Mass spectrometric measurement of helium isotopes and tritium in water samples

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ABSTRACT

The design, setup and routine performance of systems for mass spectrometric measurement of helium isotopes and tritium of water samples by the ^{3}He ingrowth method are described using two systems operated in the noble gas laboratory of the Lamont-Doherty Earth Observatory as examples. The systems are built around commercially available mass spectrometers and are equipped with specially designed sample inlet and purification systems including a series of cryogenically cooled traps for removal of water and permanent gases, as well as for separation of helium from neon. Neon isotopes are measured simultaneously to the helium isotope measurements in quadrupole mass spectrometers. The systems are fully automated for high sample throughput and high precision. Typical precisions for measurement of tritium, $\delta\ ^3$He, and the ^{4}He and neon concentrations are ± 1 to ± 2 %, ± 0.15 to ± 0.2 %, and ± 0.2 to ± 0.3 %, respectively. These values are determined by several factors including the linearity of the mass spectrometers and the individual blank and memory components.

1. Introduction

Tritium, together and its radioactive decay product ^{3}He 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 ^{3}He 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 ñ 2.5 to ñ 5 % with detection limits of 0.05 to 0.08 TU (e.g., Weiss et al., 1976; ™ 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 he 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 ^{3}He 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 ^{3}He ingrowth method for measurement of tritium, precision could be improved to ñ 1 to ñ 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 ^{3}He 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.

2. General system design

Measurement of helium isotopes, as well as tritium by the ^{3}He 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. Theycan 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. ^{3}He-free ater for tritium measurement is stored in flame-sealed glass bulbs (volume: 200 cm^3 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^{o}C during the ^{3}He 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 ^{3}He. The ion source has to be stable and at the same time yield a high ion current. The best ^{3}He 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).

3. Gas extraction

3.1. *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).

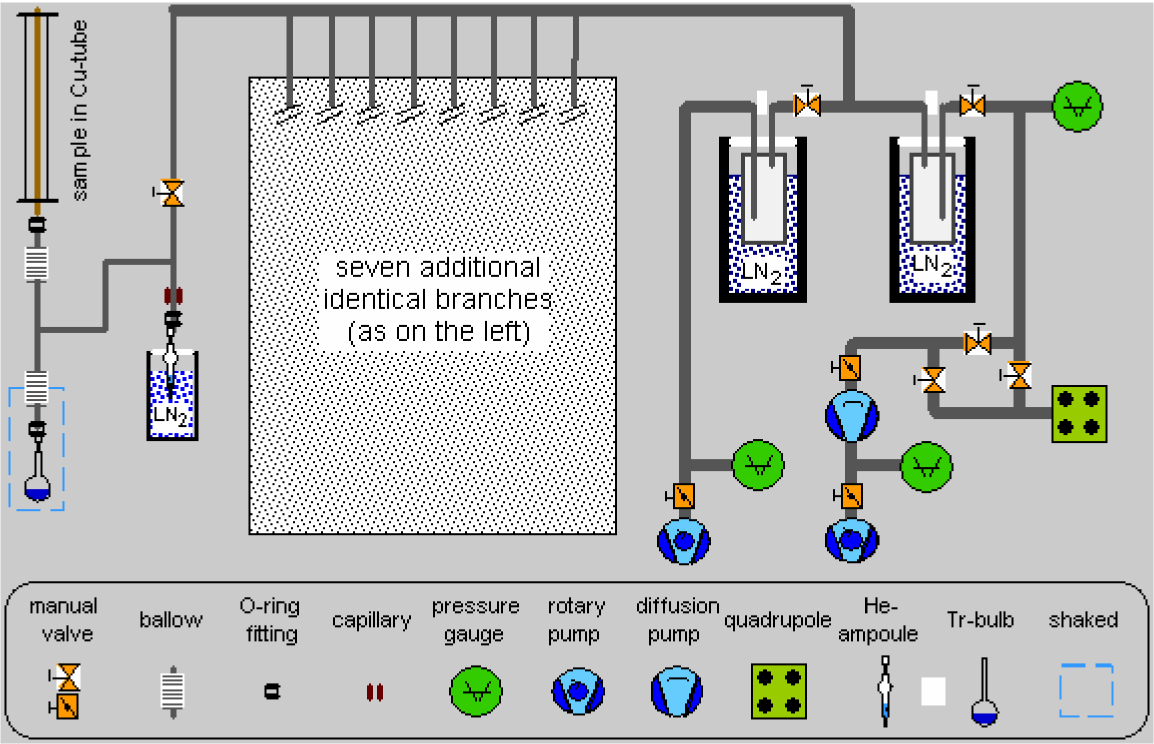

Fig. 1: Schematic diagram of the helium extraction system

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 (QPMS) 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 velocityof 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} cm^3 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.

3.2. 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 cm^3 compared to the 40 cm^3 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 effieciency for large bulbs is approximately 99.995 %). Diffusion of helium through the O-ring connecting the glass bulb to the vacuum system is negligible.

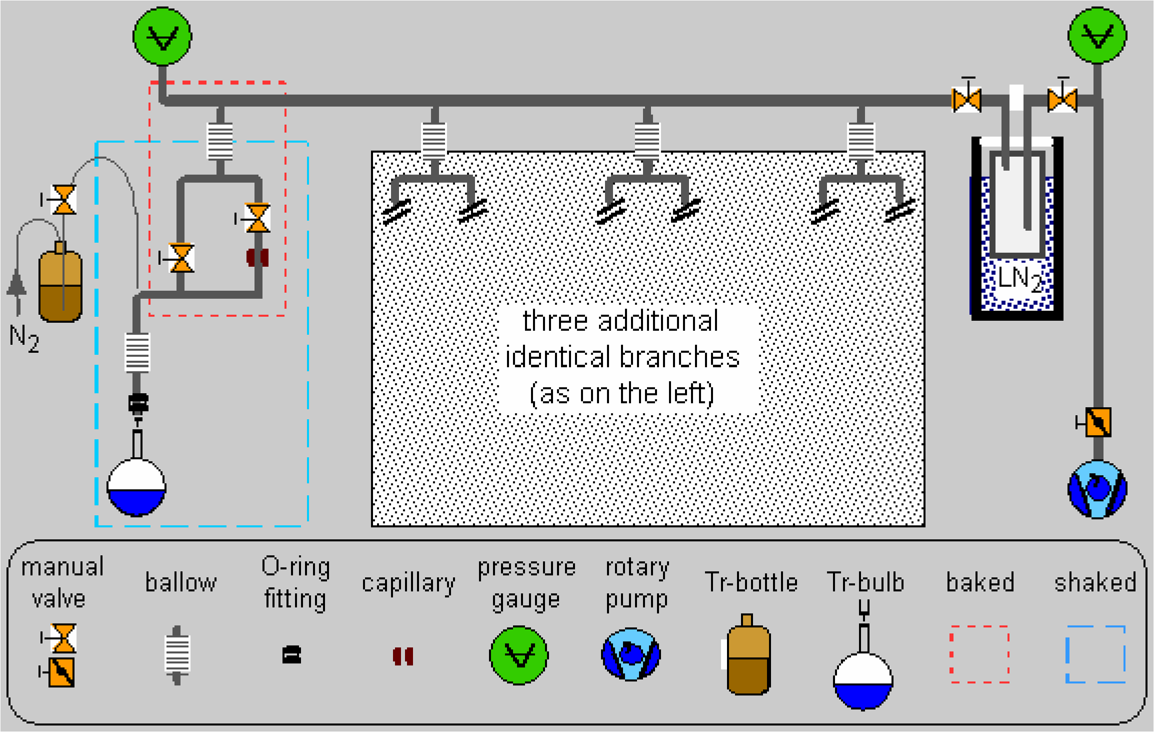

Fig. 2: Schematic diagram of the tritium extraction system.

4. Inlet System

4.1. 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.

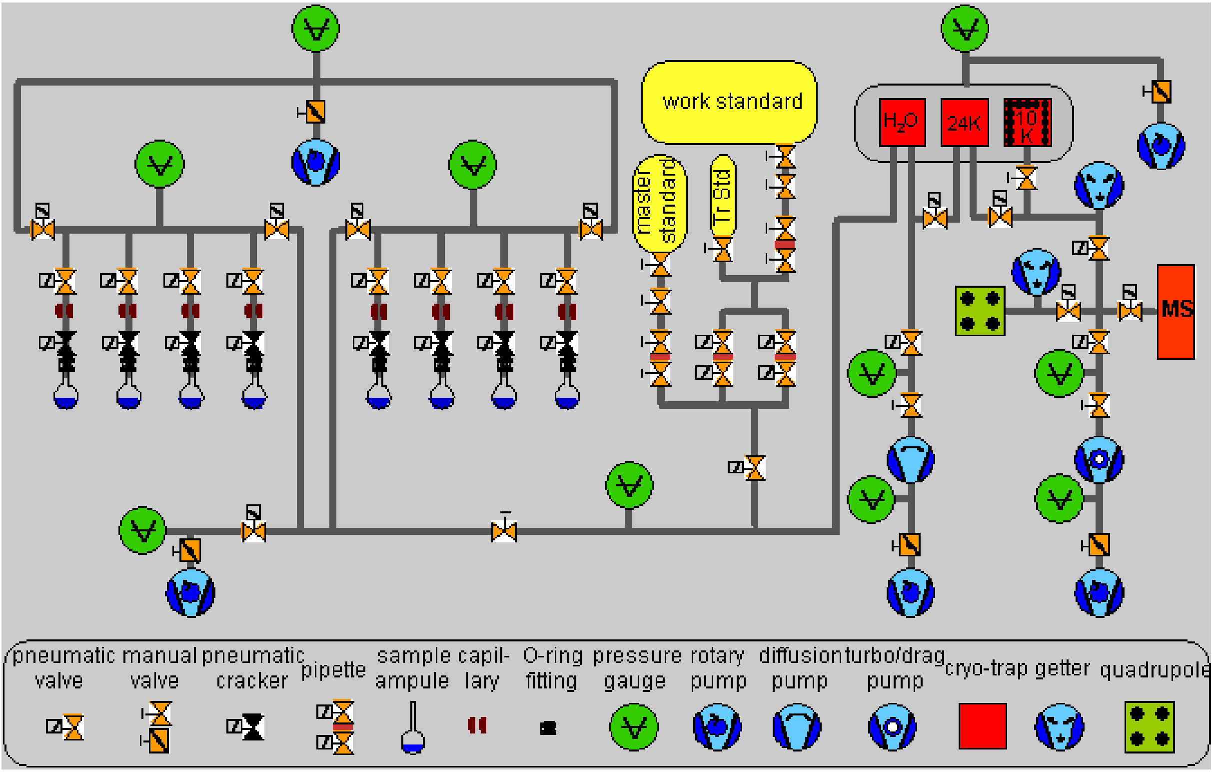

Fig. 3: Schematic diagram of the sample preparation system.

4.2. *Vacuum system*

The vacuum system consists of electropolished stainless steal 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 (ó 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 (ó 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 (Balazers, 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.

4.3. 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, pneumatcilly dirven). 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: ÷ 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 cm^3 tritium samples, and 5 minutes for 400 cm^3 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.

4.4. *Air standards*

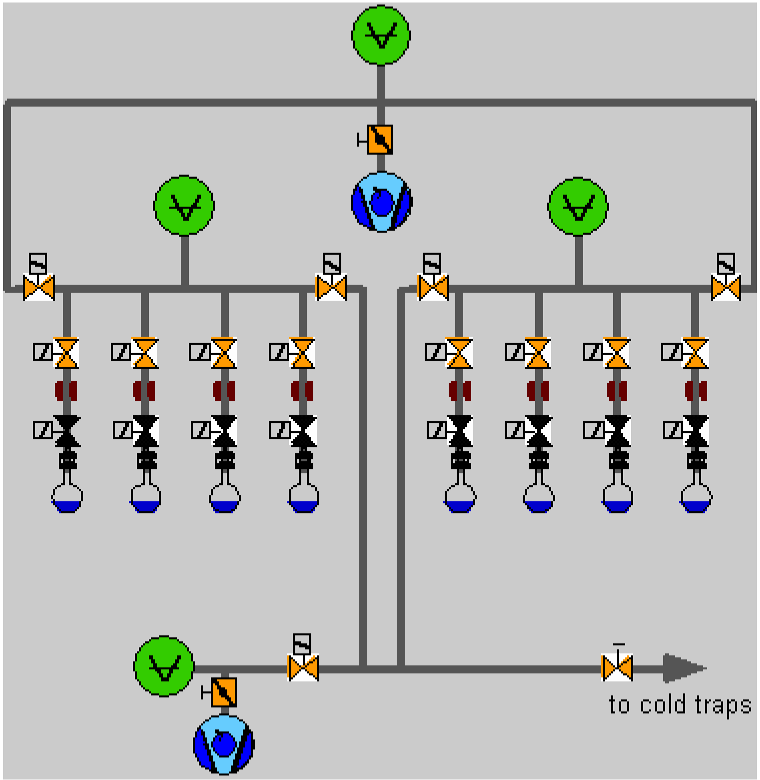

Fig. 4: Schematic diagram of inlet part of sample preparation system (for symbol legend, see Fig. 3).

The helium isotope ratio measurements, as well as the absolute ^{3}He , ^{4}He , and neon measurements are standardized against air. The He content of air (5.24 ppm; Glueckauf, 1946), as well as its ^{3}He/^{4}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 ñ 1 ‰ requires measurement precisions of ñ 1 mbar, ñ 0.3 K and ñ 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 ^{3}He 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)

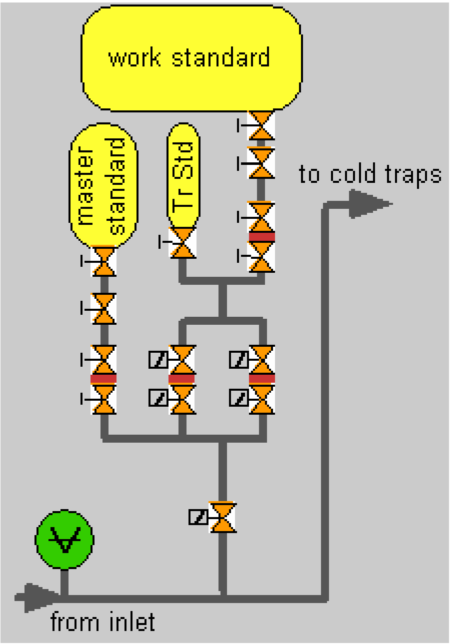

Fig. 5: Schematic diagram of the standardization part of the sample preparation system (for symbol legend, see Fig. 3).

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.

4.5. 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 ñ 0.1 K or better.

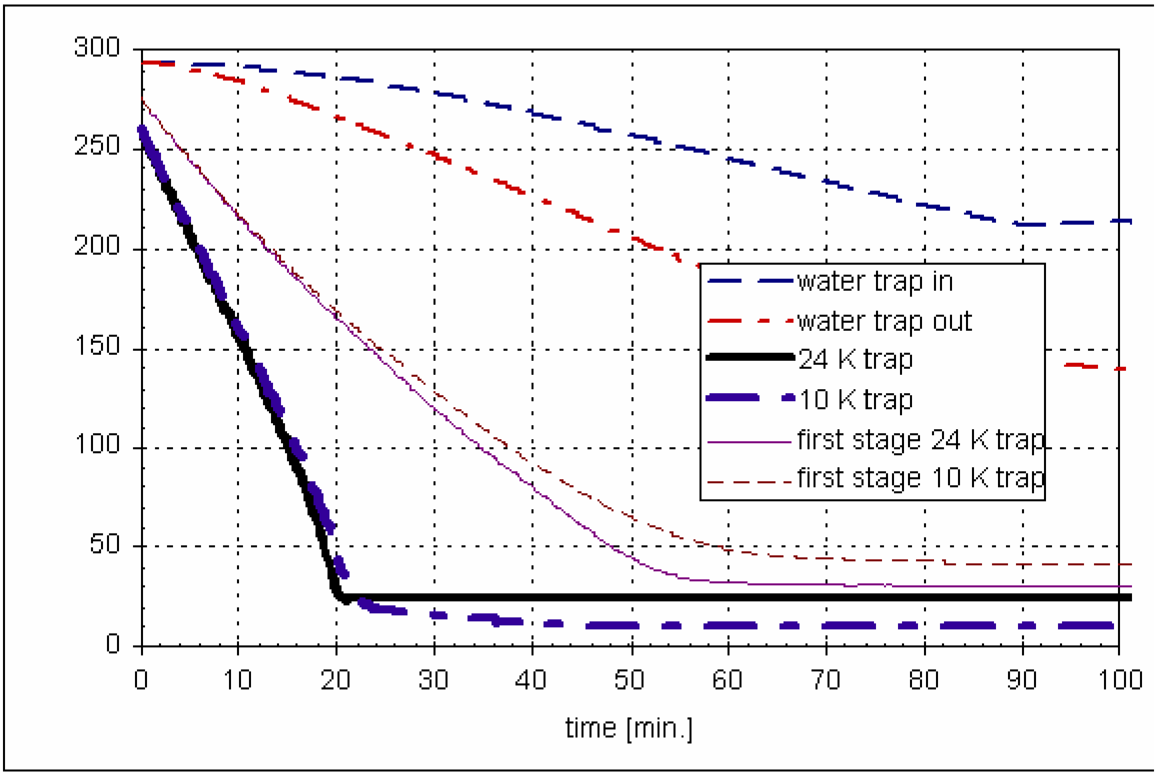

Fig. 6: Cool down times for the cryogenic cold traps.

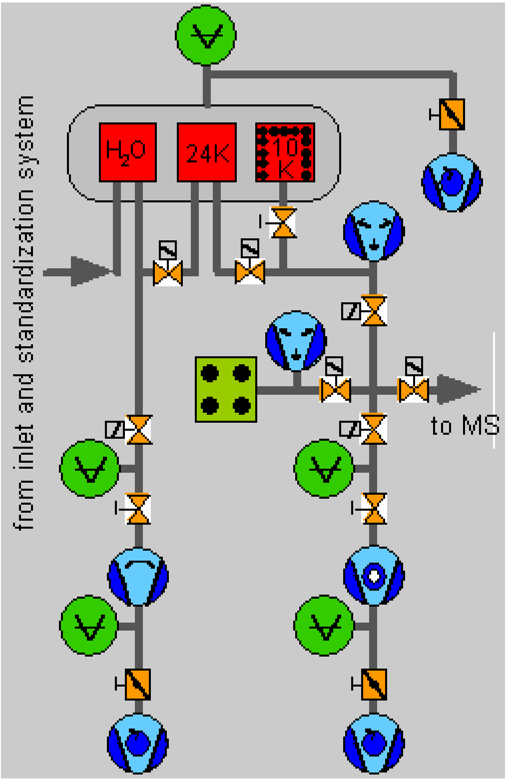

Fig. 7: Schematic diagram of the cryogenic cold trap system (for symbol legend, see Fig. 3)

The first trap (stainless steel cylinder; 2.5 cm diameter, 10 cm length, 40 cm^3 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 cm^3 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 cm^3 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 ò 45 K (Fig. 8; tritium mass spectrometer ò 38 K). The small ^{3}He to ^{4}He isotope fractionation effect (Fig. 8) is negligible at temperatures < 14 K and > 45 K.

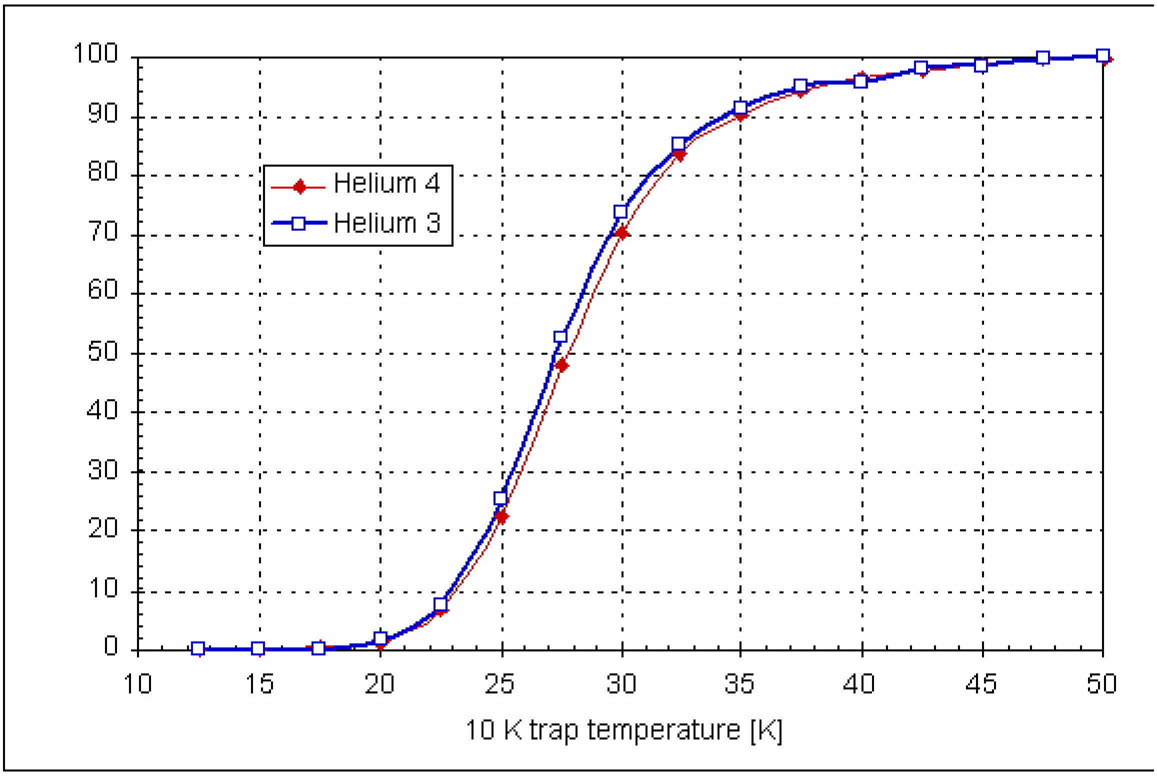

Fig. 8: 3He and 4He adsorption isotherms (measured on the helium isotope SFMS).

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.

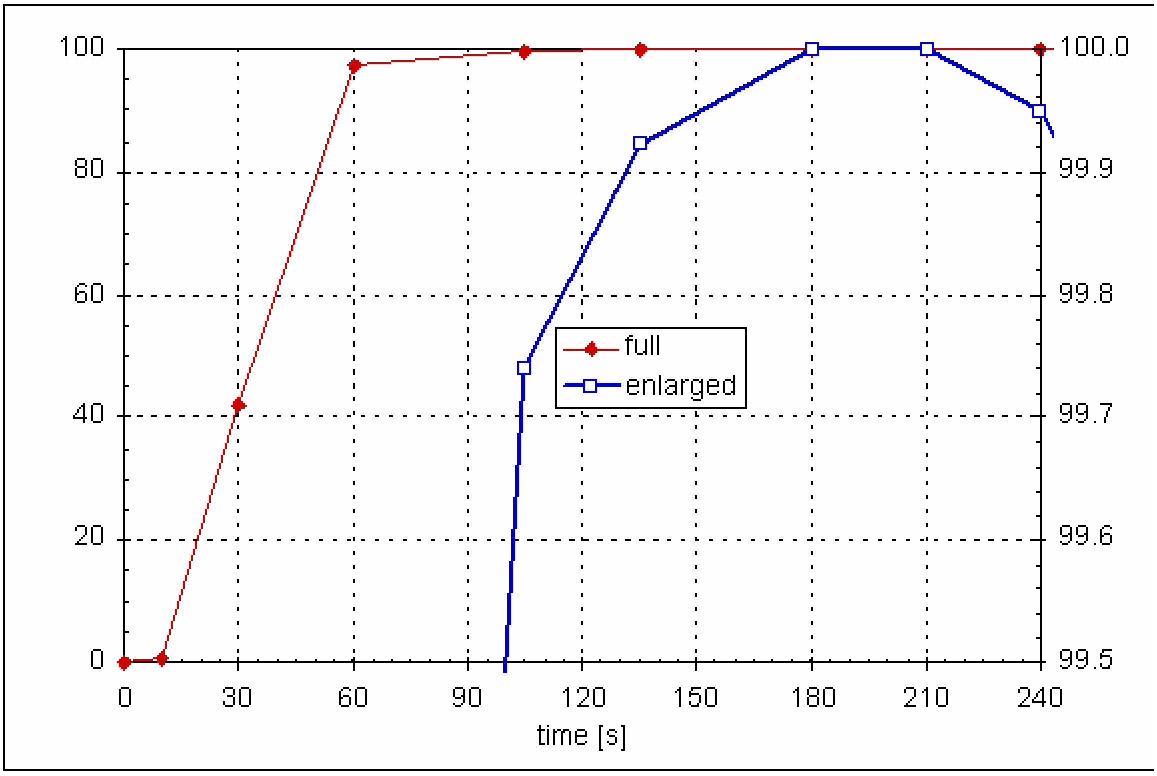

Fig. 9: Desorption time of 4He from the charcoal for a temperature of 45 K (measured on the Tritium mass spectrometer).

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).

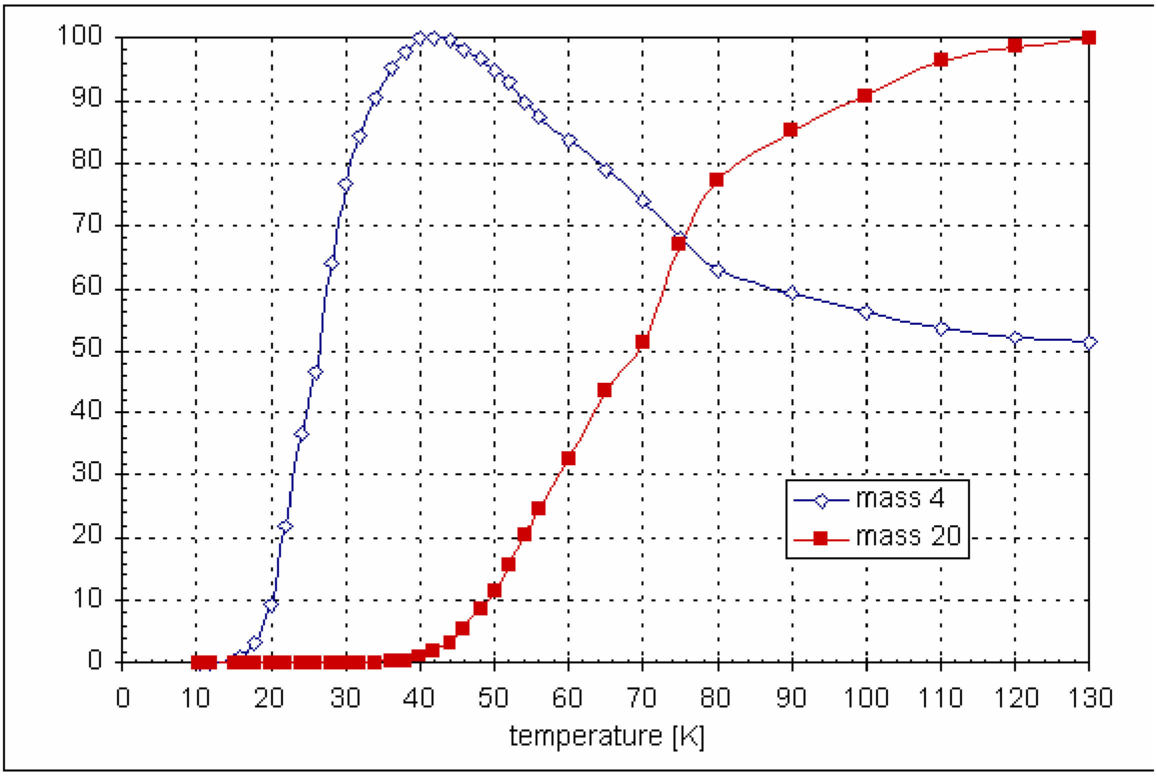

Fig. 10a: 4He discrimination by neon in the Prisma quadrupole mass spectrometer.

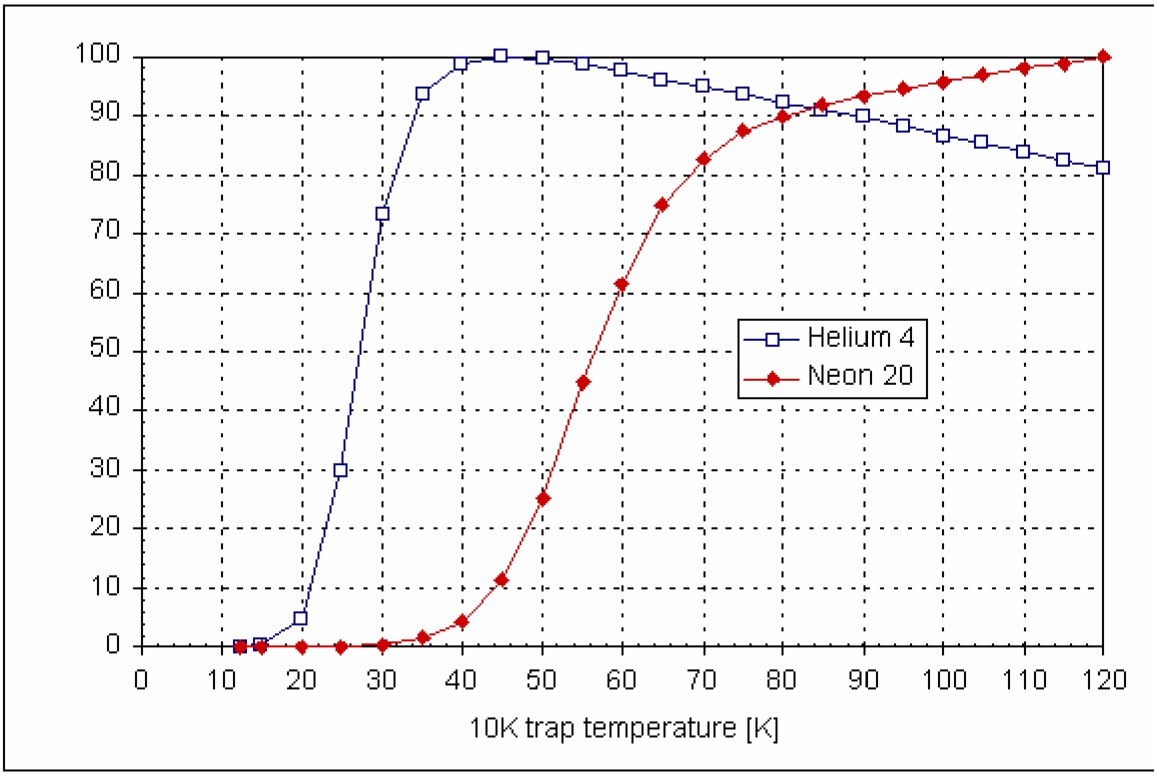

Fig. 10b: 4He discrimination by neon in the SFMS (helium isotope MS).

5. Mass spectrometer

5.1. 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.

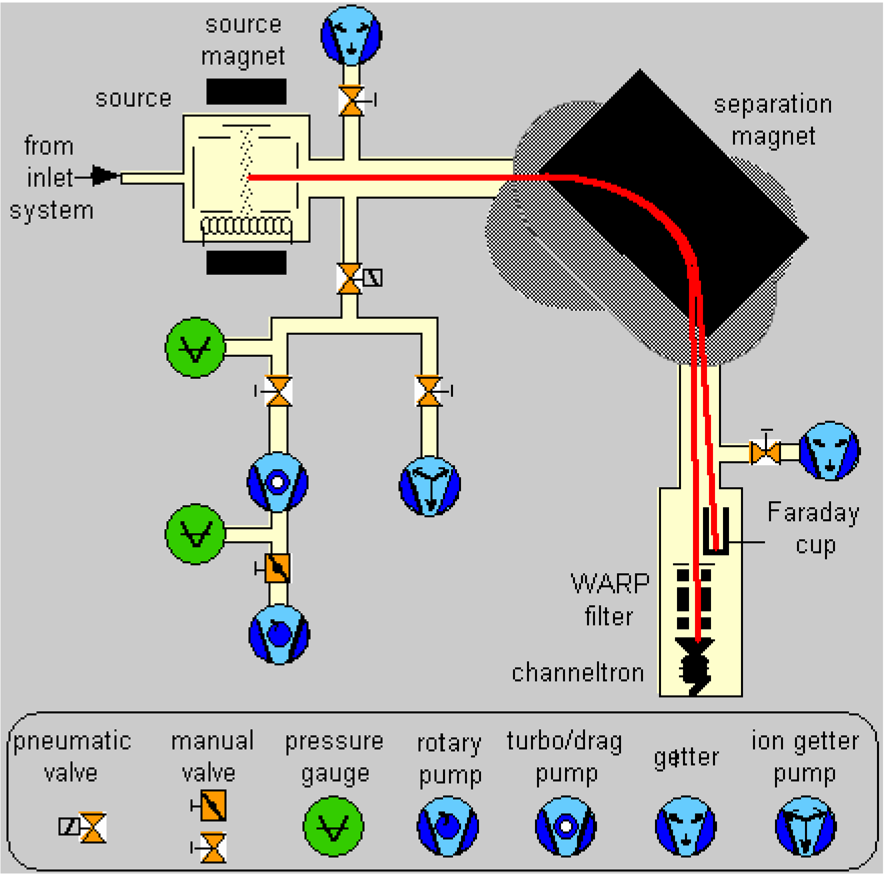

Fig. 11: Schematic diagram of the VG 5400 noble gas mass spectrometer

5.2. Vacuum system

During automated operation, the mass spectrometers are pumped between measurements of individual samples or standards by ion getter pumps (Varian, StarCell VacIon 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).

5.3. 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.

5.4. Ion detection

The ^{4}He 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 ^{4}He atoms per second.

A channeltron (Galileo, 4869 EIC) operated in the ion counting mode is used for measurement of the ^{3}He 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 ^{3}He count rate of about 2000 cps.

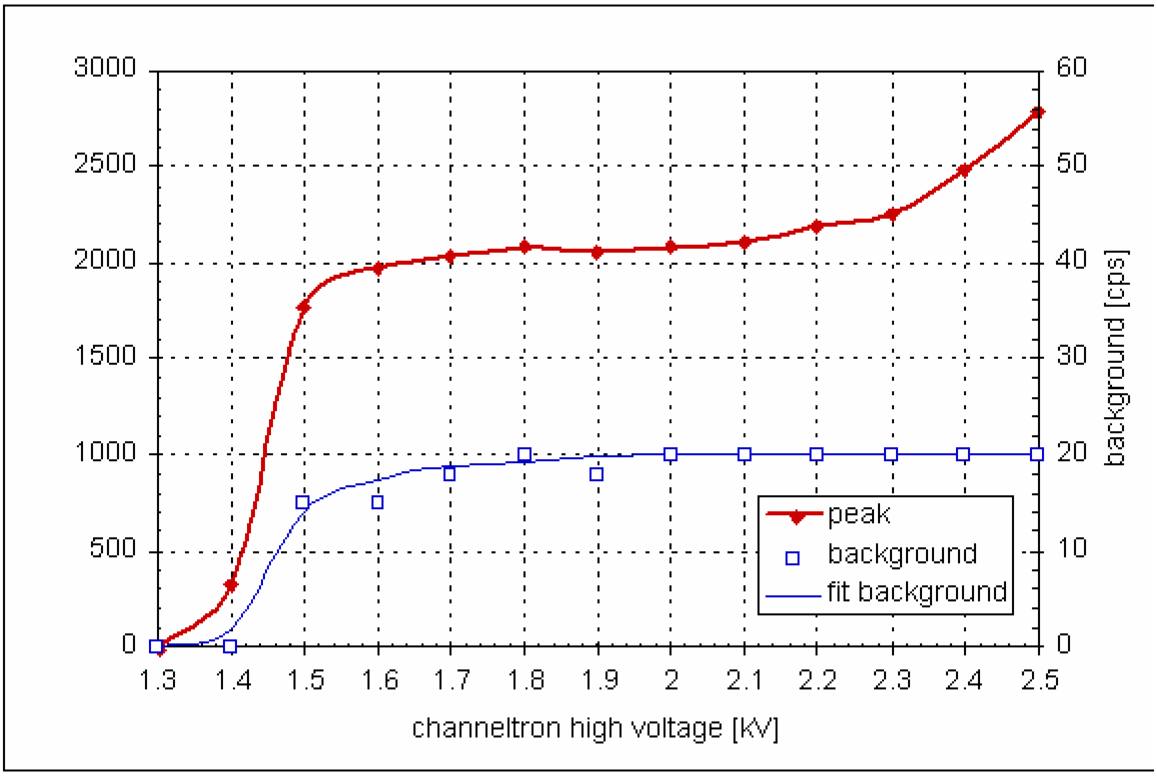

Fig. 12: Channeltron count rate versus high voltage. Note extended scale for background count rate (right Y-axis).

Before reaching the channeltron the ^{3}He 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.

5.5. 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.

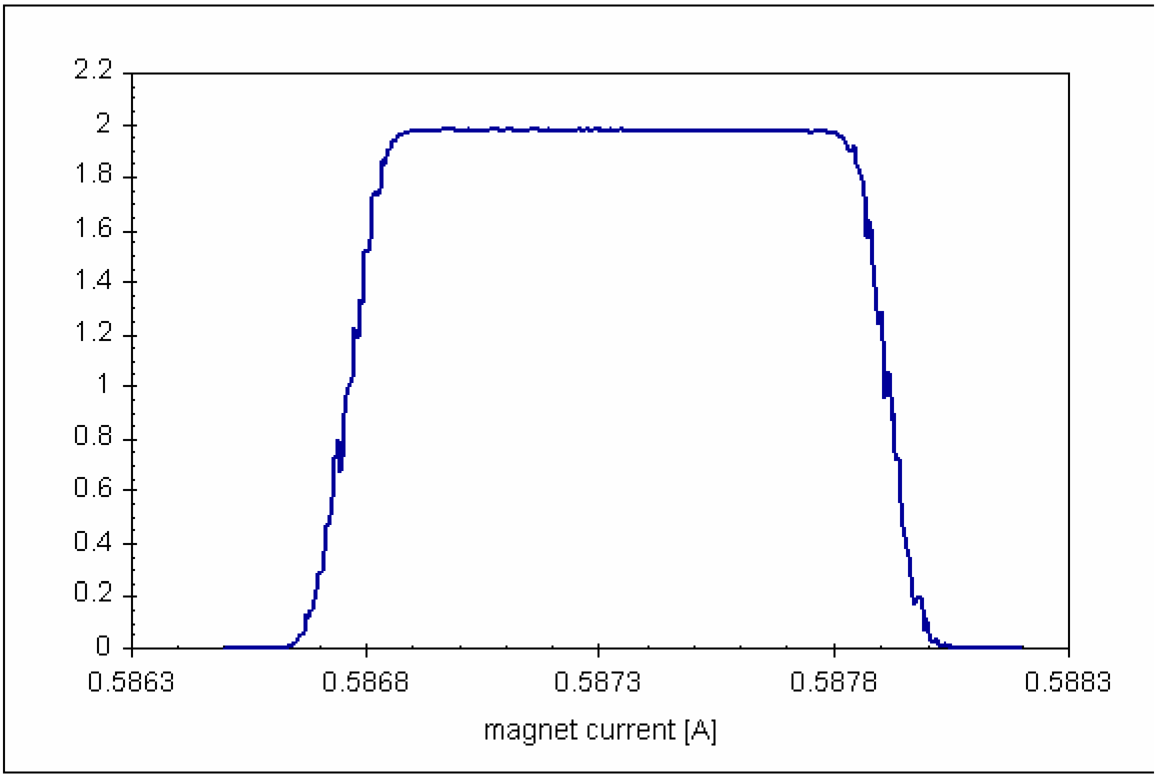

Fig. 13: 4He peak measured on the helium isotope SFMS using a Faraday cup (0.4 cm3 air standard)

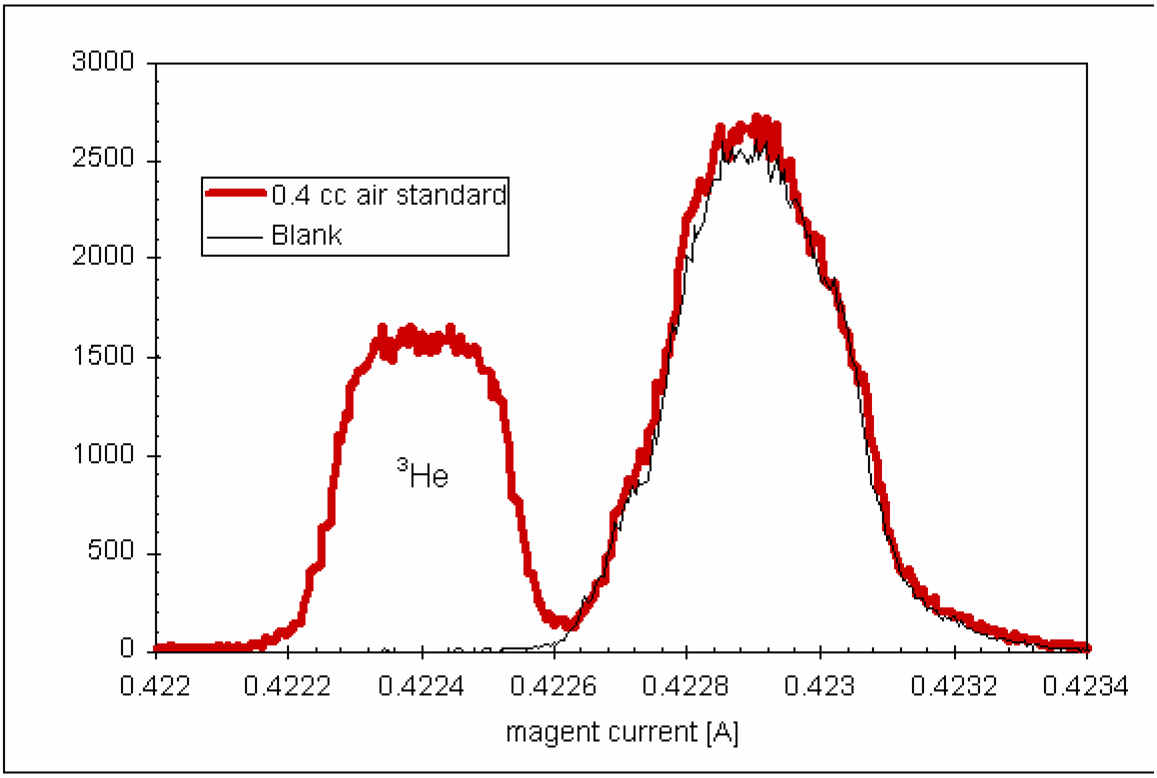

Fig. 14: 3He and HD/H3 peaks measured with a channeltron shortly after a bakeout (0.4 cm3 air standard).

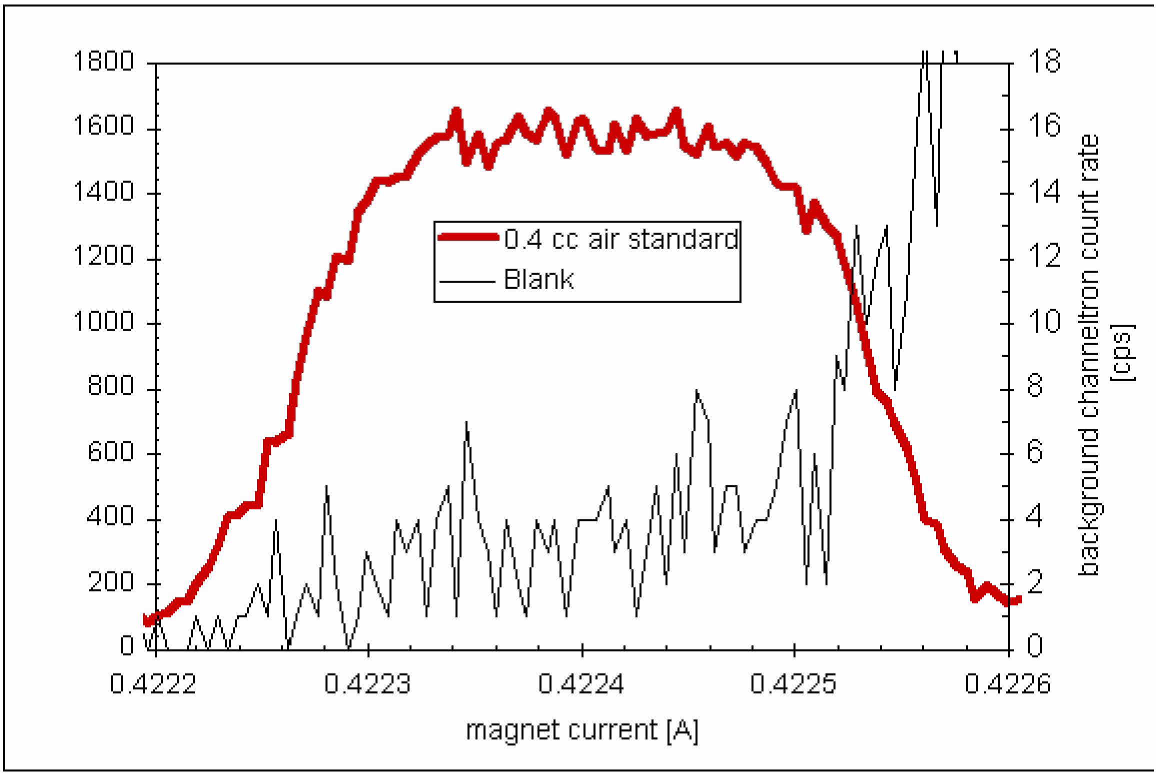

Fig. 15: 3He peak measured with a channeltron (0.4 cm3 air standard). Same 3He peak as in Fig. 4; scale for background count rate extended by a factor of 100.

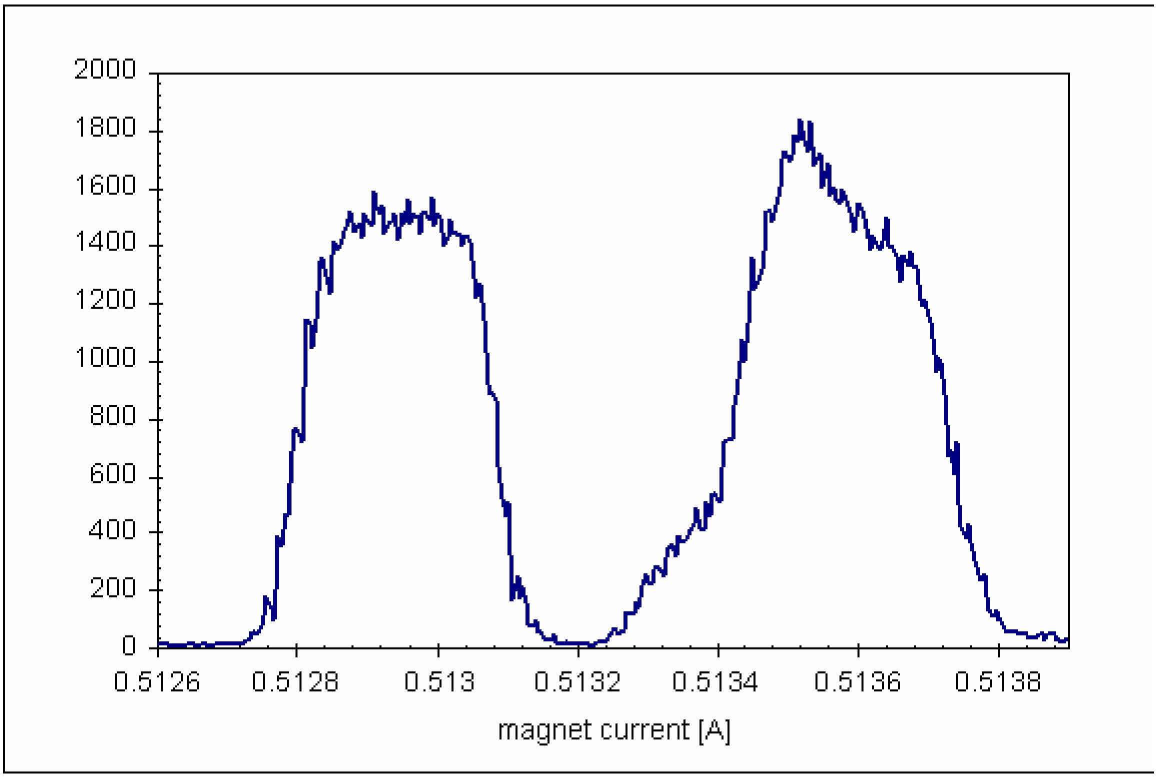

Fig. 16 3He and HD/H3 peaks measured with a channeltron 3 days after a bakeout

The ^{3}He peaks are narrower by about a factor of three compared to ^{4}He 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 ^{3}He (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 ^{3}He peak from the other peaks with mass three is an essential feature of a mass spectrometer for ^{3}He 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.

6. ^{4}He and ^{3}He/^{4}He ratio measurements

6.1. Background information

A typical 40 g water-sample is standardized by 0.4 cm^3 air standards, which contain roughly 2× 10^{-6} cm^3 STP He and 3× 10^{-12} cm^3 STP ^{3}He, corresponding to 5.6× 10^{13} ^{4}He atoms and 7.9× 10^7 ^{3}He 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 ^{4}He ions per second or 250 pA. The typical ^{3}He count rate on the channeltron is 2000 cps . With a counting time of 420 seconds, the total number of ^{3}He atoms counted on the channeltron is about 840,000 with a statistical error of ± 0.11 %. During this time, 1.4 % of all the ^{3}He atoms admitted to the mass spectrometer are counted. The ion consumption rate is about 2.7× 10^9 atoms of ^{4}He per second equivalent to 0.3 % per minute or 4 % over the measurement period (13 minutes). The memory of the SFMS for ^{4}He 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^{-06}	cm^3 STP He			
				3× 10^{-12}	cm^3 STP ^{3}He			
				5.6× 10^{13}	atoms He			
				7.9× 10^7	atoms ^{3}He			
	voltage			2.5	V			
	resistance			1.00× 10^{10}	Ohm			
	^{4}He ion current			2.50× 10^{10}	A			
	^{4}He ions per second			1.56× 10^9	^{4}He$^+$/s			
	^{3}He count rate			2000	cps			
	counting time on ^{3}He			420	s			
	statistical error			840,000	counts		± 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

6.2. 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)

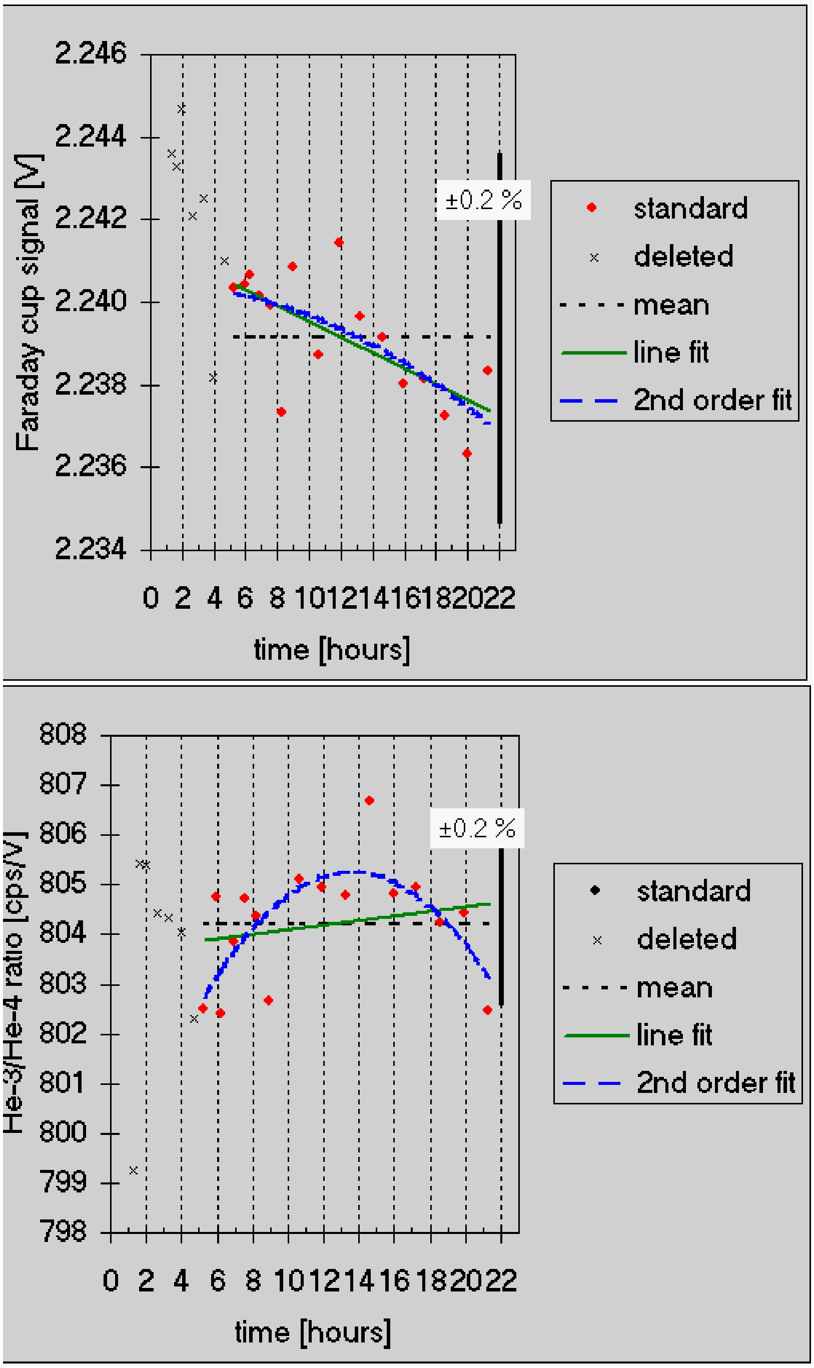

Fig. 17: Plots of 4He (a) and 3He/4He (b) standard measurements over a period of one day.

6.3. 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 ^{4}He concentration and the ^{3}He/^{4}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 ^{4}He 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 δ ^{3}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.

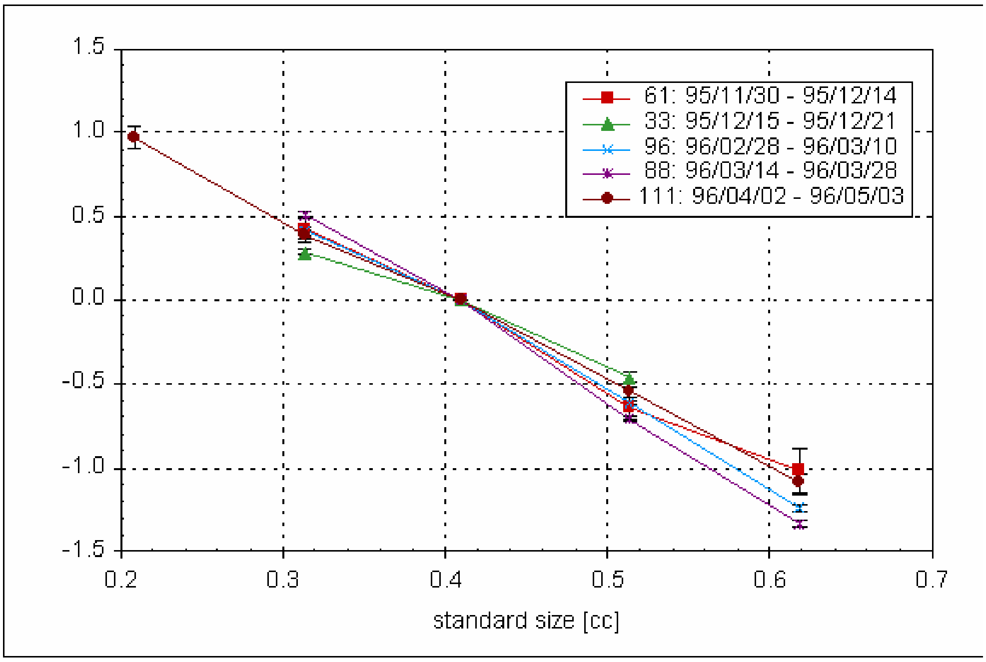

Fig. 18a: Deviation of 4He substandards from a 0.4 cm3 air standard. The numbers in the figure legend indicate the number of standards and the measurement periods. All data are collected with the same filament.

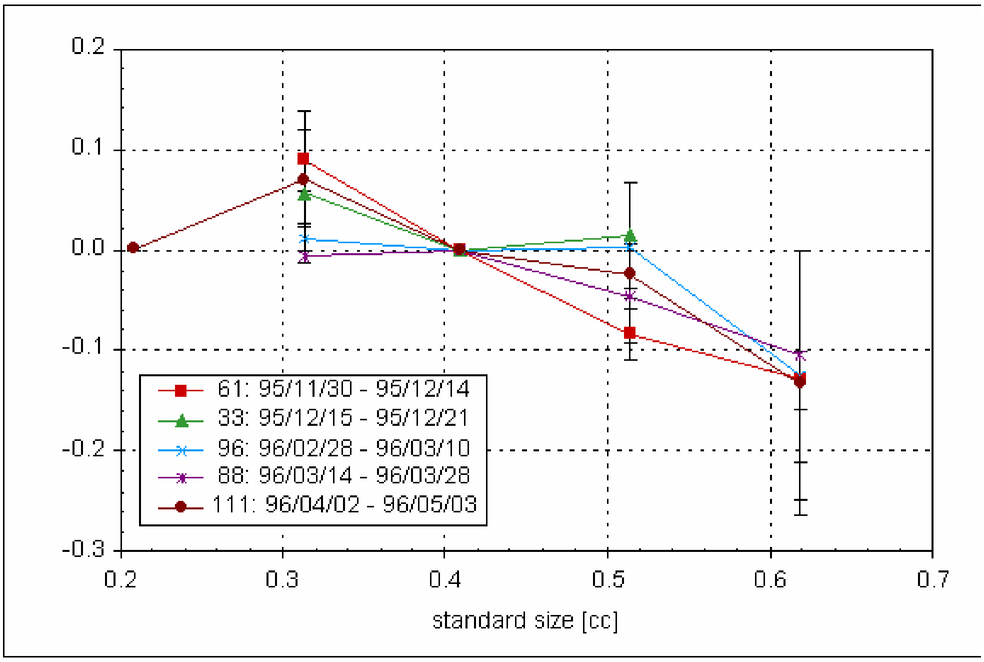

Fig. 18b: Same as 17a except for d3He.

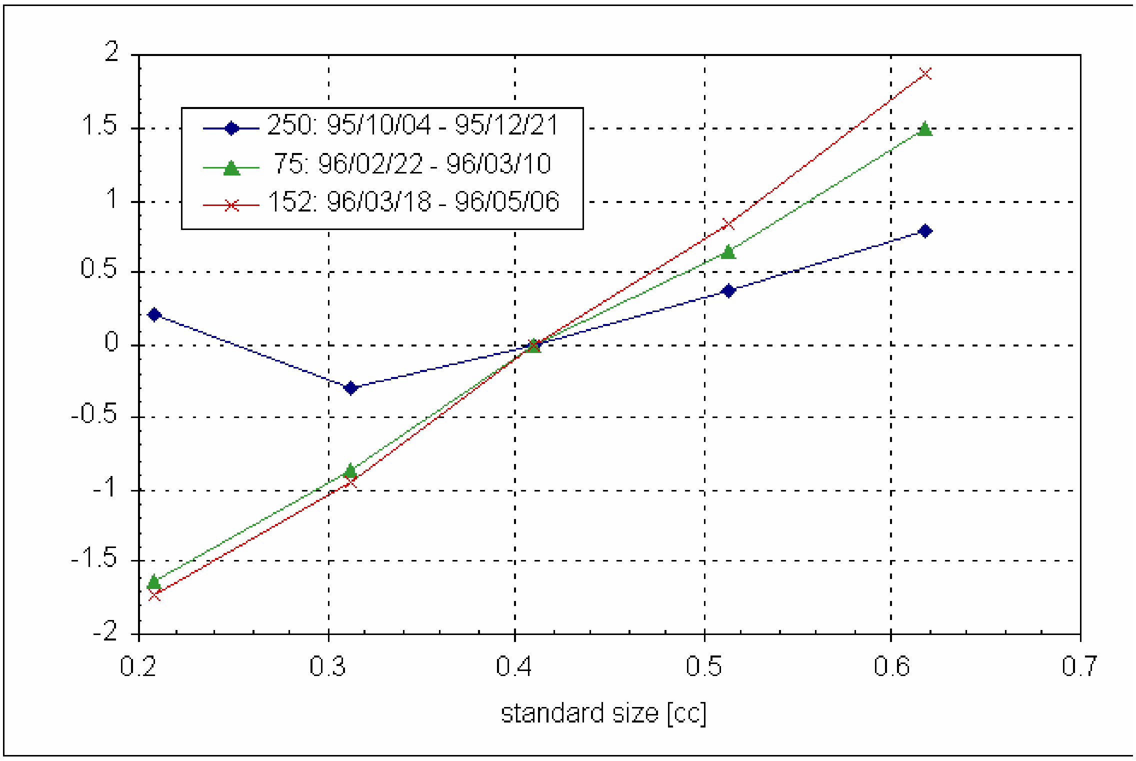

Fig. 18c: Same as 17a except for neon.

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).

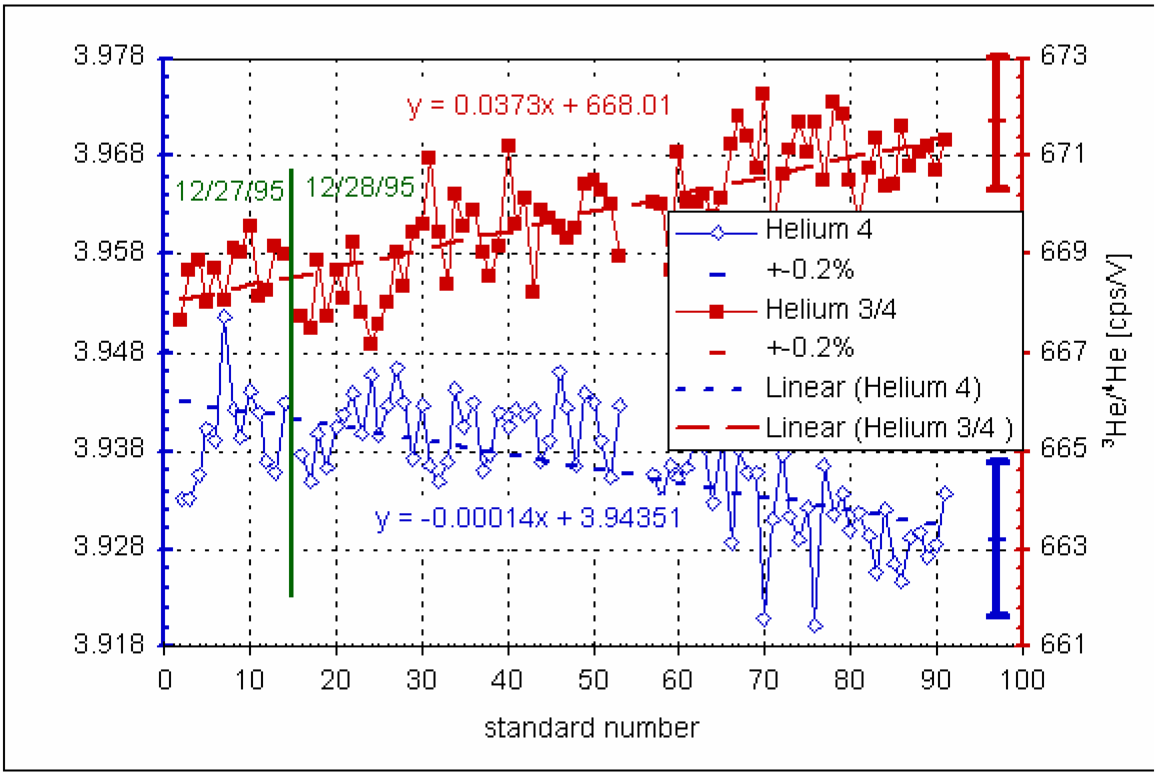

Fig. 19: Long-term stability of 4He and 3He/4He ratio measurements (86 standards). The two bars span a range of ±0.2 % of the measured 3He/4He ratios and 4He concentrations, respectively.

6.4. 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 ^{4}He and ^{3}He 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 ^{4}He peak (30 times 160 msec) to ^{4}He background (5 times 160 msec), ^{3}He peak (42 times 1 sec), and finally ^{3}He background (12 times 1 sec).

For evaluation of the raw data, we use the linear fit of the net ^{4}He signal (peak minus background) extrapolated to the inlet time and the net mean value of the ^{3}He 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

7. Tritium Measurements

7.1. Background information

A typical 400 g water sample with a tritium concentration of 0.2 TU contains 4.5×10^{-15} 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 ± 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.

7.2. 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 $^3He/^4He$ 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:

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

c_{trit} tritium concentration in TU

$^3He_{trit}$ 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}H/H fractionation due to loss of (distilled) water during gas extraction. α = 1.15 (ratio of tritium concentration in the liquid phase to tritium concentration in the water vapor (Clarke et al., 1976)

7.3. 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 (^{4}He) and count rates (^{3}He) into helium concentrations. The fit curves generally intercept the y axis at the measured blank (line blank plus memory) values.

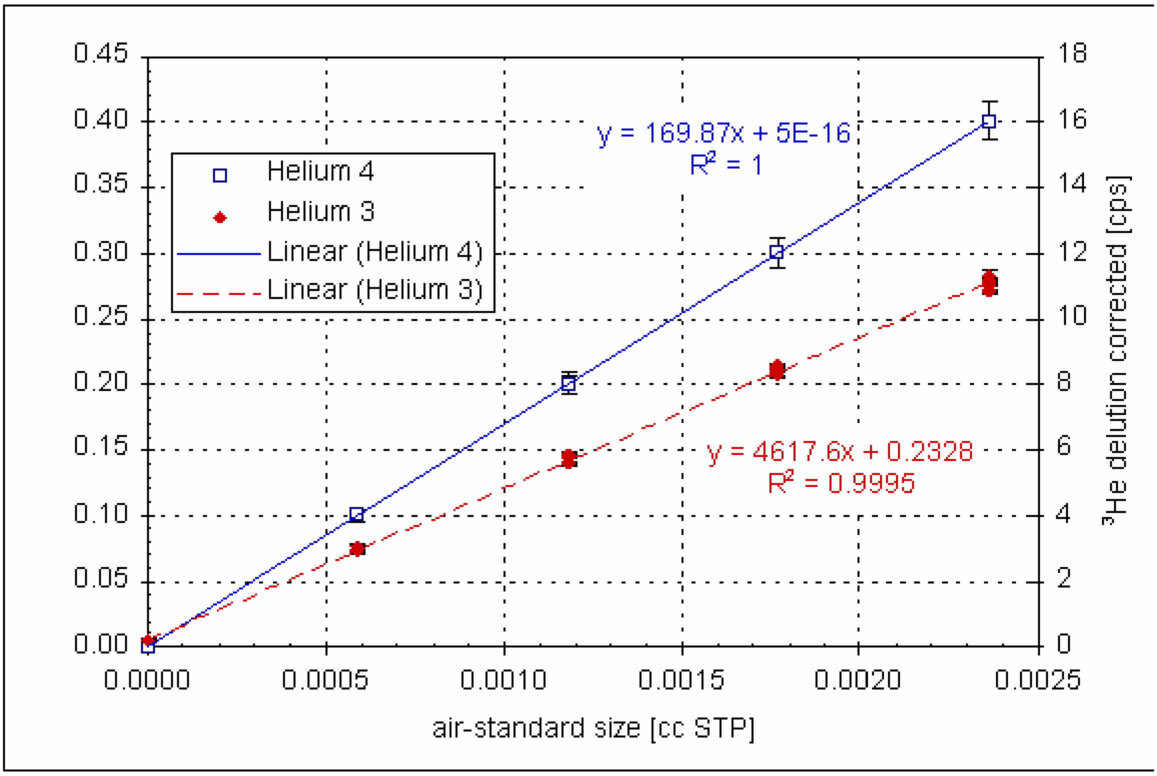

Fig. 20: 3He and 4He Linearity for a total of 93 measurements of diluted air standards and blanks

7.4. Blank

The low ^{3}He concentrations in tritium samples make them extremely sensitive to contamination. Measurement of the ^{4}He contained in the tritium samples allows us to subtract the ^{3}He 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 ^{3}He 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 tritiogenic ^{3}He concentration.

	NET	#	^{4}He	±	^{3}He	±	^{3}He/^{4}He	±	
			[cm^3 STP]	[%]	[cm^3 STP]	[%]	[to air 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 ^{3}He during the sample processing or measurement process. This includes incomplete gas extraction of the tritium sample, addition of ^{3}He through diffusion through O-rings in the extraction laboratory and in the mass spectrometer laboratory, or leaks in the vacuum system.

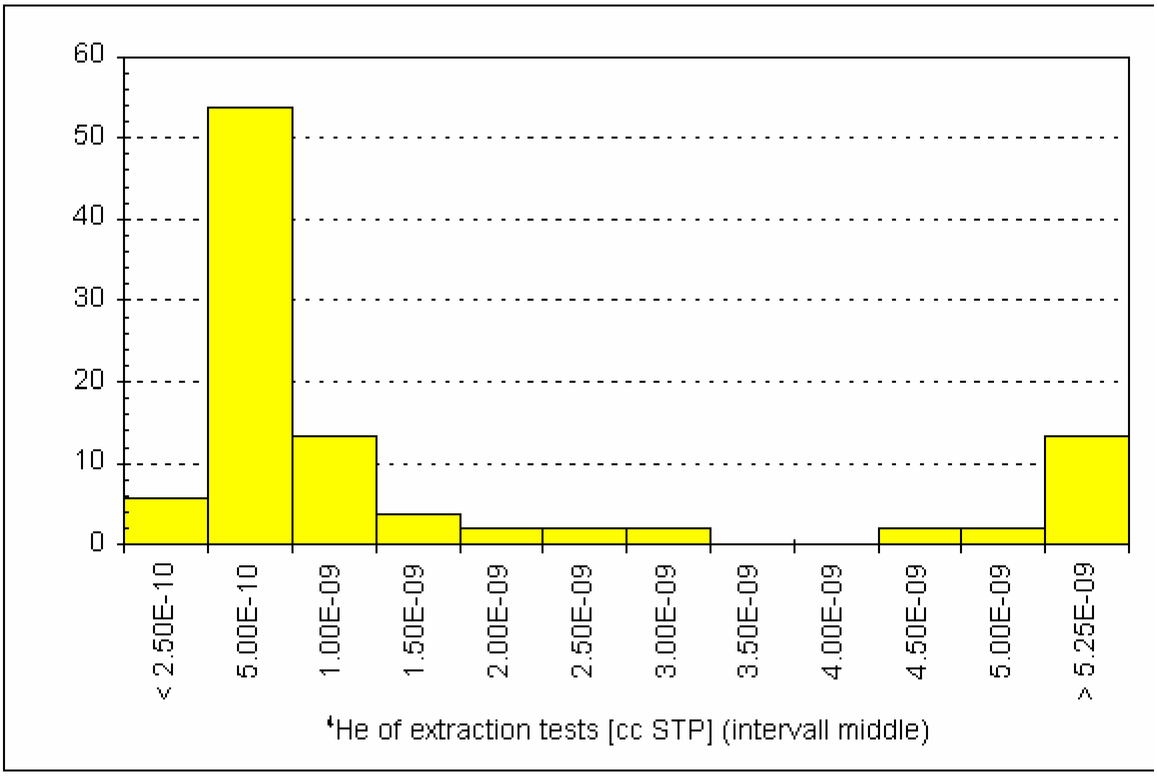

Fig. 21: 4He blanks of 52 large bulbs including 5 minutes of O-ring contribution (1 l bulbs with 400 g of water).

7.5. 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 ^{3}He 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 7×10^{-10} cm^3 STP ^{4}He for a 40 g samples and 99.995 % for a 400 g samples, respectively. These ^{4}He amounts correspond to 9.7×10^{-16} cm^3 STP ^{3}He, if we assume an atmospheric ^{3}He/^{4}He ratio.

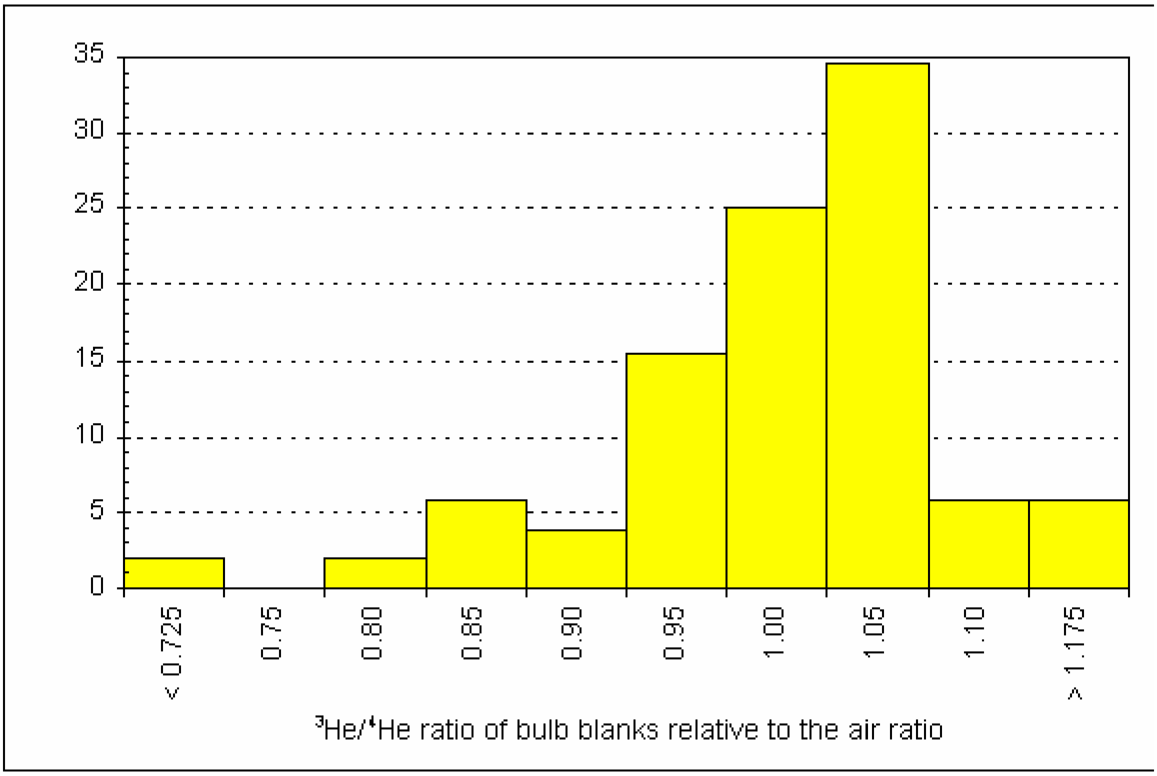

Fig. 22: 3He/4He ratio of 52 blanks measured in large bulbs. The average is 1.00 ± 0.09 times the air ratio.

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

Addition of helium during the storage of the water sample for ^{3}He 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 ^{o}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 cm^3; surface: 500 cm^2) have a ^{4}He blank approximately 10 times higher than that of the small bulbs (volume: 200 cm^3; surface: 170 cm^2; Fig. 23). The ^{4}He 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} cm^3 STP (small bulbs) and 1×10^{-8} cm^3 STP (large bulbs).

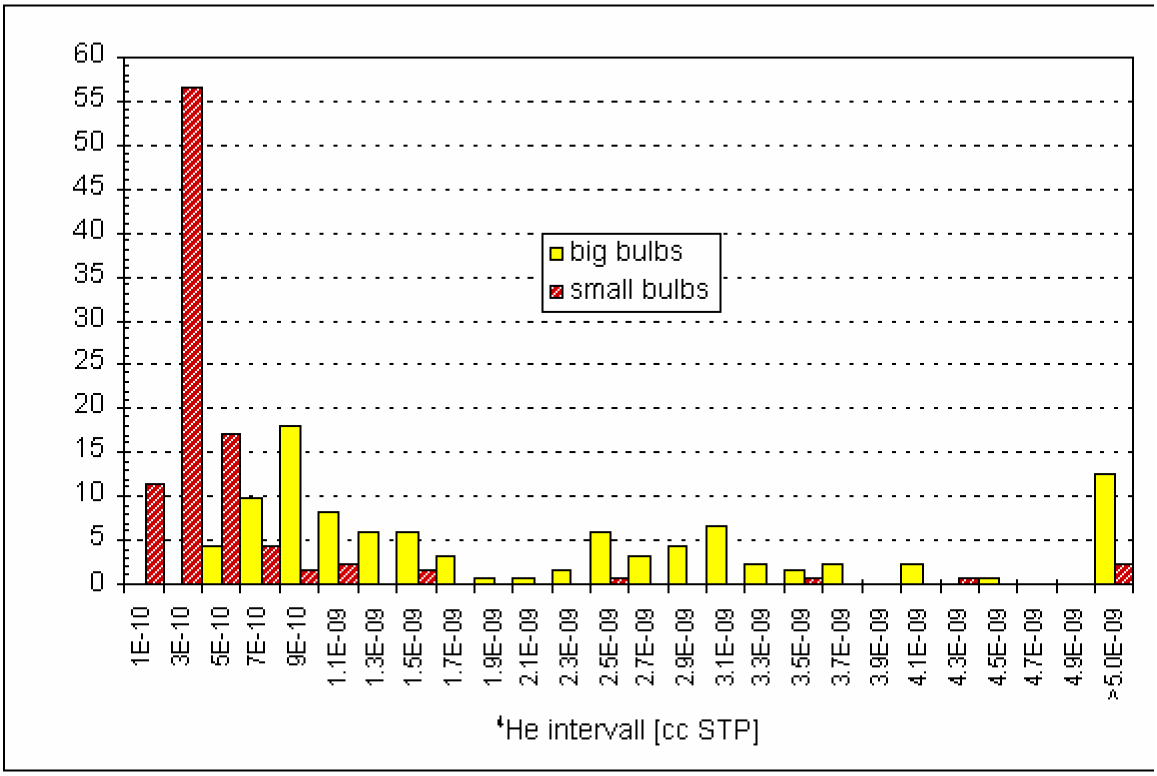

Fig. 23: 4He Blanks of 122 small bulbs extracted on the helium extraction system and of 299 large bulbs extracted on the tritium extraction system.

7.6. 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 ^{4}He and ^{3}He 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} cm^3 STP ^{4}He for 36 minutes corresponding to 2×10^{-10} cm^3 STP for samples with 5 minutes transfer time or 7×10^{-13} cm^3 STP ^{4}He per second. The fact that there is no significant trend in the ^{4}He 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}He/^{4}He ratio distribution is plotted as histogram in Fig. 25. The mean value is 1.00 ± 0.06 times the ^{3}He/^{4}He ratio of air.

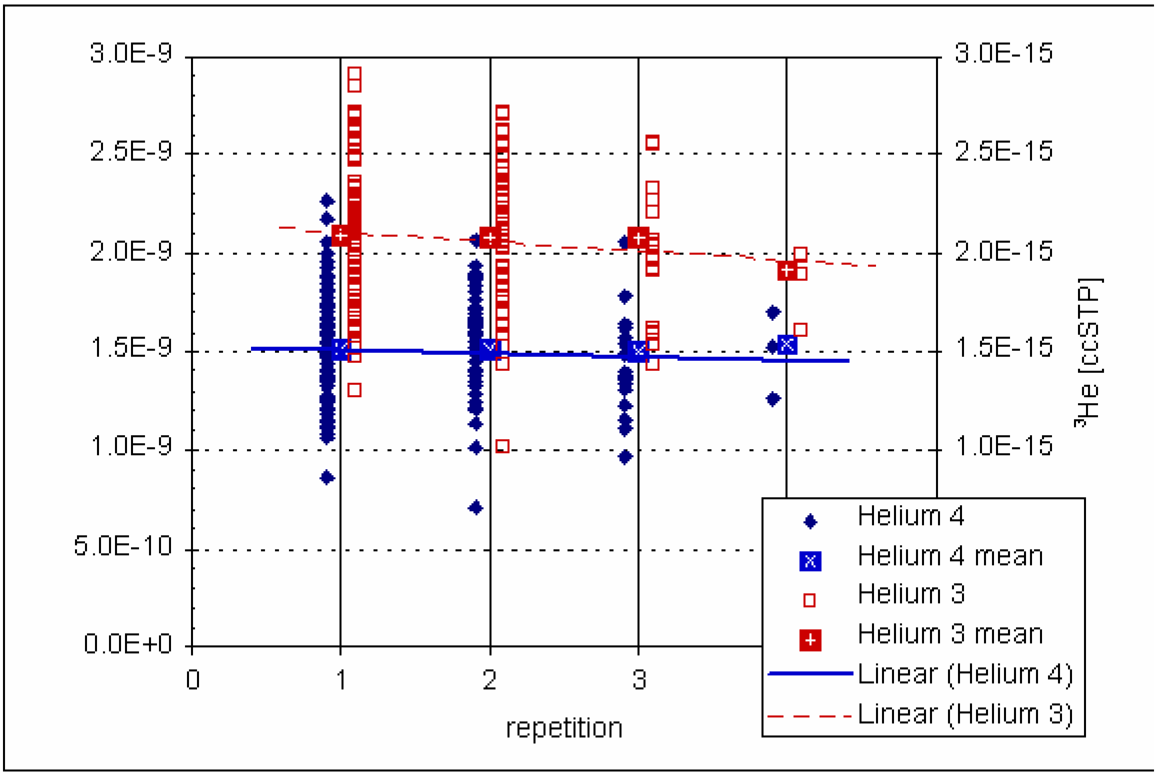

Fig. 24: 153 repeat measurements of 4He and 3He (large bulbs). The data are a check of the transfer efficiency of helium from the glass bulbs into the inlet system. Additionally, they are used to determine the diffusion rate of helium through wet O-rings.

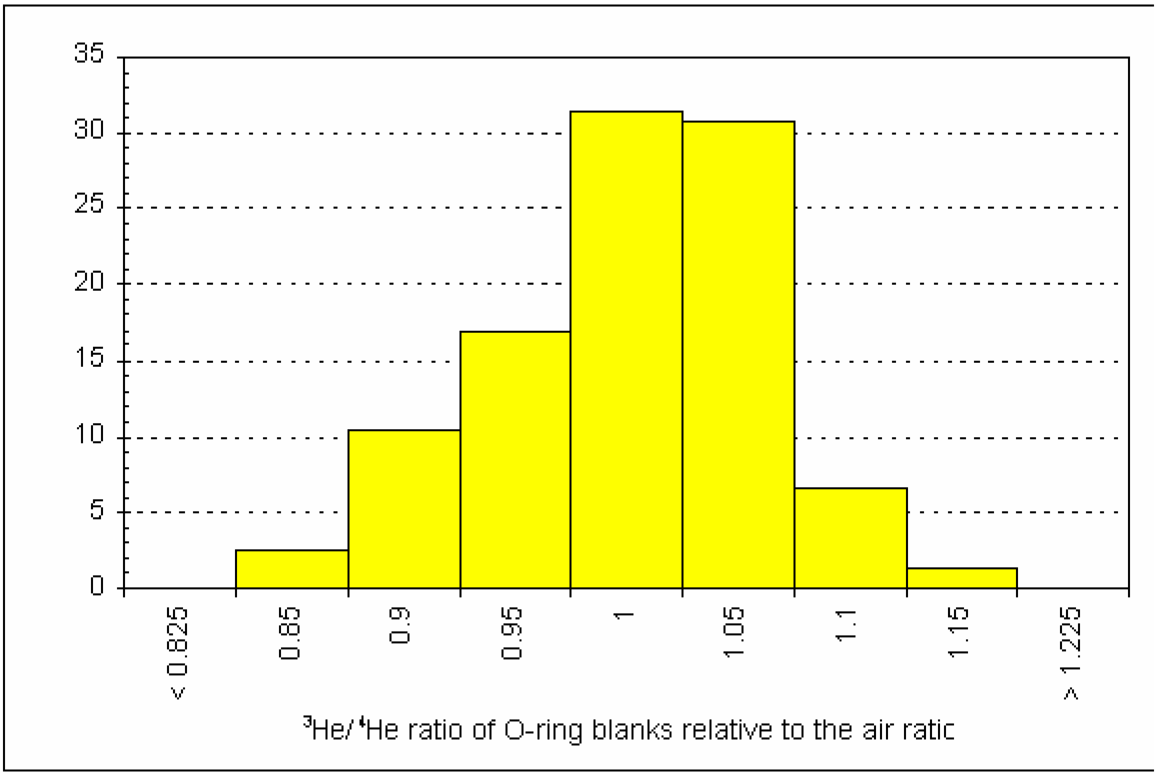

Fig. 25: 3He/4He ratio of 153 repeat measurements of the bulb blank of large bulbs.

In Fig. 26, four different types of blanks for ^{3}He and ^{4}He 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

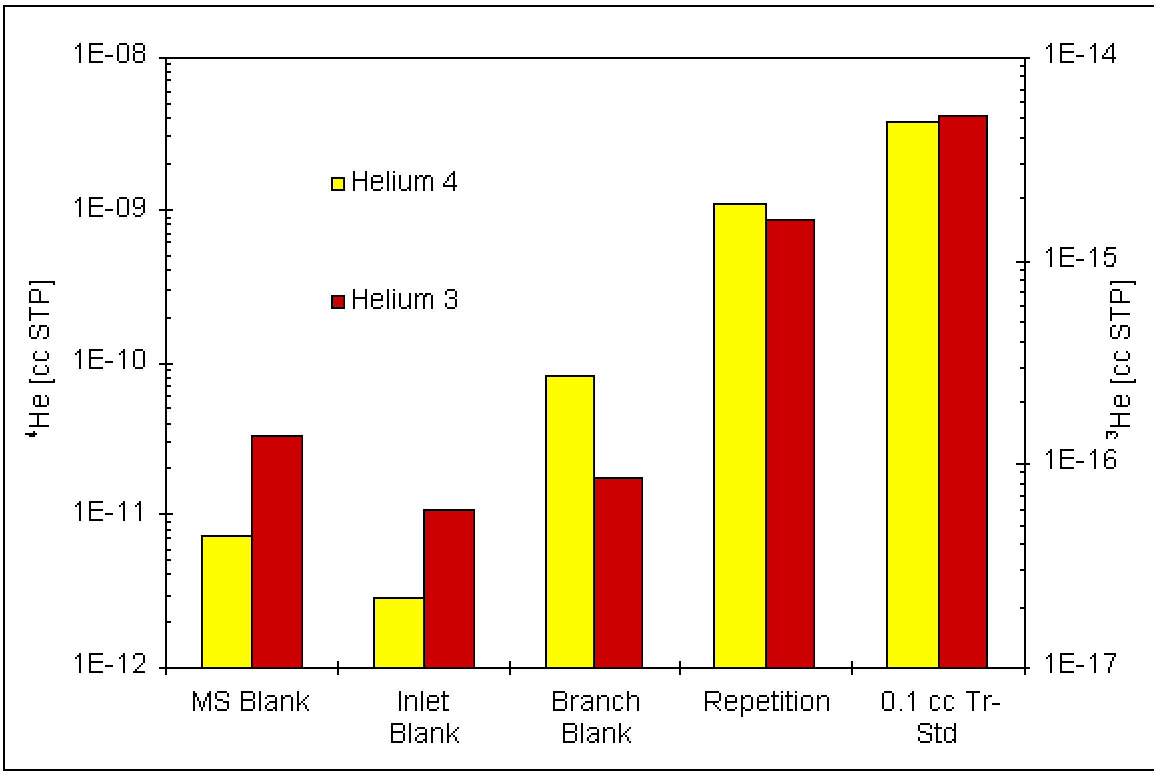

Fig. 26: Comparison of MS-, inlet system-, branch-, and repeat- measurement blanks. The 3He and 4He amounts contained in a 0.1 cm3 air standard diluted by a factor of 160 are plotted for comparison.

7.7. Measurement procedure

The procedures of measuring tritium via the ^{3}He 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 ^{3}He 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 ^{3}He signal, we use the HD/H_3 peak as indicator for the location of the ^{3}He peak. For this purpose, we determine the center of the HD/H_3 peak. The ^{3}He peak center is then determined by a predefined offset from the HD/H_3 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 m^3 pipette (approx. 160 time diluted).

Measurement of ^{4}He and ^{3}He is divided into ten intervals (Tab. 3). During each interval the magnetic field is set to the masses of ^{4}He (5 times 1280 msec), ^{4}He background (5 times 1280 msec), ^{3}He (120 times 1 sec), and ^{3}He 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 ^{4}He measurements extrapolated to the time of sample inlet and the background-corrected ^{3}He count rates are used. Following this procedure, a tritium measurement requires 36 minutes.

8. Acknowledgements

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