDS concentrations but with Na as the dominant cation); and Type 3 (Ca- HCO_3 -Cl- SO_4 type water, found upgradient and to the west of JPL, believed to be a mixture of Type 1 water and higher-TDS Colorado River water imported by the Metropolitan Water District).

Hydrogen and oxygen isotope ratios: $\delta^2\text{H}$ and $\delta^{18}\text{O}$ - Colorado River water is relatively depleted isotopically (i.e., lower $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values) compared with local meteoric water in the study area (Coplen and Kendall, 2000), and therefore it might be expected that this difference would be reflected in a distinct isotopic composition of Type 3 water relative to Types 1 and 2 in the study area. Evaluation of mixing between Colorado River water and local meteoric water may be complicated by seasonal variations. Types 1 and 2 water could also have distinct stable isotope compositions. The stable isotopic compositions of the water would complement the discrimination of water types that has been based on ionic compositions.

Tritium activity: $^3\text{H}/^3\text{He}$ dating – The age of groundwater (time since isolation from the atmosphere) can be determined fairly well for young (≤ 50 year) water using $^3\text{H}/^3\text{He}$ dating (Schlosser et al., 1988, 1989). Tritium-helium measurements can be used for groundwater sampled from selected wells to evaluate the validity of particle-tracking groundwater flow model (Battelle Technical Memorandum, October 22, 2004). The most important application of such measurements would be near the Sunset Reservoir wells (i.e. at new monitoring well #26). If $^3\text{H}/^3\text{He}$ measurements indicate that flow models are valid, then the so-called bomb tritium pulse (mid-1960s) should not yet be evident in the Sunset wells because that water should predate the mid-1960s. However, according to the flow model, the bomb pulse may have passed the location of the proposed new monitoring well #25 and may not yet have arrived at the location of proposed new monitoring well #26. The question of groundwater age would be well-constrained at a number of key locations by $^3\text{H}/^3\text{He}$ measurements.

Chlorofluorocarbons (CFCs) and Sulfur Hexafluoride (SF₆) – A useful complement (or alternative) to ³H/³He measurements for groundwater age determination of young (≤50 year) groundwater is the measurement of CFC concentrations and SF₆ (Plummer et al., 1993). The main advantage of this technique, which is based on equilibrium gas solubilities in recharge water and knowledge of the history of atmospheric concentrations of the gases, is that it is much faster and less expensive than ³H/³He measurement. The CFC and SF₆ measurements are done by gas chromatography with electron capture detector.

Approach #3: Tracing the Extent of JPL Contaminant Plume

Depending on the results of the first two approaches, the third approach may be redundant. For example, if perchlorate derived from JPL is found to be isotopically distinct from that found in upgradient monitoring wells and that found in the Sunset Reservoir wells, then the objectives of the study will have been achieved and this approach will be unnecessary. However, if the first two approaches yield ambiguous results and further data are required to resolve the issues, then the third approach will be worth pursuing.

Tracing the extent of carbon tetrachloride migration from JPL – According to available data (Battelle, 2004; Battelle Technical Memorandum, October 22, 2004) the only known source of carbon tetrachloride (CCl₄) in the study area is JPL. Standard EPA methods for VOC analysis have a detection limit near 1 ppb. Much lower detection limits (~0.01 ppb) can be obtained by using a combination of large sample volumes, purge-and-trap methods (Holt et al., 2001), and solid-phase microextraction, combined with GC-combustion-IRMS techniques. This approach would also provide C isotope ratio analysis of the CCl₄. It could be attempted with the caveat that there could be sub-ppb concentrations in the study area that are unrelated to JPL discharges, resulting in false positive identification of the extent of the JPL contaminant plume.

Isotope ratios of other trace contaminants in JPL contaminant plume – If other contaminants can be identified that are unique to the JPL contaminant plume, then they can be used to trace its extent. Their uniqueness may be either in their identity (as constituents not normally found in groundwater) or their characteristic isotope ratios (e.g., reagent Li; Qi et al., 1997). This approach may require initial assays of on-site groundwater to identify constituents that might serve well as off-site tracers.

Other indicators of natural attenuation - Chemical measurements of redox-sensitive parameters such as dissolved oxygen, Eh, nitrate-nitrite-ammonium, ferrous-ferric iron, and others, as well as the amount of dissolved organic carbon, can also give useful information about the potential for occurrence of natural attenuation. In addition, the presence of the products of reductive dechlorination of known contaminants PCE and TCE (cis-DCE and vinyl chloride) would indicate that conditions favorable for natural attenuation are present within the aquifer or the overlying vadose zone. These types of measurements could be useful in assessing the potential for (or, if found, the rate of) natural attenuation of perchlorate in the JPL plume.

Recommendations for Sampling

Sampling locations recommended for this project are:

MW-1, -9, and -15 upgradient wells
MW-17 within known plume
MW-19, -20, -21 downgradient near site
MW-24 source area at JPL
MW-25 and -26 new wells between MW-19 and Sunset Reservoir wells
MWD Colorado River water

Time line for sampling – It is recommended that the next round of sampling (early 2005) should include analysis of at least 15-20 samples for some or all of the following parameters. These are grouped into two priority levels and it is assumed that a standard suite of analyses will also be done for each sample (i.e., temperature, pH, major cations and anions, VOCs). For optimal results, in terms of limiting the scope and expense of the study, the first-level priority analyses should be sampled for and performed as soon as possible. If budgetary constraints permit, the second-level priority analyses should also be done in the same sampling round as the first-level priority analyses. However, the second-level priority analyses may also be viewed as optional measurements that could be obtained in a subsequent round of sampling, after considering the results of the first-level round of sampling, for the purpose of resolving issues that may arise from the results of the first-level sampling. It is recommended that, in any case, all measurements be performed on duplicate samples to increase the confidence level of the results.

First-level priority:

1. Perchlorate for $\delta^{37}\text{Cl}$ and $\delta^{18}\text{O}$, and $\Delta^{17}\text{O}$
2. Water for $\delta^2\text{H}$ and $\delta^{18}\text{O}$
3. CFCs and SF_6

Second-level priority:

1. Tritium-helium dating
2. low-level CCl_4 , $^{87}\text{Sr}/^{86}\text{Sr}$ and other JPL-specific groundwater tracers
3. Redox-sensitive parameters, organic carbon, other indicators of natural attenuation

Perchlorate for stable isotope analysis - In multi-port monitoring wells, samples should be taken from individual screened levels where perchlorate was detected in the most recent sampling. More than one screened level per well should be sampled where data indicate that there is a variation in water type with depth. Sampling for perchlorate should be done using highly perchlorate-selective bifunctional ion exchange resin (Purolite A-530E or equivalent) in columns designed for the perchlorate concentration range expected, based on available data from most recent sampling. Water should be pre-filtered through a 5-micrometer pore-size filter before the resin column. Flow rate through the resin column should not exceed 0.5 L/minute. A volume of water containing at least 20 mg of perchlorate should be passed through the column to ensure sufficient yield of perchlorate for multiple stable isotope analyses.

Water for stable isotope analysis – Unfiltered or filtered water is collected in glass bottle (at least 20 mL) with Polyseal cap. Isotopic measurements will be made by gas-source isotope ratio mass spectrometry following hydrogen equilibration or Zn reduction (for $\delta^2\text{H}$) and CO_2 equilibration (for $\delta^{18}\text{O}$).

CFCs and SF_6 – Water must be sampled in a way that carefully avoids entrapment of air bubbles. A simple but effective method for sampling is described on the web site of the USGS Reston Chlorofluorocarbon Laboratory (<http://water.usgs.gov/lab/cfc/sampling/newmethod.htm>).

Tritium-helium dating – Unfiltered water is collected in a length of 3/8-inch diameter copper tube that is clamped shut after removal of air bubbles. Dissolved gases are extracted in the laboratory for measurement of He and Ne concentrations and $^3\text{He}/^4\text{He}$. Degassed water is maintained to allow ingrowth of additional ^3He from tritium and then re-extracted after about 6 months for measurement of ^3He concentration.

Other constituents – Sampling and analysis of other constituents to be determined following identification of appropriate constituents in JPL groundwater and refinement of strategy.

Cost estimate for analytical work – The cost estimate shown here is based on a per-sample fee for analysis in the 10-50 sample range. The total can be pro-rated for additional samples. Recommendation for minimum sampling density is 15 samples from the study area, analyzed in duplicate for perchlorate isotopes, water isotopes, CFCs and SF_6 , along with 6 samples analyzed in duplicate for tritium-helium dating. (Data interpretation and report writing costed separately.)

Stable isotope analysis of perchlorate \$1500./sample

Including provision of custom ion-exchange column and pre-filter assembly for sampling; extraction and purification of perchlorate from ion-exchange column; duplicate analysis of $\delta^{37}\text{Cl}$, $\delta^{18}\text{O}$, and $\Delta^{17}\text{O}$

Recommended lab: UIC Environmental Isotope Geochemistry Laboratory

Stable isotope analysis of water \$150./sample

Including duplicate $\delta^2\text{H}$ and $\delta^{18}\text{O}$ analysis by standard methods

Recommended lab: UIC Environmental Isotope Geochemistry Laboratory

CFC and SF_6 analysis of water \$600./sample

Including duplicate GC-ECD measurements by standard methods

Recommended lab: USGS Reston CFC Laboratory

Tritium-helium analysis of water \$1000./sample

Including provision of aluminum frame, clamps, and copper tubing for sample collection.

(Requires a separate sample for duplicate measurement)

Recommended lab: Environmental Tracer Group, LDEO, Columbia University

Cost for minimum sample density (15 samples in duplicate for perchlorate stable isotopes, $\delta^2\text{H}$ and $\delta^{18}\text{O}$ of water, CFCs and SF_6) \$33,750.

Cost for 6 samples for tritium-helium dating (counts as 12 for duplicates) \$24,000.

Total Cost as described for minimum recommended sample density \$57,750.

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ATTACHMENT 2

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November 12, 2004

Technical Memorandum: NASA-JPL Perchlorate Plume Investigation

Objectives: Forensic Biogeochemical Component

This segment of the Scope of Work focuses on the use of naturally-occurring isotopes, integrated with other hydrogeochemical data to:

- delineate, as much as possible, the location of the leading edge of the perchlorate plume;
- assess the fate of the perchlorate plume, focusing especially on the potential transport of perchlorate down hydrologic gradient to the Sunset Reservoir; and
- discriminate NASA-JPL perchlorate from other potential sources of perchlorate in the Raymond Basin.

In order to accomplish these objectives, aqueous samples will be collected for biogeochemical analyses from: (1) ~ 10 groundwater monitoring wells, both on- and off-site; and (2) MWD Colorado River water. The analyses to be performed and their rationale are discussed in the subsequent section.

Analyses to be Performed to Achieve Objectives

Although the analyses described herein will be done in parallel, they are discussed in sequence from those that are more routinely performed in the course of groundwater investigations to those, such as isotopic ratio analyses, that are more specialized, being used in cases where discriminating among sources of contaminants is an issue.

General Groundwater Chemistry: Analyses of major cations and anions, pH, temperature, and potential contaminants of concern (perchlorate, nitrate) will be performed on the samples to be collected. These data will be compared and contrasted, using statistical evaluations, to each other and available historic groundwater chemical analyses of not only perchlorate-impacted groundwater, but also groundwater that has not been impacted by perchlorate (i.e., natural groundwater). The intent is to provide a geochemical framework that contributes to defining the characteristics of perchlorate-impacted groundwater from MWD Colorado River water and natural groundwater. It is clear that general groundwater chemistry, up to this point, has not successfully provided the level of resolution possible to achieve the objectives discussed above, however, detailed statistical analyses of larger data bases (current plus historic analyses), when integrated with isotopic analyses, have been shown to be very effective in investigations involving contaminant fate and transport (e.g. delineating plume boundaries, identifying potential sources of contamination).

Perchlorate Degradation (Chemical/Microbiological Indicators): Another factor that should be evaluated with regard to the fate and transport of perchlorate is the potential for perchlorate to degrade as the result of reduction reactions (i.e., oxygen deficient) and/or the presence of perchlorate-reducing microorganisms in an aquifer. In order to assess the potential for perchlorate degradation in the aquifers involved, the following analyses will be performed:

- dissolved oxygen and oxidation – reduction potential (DO and ORP, respectively)
- oxidation – reduction pairs (e.g., nitrite/nitrate, ferrous/ferric, sulfite/sulfate)
- dissolved and total organic carbon (DOC and TOC, respectively)
- microbial assays

The first three analyses evaluate either directly or indirectly, relative abundances of oxygen; higher abundances of oxygen stabilize perchlorate ions, thereby inhibiting its degradation via reduction. The fourth analysis, microbial assays, is important given the presence or absence of perchlorate-reducing microorganisms (e.g., *Dechlorosoma suillum*) influences the overall fate of perchlorate in groundwater systems. Evaluation of these factors is important, not only in the short term, but also in the long term, to the fate of perchlorate in groundwater systems within the Raymond Basin.

Tritium: Tritium, a radioactive isotope of the element hydrogen, provides information about the age of groundwater (i.e., time since groundwater has been out of contact with the atmosphere) and hence, contributes to characterizing groundwaters. Specifically, high precision tritium analyses (to 0.1 TU, tritium units) can assist in constraining whether or not perchlorate contamination is recent, old, or a mixture of old-new sources.

Stable Isotope Analyses: Both oxygen/hydrogen ($\delta^{18}\text{O}$ and δD , respectively) and strontium ($^{87}\text{Sr}/^{86}\text{Sr}$) isotope analyses will be performed on each aqueous sample collected for the purpose of:

- characterizing the isotopic characteristics of each water;
- assessing the fate/transport of perchlorate and delineating the plume (e.g., leading edge);
- discriminating the NASA-JPL perchlorate source from other potential sources of perchlorate and/or fingerprinting NASA-JPL perchlorate;
- assessing if NASA-JPL derived perchlorate is contributing to perchlorate contamination at the Sunset Reservoir; and
- modeling the relative contribution of NASA-JPL perchlorate to groundwater resources in the Raymond Basin (if multiple perchlorate sources are determined to be present).

The advantage of stable isotope analyses resides in the higher precision and accuracy possible when compared to those achievable via general groundwater chemistry ($\ll 0.01\%$ versus $> 1-10\%$ respectively). Hence, important variations in groundwater chemistry pertinent to perchlorate source identification and tracing the migration of perchlorate that may escape the scrutiny of general groundwater chemical analyses are far more discernible via isotopic analyses. It is also possible, using isotope geochemistry mixing models, to assess contributions of perchlorate from each source to groundwater in cases where more than one source of contamination is present.

Cumulative Data Integration

Lastly, it should be emphasized that potential covariations and groupings will be statistically evaluated utilizing the entire data set in order to define the biogeochemical characteristics of the NASA-JPL perchlorate sources in order to trace their migration and discriminate them from other sources of perchlorate, as well as natural, unimpacted groundwater.

Furthermore, these data can also be used to help constrain other modeling (e.g. hydrogeological flow models) that bear significantly on the fate/transport of perchlorate in the region.

Although each data set (e.g., general groundwater chemistry, tritium, stable isotopes, etc.) leads to independent conclusions, statistically significant covariations and groupings of independent data populations provide valuable information pertinent to achieving objectives that would be otherwise overlooked. Hence, for groundwaters collected during this sample round, and, if necessary, future sampling rounds in which the analyses discussed herein are performed, data sets will be interpreted both independently and cumulatively in order to achieve, to the highest degree possible, the stated objectives.

General Sampling Protocols

All sampling (general water chemistry, DO, ORP, DOC, TOC, microbial assays) will follow established regulatory protocols including Chain of Custody procedures. In the case of samples collected for isotope analyses, Chain of Custody procedures will be followed; in samples where a preservative (e.g. acid) may extract an element/isotope of interest from suspended particulate matter, preservatives will not be added. Samples will be filtered, preferably in an ultraclean laboratory environment, in order to remove particulates.

With regard to sampling for isotopes, it is best to keep the protocols as uniform as possible to avoid problems that may be encountered by those charged with field sampling. In general, all samples for isotope analyses should be collected in airtight, precleaned glass containers which should be filled to the rim to avoid aqueous-air exchange; splits should be taken for each isotope to be analyzed. Specific details will be provided and discussed with field technicians prior to sampling. Typical aqueous sample volumes required are as follows:

Hydrogen/Oxygen/Strontium	40-50 ml
Tritium	~ 1 L

ATTACHMENT 3
LABORATORY PROCEDURES

3A: PERCHLORATE ISOTOPE ANALYSIS

Environmental Isotope Geochemistry Laboratory
University of Illinois at Chicago (UIC)
Contact: Leslie Patterson at (312) 413-0098, e-mail lpatte2@uic.edu

Perchlorate is adsorbed from groundwater onto a highly perchlorate-selective bifunctional anion exchange resin (Purolite A530E). Up to 100,000 bed volumes of groundwater can be passed through this resin before perchlorate breakthrough is observed (Gu et al., 2000). In the laboratory, the perchlorate is desorbed from the resin using a FeCl₃-HCl solution (Gu et al., 2001), purified by ion exchange chromatography, and concentrated by evaporation and precipitated as a pure alkali perchlorate salt (Bao and Gu, 2004). Recovery of perchlorate at each step is monitored by ion chromatography measurements. The recovered perchlorate salt is decomposed in vacuo for analysis of Cl and O isotope ratios. Oxygen gas is purified for isotope ratio analysis of oxygen (including both ¹⁸O/¹⁶O and ¹⁷O/¹⁶O). Alkali chloride residue from perchlorate combustion is converted to AgCl and analyzed for Cl isotope ratio according to the inorganic chloride method summarized in Section 3F of this Attachment. Conversion yields are monitored by capacitance manometry and are near quantitative. In addition, O isotopic analyses will be performed on CO produced quantitatively by reaction of perchlorate with carbon at 1350°C, with procedures and calibrations as reported in Bohlke et al. (2003). Isotope ratios are measured by gas-source isotope ratio mass spectrometer using reference gases calibrated against standard isotopic reference materials. The standard isotopic reference materials against which all chlorine and oxygen isotope data are normalized are SMOC (Standard Mean Ocean Chloride; Godon et al., 2004) and V-SMOW (Vienna Standard Mean Ocean Water; Coplen, 1996). Precision of perchlorate Cl and O isotope ratios determined by this method is better than ±0.3‰.

Bao, H. and Gu, B. 2004. *Environ. Sci. Technol.* 38, 5073.

Bohlke, J. K., Mroczkowski, S. J., Coplen, T. B., 2003. *Rapid Comm. Mass Spectrom.* 17, 1835.

Coplen, T.B., 1996. *Geochim. Cosmochim. Acta* 60, 3359.

Godon, A. et al., 2004. *Chem. Geol.* 2004, 207, 1.

Gu, B., Brown, G. M., Alexandratos, S. D., Ober, R., Dale, J. A.,

Plant, S., 2000. In *Perchlorate in the Environment*. Urbansky, E. T., Ed., Kluwer/Plenum, New York, p. 165.

Gu, B, Brown, G.M., Maya, L., Lance, M.J., Moyer, B.A., 2001. *Environ. Sci. Technol.* 35, 3363.

3B: OXYGEN ISOTOPE ANALYSIS IN GROUNDWATER

Equilibrating Water Samples for $\delta^{18}\text{O}$ Analysis

- I. This SOP is to explain the procedure for preparing water samples by the equilibration technique for analysis of $\delta^{18}\text{O}$ on a ThermoFinnigan Delta Plus XP using a Gas Bench II peripheral unit equipped with a GC-Pal autosampler.
- II. Equipment
 - A. Exetainer tubes with caps
 - B. 0.3% CO_2 in Helium
 - C. 0.5mL Pipette
 - D. Pipette tips
 - E. Internally calibrated water standards and/or VSMOW, GISP and SLAP
 - F. Sample/flush needle from the Gas Bench
 - G. Gas Bench II
 - H. Delta Plus XP
 - I. Isodat v1.5 Software (Service Pack v1.8)
 - J. ThermoFinnigan Delta Plus XL
 - K. Timer
- III. Procedure
 - A. Label the exetainers with the sample ID's and prepare exetainers for the standards at the beginning, middle and end of the run. Also prepare exetainers for one of the standards to be analyzed every eight samples.
 - B. Pipette out 0.5ml of each standard and sample into the appropriate exetainer and close tightly. The septa should have a pucker when the seal is good.
 - C. Attach a sample/flush needle using a Swagelok fitting by the stainless steel line to the regulator on the 0.3% CO_2 in He tank.
 - D. Put the needle into an empty exetainer, turn on the tank and measure the flow out of the capillary line. It should be set to 40mls/min.
 - E. After the flow rate is set, use the needle to flush all the standards and samples. Start with the first standard and push the needle as far as it will go into the exetainer through the septa. Allow it to flush for 1 minute and move it to the next vial by holding onto the metal knurled-knob to avoid breaking the capillary line. To ensure consistency a timer is used here.
 - F. When all the samples and standards are flushed, push the needle into an empty exetainer for safety and turn off the 0.3% CO_2 in He tank.
 - G. The samples are then left to equilibrate at 25°C for 48 hours.
 - H. The samples and standards are then analyzed using a run that has three standard gas injections followed by seven sample gas measurements.
- IV. References
 - A. Nelson, Stephen T. Rapid Commun. Mass Spectrom. 2000;14:1044-1046.

- B. Nelson, Stephen T. Rapid Commun. Mass Spectrom. 2000;14:93-297
- C. Coplen, Tyler B., Wildman, Joe D. and Chen, Julie Anal. Chem. 1991;63:910-912

3C: HYDROGEN ISOTOPE ANALYSIS

Equilibrating Water Samples for δD Analysis*

*Alternate method to be implemented starting 02/05:

Direct injection of water samples into TC/EA, pyrolysis decomposition to CO and H₂ using a glassy carbon reactor at 1400 °C. H₂ gas analyzed using ConFlo III interface to Delta Plus XL; SOP in progress.

- I. This SOP is to explain the procedure for preparing water samples by the equilibration technique for analysis of δD on a ThermoFinnigan Delta Plus XP using a Gas Bench II peripheral unit equipped with a GC-Pal autosampler.

- II. Equipment
 - A. Exetainer tubes with caps
 - B. 2.0% H₂ in Helium
 - C. 0.5mL Pipette
 - D. Pipette tips
 - E. Internally calibrated water standards and/or VSMOW, GISP and SLAP
 - F. Sample/flush needle from the Gas Bench
 - G. Gas Bench II
 - H. Delta Plus XP
 - I. Isodat v1.5 Software (Service Pack v1.8)
 - J. ThermoFinnigan Delta Plus XP
 - K. Timer
 - L. Platinum catalyst rods
 - M. Drying oven
 - N. Forceps

- III. Procedure
 - A. Label the exetainers with the sample ID's and prepare exetainers for the standards at the beginning, middle and end of the run. Also prepare exetainers for one of the standards to be analyzed every eight samples.
 - B. Pipette out 0.5ml of each standard and sample into the appropriate exetainer and close.
 - C. The platinum rods are stored in a 60 degrees C oven in between runs in cell wells to keep them apart. Remove the rods from the oven and let them sit for 5 minutes before they are needed.
 - D. Using forceps drop one rod into each vial and close tightly. The septa should be puckered when the seal is good.
 - E. Attach a sample/flush needle using a Swagelok fitting by the stainless steel line to the regulator on the 2.0% H₂ in He tank.
 - F. Put the needle into an empty exetainer, turn on the tank and measure the flow out of the capillary line. It should be set to 90mls/min.
 - G. After the flow rate is set, use the needle to flush all the standards and samples. Start with the first standard and push the needle as far as it will go into the

exetainer through the septa. Allow it to flush for 3 minute and move it to the next vial by holding onto the metal knurled-knob to avoid breaking the capillary line. To ensure consistency between samples a timer is used here.

- H. When all the samples and standards are flushed, push the needle into an empty exetainer for safety and turn off the 2.0% H₂ in He tank.
- I. The samples are then left to equilibrate in the heated block on the Gas Bench for 16 hours at 22 degrees C. Since the samples are going to equilibrate in the Gas Bench II, you will need to create the sequence in ISODAT before loading them so you don't have to open the top of the Gas Bench II after loading the samples.
- J. The samples and standards are then analyzed using a run that has three standard gas injections followed by seven sample gas measurements.

IV. References

- A. Nelson, Stephen T. Rapid Commun. Mass Spectrom. 2000;14:1044-1046.
- B. Nelson, Stephen T. Rapid Commun. Mass Spectrom. 2000;14:93-297
- C. Coplen, Tyler B., Wildman, Joe D. and Chen, Julie Anal. Chem. 1991;63:910-912

3D: TRITIUM-HELIUM ISOTOPE ANALYSIS

Mass spectrometric measurement of helium isotopes and tritium in water samples

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Palisades, NY 10964

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Introduction

Tritium, together and its radioactive decay product ^3He are among the most frequently measured transient tracers applied to studies of the ocean. Tritium measurements of oceanographic water samples started in the 1950s (e.g., Begemann and Libby, 1957), whereas the application of ^3He was added in the late 1960s as part of the preparation for the GEOSECS program (e.g., Clarke et al., 1969). Most of the early oceanographic tritium measurements were based on radiometric methods. In order to achieve the sensitivity and precision needed for oceanographic studies, the radiometric measurement has to be preceded by electrolytic and/or thermodiffusive enrichment by factors of the order of 100. Overall precisions of radiometric tritium measurements using enrichment are in the range of ≈ 2.5 to ≈ 5 % with detection limits of 0.05 to 0.08 TU (e.g., Weiss et al., 1976; TM stlund and Grall, 1987; one TU means a tritium to hydrogen ratio of 10^{-18}). These precisions and detection limits provided sufficient resolution of the oceanographic tritium distributions observed during the 1960s and 1970s. However, tritium decay and mixing led to decreased tritium concentrations in the ocean, especially in the southern hemisphere, where surface concentrations hardly exceeded one TU during the peak time (compared to about 17 TU in the northern hemisphere) preventing the use of radiometric tritium measurements to delineate the oceanic tritium distributions at high resolution.

This problem was overcome by the development of mass spectrometric methods for measurement of tritium by the ^3He ingrowth method (e.g., Clarke et al., 1976; Jenkins et al., 1979; Lynch and Kay, 1981; Bayer et al., 1989; Jenkins et al., 1991). By using the ^3He ingrowth method for measurement of tritium, precision could be improved to ≈ 1 to ≈ 2 % and the detection limit to about 0.005 TU. Whereas early mass spectrometric tritium and helium isotope measurements were performed on dedicated mass spectrometers typically developed in specialized physics departments (e.g., Clarke et al., 1976), the more recently installed systems mainly use commercially available mass spectrometers in combination with specially designed sample purification and inlet systems (e.g., Bayer et al., 1989). This contribution describes two state of the art systems for measurement of helium isotopes and tritium by the ^3He ingrowth method installed and operated at the Lamont-Doherty Earth Observatory (L-DEO). The description includes the design and setup of the systems, as well as their performance during routine measurements. The principal features of the mass spectrometric systems operated in the L-DEO laboratory, as well as the measurement procedures, are similar to those applied in most of the other tritium/helium laboratories actively involved in oceanic tracer studies. In the case of the L-DEO laboratory, tritium and helium isotopes are measured on separate, dedicated mass spectrometric systems to increase throughput and efficiency. However, each system can be used for both helium isotope and tritium measurements.

General system design

Measurement of helium isotopes, as well as tritium by the ^3He ingrowth method, in water samples require several steps that determine the design of the mass spectrometric systems used for such measurements.

(1) Water samples for measurement of helium isotopes, neon and tritium are drawn at sea from Niskin bottles. They can either be stored in copper tubes for shore based gas extraction or be processed at sea. For high precision tritium measurements water samples are collected in 1 liter glass bottles. Detailed descriptions of laboratory-based gas extraction systems can be found in Bayer et al. (1989) or Jenkins et al. (1991). Additionally, we briefly describe the design of the L-DEO laboratory-based gas extraction systems in chapter 3 of this contribution.

(2) The gases extracted from the water samples using either seagiong or laboratory-based extraction systems are stored in flame-sealed glass ampoules to minimize addition of helium to the sample during the storage time. ^3He -free water for tritium measurement is stored in flame-sealed glass bulbs (volume: 200 cm³ or 1 l). Although there is some permeation of helium from glass into the water samples during storage, low-permeability glass is the best material for this purpose because stainless steel containers would be expensive and need valves which always have a certain leak rate. The use of glass bulbs and ampoules requires a design of the gas extraction and sample inlet systems that minimizes the use of O-ring fittings for metal-glass transitions. To further decrease the helium addition from the glass, the samples are stored at -30°C during the ^3He ingrowth period.

(3) Although commercially available mass spectrometers can be used, attention has to be paid to certain design features, especially with respect to the ion source and the detection of ^3He . The ion source has to be stable and at the same time yield a high ion current. The best ^3He detection mode seems to be the utilization of a channeltron connected to a fast ion counting system.

(4) Fully automated measurement is an absolute necessity for high sample throughput, as well as high precision of the measurements. Therefore, the hardware has to be designed in a way that allows effective computer control of all essential components of the system (mass spectrometer plus inlet system). The system control software is too complex for inclusion into this contribution. It is described in a separate contribution by Zaucker et al. (1996).

Gas extraction

Helium isotope samples

Before the mass spectrometric measurement of helium isotopes of water samples, the dissolved gases have to be extracted quantitatively from the water sample and stored in flame sealed glass ampoules. For this purpose, a vacuum extraction system with the capacity for simultaneous handling eight samples is used (for schematic view, see Fig. 1).

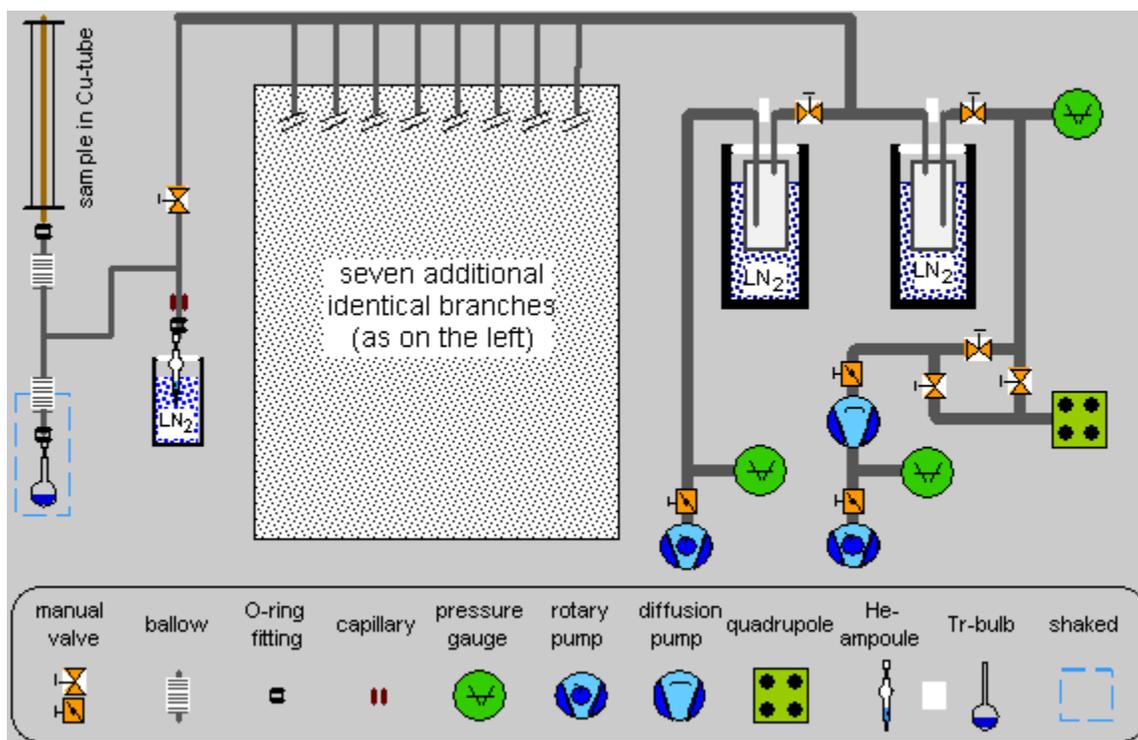


Fig. 1: Schematic diagram of the helium extraction system

The portion of the extraction system operated in a static vacuum mode during gas extraction is an all-metal design except for three Viton® O-rings used to attach the sample container (copper tube), the glass ampoule (filled with 1 g of activated charcoal), and a 200 ml glass bulb to the system. The rough vacuum is produced by a rotary pump protected from the water vapour in the system by a liquid nitrogen cooled all-metal water trap. To pump the system down to about 10^{-6} mbar, a combination of a rotary and a diffusion pump is used. Additionally, the vacuum system is equipped with a quadrupole mass spectrometer (QPM) for leak detection.

After establishing high vacuum, each branch of the extraction system is separated from the vacuum pumps by a stainless steel valve. In a static vacuum mode, the pinch-off clamps of the copper tubes are opened and the water is released into the glass bulb. During expansion of the water into the bulb, most of the dissolved gases are transferred to the gas phase. To enhance the removal of the remaining gases from the water phase, the glass bulbs are shaken mechanically to produce turbulence in the molecular boundary layer of the water contained in the glass bulbs. The extracted gases are transported by water vapour into the glass ampoule which at this time is cooled by liquid nitrogen, thus maintaining a strong pressure gradient and a related water vapour flow. The water vapour flow is controlled by a capillary mounted above the O-ring connection used to attach the glass ampoule to the system. In the glass ampoule, the water vapour is frozen out and all gases except for neon and helium are adsorbed on the

activated charcoal. Helium and neon are trapped dynamically by the high velocity of water vapour through a 'glass capillary' used for flame-sealing the ampoule. Diffusion of helium against the strong water vapour advection in this glass capillary is negligible. After about 30 minutes, the gas transfer is complete and the glass ampoule is flame-sealed. A leak check is performed to ensure the quality of the samples by checking the pressure increase in the system after opening the vacuum valve connecting the specific sample branches to the main vacuum system. The preparation of the system and the extraction of eight samples requires about 4 hours.

The extraction efficiency of this system is about 99.9 % or higher (Bayer et al., 1989). Diffusion of helium through 3 O-rings over a period of about 30 minutes adds a blank of roughly 4×10^{-9} cm³ STP ⁴He or about 0.2 % of the He amount of a sample. The water in the glass bulb can be flame-sealed for ³He ingrowth from tritium decay. Before flame-sealing of the bulbs, the vacuum valve connecting the individual branches to the main pumping line is opened for a period of about 3 minutes to ensure complete removal of ³He.

Tritium samples

Water samples for measurement of tritium are either flame-sealed after the helium extraction (small-volume samples, used for tritium concentrations between 0.2 to 10 TU; see above) or prepared for ³He ingrowth using a separate system (large volume samples, used for tritium concentrations below 0.2 TU: see Fig. 2). This system is capable of handling samples with a volume of about 500 cm³ compared to the 40 cm³ used for small volume samples. It consists of 4 identical branches and a simple vacuum system (rotary pump plus all-metal water trap). The samples (typically one liter glass bottles) are attached to the extraction system after a pressure of about 10^{-3} mbar has been achieved. About 400 to 500 grams of water are transferred through a capillary into one liter bulbs fabricated from special glass with low He permeability (GW or Corning; e.g., Suckow et al., 1990). After completion of the water transfer, the water samples are shaken to enhance the gas transfer from the water into the gas phase. All extracted gases are pumped away by the rotary pump. Loss of water is reduced by a capillary mounted into the vacuum line. The partial pressure of helium in the glass bulbs is lower than that in the vacuum lines because water vapor constantly flushes the helium extracted from the water out of the bulbs through a glass capillary used for flame-sealing of the bulbs after the extraction is completed. Typically, an extraction efficiency of at least 99.95 % is achieved for small bulbs (the gas extraction efficiency for large bulbs is approximately 99.995 %). Diffusion of helium through the O-ring connecting the glass bulb to the vacuum system is negligible.

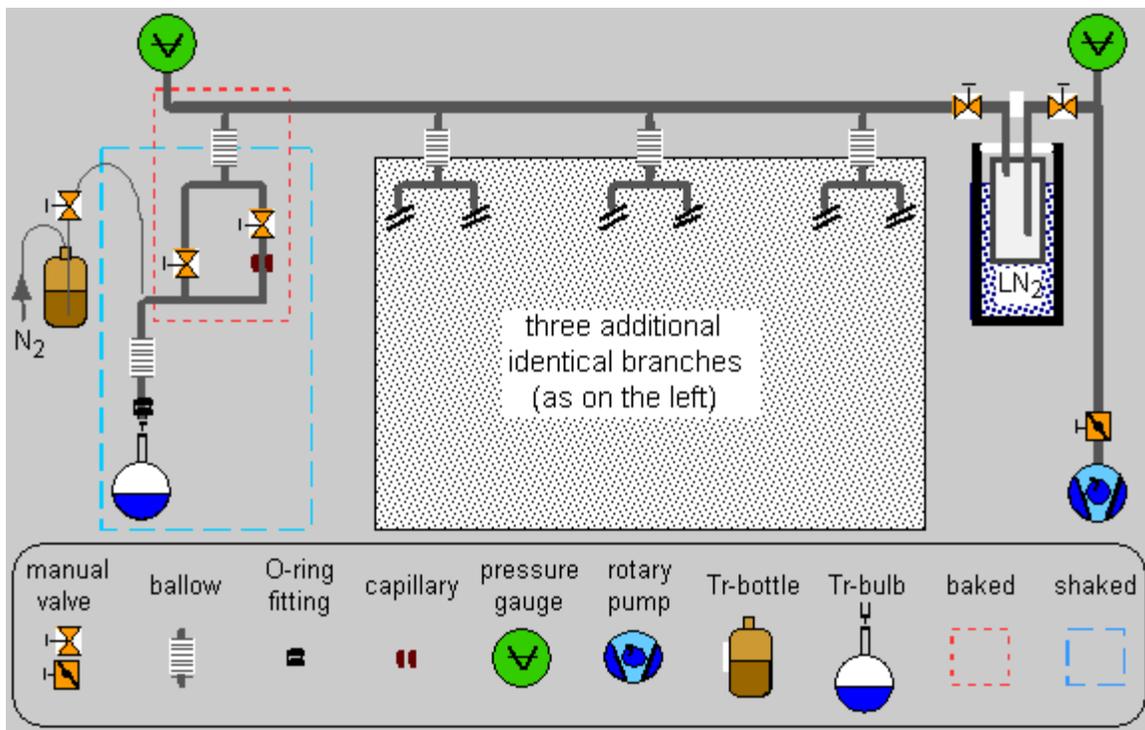


Fig. 2: Schematic diagram of the tritium extraction system.

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Inlet System

General Design

The "inlet" or sample preparation system is designed to produce pure helium and neon fractions from the gas mixtures extracted from the water samples and stored in the glass ampoules. It is optimized for fully automated operation and high sample throughput. It consists of three main parts (Fig. 3):

a manifold of eight vacuum and cracking valves for attachment of the glass ampoules to a high-vacuum system and cracking of the glass seals to admit the gas samples into the purification part of the inlet system,

an air standard preparation system, and

three traps cryogenically cooled by a helium compressor for separation of helium and neon from water vapour and permanent gases.

The inlet system also contains a QPMS for measurement of neon.

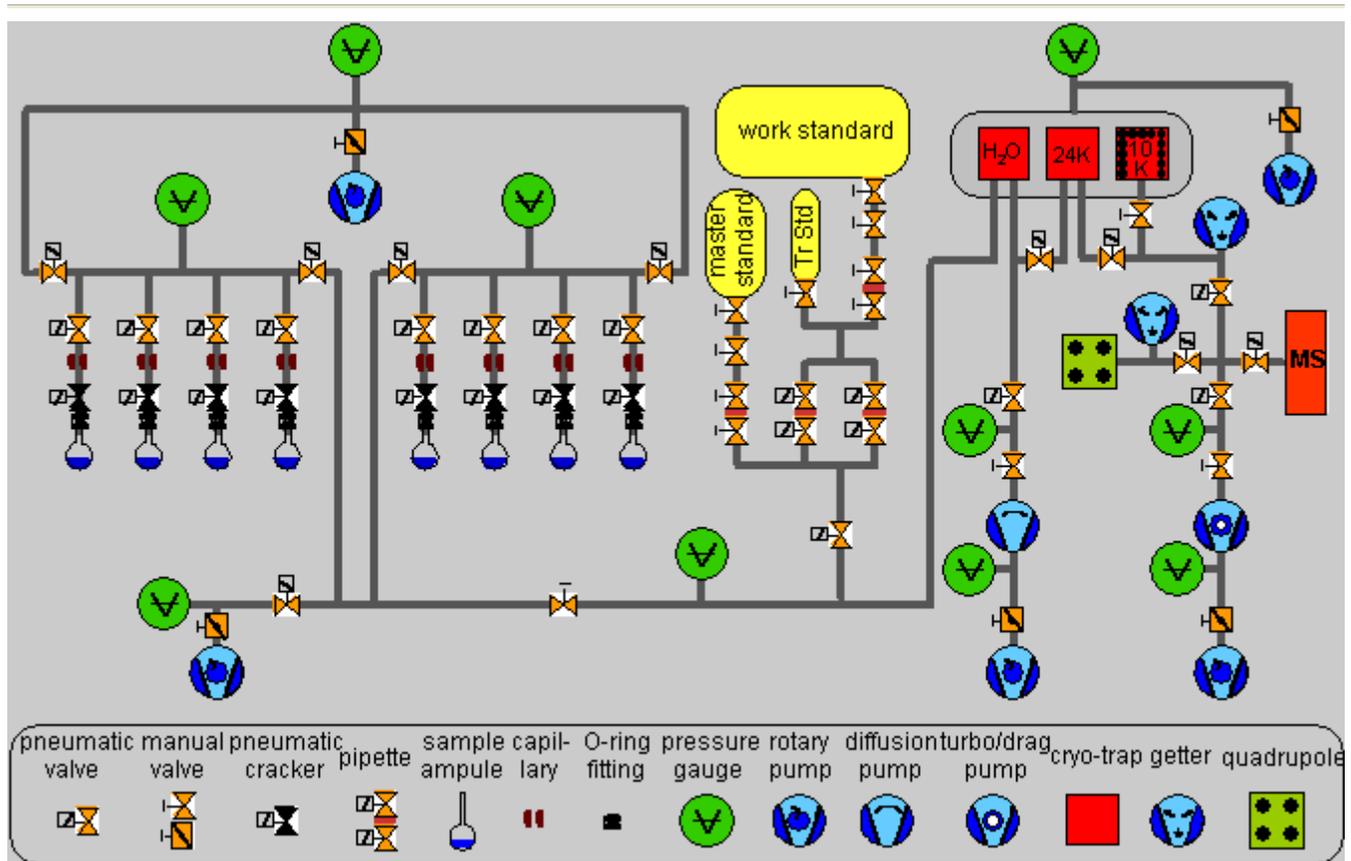


Fig. 3: Schematic diagram of the sample preparation system.

Vacuum system

The vacuum system consists of electropolished stainless steel tubing (1/4" or 3/8" outer diameter) with all-metal fittings (mostly VCR). The 3/8" tubing is used in the sample inlet and air standardization parts for more efficient pumping, whereas 1/4" tubing is used in the cryogenic cold trap part of the system to minimize the volume (the ratio of the trap volume to

the mass spectrometer volume determines the fraction of the helium that is admitted to the mass spectrometer).

We used all-metal valves and vacuum fittings wherever possible to minimize the helium background in the system. The only parts that contain material other than stainless steel are the O-ring fittings in the system that are used to attach the glass ampoules to the all-metal inlet system (Cajon Ultra Torr). The all-metal fittings are well suited for relatively high bakeout temperatures of the vacuum lines and keep the helium background levels low. The Pirani and Penning pressure gauges are also all-metal designs and are attached to the vacuum lines through CF flanges (16 and 40 mm for the Pirani and Penning gauges, respectively). The valves are equipped with copper stamps (Nupro SS-4BG-V51-CU3C). Most of the valves are pneumatically driven, allowing for fast manual or computer-controlled valve operation. We use normally closed valves to secure the system in case of power or compressed air loss.

Rough vacuum ($\approx 10^{-3}$ mbar) is produced by rotary pumps (Leybold, Trivac D4B). Oil filters (Edwards, activated alumina) prevent back-flow of oil vapour from the rotary pumps in case of a pump failure. A diffusion pump (Balzers, DIF 063) backed up by a rotary pump achieves a finer vacuum ($\approx 10^{-5}$ mbar). The diffusion pump is protected from the water vapour by a water trap (see below). The ultra-high vacuum section, which consists of the 10 K charcoal trap and the QPMS (Balzers, Prisma or QMG 112 with Faraday cup), is pumped by a turbomolecular/drag pump (Balzers, TMU 065) or by a combination of a diffusion pump (Balzers, DIF 063) and a turbomolecular pump (Balzers, TPU 60). Either combination is backed by a rotary pump.

The pressures of the five rotary pumps are monitored by Pirani pressure gauges (Balzers, TPR 250). In the all-metal section, three all-metal Piranis (Balzers, TPR 260) are used. The vacuum of the diffusion and turbo/drag pumps is controlled by two Penning pressure gauges (Balzers, IKR 260). The pressure readings of the ten gauges are displayed by five dual controllers (Balzers, TPG 252). They are also monitored by the system control computer.

Sample Inlet

To open the flame-sealed glass ampoules and bulbs for gas transfer into the inlet system, we use modified Nupro SS-8BK-TW-10 valves (normally open, pneumatically driven). The modification of the valves includes drilling open the inlet port of the valve to accommodate the glass neck of the ampoules next to the modified stamps (stamps have been replaced by stainless-steel screws). Before cracking the glass ampoules or bulbs by closing the cracking valves, the inlet system is evacuated in two steps by a rotary and a diffusion pump to decrease the partial pressure of helium to a negligible level.

During the extraction procedure, water vapour is used as carrier gas to transport the gases released from the water samples into the glass ampoules. This water is utilized to flush the gases contained in the glass ampoules into the inlet system. More than 99 % of the He is in the gas phase of the head space of the ampoules or bulbs. A capillary mounted just above the cracking valves (Fig. 4; inner diameter: 0.069 cm, length: \approx 2.5 cm) prevents back-diffusion of helium into the glass container and reduces the amount of water transferred into the inlet system. The transfer times through the capillary are set to 1 minute for helium isotope samples, 2.5 minutes for 40 cm³ tritium samples, and 5 minutes for 400 cm³ tritium samples, respectively. These transfer times are checked by repeat measurements to ensure complete transfer of the sample gas from the glass ampoules or bulbs into the inlet system.

Air standards

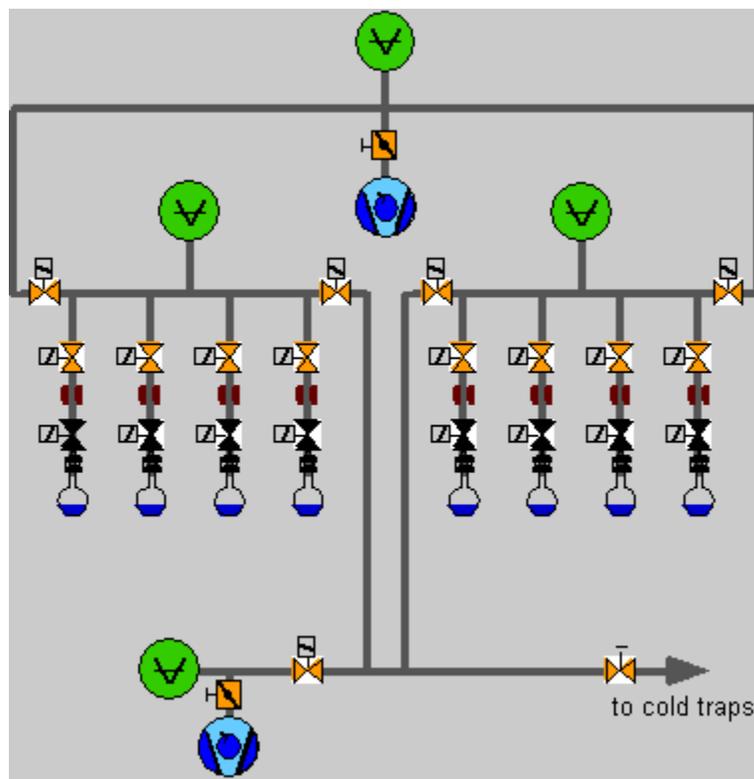


Fig. 4: Schematic diagram of inlet part of sample preparation system (for symbol legend, see Fig. 3).

The helium isotope ratio measurements, as well as the absolute ^3He , ^4He , and neon measurements are standardized against air. The He content of air (5.24 ppm; Glueckauf, 1946), as well as its $^3\text{He}/^4\text{He}$ ratio (1.384×10^{-6} ; Clarke et al., 1976) and He/Ne ratio (0.288, Ozima et al., 1983) are well known. Therefore, atmospheric air is well suited as a standard for helium isotope measurements. As working standard, we use a stainless steel container with known volume (13 l) filled with atmospheric air (Fig. 5). The container is filled sufficiently far away from laboratory buildings to avoid contamination with tank He. For precise determination of the amount of helium contained in the air standard, atmospheric pressure, temperature, and humidity have to be measured accurately. Determination of the helium content in the standard container with a precision of $\approx 1\%$ requires measurement precisions of ≈ 1 mbar, ≈ 0.3 K and $\approx 2\%$ for atmospheric pressure, temperature, and relative humidity, respectively.

Besides the working standard, we use a master standard (3.9 l) to calibrate the individual working standards which are changed after a depletion of about 10 percent (Fig. 5). For tritium measurement by the ^3He ingrowth method, very small amounts of helium are used for standardization. Therefore, the air standards are diluted in an expansion volume (volume of about 1 l) by a factor of about 160 (Fig. 5)

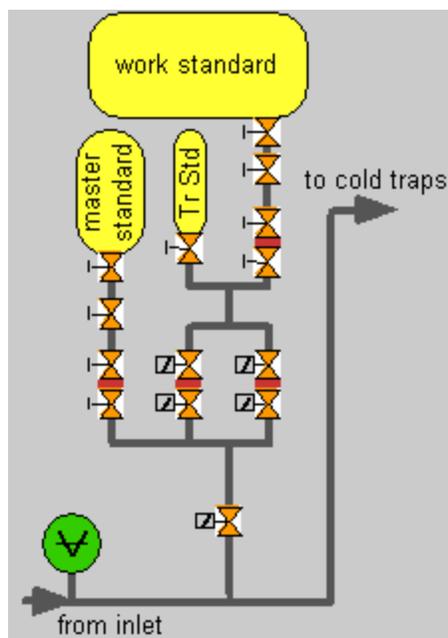


Fig. 5: Schematic diagram of the standardization part of the sample preparation system (for symbol legend, see Fig. 3).

The individual air standards are taken from the standard containers by pipettes, which consist of calibrated volumes mounted between two Nupro valves. The pneumatically operated (automatic) pipettes (custom-made by D. Doerflinger, Heidelberg, Germany) are equipped with counters mounted into the pneumatic air lines to account for the depletion of the standard. The depletion has to be known for correction of the absolute amount of helium contained in the volume of one air standard taken by a pipette. The air standards are treated in the same way as the extracted gases from water samples.

Cryogenic cold traps

Three different traps (custom-made by Leybold and Janis Research Co. for the helium isotope and tritium mass spectrometers, respectively) are cooled by two cryogenic pumps (Leybold, RGD 510, with compressor, Leybold, RW4200, for cool down times of traps see Fig. 6). They are used to separate helium and neon from all other gases contained in a water sample or air standard (Fig. 7). All traps are housed in a protection vacuum maintained by a rotary pump for proper thermal insulation and to avoid water vapour condensation on the cold surfaces. Their temperatures are measured by silicon diodes and set by several controllers (2 Leybold LTC 60 in the helium isotope system, and 4 Lakeshore, Temperature Controller 330 in the tritium system, respectively). The temperatures are stable within about ± 0.1 K or better.

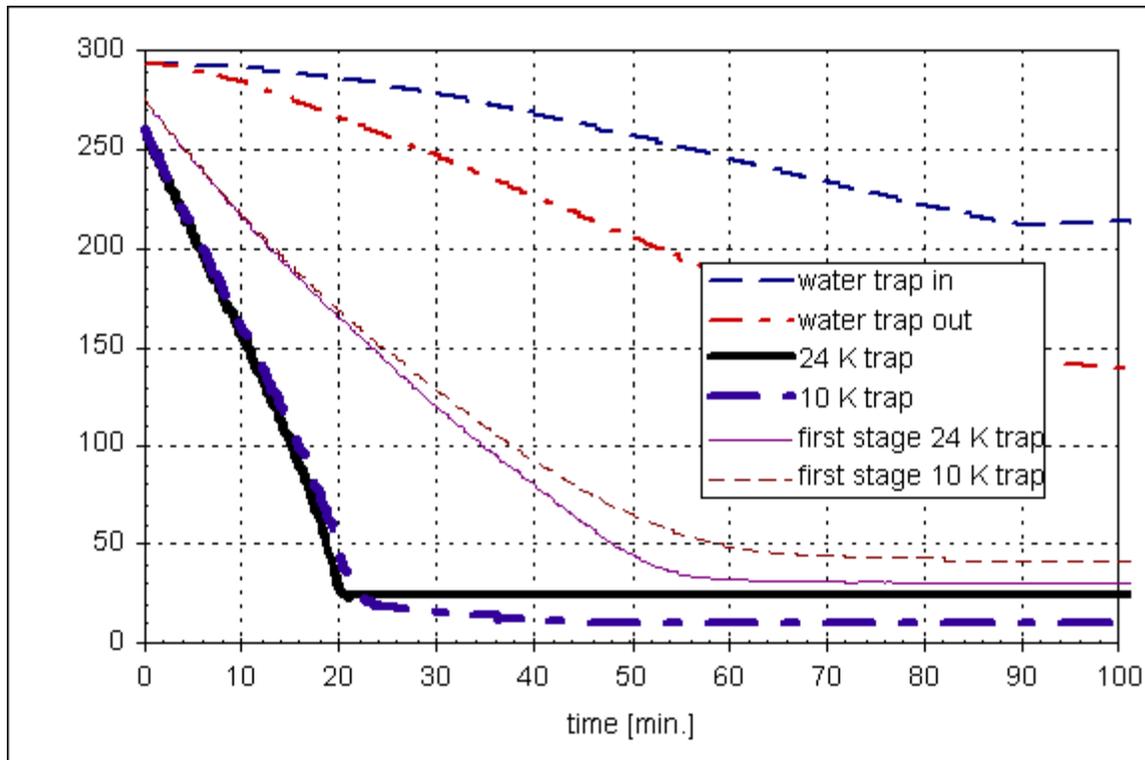


Fig. 6: Cool down times for the cryogenic cold traps.

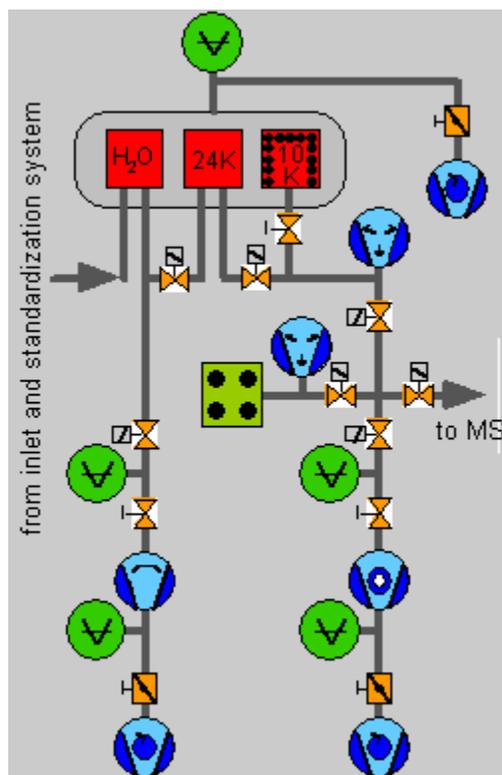


Fig. 7: Schematic diagram of the cryogenic cold trap system (for symbol legend, see Fig. 3)

The first trap (stainless steel cylinder; 2.5 cm diameter, 10 cm length, 40 cm³ volume) is connected by copper wires to the first stage of one of the cryogenic pumps. Two silicon diodes and heaters are stabilizing the temperatures at 253 K at the trap inlet and 123 K at the trap outlet to distribute the freeze-out of the water over the entire length of the trap. An additional

temperature controller keeps the inlet line before the water trap above the freezing point of water to avoid any freezing and clogging.

The second trap (stainless steel cylinder of 2.3 cm diameter, 2.0 cm length, about 4 cm³ volume) mounted directly onto the second stage of one cryogenic pump with a stabilized temperature of 24 K liquefies all gases except helium and neon. About 5 minutes are required for removal of the water vapour and condensation of the permanent gases.

The inner surface of the final cold trap (cylinder of 2.3 cm diameter, 2.0 cm length, about 4 cm³ volume) are covered with charcoal (DESOREX, F11) by using a cold-temperature epoxy glue for good thermal contact. The adsorption coefficient of gases on the activated charcoal is a function of the partial pressure in the cold trap, the volume of the trap, the amount and type of activated charcoal, and the temperature of the trap. The adsorption and desorption of helium (and neon) onto and from the charcoal can be measured directly by using the sector field mass spectrometer (SFMS). The same holds true for neon if the QPMS is used. Quantitative (> 99.5 percent) adsorption of helium on the charcoal requires temperatures below 14 K. Quantitative desorption is achieved at temperatures of \approx 45 K (Fig. 8; tritium mass spectrometer \approx 38 K). The small ³He to ⁴He isotope fractionation effect (Fig. 8) is negligible at temperatures < 14 K and > 45 K.

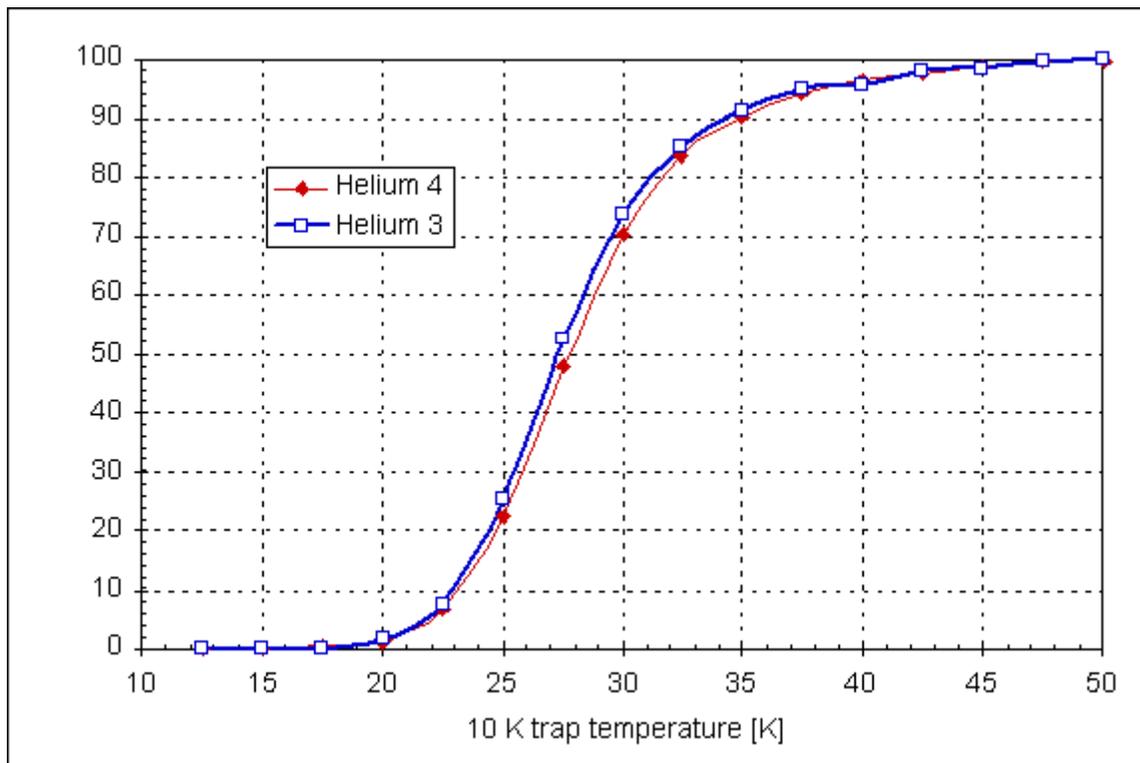


Fig. 8: ³He and ⁴He adsorption isotherms (measured on the helium isotope SFMS).

We determined the absorption of helium and neon onto the charcoal as a function of time using the QPMS. For this purpose, both helium and neon were adsorbed quantitatively onto the charcoal at 10 K. This process took about 2.2 minutes for helium. The following desorption of helium to >99 percent of the original signal (at 45 K) required about 1.5 minutes (Fig. 9). The equivalent numbers for neon are about 4.5 and 7 minutes (120 K), respectively.

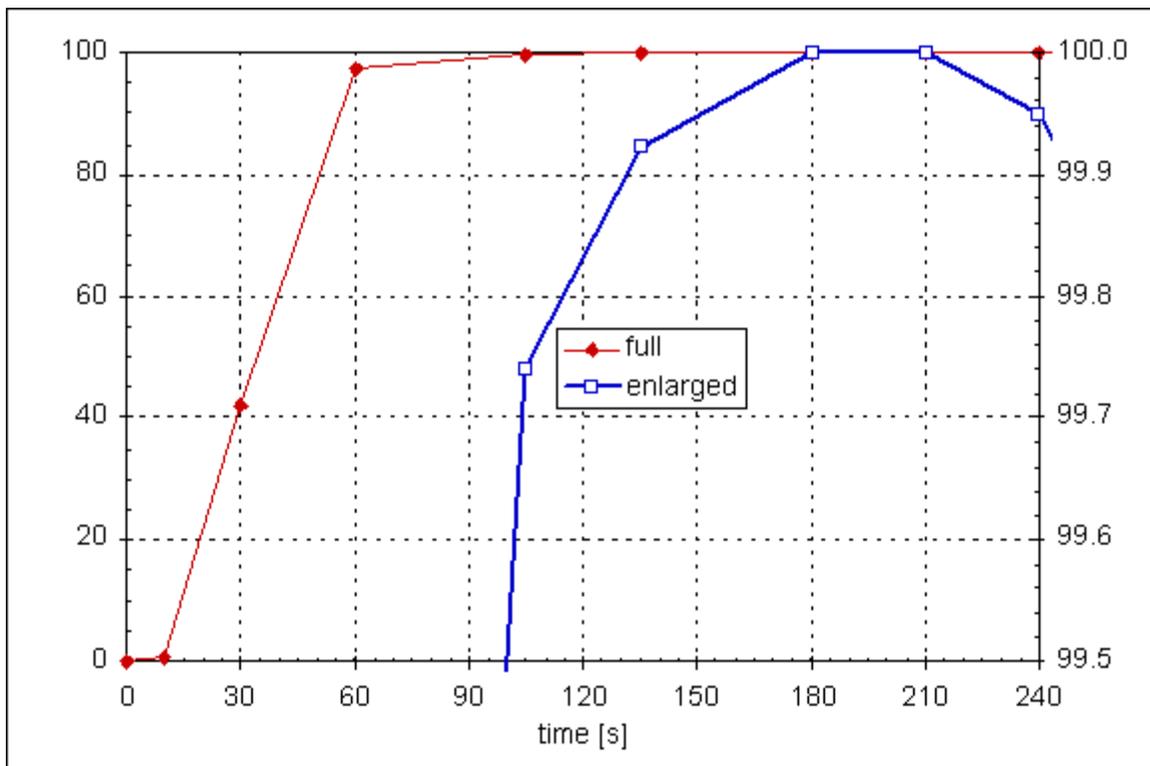


Fig. 9: Desorption time of 4He from the charcoal for a temperature of 45 K (measured on the Tritium mass spectrometer).

There is discrimination of helium by neon in the QPMS (Balzers Prisma). At the helium inlet temperature of 38 K (tritium mass spectrometer), less than 0.5 % of the neon is in the gas phase (Fig. 10a). With the full neon signal in the QPMS (120 K), the helium signal is reduced by about 50 % (Fig. 10a). In the SFMS, the discrimination for a 0.2 cc air standard at 120 K is about 20 % (Fig. 10b).

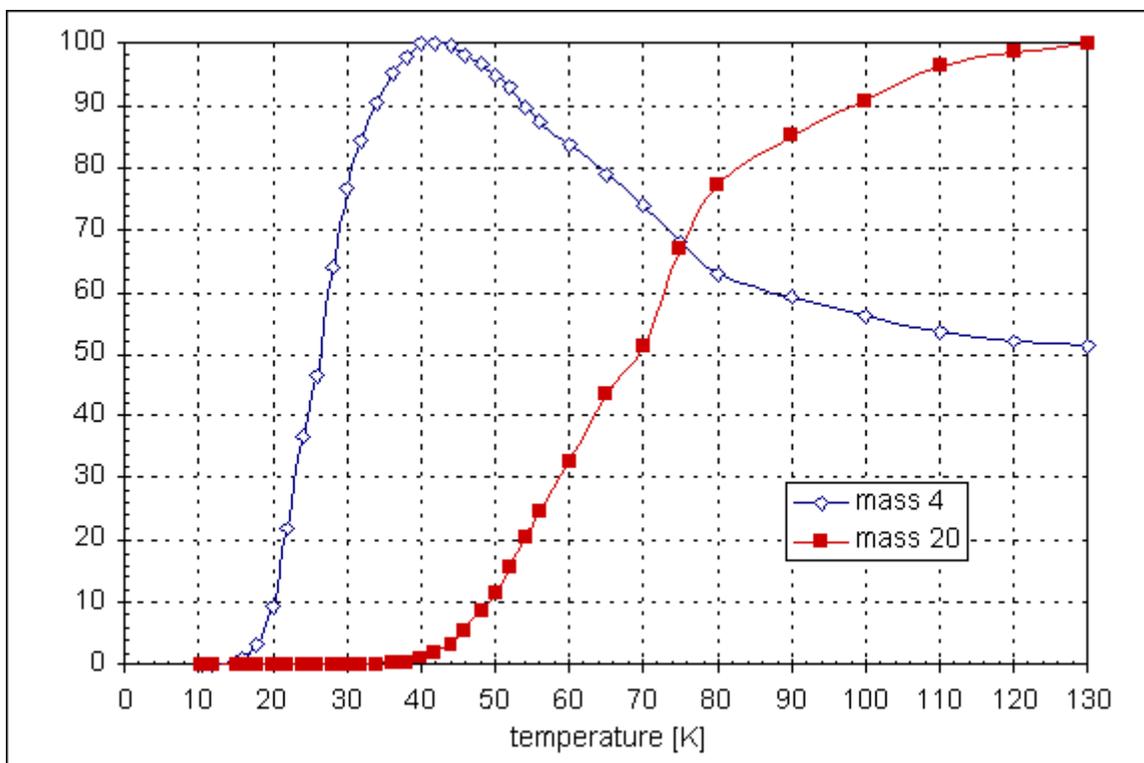


Fig. 10a: 4He discrimination by neon in the Prisma quadrupole mass spectrometer.

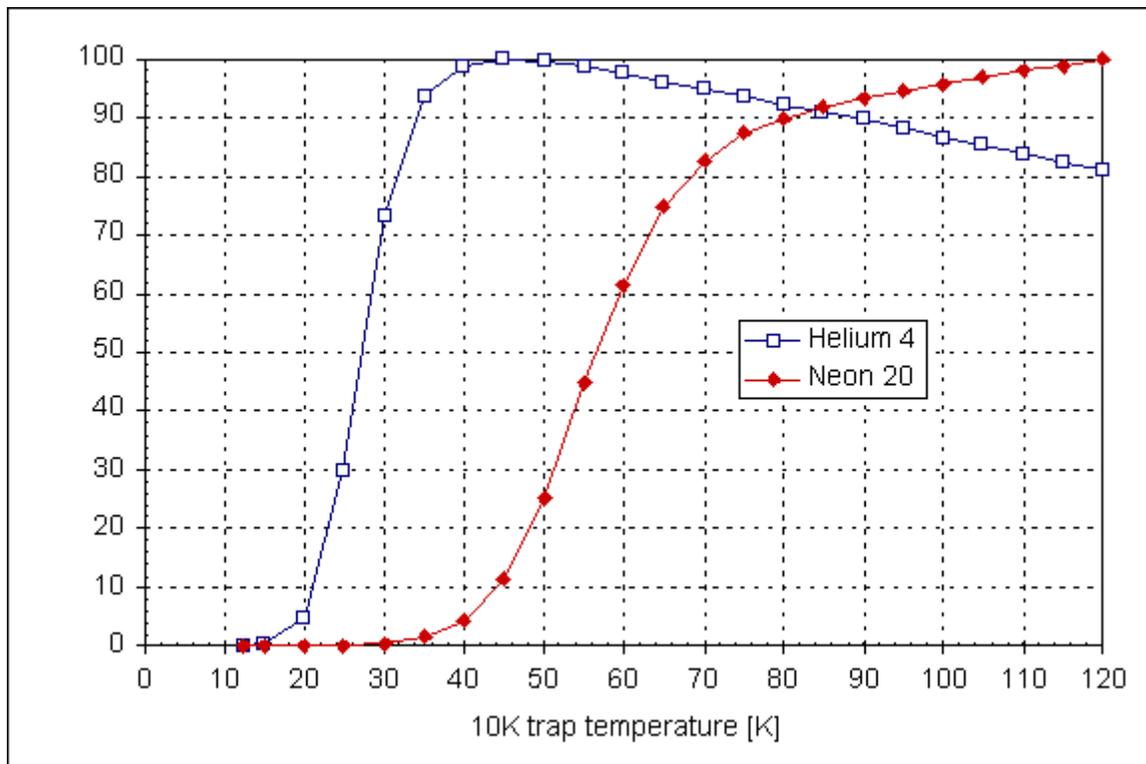


Fig. 10b: 4He discrimination by neon in the SFMS (helium isotope MS).

Mass spectrometer

General Design

The sector field mass spectrometers (SFMS) used for helium isotope and tritium measurement are commercial instruments (Fig. 11, VG 5400; Micromass; Manchester, UK). They are designed for measurement of all noble gases (He, Ne, Ar, Kr, Xe) and their isotopes. For our purpose, they are dedicated to helium isotope measurements. They are operated in a static mode, i.e., all pumps with the exception of two SAES getters are disconnected from the mass spectrometers during sample measurement. The SAES getters keep the background pressure low, especially that arising from hydrogen and HD without pumping the noble gases.

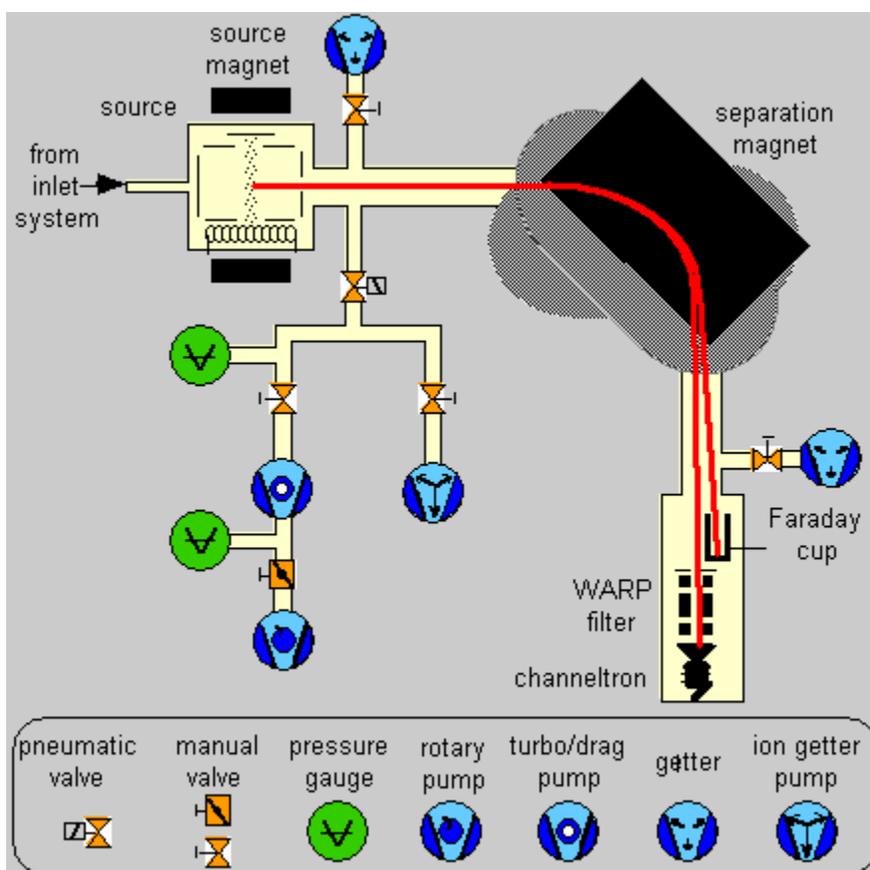


Fig. 11: Schematic diagram of the VG 5400 noble gas mass spectrometer

Vacuum system

During automated operation, the mass spectrometers are pumped between measurements of individual samples or standards by ion getter pumps (Varian, StarCell Vaclon Plus 40) attached to the flight tubes by pneumatically operated valves (VG, CR 38 TU, and VAT, Series 57, respectively). The advantages of ion getter pumps are (1) the absence of any oil (low hydrogen and HD levels), and (2) a closed system in case of a power failure. An additional pumping line consisting of a turbomolecular - drag pump (Balzers, TMU 065; tritium mass spectrometer) backed by a rotary pump (Edwards, E2M2) is used for initial pumping after venting the system. An oven can be mounted over all vacuum parts for bakeouts at temperatures of up to 350 °C. A Penning gauge (Balzers, IKR 260) is used to monitor the pressure in the turbomolecular - drag pumping line (usually this pressure is below the detection limit of 2×10^{-9} mbar).

Ion source

The VG 5400 uses a Nier-type electron impact ion source (Bright source). The electron emission is controlled by the trap current which regulates the filament current. To achieve the sensitivity required for high-precision helium isotope and tritium measurements, we have to use a relatively high trap current of 800 μA . The electrons emitted from the filament are forced onto circular trajectories by a magnetic field (source magnets) to increase the ionization probability of gas atoms in the source. The ions are extracted from the ionization cage and accelerated to 4.5 keV. The field of the separation magnet is controlled by a Hall probe through adjustment of the magnet current.

Ion detection

The ^4He ion beam is measured with a Faraday cup as the voltage produced over a 10^{10} Ohm resistance. A 0.4 cm^3 STP air standard produces a signal of about 2.5 V (measured by a 7-digit-voltmeter; Solartron Instruments, 7060 system), which is equivalent to 250 pA or 1.5×10^9 ^4He atoms per second.

A channeltron (Galileo, 4869 EIC) operated in the ion counting mode is used for measurement of the ^3He beam. The channeltrons produce a good plateau in the HV (Brandenburg, alpha III unit) versus count rate plot (Fig. 12). This plateau is typically located between 1.6 and 2.4 kV and its absolute position on the HV axis varies between individual channeltrons. The high voltage used for sample measurement has to be adjusted during the aging process of the channeltron (typically requiring increased high voltages). The ion beam produces a pulse in the channeltron (about 15 mV) which is amplified by about a factor of 10 in a preamplifier (Ortec, 9301), and another factor of 10 in the main amplifier (Phillips, 9650). The amplified signal is processed by using a discriminator (Phillips, 6930) and registered by a 100 MHz timer - counter unit (Ortec, 996). A 0.4 cm^3 air standard results in a ^3He count rate of about 2000 cps.

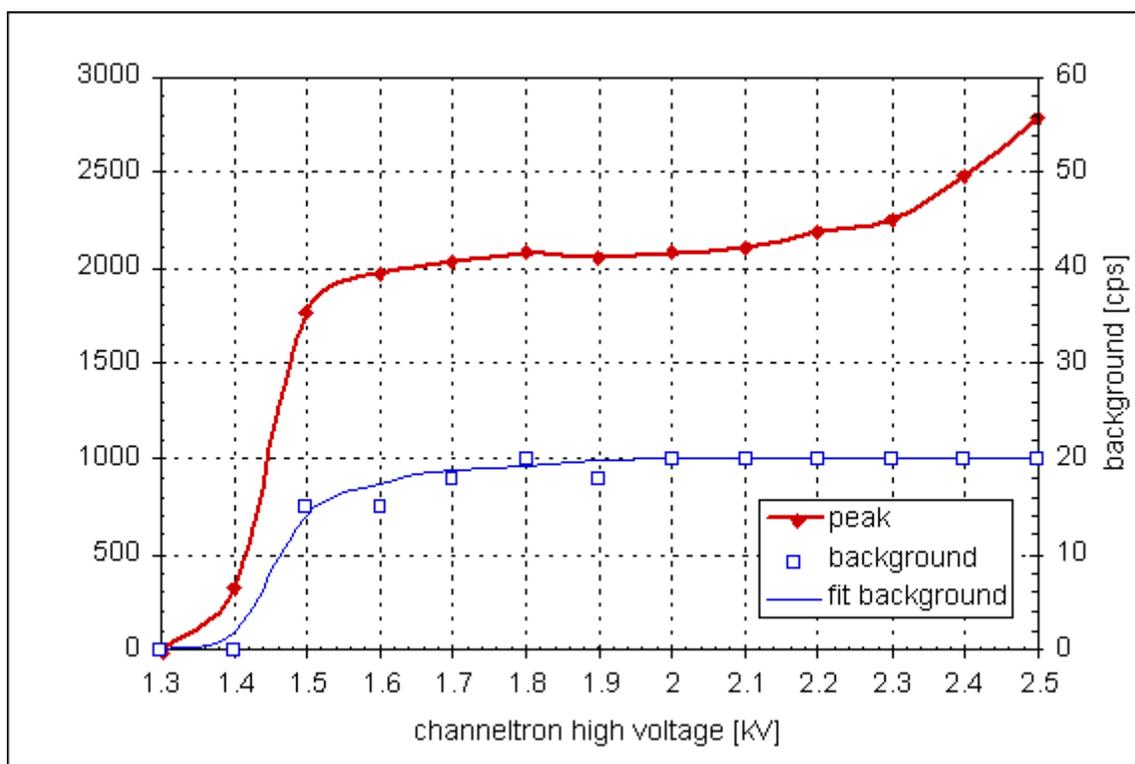


Fig. 12: Channeltron count rate versus high voltage. Note extended scale for background

count rate (right Y-axis).

Before reaching the channeltron the ^3He beam passes a velocity filter (WARP spell out the acronym filter from Micromass) to reduce the background by stopping scattered ions (tritium mass spectrometer only). This filter acts also as a protection for the channeltron. In case of high channeltron count rates, it blocks all incoming ions.

Tuning and peak shapes

The sensitivity of the mass spectrometers is mainly a function of the source parameters: repeller, electron energy, focus, beam center and source magnet position. The peak shape, on the other hand, is mainly determined by the position of the separation magnet. The position of the magnet can be adjusted in 3 dimensions. Additionally, there is an adjustable "pole shoe". The observed helium peak shapes (Figs. 13 to 16) are also a function of the ratio of the aperture to the peak width ratio, which determines the flatness of the peaks.

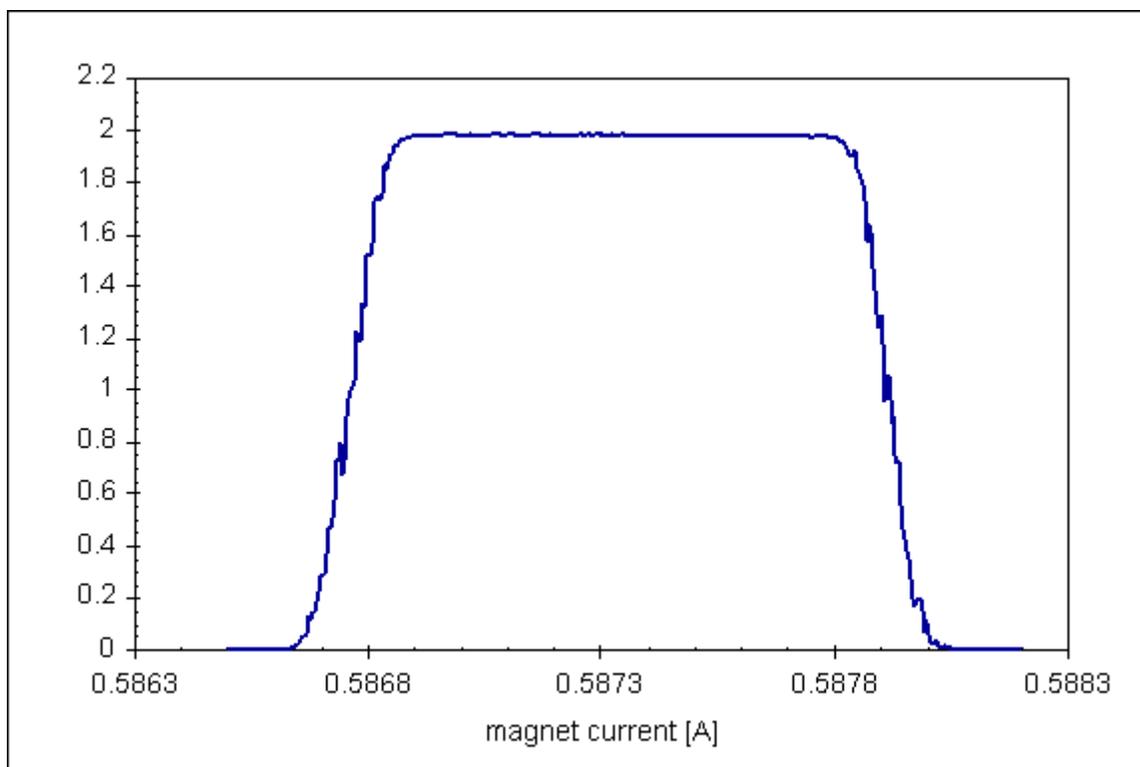


Fig. 13: ^4He peak measured on the helium isotope SFMS using a Faraday cup (0.4 cm³ air standard)

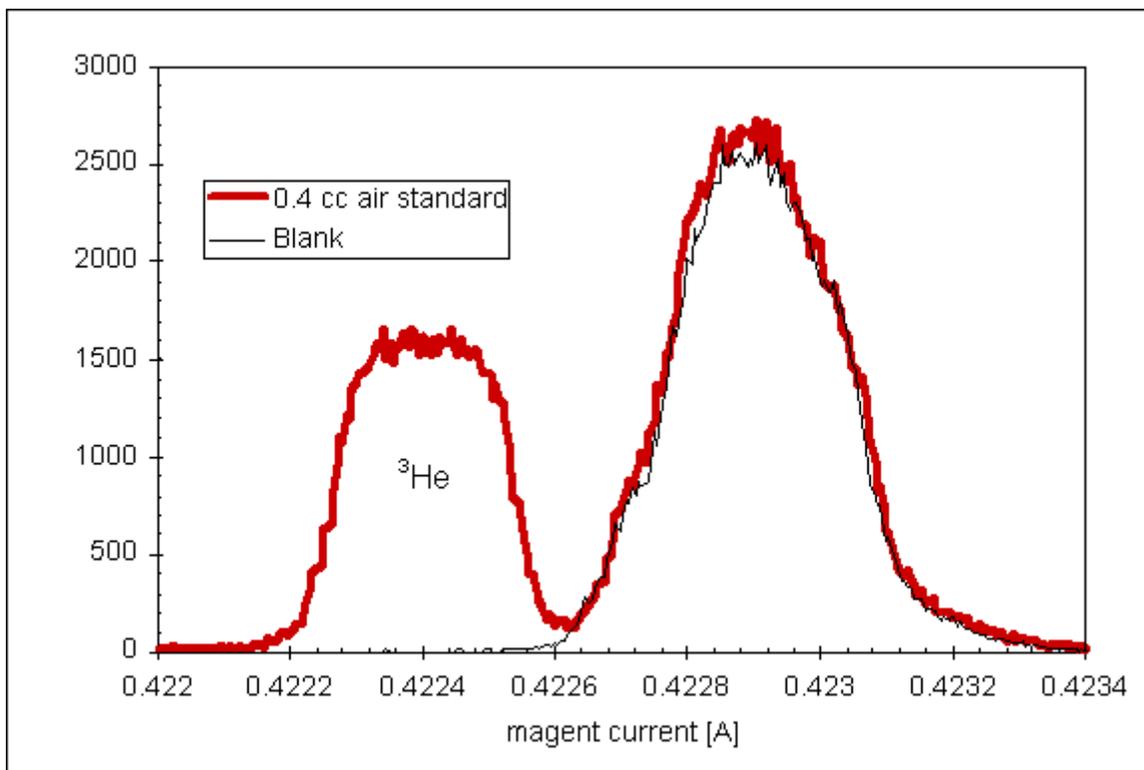


Fig. 14: ^3He and HD/H3 peaks measured with a channeltron shortly after a bakeout (0.4 cm³ air standard).

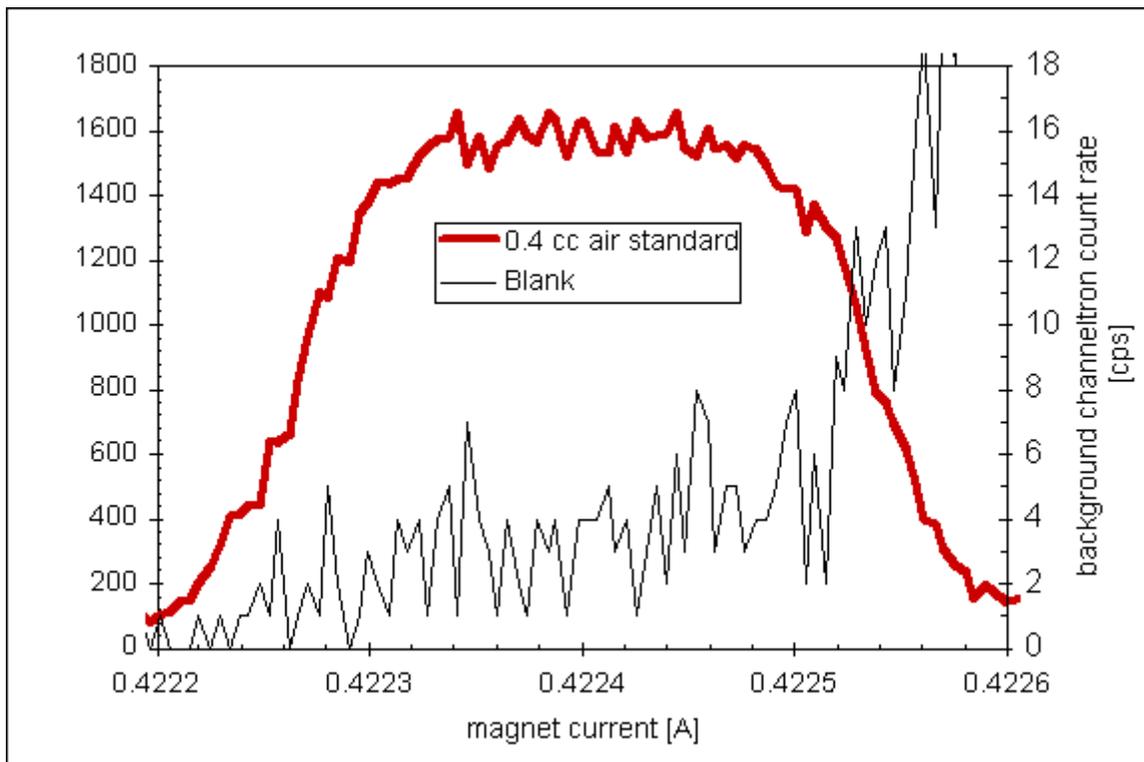


Fig. 15: ^3He peak measured with a channeltron (0.4 cm³ air standard). Same ^3He peak as in Fig. 4; scale for background count rate extended by a factor of 100.

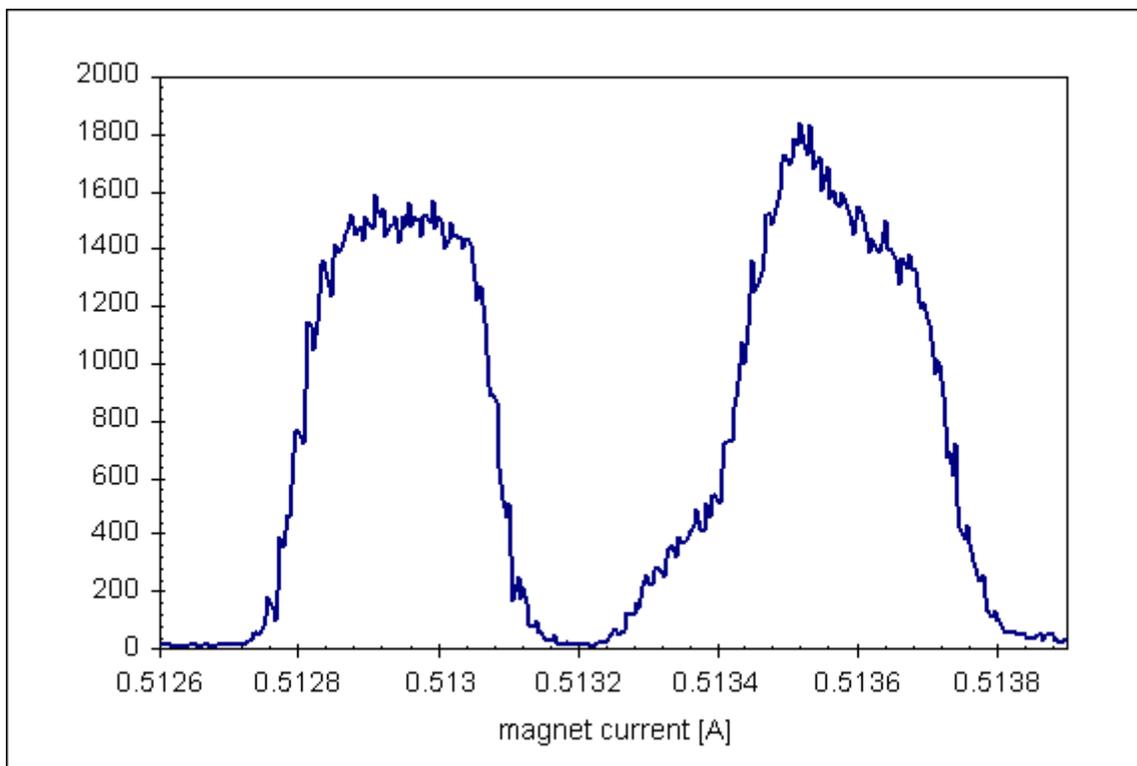


Fig. 16 ^3He and HD/ H_3 peaks measured with a channeltron 3 days after a bakeout

The ^3He peaks are narrower by about a factor of three compared to ^4He due to the different apertures (2 mm in front of the Faraday cup and 0.6 mm in front of the channeltron). In Figs. 14 and 16, the left peaks correspond to mass ^3He (3.01603 AMU) and the right peaks are a combination of HD (hydrogen-deuterium molecule, 3.02193 AMU) and H_3 (3.02348 AMU). The separation of the ^3He peak from the other peaks with mass three is an essential feature of a mass spectrometer for ^3He measurements. The scans plotted in Figs. 14 and 15 were produced a few days after a system bakeout following a change of both the filament and the channeltron. The HD/ H_3 peak decreases significantly over a period of about one week (Fig. 16) and reaches a fraction of a 0.4 cm^3 STP air standard count rate after several weeks.

^4He and $^3\text{He}/^4\text{He}$ ratio measurements

Background information

A typical 40 g water-sample is standardized by 0.4 cm^3 air standards, which contain roughly $2 \times 10^{-6} \text{ cm}^3$ STP He and $3 \times 10^{-12} \text{ cm}^3$ STP ^3He , corresponding to 5.6×10^{13} ^4He atoms and 7.9×10^7 ^3He atoms, respectively. A typical signal on the Faraday cup for such a sample or standard is 2.5 V over a 10^{10} Ohm resistance, equivalent to 1.6×10^9 ^4He ions per second or 250 pA. The typical ^3He count rate on the channeltron is 2000 cps. With a counting time of 420 seconds, the total number of ^3He atoms counted on the channeltron is about 840,000 with a statistical error of $\pm 0.11\%$. During this time, 1.4 % of all the ^3He atoms admitted to the mass spectrometer are counted. The ion consumption rate is about 2.7×10^9 atoms of ^4He per second equivalent to 0.3 % per minute or 4 % over the measurement period (13 minutes). The memory of the SFMS for ^4He in the range of a typical air standard (0.4 cm^3 air) is about 0.2 %.

air standard size	0.40	cm^3 air (or about 40 g H_2O)	
	2×10^{-6}	cm^3 STP He	
	3×10^{-12}	cm^3 STP ^3He	
	5.6×10^{13}	atoms He	
	7.9×10^7	atoms ^3He	
voltage	2.5	V	
resistance	1.00×10^{10}	Ohm	
^4He ion current	2.50×10^{10}	A	
^4He ions per second	1.56×10^9	$^4\text{He}^+/\text{s}$	
^3He count rate	2000	cps	
counting time on ^3He	420	s	
statistical error	840,000	counts	$\pm 0.11\%$
counted He atoms	1.44%	efficiency	
ion consumption rate	2.70×10^9	He/s	
relative ion consumption rate	0.30	%/s	

Tab. 1 Typical numbers for a helium isotope measurement

Standardization

The standardization is accomplished by measuring a sufficient number of air standards of

varying size before and between sample measurements. The air standards are prepared by using pipettes with pneumatically operated valves. During a typical measurement day, we measure about 20 air standards and about 5 substandards (for correction of non-linearity effects). The precision of the measurements are derived from the quality of a fit through the air standards (zero, first or second order; for an example, see Fig. 17)

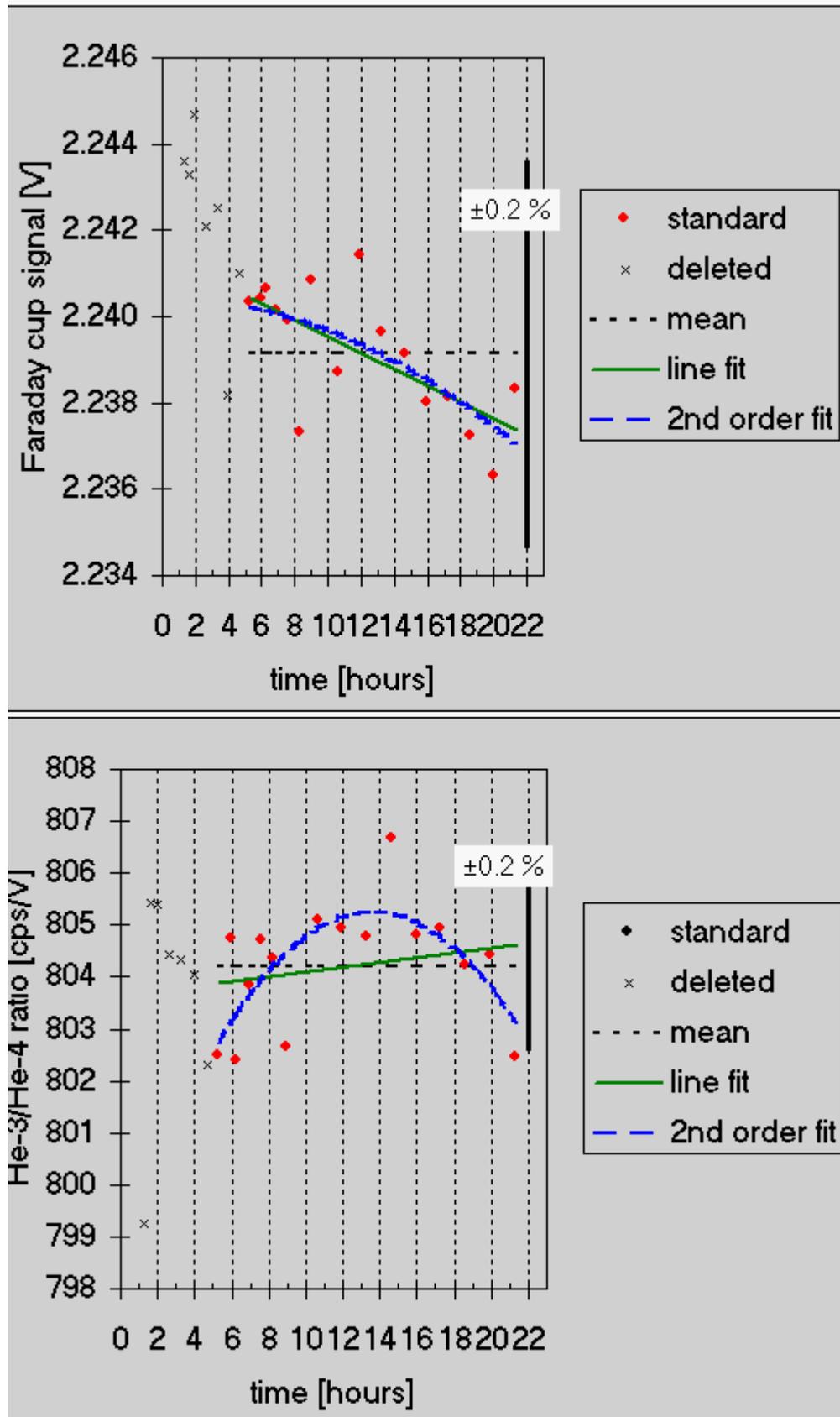


Fig. 17: Plots of ^4He (a) and $^3\text{He}/^4\text{He}$ (b) standard measurements over a period of one day.

Linearity and stability

Most mass spectrometers are not completely linear. Non-linearity means, that, for example, measurement of a standard with twice the amount of helium does not result in a signal on the Faraday cup or the channeltron that is exactly a factor of two higher. To correct for this non-linearity, substandards have to be measured. Their size should be chosen in a way, that the sample size is always bracketed by those of substandards and standards.

Typical deviations of the ^4He concentration and the $^3\text{He}/^4\text{He}$ ratio from linearity for a variation of 0.1 cm^3 STP around the 0.4 cm^3 STP standard are 0.5 % and less than 0.1 %, respectively (Figs. 18a and 18b). The data plotted in Figs. 18a-c are measured with one filament, but are divided into five individual periods with different tuning of the ion source. The deviations are calculated relative to a 0.4 cm^3 STP air standard. The data points are mean values from at least 10 substandards (the plotted error represents the standard deviation from the mean value). The helium concentrations of most 40 g water samples fall between 0.3 and 0.4 cm^3 . For the specific example shown in Figs. 18a-c, the ^4He non-linearity of about 0.5 % is significantly higher than the measurement precision of 0.2 to 0.3 % and has to be corrected. The $\delta ^3\text{He}$ non-linearity of about 0.1% is of the same order as the measurement precision of about 0.2 % and is also corrected. The linearity correction is different for each filament and is also a function of the tuning of the source. The linearity of the QPMS is shown for three measurement periods (Fig. 18c). Between these periods we changed the electronics and had an extended shutdown of the QPMS (tritium measurements). Usually, the Ne concentration of a 40 g water sample falls between those of 0.4 or 0.5 cm^3 STP of air. The non-linearity can be up to 0.8 % and has to be corrected for.

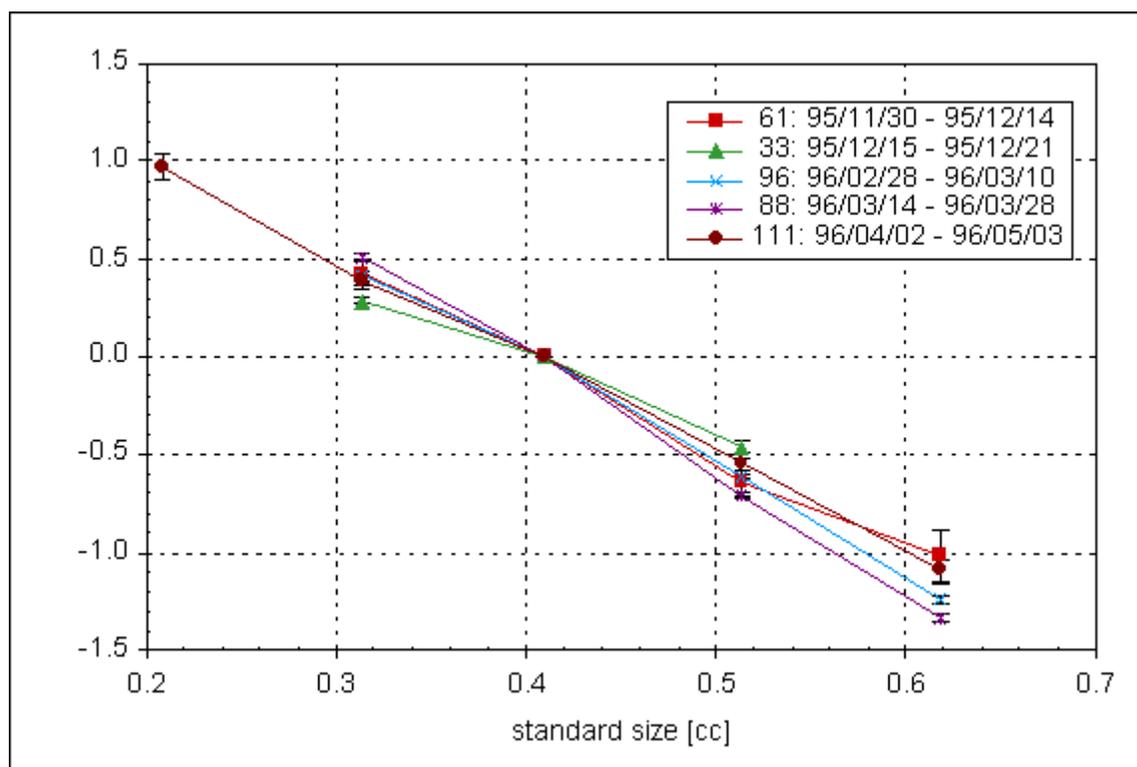


Fig. 18a: Deviation of ^4He substandards from a 0.4 cm^3 air standard. The numbers in the figure legend indicate the number of standards and the measurement periods. All data are

collected with the same filament.

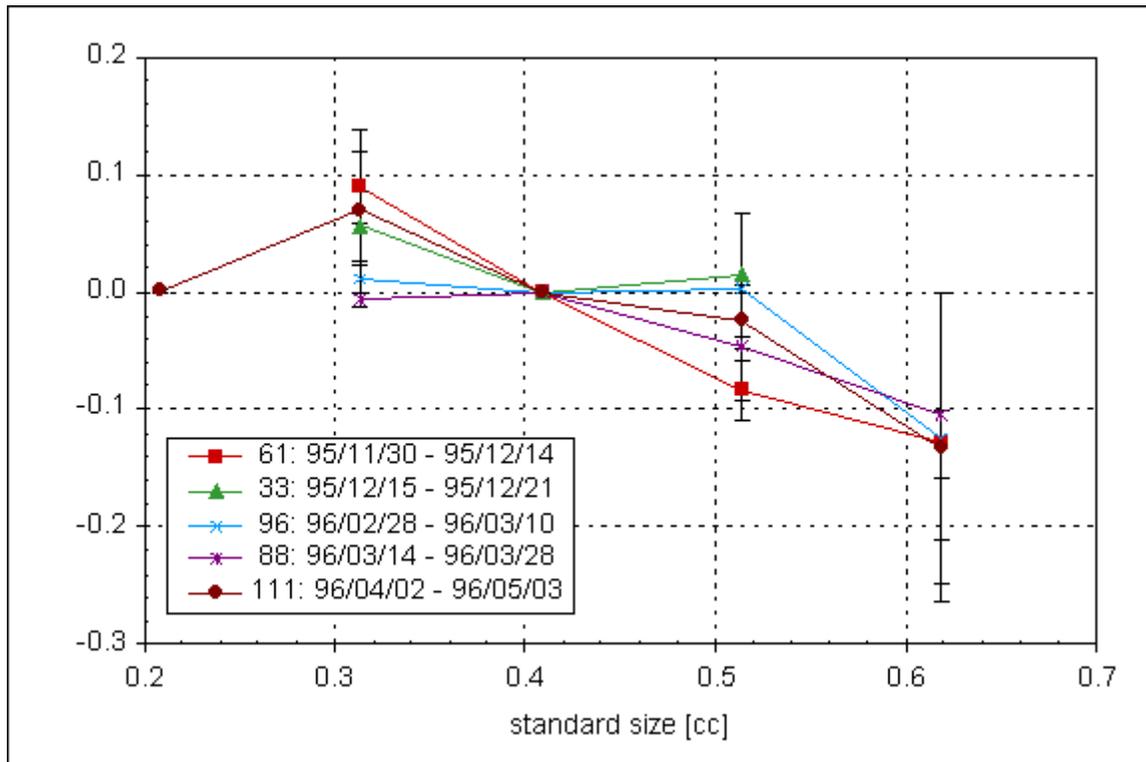


Fig. 18b: Same as 17a except for d3He.

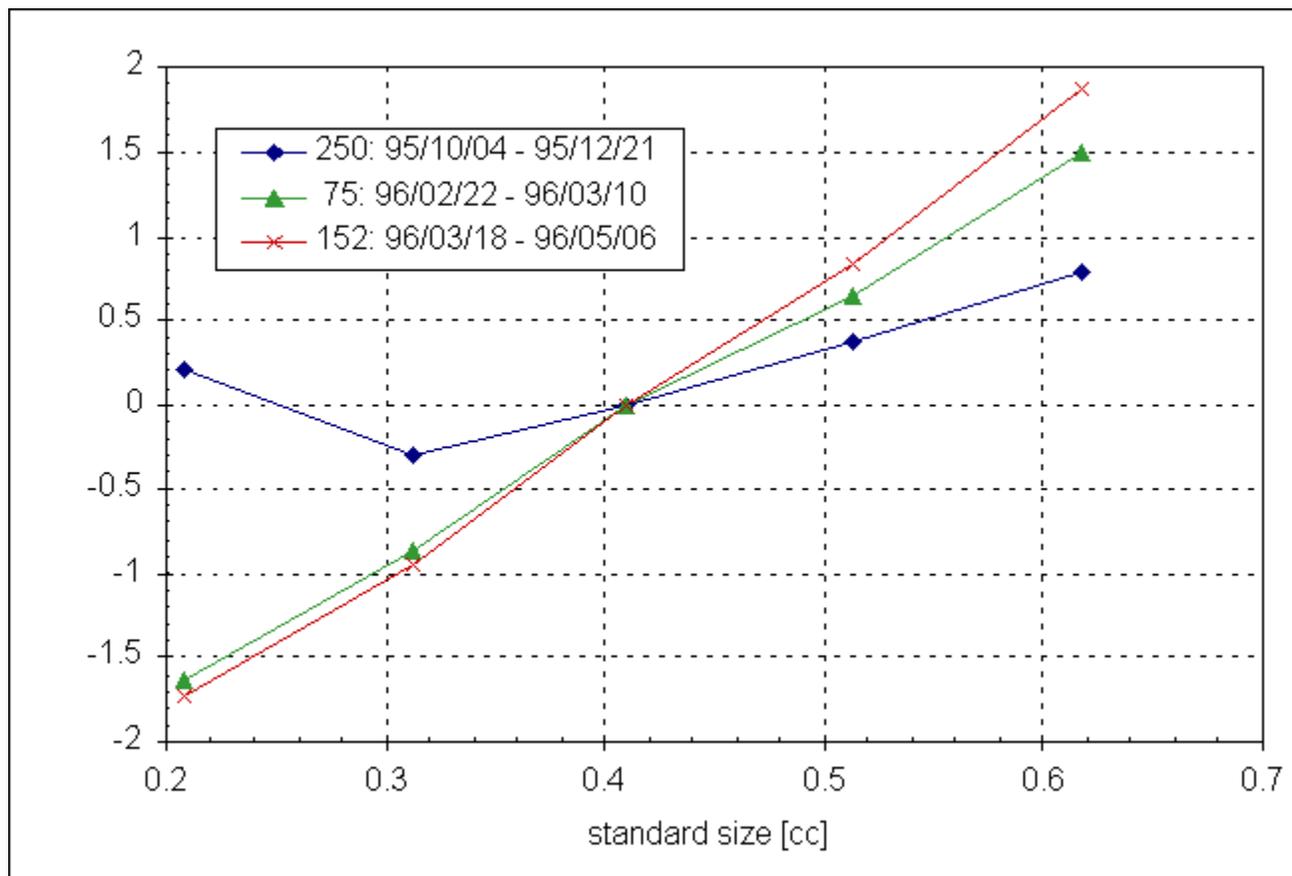


Fig. 18c: Same as 17a except for neon.

Fig. 19 shows the long-term stability (30 hours) during the initial testing of one of the mass spectrometers. Trends in the measured standard signals do not influence the precision of the measurements, as long as they can be corrected for by a reasonably tight fit curve (zero to second order).

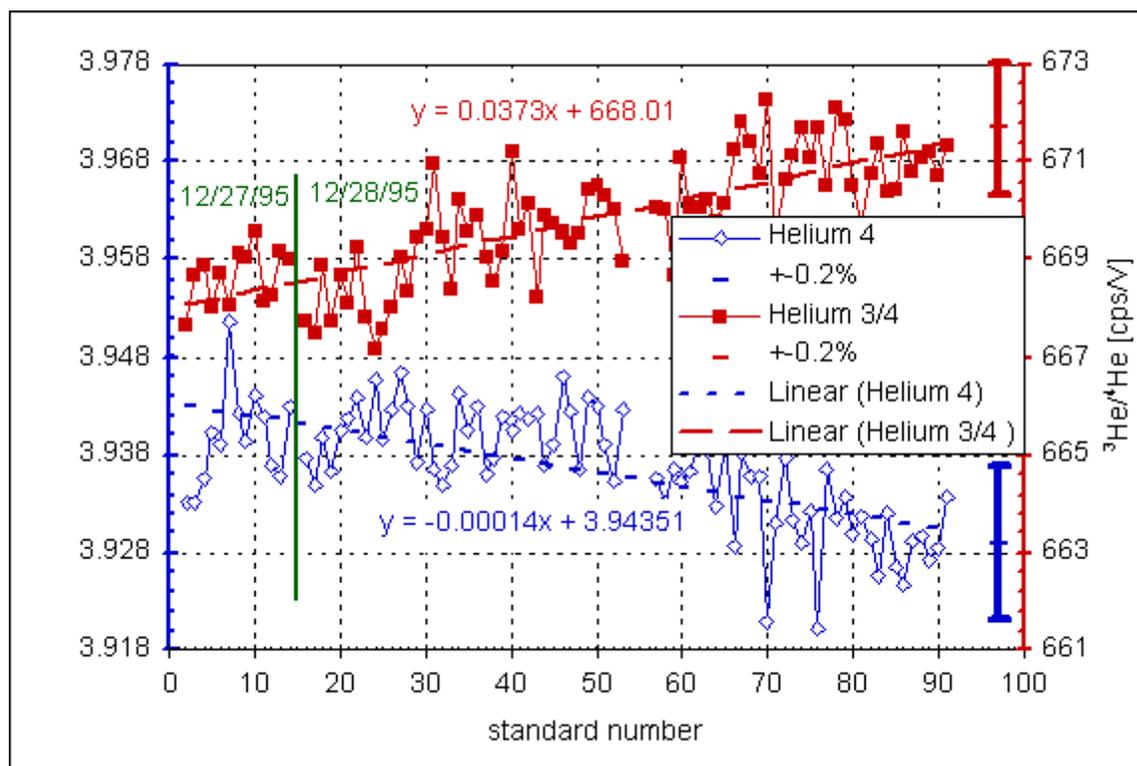


Fig. 19: Long-term stability of ^4He and $^3\text{He}/^4\text{He}$ ratio measurements (86 standards). The two bars span a range of $\pm 0.2\%$ of the measured $^3\text{He}/^4\text{He}$ ratios and ^4He concentrations, respectively.

Measurement Procedure

The procedure of measuring a standard or sample is shown in table 2, which is an excerpt from the log-file of the data acquisition computer. The measurement starts with scans over the ^4He and ^3He peaks. On the basis of these scans, specific magnetic field values are assigned for the measurement period following the scans. The measurement is divided into 10 blocks. During each block, the magnetic field is switched from ^4He peak (30 times 160 msec) to ^4He background (5 times 160 msec), ^3He peak (42 times 1 sec), and finally ^3He background (12 times 1 sec).

For evaluation of the raw data, we use the linear fit of the net ^4He signal (peak minus background) extrapolated to the inlet time and the net mean value of the ^3He count rates. The total time required for measurement of a helium isotope sample including the scans, the 10 measurement blocks, and the pumping is about 22 minutes.

Cold_head(2) at 44.95 K

Calling Admit_sample() at Thu Jun 27 10:37:52 1996

Sample in MS at Thu Jun 27 10:38:18 1996

Std : S15b-0278-4

Ok

0 * Pip1, 1 * Pip2

Measurement started at Thu Jun 27 10:40:47 1996

	He4	He3		
Magnet setting:	0.49332	0.49	0.43067	0.4245
Integration time:	160	160	1000	1000
Repeat:	30	5	42	12

	Peak1:	Backgrd1:	Peak2:	Backgrd2	Ratio
--	--------	-----------	--------	----------	-------

	[V]	[V]	[cps]	[cps]	[cps/V]
--	-----	-----	-------	-------	---------

Cycle:

0	10:40:58	2.4641	0.0020083	2055.8	42.583	817.7
1	10:42:18	2.4515	0.0019588	2043.1	42.5	816.74
2	10:44:02	2.4312	0.0019268	2035.1	44.75	819.32
3	10:45:59	2.4179	0.0019807	2010.4	43.667	814.07
4	10:47:19	2.4061	0.0019521	2015.7	45	819.7
5	10:48:40	2.3941	0.0019338	2013.9	45.833	822.72
6	10:50:00	2.382	0.0019425	1995.7	42.333	820.73
7	10:51:21	2.3696	0.001934	1986.8	41.5	821.61
8	10:52:40	2.3588	0.0019645	1983.7	45	822.58
9	10:53:59	2.3471	0.0019362	1983.9	43.333	827.49

Total:	---	---	8.4521e+05	5238		
--------	-----	-----	------------	------	--	--

Average (counts per cycle for He-3): 72.067 0.0097688 84521 523.8 820.27

Mean He4: 2.4003 +- 0.01239 (0.516 %)

Fitted values are extrapolated to Thu Jun 27 10:38:18 1996

Fit He4: 2.484 +- 0.0012203 (0.0491 %)

Mean He3: 1968.8 +- 2.2705 (0.115 %)

Total He3: 8.3997e+05 (0.109 %)

Fit He3: 2022.5 +- 4.5701 (0.226 %)

Mean He3/He4: 820.27 +- 1.1762 (0.143 %)

Fit He3/He4: 814.01 +- 1.8989 (0.233 %)

Ne20: 1.563e-09 +- 2.1947e-13 (0.014 %), range:0

Ne22: 1.5728e-09 +- 1.5519e-13 (0.00987 %), range:0

He-measurement ended at Thu Jun 27 10:55:30 1996

Tab. 2 Excerpt from the measurement log-file of one 0.4 cm³STP air standard

Tritium Measurements

Background information

A typical 400 g water sample with a tritium concentration of 0.2 TU contains $4.5 \times 10^{-15} \text{ cm}^3$ STP ^3He or 1.2×10^5 ^3He atoms after an ingrowth time of 150 days (one TU is defined as the ratio of one tritium atom per 10^{18} hydrogen atoms.). A 0.1 cm^3 air standard pipette diluted by a factor of 160 contains about the same amount of ^3He . For this amount of ^3He we obtain a count rate of approximately 3 cps. Integration over a period of 1200 sec results in 3600 total counts with a statistical error of $\pm 1.7\%$. Consequently, about 3% of all ^3He atoms admitted to the mass spectrometer are detected during measurement. The background count rates vary considerably, mainly as a function of time since the last bakeout of the SFMS. The maximum background count rate tolerable for tritium measurements is about 1 cps. During extended tritium measurement periods the background count rate decreases to values below 0.15 cps.

Standardization

Compared to the helium isotope measurements, the tritium samples typically contain more than a factor of 100 less ^3He . Therefore, the standard size has to be adjusted. To utilize the same automatic pipettes used for helium isotope measurement, the air standard is diluted by a factor of about 160. The dilution is accomplished by expanding about 1 cm^3 STP of air drawn from the working standard container into a volume of approximately 1 liter. The standards used for tritium measurement are then drawn from this volume using the automated pipettes (Fig. 5). The $^3\text{He}/^4\text{He}$ ratio of samples can differ considerably from that of air used for standardization. For this reason it should be kept in mind that a possible discrimination of ^3He by ^4He is not necessarily corrected by the air standards.

The measured ^3He concentrations are converted from cm^3 STP to TU by using the following equation:

$$c_{\text{trit}} = \frac{{}^3\text{He}_{\text{trit}}}{C} \cdot \frac{e^{\lambda(t_s - t_e)}}{1 - e^{-\lambda(t_e - t_m)}} \cdot \frac{1}{W \cdot [1 - (S/1000)]} \cdot \left[1 - (\alpha - 1) \cdot \frac{W_0 - W}{W_0} \right]$$

c_{trit} tritium concentration in TU

${}^3\text{He}_{\text{trit}}$ measured tritiogenic ^3He in cm^3 STP

C conversion factor from cm^3 STP to TU (2.4889×10^{-15} [(cm^3 STP/g)/TU])

λ radioactive decay constant of tritium (17.93 years., Clarke et al., 1976)

t_s , t_e , t_m dates of sampling, extraction and measurement, respectively

W_0 , W weights of the sample before and after the extraction, respectively

S salinity in permille

α correction for the $^3\text{H}/\text{H}$ fractionation due to loss of (distilled) water during gas extraction. $\alpha = 1.15$ (ratio of tritium concentration in the liquid phase to tritium concentration in the water vapor)

(Clarke et al., 1976)

Linearity

Typically, the mass spectrometers perform fairly linearly in the partial pressure range for helium introduced into the SFMS during tritium measurement (Fig. 20). However, in some instances, we have to use a second-order fit to convert the measured voltages (^4He) and count rates (^3He) into helium concentrations. The fit curves generally intercept the y axis at the measured blank (line blank plus memory) values.

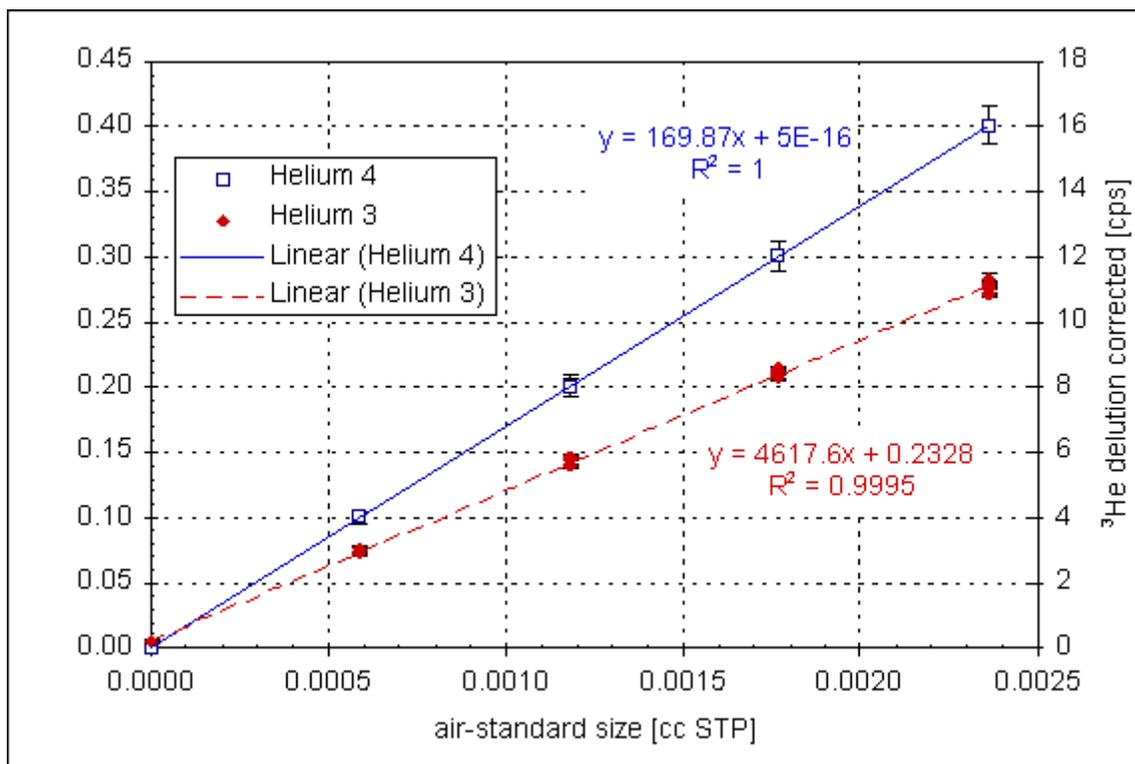


Fig. 20: ^3He and ^4He Linearity for a total of 93 measurements of diluted air standards and blanks

Blank

The low ^3He concentrations in tritium samples make them extremely sensitive to contamination. Measurement of the ^4He contained in the tritium samples allows us to subtract the ^3He left in the bulb due to incomplete gas extraction, as well as that introduced into the sample via diffusion or channeling through O-rings during the gas transfer from the bulbs into the inlet system of the mass spectrometer. Correction for atmospheric ^3He is possible as long as its signal is smaller than that of the sample. Therefore, the maximum amount of atmospheric helium that can be tolerated in a sample is a function of its tritogenic ^3He concentration.

NET	#	^4He	\pm	^3He	\pm	$^3\text{He}/^4\text{He}$	\pm
			[%]		[%]	[to air]	[%]

		[cm ³ STP]		[cm ³ STP]		ratio]	
MS Blank	6	7.28× 10 ⁻¹²	53	1.40× 10 ⁻¹⁶	13	13.90	55
Inlet Blank	6	2.86× 10 ⁻¹²	200	5.95× 10 ⁻¹⁷	63	15.02	210
Branch Blank	16	8.31× 10 ⁻¹¹	18	8.64× 10 ⁻¹⁷	51	0.75	54
Repetition	6	1.09× 10 ⁻⁰⁹	27	1.58× 10 ⁻¹⁵	25	1.05	37
0.1 cm ³ Tr-Std	21	3.77× 10 ⁻⁰⁹	2	5.19× 10 ⁻¹⁵	2	0.99	3

Tab. 3 Comparison of blanks

A tritium sample can be affected by several processes: (1) direct tritium contamination of the water during sample collection or processing in the laboratory (e.g., tritium addition from watches with tritiated dials or addition of water with high tritium concentrations to the samples). (2) indirect 'contamination' through addition of ³He during the sample processing or measurement process. This includes incomplete gas extraction of the tritium sample, addition of ³He through diffusion through O-rings in the extraction laboratory and in the mass spectrometer laboratory, or leaks in the vacuum system.

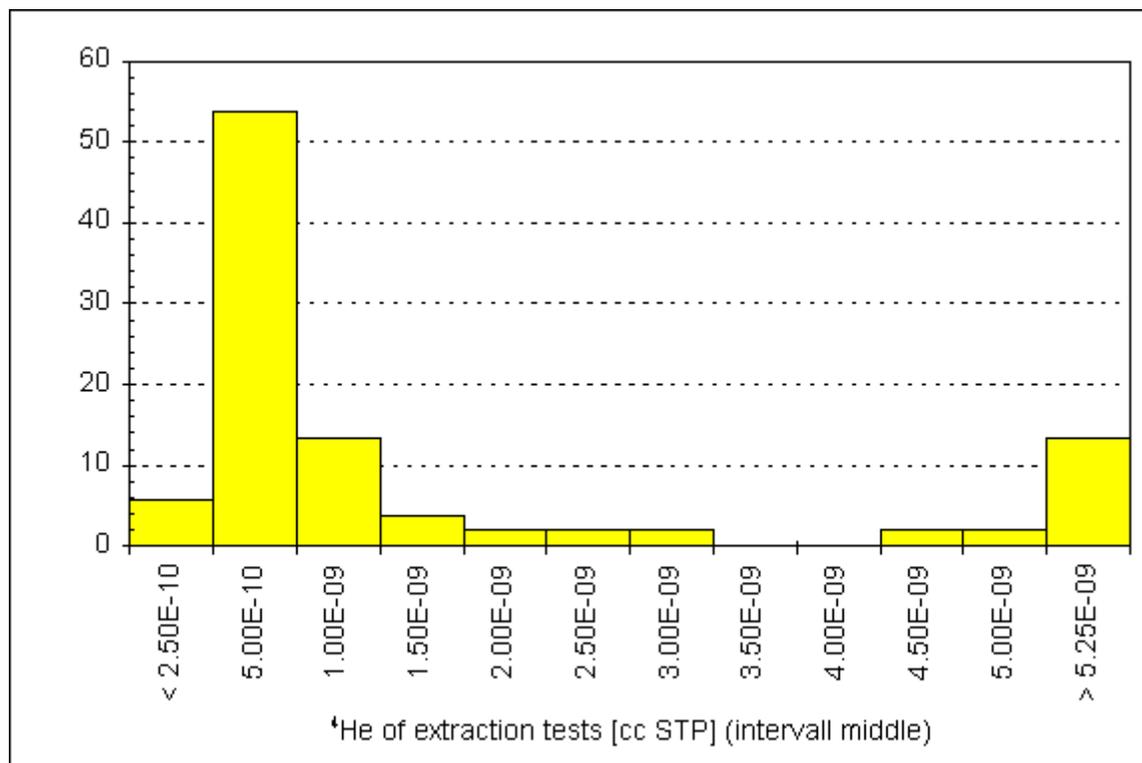


Fig. 21: 4He blanks of 52 large bulbs including 5 minutes of O-ring contribution (1 l bulbs with

400 g of water).

Bulb Blank

The so-called bulb blank is the sum of the helium components accumulated in the glass bulbs used for storage of the water sample for ^3He ingrowth from tritium decay. They represent the contamination factor of the extraction and the storage including: (1) helium from a leak in the vacuum system, which might not be detected because of the high water vapor pressure, (2) helium diffusion or channeling through an O-ring, (3) helium released from the glass bulb during flame sealing and storage, and (4) helium remaining in the water due to incomplete gas extraction.

The extraction efficiency has to be higher than 99.95 % to reduce the rest helium to levels of less than $7 \times 10^{-10} \text{ cm}^3 \text{ STP } ^4\text{He}$ for a 40 g samples and 99.995 % for a 400 g samples, respectively. These ^4He amounts correspond to $9.7 \times 10^{-16} \text{ cm}^3 \text{ STP } ^3\text{He}$, if we assume an atmospheric $^3\text{He}/^4\text{He}$ ratio.

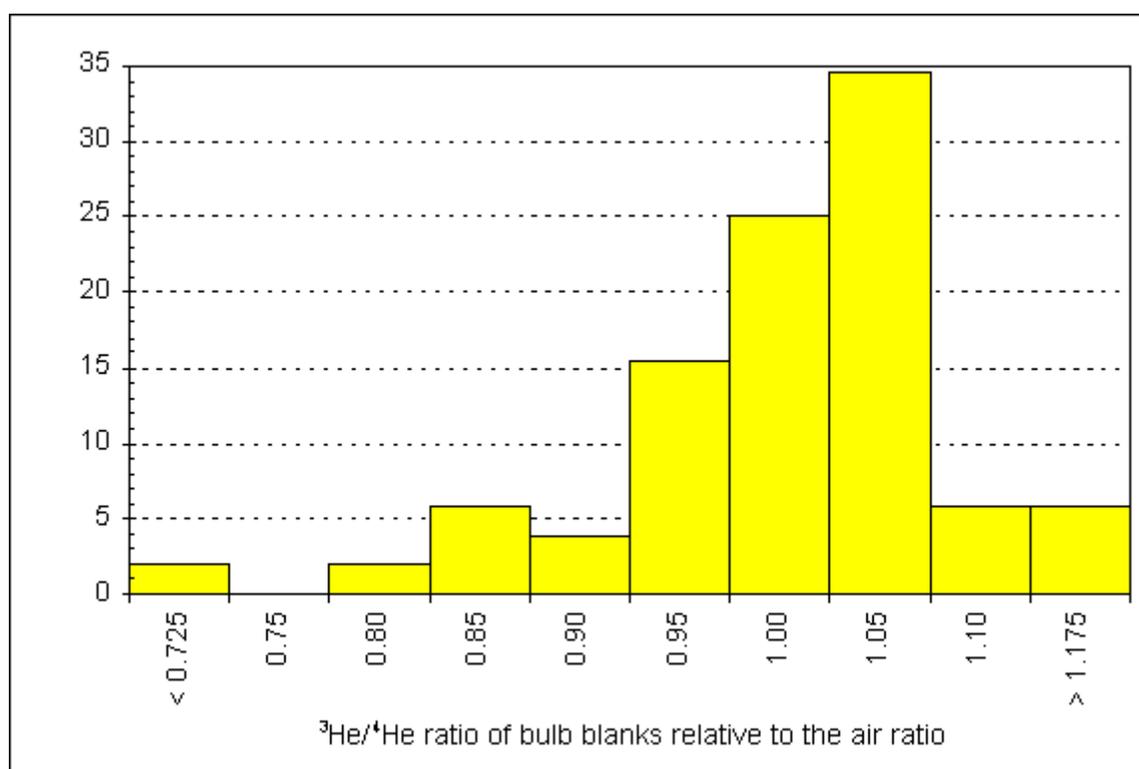


Fig. 22: $^3\text{He}/^4\text{He}$ ratio of 52 blanks measured in large bulbs. The average is 1.00 ± 0.09 times the air ratio.

The blanks of 52 test tritium extractions with large bulbs show that the contribution of the extraction is generally smaller than $10^{-9} \text{ cm}^3 \text{ STP } ^4\text{He}$ (Fig. 21). For these tests, low-tritium water was extracted and measured immediately after extraction. The $^3\text{He}/^4\text{He}$ ratio of these 52 test extractions is 1.00 ± 0.09 times the $^3\text{He}/^4\text{He}$ ratio of air (Fig. 22).

Addition of helium during the storage of the water sample for ^3He ingrowth is mainly caused by diffusion of from the glass into the sample. The use of special glass with low helium permeability and the storage of the extracted and flame-sealed samples at about $-25 \text{ }^\circ\text{C}$

reduce helium contributions to the bulb blank from this source (Suckow et al., 1990). Additionally, baking of the glass bulbs in a nitrogen atmosphere before sample extraction further reduces the amount of helium added to the bulb blank through diffusion from the glass (Bayer et al., 1985).

The large bulbs (volume: 1000 cm³; surface: 500 cm²) have a ⁴He blank approximately 10 times higher than that of the small bulbs (volume: 200 cm³; surface: 170 cm²; Fig. 23). The ⁴He blanks of both the small and the large bulbs span a fairly broad concentration range around the mean value. In both cases, a certain fraction of the blanks falls above the acceptable limit of 1× 10⁻⁹ cm³ STP (small bulbs) and 1× 10⁻⁸ cm³ STP (large bulbs).

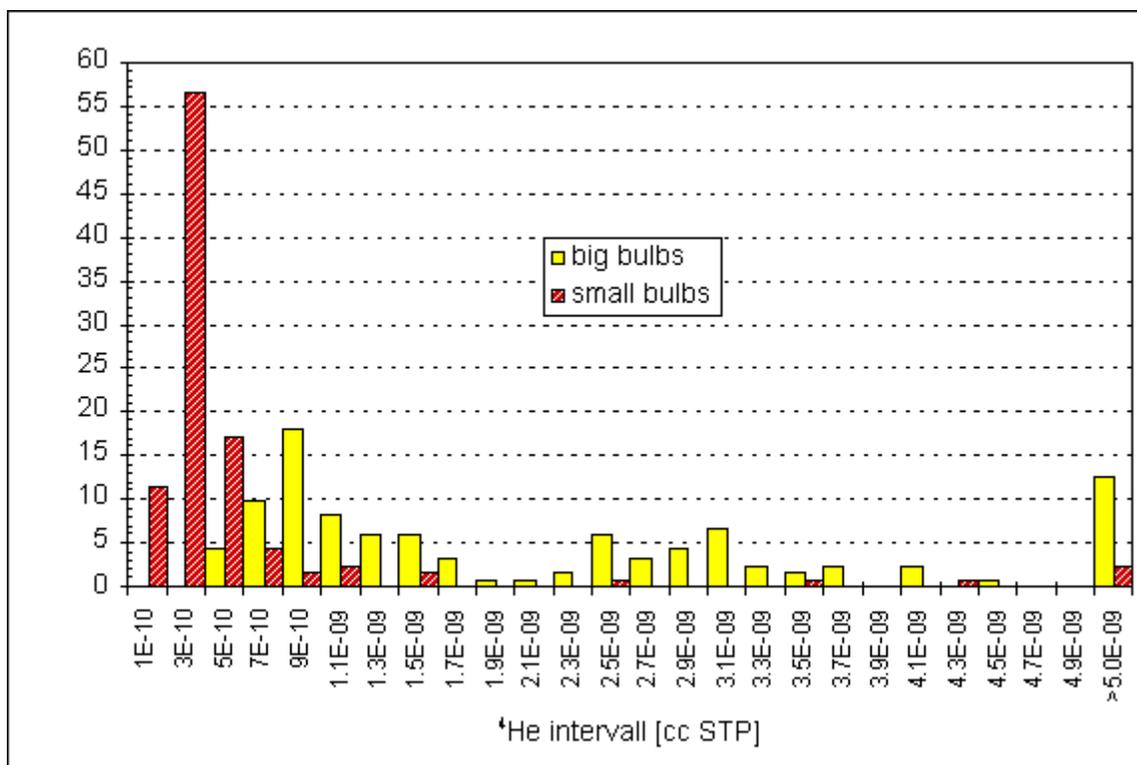


Fig. 23: ⁴He Blanks of 122 small bulbs extracted on the helium extraction system and of 299 large bulbs extracted on the tritium extraction system.

O-Ring Blanks

The main blank contribution during measurement is caused by diffusion and channeling of helium through the O-rings which are used to attach the glass bulbs to the all-metal inlet system. To determine the diffusion rate through the O-rings and at the same time to check the transfer efficiency of helium from the bulbs into the inlet system, we perform repeat measurements. During these measurements, a previously measured sample is subjected to one or more additional sample cycles without pumping the head space. If the helium transfer during the first measurement was complete, the repeat measurements should yield constant ⁴He and ³He amounts which reflect the diffusion of helium through the O-ring for the entire period between two measurements (about 36 min; the glass bulb is not pumped between repeat measurements). Evaluation of 153 repeat measurements (large bulbs, Fig. 24) yields an average O-ring contribution of 1.5× 10⁻⁹ cm³ STP ⁴He for 36 minutes corresponding to 2× 10⁻¹⁰ cm³ STP for samples with 5 minutes transfer time or 7× 10⁻¹³ cm³ STP ⁴He per second. The fact that there is no significant trend in the ⁴He amounts of the repeat measurements

provides evidence for complete sample transfer during a 5 minutes interval (large bulbs). For the same 153 repeat measurement the $^3\text{He}/^4\text{He}$ ratio distribution is plotted as histogram in Fig. 25. The mean value is 1.00 ± 0.06 times the $^3\text{He}/^4\text{He}$ ratio of air.

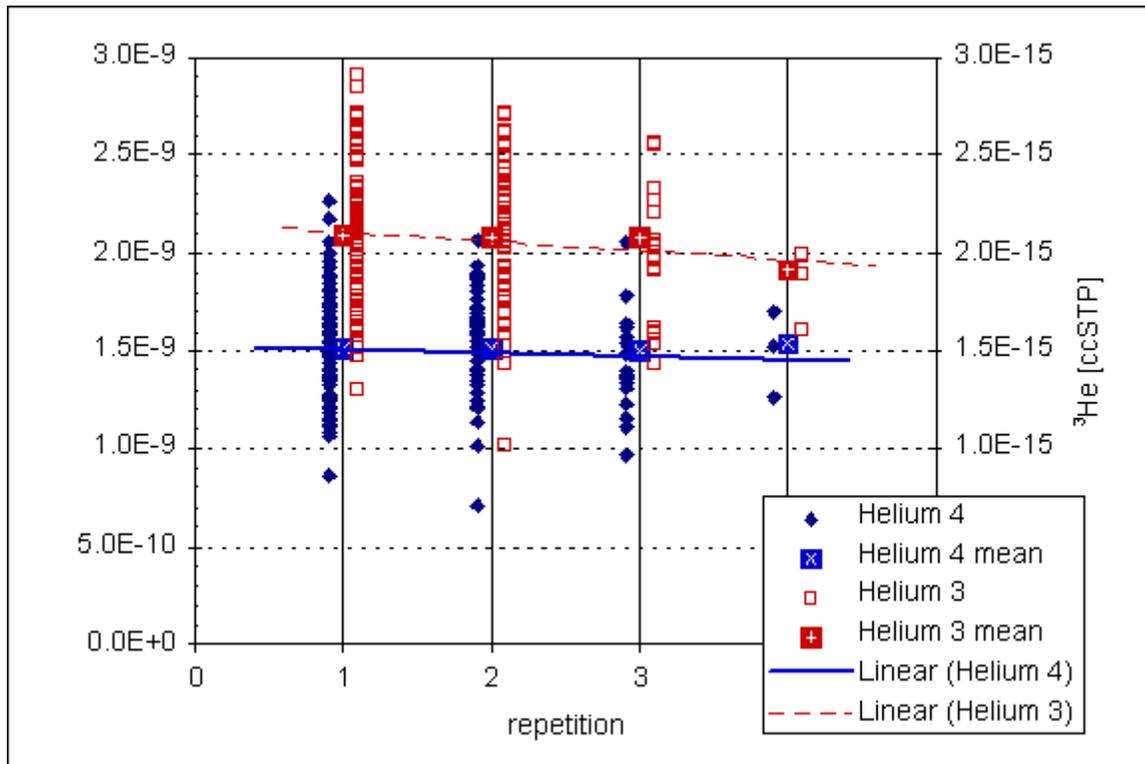


Fig. 24: 153 repeat measurements of ^4He and ^3He (large bulbs). The data are a check of the transfer efficiency of helium from the glass bulbs into the inlet system. Additionally, they are used to determine the diffusion rate of helium through wet O-rings.



Fig. 25: $^3\text{He}/^4\text{He}$ ratio of 153 repeat measurements of the bulb blank of large bulbs.

In Fig. 26, four different types of blanks for ^3He and ^4He are plotted on a logarithmic scale. MS blank means a measurement with no sample inlet into the previously pumped mass spectrometer. It practically represents the memory of the mass spectrometer which depends on the type and size of samples measured since the last bakeout. The inlet blank is the amount of helium accumulating in the vacuum lines and traps used for preparation of an air standard. The branch and repetition blanks contain 2.5 and 36 minutes of O-ring contribution, respectively

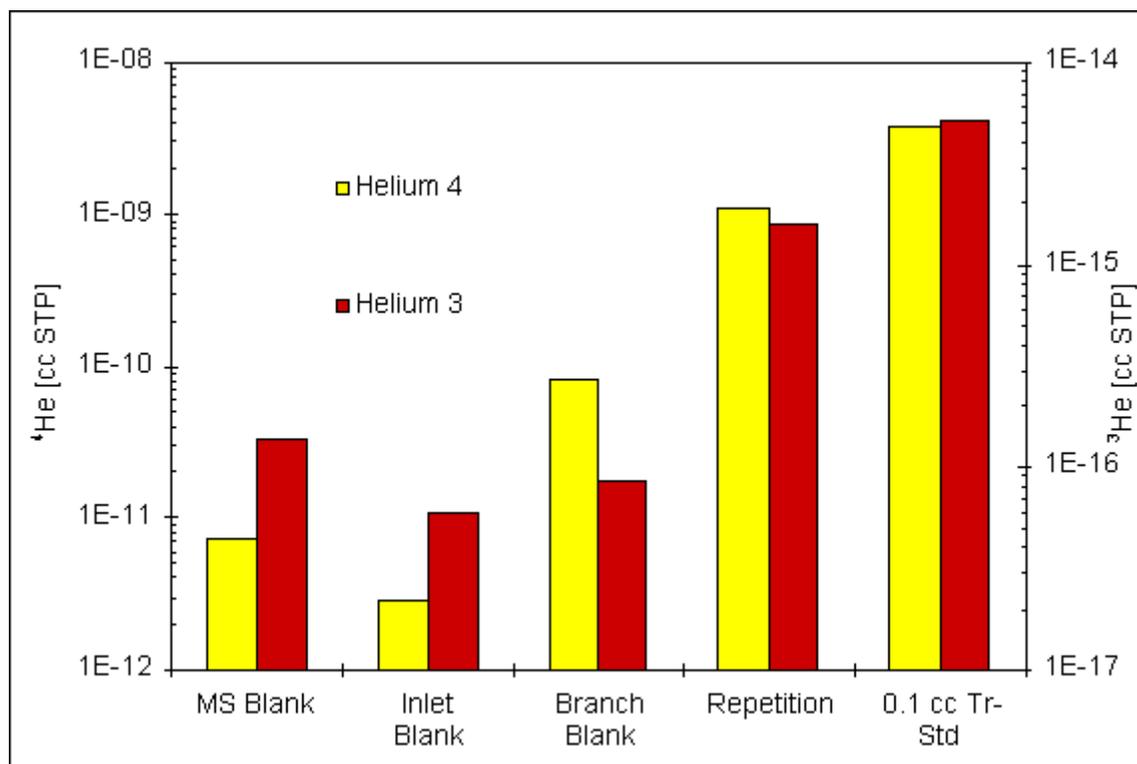


Fig. 26: Comparison of MS-, inlet system-, branch-, and repeat- measurement blanks. The ^3He and ^4He amounts contained in a 0.1 cm³ air standard diluted by a factor of 160 are plotted for comparison.

Measurement procedure

The procedures of measuring tritium via the ^3He ingrowth method are mainly the same as those for the measurement of helium isotopes with the exception of the determination of the center of the ^3He peak and the counting time required to achieve the appropriate counting statistics. Additionally, no neon measurement is performed simultaneously with the tritium measurements.

Because of the low ^3He signal, we use the HD/H₃ peak as indicator for the location of the ^3He peak. For this purpose, we determine the center of the HD/H₃ peak. The ^3He peak center is then determined by a predefined offset from the HD/H₃ peak.

Cold_head(2) at 0 K

Calling Admit_sample() at Wed Jul 10 14:19:17 1996

Sample in MS at Wed Jul 10 14:19:55 1996

Std : A-Std1-10-10

1 * Pip1, 0 * Pip2

Measurement started at Wed Jul 10 14:21:52 1996

	He4	He3		
Magnet setting:	0.636045	0.65	0.55584	0.57
Integration time:	1280	1280	1000	1000
Repeat:	5	5	120	20

	Peak1:	Backgrd1:	Peak2:	Backgrd2	Ratio
	[V]	[V]	[cps]	[cps]	[cps/V]
Cycle:					
0 14:21:57	0.0059913	0.0023416	2.7	0	739.79
1 14:24:56	0.005985	0.0023331	2.9917	0	819.21
2 14:27:55	0.0059559	0.0023456	3.0667	0.05	835.56
3 14:30:55	0.0059367	0.0023429	2.9583	0	823.19
4 14:33:54	0.0059026	0.0023407	3.0583	0.1	830.55
5 14:36:53	0.0058708	0.0023346	2.9	0	820.09
6 14:39:53	0.0058443	0.0023406	2.8583	0	815.81
7 14:42:52	0.0058161	0.002339	2.825	0	812.47
8 14:45:52	0.0057919	0.0023406	3.0083	0.05	857.17
9 14:48:51	0.0057618	0.0023449	2.7583	0	807.26

Total: --- --- 3495 4

Average (counts per cycle for He-3): 0.029428 0.011702 349.5 0.4 816.11

Mean He4: 0.0035453 +- 2.5802e-05 (0.728 %)

Fitted values are extrapolated to Wed Jul 10 14:19:55 1996

Fit He4: 0.0036853 +- 5.5774e-06 (0.151 %)

Mean He3: 2.8925 +- 0.05027 (1.74 %)

Total He3: 3491 (1.69 %)

Fit He3: 2.9247 +- 0.071378 (2.44 %)

Mean He3/He4: 816.11 +- 9.5821 (1.17 %)

Fit He3/He4: 793.37 +- 18.828 (2.37 %)

He-measurement ended at Wed Jul 10 14:52:11 1996

Tab. 4 Excerpt from the log-file of the measurement of one 0.1 c m³ pipette (approx. 160 time diluted).

Measurement of ⁴He and ³He is divided into ten intervals (Tab. 3). During each interval the magnetic field is set to the masses of ⁴He (5 times 1280 msec), ⁴He background (5 times 1280 msec), ³He (120 times 1 sec), and ³He background (20 times 1 sec). For all further calculations of the helium blanks and tritium concentrations of the samples, the linear fit through the 10 background-corrected ⁴He measurements extrapolated to the time of sample inlet and the background-corrected ³He count rates are used. Following this procedure, a tritium measurement requires 36 minutes.

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