A Mass Spectrometric System for the Analysis of Noble Gases and Tritium from Water Samples

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The design, setup, and performance of a mass spectrometric system for the analysis of noble gas isotopes (^{3}He, ^{4}He, ^{20}Ne, ^{21}Ne, ^{22}Ne, ^{36}Ar, ^{40}Ar, ^{84}Kr, ^{136}Xe) and tritium (^{3}H) from water samples are described. The ^{3}H concentration is measured indirectly by the ^{3}He ingrowth from radioactive decay. After extraction, purification, and separation, the noble gases are measured in two noncommercial double-collector 90° magnetic sector mass spectrometers. We present a new approach for the analysis of the heavy noble gas isotopes that enables, in principle, simultaneous measurement of Ar, Kr, and Xe. Typical precisions of the measurements of ^{3}H, He, Ne, Ar, Kr, and Xe concentrations are ±2.7%, ±0.3%, ±0.9%, ±0.3%, ±0.8%, and ±1.0%, respectively. For the isotopic ratios ^{3}He/^{4}He, ^{20}Ne/^{22}Ne, and ^{40}Ar/^{36}Ar the typical precisions are ±0.7%, ±0.3%, and ±0.2%. These values express the reproducibility of the measurement of an internal freshwater standard and include the overall stability of the system as well as of the extraction procedure. To verify the method, the noble gas concentrations of air-saturated water samples prepared under controlled conditions are compared with noble gas solubility data. The ^{20}Ne/^{22}Ne and ^{36}Ar/^{40}Ar fractionation during solution is estimated from 70 surface water samples to be −2.0 ± 0.2‰ and −1.3 ± 0.2‰, respectively.

Introduction

The noble gas isotopes of He, Ne, Ar, Kr, Xe and the hydrogen isotope tritium are widely used as environmental tracers to study the dynamics of natural water systems such as the ocean, lakes, and groundwaters. Tritium (^{3}H, half-life 12.38 yr, (*1*)) in combination with its decay product ^{3}He enables the determination of the mean water residence time or "water age". The ^{3}H/^{3}He dating method is used in oceanography and limnology (e.g., refs *2*—*5*) to study the circulation of water masses and large-scale mixing processes. Applied to groundwater systems, the ^{3}H/^{3}He water age is used to determine

recharge rates, groundwater flow velocities, and mixing ratios (*6, 7*). In addition, radiogenic production of ^{4}He (from U and Th decay series (*8*)), of ^{40}Ar (from ^{40}K decay (*9*)), or even of ^{21}Ne (from α-induced nuclear reactions (*10*)) in rocks and subsequent accumulation in groundwater offers the possibility to derive estimates of groundwater residence times up to millions of years.

Since noble gases are chemically inert under natural conditions, they are ideal tracers. In water the concentration of dissolved atmospheric noble gases is determined by the temperature and salinity of the water and the atmospheric pressure. Hence the noble gas concentrations of a water body isolated from the atmosphere provide information about the conditions prevailing during gas exchange with the atmosphere (*11*). In old groundwater, the measured concentrations of atmospheric noble gases are used to deduce paleotemperatures back to the last glacial period (*12*—*14*).

Mass spectrometric methods to measure He isotopes and ^{3}H in water have been outlined by several authors (*15*—*21*). In this contribution a combined system is described for the measurement of ^{3}H (using the ^{3}He ingrowth method) and the most abundant isotopes of all stable noble gases (He, Ne, Ar, Kr, Xe) in water samples. We present a new approach for the analysis of the heavy noble gas isotopes that enables, in principle, the simultaneous determination of Ar, Kr, and Xe and that minimizes the problem of eliminating interfering gases. Further new aspects of our method are the direct high-vacuum connection of the sample container (copper tube) to the extraction line and the reuse of the same container and sample for the ^{3}H analysis, avoiding the use of glass ampules and O-ring connections. The analytical precision of the technique is derived from the stability of calibrations and verified by repeated measurements of an internal water standard. The accuracy is checked by comparing noble gas concentrations of air-equilibrated water samples with published solubility data.

Experimental Section

The determination of noble gas and ^{3}H concentrations in natural water samples requires several steps. Water samples are collected in the field in appropriate containers. In the laboratory the dissolved gases are extracted from the water. After purification and separation the noble gases are measured mass spectrometrically. The completely degassed water samples are resealed in the original container, and a few months later the ^{3}He produced by decay of ^{3}H is analyzed.

Sampling. As noble gases are highly volatile it is extremely important to avoid gas exchange between the water sample and the atmosphere during sampling, transport, or storage. Samples from oceans or lakes can be collected with the aid of Niskin bottles. In the case of supersaturated lake or seawater (e.g. high CO_2 concentrations), we also use an in situ sampling technique to seal samples under water (*22*). Since groundwater is commonly supersaturated with respect to atmospheric gases—known as excess air phenomenon (*23*)—and may contain excesses of subsurface produced gases (e.g. CO_2, CH_4, He), it is essential to keep the groundwater under pressure during sampling to avoid degassing. Sufficient pressure can usually be achieved by the use of submersible pumps and tight connections.

In any case the water has to be transferred as fast as possible into sealed containers. Usually about 45 g of water is filled in copper tubes which are mounted on an aluminum channel with adjustable length and with stainless steel pinch-off clamps at either side (Figure 1). To avoid any air bubbles being generated or captured during sampling the copper

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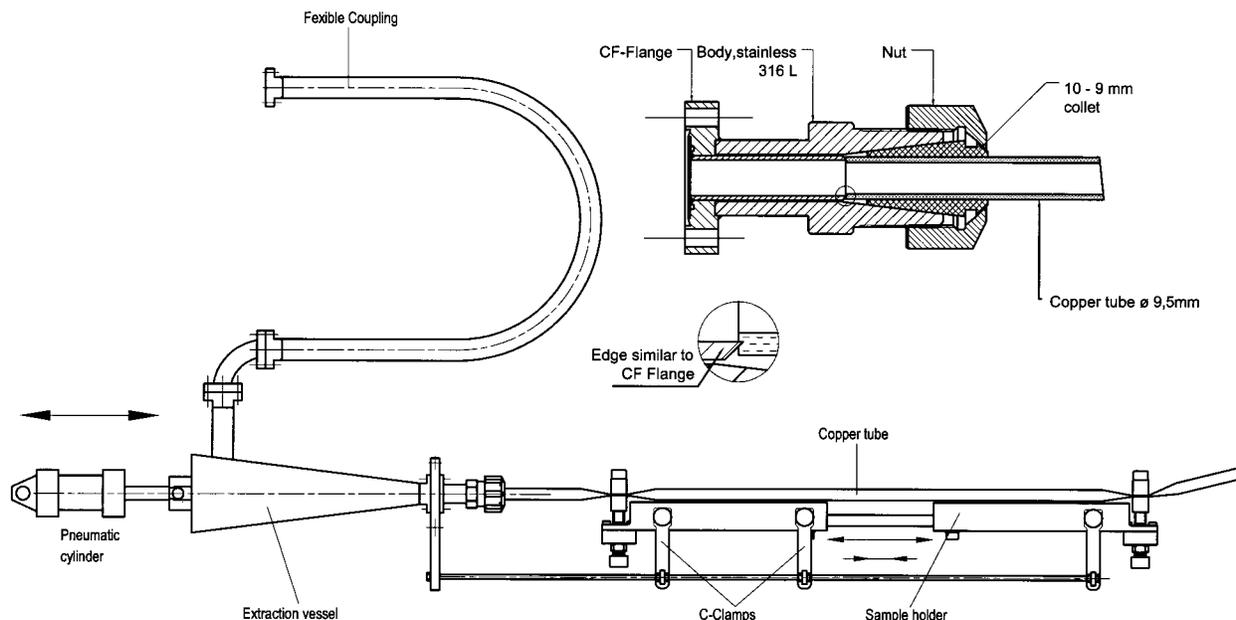‡ Isotope Geology, Department of Earth Sciences, Swiss Federal Institute of Technology (ETH).

FIGURE 1. Drawing of the sample container and its connection to the extraction vessel and line. The copper tube (internal diameter 7.7 mm) is mounted on a sample holder (steel clamps on aluminum channels with a sliding connection). The distance between the clamps is either 1 m (usual 45 g water samples) or 0.5 m (22 g samples) and can be reduced by a few cm to open and reseal the copper tube. For UHV-tight connection to the extraction vessel (stainless steel, volume $\approx$ 500 cm^3) the front of the copper tube is pressed onto a cutting edge (see enlargements). An external stiff support links the vessel and sample holder to avoid relative movements during extraction, when the entire setup is shaken by a pneumatic cylinder. A metal bellows (length $\approx$ 1 m) provides a flexible connection to the extraction line. For further details see ref *24*.

tube is rinsed thoroughly. Afterward, the pinch-off clamps are closed to seal off the tube. The sample can now be stored without any significant gas loss or gain. Even for the most mobile gas, He, the maximum leak rate to vacuum is smaller than 10^{-9} cm^{3}STP yr^{-1} (*24, 25*), whereas the amount of He in the copper tube is typically $2 \cdot 10^{-6}$ cm^{3}STP for surface waters and can be orders of magnitude higher for groundwaters.

For low-level or high-precision ^{3}H measurements about 1 L of water is sampled. In the laboratory, the water is transferred to a full-metal stainless steel bottle with a copper tube neck. After gas extraction, the copper bottleneck is tightly closed using a clamp. Several months later the ^{3}He produced by the decay of ^{3}H is measured.

Gas Extraction. To quantitatively extract the noble gases from the water sample, the copper tube is directly connected to the ultrahigh vacuum (UHV) extraction and purification line by means of a device which presses the front of the copper tube UHV-tight onto a metal cutting edge (Figure 1) (*24*). Note that in contrast to the common extraction procedure (*18−21*), our system does not use any O-ring fittings and glass ampules. This design minimizes air contamination during extraction and storage and eliminates the work, cost, and risk involved in glass handling.

Figure 2 illustrates the setup of the extraction and purification line. The line consists of stainless steel tubes (diameter 19 mm) connected with Varian ConFlat flanges. Valves are either manually operated Nupro SS-4H-TSW (N) and all-metal Varian 9515014 valves (VM) or pneumatically actuated Varian valves (V). The automatic valves are controlled by the two mass spectrometer computers. For cleaning the whole line can be heated to 300 °C.

A cascade of pumps produces the UHV in the extraction vessel (EX). First, a diaphragm pump (DP1, Vacuubrand MZ4) is used to remove the water vapor from the system. Second, a rotary pump (RP1, Welch 1400) produces a rough vacuum of about 10^{-1} mbar. Finally, a combination of a diaphragm (DP2) and turbomolecular pump (TP2, Pfeiffer TPU 050) reduces the pressure to about 10^{-7} mbar. After establishing

UHV, the extraction line is separated from the vacuum pumps (close valves N4, VM8, VM8a, Figure 2). Then the pinch-off clamp (PC1) of the copper tube on the UHV-system side is opened, and the sealed part of the copper tube is reopened by a special pair of pliers (*24*). The use of pure copper guarantees that the tube can be reopened without breaking. Subsequently the water is transferred from the copper tube into the extraction vessel, which is connected to the extraction line by a flexible metal bellows (MB) (Figures 1 and 2). To enhance the removal of the gases from the water phase the extraction vessel is shaken mechanically to produce turbulence in the molecular boundary layer of the water and to enlarge the active surface area of gas exchange.

The water vapor and the extracted gases are adsorbed on an all-metal trap (T1) and a trap filled with zeolite (ZEO1, Varian, molecular sieve of 5 Å pore diameter), both cooled by liquid nitrogen. Water vapor is adsorbed mainly on T1 (less than 0.5 g during the entire extraction procedure). The adsorption of the condensable gases maintains a strong pressure gradient between the extraction vessel and the traps, inducing a continuous flow of water vapor and extracted gases. This flow is controlled by a capillary (C) (internal diameter 0.5 mm, length 2 cm), which reduces the amount of transported water vapor and increases the flow velocity in order to prevent back diffusion of noncondensable gases (such as He and Ne). The pressure in the extraction line can be monitored by 3 Pirani cells (P1 − P3, Edwards PRM 10), allowing the detection of large leaks and the control of the removal efficiency of condensable gases. All along, the capillary and the metal bellows are gently heated (50 °C and 30 °C, respectively) to prevent condensation of water vapor and thus guarantee a complete gas extraction. After 5 min, the gas extraction is terminated by closing the valve just before the capillary (V8). For He, the extraction efficiency is higher than 99.995% (*25*).

He−Ne Measurement. After extraction the gas remains exposed to the cold trap and the zeolite for 10 min to ensure complete adsorption of the condensable gases, whereas
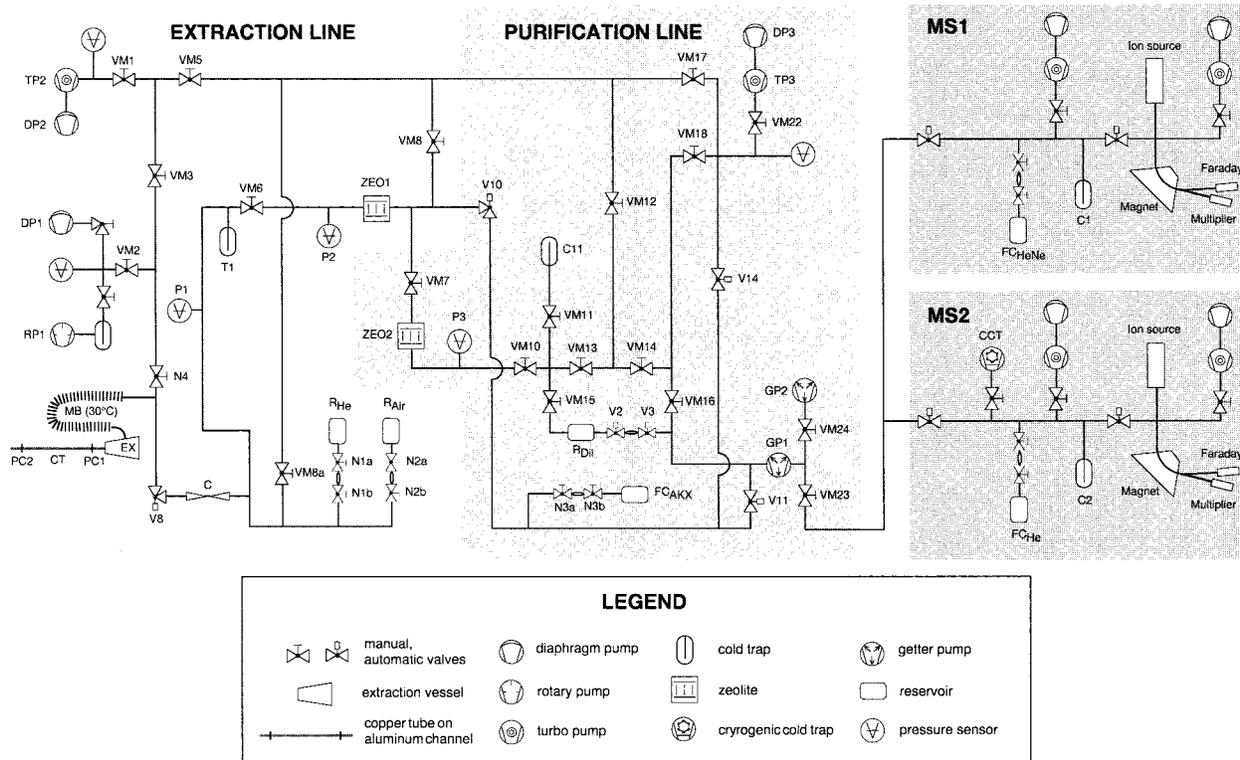
FIGURE 2. Schematic diagram of the extraction and purification line and the two mass spectrometers MS1 and MS2. Abbreviations see text.

noncondensable gases, mainly He and Ne, remain in the gas phase. Then the extraction line is connected to the purification line (open V10), where all remaining active gases are caught in two getter pumps (GP1, Zr−Ti bulk getter at 700 °C and GP2, SAES GP 50 Zr−Al alloy St101). Note that the noble gases are unaffected by the two getters. To ensure complete pressure equilibrium between all involved parts of the extraction and purification line, the cold traps (T1 and ZEO1) are bypassed (open VM8, VM8a).

In the first step a minor split (about 1/4) of the He and Ne phase is expanded to a noncommercial, all-metal, statically operated 90° magnetic sector spectrometer (MS1) equipped with the highly linear Baur-Signer source (26) for simultaneous measurement of He and Ne isotopes. The noble gas isotopes ^{4}He, ^{20}Ne, and ^{22}Ne are detected and measured using a Faraday cup, and ^{21}Ne can be counted on an electron multiplier (specifications see Table 1).

In the second step the remaining He and Ne phase is admitted to the second mass spectrometer (MS2) for simultaneous measurement of ^{4}He and ^{3}He. To avoid Ne ion

backscattering on ^{3}He during the measurement it is necessary to separate He from Ne quantitatively. Therefore, the He and Ne phase is transferred to a cryogenic cold trap (CCT) at 14 K containing a high porosity filter of sintered stainless steel (Nupro SS-2FE-5, 0.5 μm) that adsorbs Ne quantitatively while He remains in the gas phase. The temperature of the CCT can be set by computer control and is stable within ±0.1 K or better during Ne adsorption. After 20 min the He fraction is transferred to the spectrometer and the CCT is heated to 100 K to release Ne, which is pumped off.

The MS2 is also a noncommercial 90° sector mass spectrometer equipped with a Baur-Signer source (26) and a double collector system (Table 1). The MS2 is tuned for maximum linearity and not necessarily for maximum sensitivity. The ^{4}He$^+$ ion current is integrated on a Faraday cup. The small ^{3}He$^+$ ion beam is counted by an electron multiplier (16-stage, discrete Cu−Be dynode). The typical ^{3}He signal of 100 cps is integrated over 1200 s to achieve a counting error of 0.3%. The sensitivity, resolution, and the background of the system are designed to permit He measurements down to 10^{-10} cm^{3}STP for ^{4}He and 10^{-15} cm^{3}STP for ^{3}He. The mass resolution is set to about 750 (50% valley), allowing accurate separation of ^{3}He$^+$ and HD$^+$/H$_3^+$ peaks.

The UHV before and in both spectrometers (about 10^{-9} mbar and 10^{-10} mbar, respectively) is established with turbomolecular pumps (Alcatel 2040 or Pfeiffer TPU 062H) backed up by diaphragm pumps (Varian or Vacuubrand). Both spectrometers are equipped with a SAES GP 50 getter near the inlet valve (not shown in Figure 2).

Ar−Kr−Xe Measurement. For the measurement of the heavy noble gases, the water and all other condensable gases including Ar, Kr, and Xe which were adsorbed on the cold traps during the extraction are released by heating T1 and ZEO1 to 180 °C. The released wet gas phase is dried by transferring it to a charcoal trap (C11) cooled by liquid nitrogen, dynamically passing a zeolite trap (ZEO2, Merck, molecular sieve 3 Å) which is kept at room temperature (open

TABLE 2. Typical Analytical Errors

isotope or ratio	spectrometer	collector	signal of a standard sample (A)	signal of a standard sample (cps)	error of the signal[a] (%)	reproducibility of calibrations[b] (%)	total measurement error[c] (%)
^{4}He	MS1	Faraday	$5 \cdot 10^{-13}$		0.1	0.6	0.6
^{20}Ne	MS1	Faraday	$5 \cdot 10^{-12}$		0.02	0.9	0.9
^{20}Ne/^{22}Ne	MS1	Faraday			0.1	0.1	0.2
^{21}Ne	MS1	Multiplier		10^4	0.4	0.9	1.0
^{40}Ar	MS1	Faraday	10^{-10}		0.1	0.8	0.8
^{36}Ar/^{40}Ar	MS1	Faraday			0.1	0.1	0.1
^{84}Kr	MS1	Multiplier		$5 \cdot 10^4$	0.3	1.0	1.0
^{136}Xe	MS1	Multiplier		10^4	0.3	1.3	1.3
^{4}He	MS2	Faraday	10^{-11}		0.01	0.5	0.5
^{3}He	MS2	Multiplier		100	0.3	0.5	0.6
^{3}He$_{tri}$	MS2	Multiplier		1	2–3	1	2–3

[a] Typical error of the signal of a single measurement (SS_j in eq 2). [b] Typical long-term standard deviation of drift-corrected calibration signals (E_i in eqs 1 and 2). [c] Typical total error of a measurement (SA_j in eq 2).

VM7, VM10 and VM11). ZEO2 adsorbs water vapor but allows the heavy noble gases to pass through to be adsorbed on C11. To ensure complete gas transfer to C11, the heated ZEO1 is directly connected to C11 after 10 min by bypassing ZEO2 (open VM8, VM8a, VM12, and VM13). After 5 more min, C11 is cut off (close VM10, VM13), and the dry adsorbed gases are released by heating C11 to 180 °C.

Since less than 1‰ of the gas extracted from 45 g of water is needed for mass spectrometric analysis of the heavy noble gases, the dry gas phase is expanded into a large reservoir (R_{Dil}, 2000 cm^3, open VM15). Out of R_{Dil} small splits (0.7 cm^3) are taken for mass spectrometric analysis. The first gas split, about 0.35‰ of the total heavier gas fraction, passes by getters (GP1, GP2) that remove all reactive gases and is then admitted to the first mass spectrometer (MS1) for simultaneous analysis of Ar, Kr, and Xe isotopes. Advantages of using only a small split of the total gas phase in this step are that reactive gases such as CH$_4$ are easily removed and that repeated measurements are possible. Most importantly, however, the heavy noble gases need not be separated from each other. The noble gas amount is adjusted such that Ar can be measured on the Faraday cup, whereas Kr and Xe ions are counted by the electron multiplier of MS1.

Repeated measurements proved that commonly the heavy noble gases (Ar, Kr, and Xe) can be adequately measured simultaneously in the small gas aliquot and that there are basically no ^{40}Ar interferences on the Kr and Xe measurement. In particular, there is no significant increase of background due to ion backscattering on mass 136 which is used for Xe counting. But even when the electron multiplier is set to maximum sensitivity, the ^{136}Xe count rate of an unseparated gas aliquot (<1000 cps, integrated for 60 s) is too low to reach the desired 1% overall precision of the Xe concentration measurement. Therefore, Xe is reanalyzed in a second gas aliquot in which the Xe is separated form Ar and Kr by selective adsorption on an activated charcoal cold trap (C1) at −100 °C. Later, Xe is released from C1 by heating to 180 °C. Note that there is no requirement for complete separation of Xe and Kr but only for quantitative trapping of Xe. Due to the active transfer of Xe to C1 next to MS1, the amount of Xe in the second Xe analysis is increased by more than a factor of 10. The second ^{136}Xe analysis yields a count rate of about 10 000 cps (integrated for 140 s), reducing the combined error of counting statistics and regression to compensate for ion-pumping to 0.3%. An analysis of all noble gases takes about 2 h; the additional second Xe measurement requires another 50 min.

Tritium Measurement. After noble gas analysis, the degassed water is transferred back into the original copper tube. To reclose the sample, the length of the sample holder is reduced by about 3 cm, and the copper tube is sealed again (Figure 1). Several months later, ^{3}H is determined indirectly by measuring the ^{3}He that was produced by the decay of ^{3}H during storage. The extraction, purification, and measuring procedure is analogous to a He−Ne measurement but simpler. Due to the fact that the extracted gas contains practically only ^{3}He but no Ne, He needs not to be separated from Ne. After extraction both He isotopes are measured in mass spectrometer MS2.

A typical tritium sample contains about 10^6 atoms of tritiogenic ^{3}He (e.g., 45 g of water with 25 TU after 3 months storage) and yields a ^{3}He count rate of about 1 cps, 2 orders of magnitude less than in a typical noble gas analysis. Therefore the error due to counting statistics is larger (2−3% using the same integration time of 1200 s, Table 2). The detection limit for a standard water sample of 45 g is about 0.1 TU. Using larger water samples (typically 1 kg), the amount of ^{3}He produced by the decay of tritium during storage is higher, and the tritium concentration can be measured down to about $5 \cdot 10^{-3}$ TU.

^{4}He signals in the tritium measurement are typically close to the blank level of $5 \cdot 10^{-16}$ A, indicating that less than 10^{-10} cm^{3}STP ^{4}He have remained in the degassed water after the gas extraction or leaked in during storage. Usually a measurable amount of ^{4}He indicates a contamination with air during storage or extraction and is therefore used for atmospheric correction. However, in samples with very high initial He concentrations (>10^{-6} cm^{3}STP/g) sometimes a measurable He residue remains in the water after the noble gas analysis, although the concentrations are reduced by a factor of at least 10^4. In such cases the ^{3}He/^{4}He ratio measured during noble gas analysis may be used to correct for the remaining ^{3}He which otherwise would distort the ^{3}H measurement.

Calibration. Noble gas concentrations and isotopic compositions are calibrated against an air standard by peak height comparison. Air aliquots of about 0.6 cm^{3}STP (volume known with an accuracy of 0.3%) are taken from reservoir R_{Air}. This reservoir was filled with atmospheric air at a known temperature, pressure, and humidity. The noble gas amounts of the air aliquots are calculated using the atmospheric abundances given by Ozima and Podosek (27), and the ^{3}He/^{4}He ratio given by Clarke et al. (15). Air aliquots, in the following called slow calibrations, are usually measured after every fifth sample and are prepared with exactly the same procedures as a water sample. Note that slow calibrations are processed either as dry or wet air. In the latter case water vapor from a previously completely degassed water sample is mixed with the air aliquot in order to simulate the cleanup conditions for a water sample. No significant difference between dry and wet calibrations is observed.

To monitor sensitivity changes of the spectrometer, fast calibrations are always carried out immediately before each noble gas analysis. In case of the He and Ne measurement, the fast calibration gas contains either pure He (reservoir FC_{He}) or a mixture of He and Ne (reservoir FC_{HeNe}) and is directly injected into the spectrometer. In contrast, the Ar, Kr, and Xe fast calibration gas (reservoir FC_{AKX}) is the dried gas of a completely degassed water sample, which has been additionally enriched in Xe by a factor of 4 to increase the Xe count rate in the mass spectrometer. As the AKX fast calibration gas from reservoir FC_{AKX} still contains all atmospheric gases with the exception of water, the aliquot is first cleaned at the getter pumps (GP1 and GP2) before being admitted to the spectrometer MS1.

Each aliquot taken from the standard reservoirs (R_{Air}, FC_{He}, FC_{HeNe}, FC_{AKX}) reduces the total gas amount in the reservoir. Therefore the measured signal has to be corrected using the known individual dilution factors given by the volume of the reservoir divided by the sum of the volume of the reservoir and the volume of the pipet. To compensate for systematic sensitivity changes, the ratios between slow calibration and fast calibration signals, both corrected for dilution, are calculated

$$E_i = \frac{\overline{FS_i}}{CS_i} \qquad (1)$$

where $\overline{FS_i}$ is the average signal of the fast calibrations measured before and after each slow calibration i and CS_i is the slow calibration signal. The gas volume dissolved in a sample j, SA_j (cm³STP), is calculated as

$$SA_j = \overline{E_i} \cdot CA \cdot \frac{SS_j}{\overline{FS_j}} \qquad (2)$$

where SS_j is the measured signal of the sample j, $\overline{FS_j}$ is the average signal of the fast calibrations measured before and after sample j, CA is the volume of the slow calibration gas (cm³STP), and $\overline{E_i}$ is the long-term mean of the ratios between fast and slow calibrations, calculated over uninterrupted measurement periods of typically 1 month. The standard deviation of the E_i is a measure of the reproducibility of the analysis, including errors associated with sensitivity fluctuations and with gas purification (Table 2). Dividing SA_j by the sample weight yields the noble gas concentration in cm³-STP/g.

The error of a single measurement in a spectrometer is given by the uncertainty associated with the regression algorithm applied to compensate for ion-pumping or memory effects during the analysis. In case of a small multiplier signal as for ³He, this error is mainly determined by counting statistics. In general, the error of a signal measured on a Faraday cup is much smaller than the error of a multiplier signal (Table 2). The total error of a measured gas amount SA_j corresponds to the standard deviation of E_i combined with the error of the individual signal SS_j (Equation 2). Compared to the long-term stability given by the reproducibility of E_i, the errors of Faraday measurements are negligible, whereas the errors of multiplier measurements are smaller but relevant (Table 2).

In the case of the ³H measurement the analyzed gas consists of almost pure ³He. Therefore it is calibrated only against a pure He standard with a known ³He/⁴He ratio (reservoir R_{He}). To avoid an increase of the ³He background no fast calibrations are carried out between the individual ³He measurements. Thus the amount of ³He in the sample is calculated directly by peak height comparison with the calibration gas.

Results and Discussion

Standard Water Samples. To monitor the overall reproducibility of sampling, sample storage, gas extraction, purification, and separation, it is useful to routinely measure aliquots of a water standard. The water standard consists of lake water from Lake Alpnach, Switzerland, and was taken in July 1995. Up to now, 24 standard water samples have been analyzed for He and Ne isotopes, and the heavy noble gases Ar, Kr, and Xe have been measured on 13 of these samples. Of the extracted standard water samples, 15 have been processed for tritium analysis.

The results of all measured standard water samples are shown in Figure 3 and summarized in Table 3. The standard deviations of the noble gas concentrations are equal to or even smaller than the total errors of the individual measurements, proving that the error calculation of the individual measurement includes all major error sources. Since there are no systematic trends in the measured noble gas concentrations over the last 3 years, any gas loss or gain during storage can be neglected. In contrast to the concentrations, the errors of the isotope ratios seem to be slightly underestimated by the total measurement error (Table 3). A higher standard deviation of the measured ³He/⁴He ratios can be explained by the applied correction for the ³He produced in the samples by ³H decay since sampling.

In general, noble gas concentrations in lake waters are expected to be close to solubility equilibrium with the water vapor saturated atmosphere (*11*). The equilibrium concentrations depend on temperature, salinity, and atmospheric pressure. Using the mean atmospheric pressure of 0.953 atm measured at meteorological stations near Lake Alpnach and a salinity of 0.3‰, the equilibrium temperature can be calculated from the measured noble gas concentrations. Equilibrium temperatures were derived with three sets of solubility data (Table 3): (i) the *Weiss solubilities*: the data of Weiss (*28−30*) for He, Ne, Ar, and Kr; (ii) the *Clever solubilities*: the data of Clever (*31−33*) combined with Smith and Kennedy (*34*) for salinity correction; and (iii) the *Benson solubilities*: the data of Benson and Krause (*35*) combined with Smith and Kennedy (*34*).

The equilibrium temperatures calculated from Ar, Kr, and Xe are almost independent of the choice of solubility data and in good agreement with each other. However, they are about 1 °C lower than the in situ water temperature of 6.7 °C. Since the samples were taken in July during the period of warming of the lake water, presumably the heavy noble gases had not yet attained equilibrium at the present water temperature. Lower noble gas temperatures compared to in situ water temperatures have also been observed in the surface layer of Lake Baikal (*11*). The equilibrium temperature calculated from Ne using the Weiss solubilities agrees with the results from the heavier noble gases, whereas the other solubilities yield a higher temperature, consistent with the in situ temperature. The low temperatures obtained from He are due to a small He excess of 10^{-9} cm³STP/g that originates from radiogenic ⁴He emanation from the lake bottom (*25*).

Equilibrated Samples. To verify the overall analytical procedure, water equilibrated with atmospheric air was analyzed. To this end three open containers (30 dm³) containing freshwater were placed in temperature stabilized rooms at different temperatures for at least 7 days. The water was gently stirred to accelerate and facilitate gas exchange but avoiding any occurrence of bubbles. Samples were taken at the bottom outlet of the containers using standard copper tubes. Both water temperature and total ambient atmospheric pressure were monitored (Table 4). Whereas temperature became stable within the precision of the measurement (± 0.1 °C), the pressure varied typically by a few mbar over the time of exposure. All pressure readings of the last 7 days
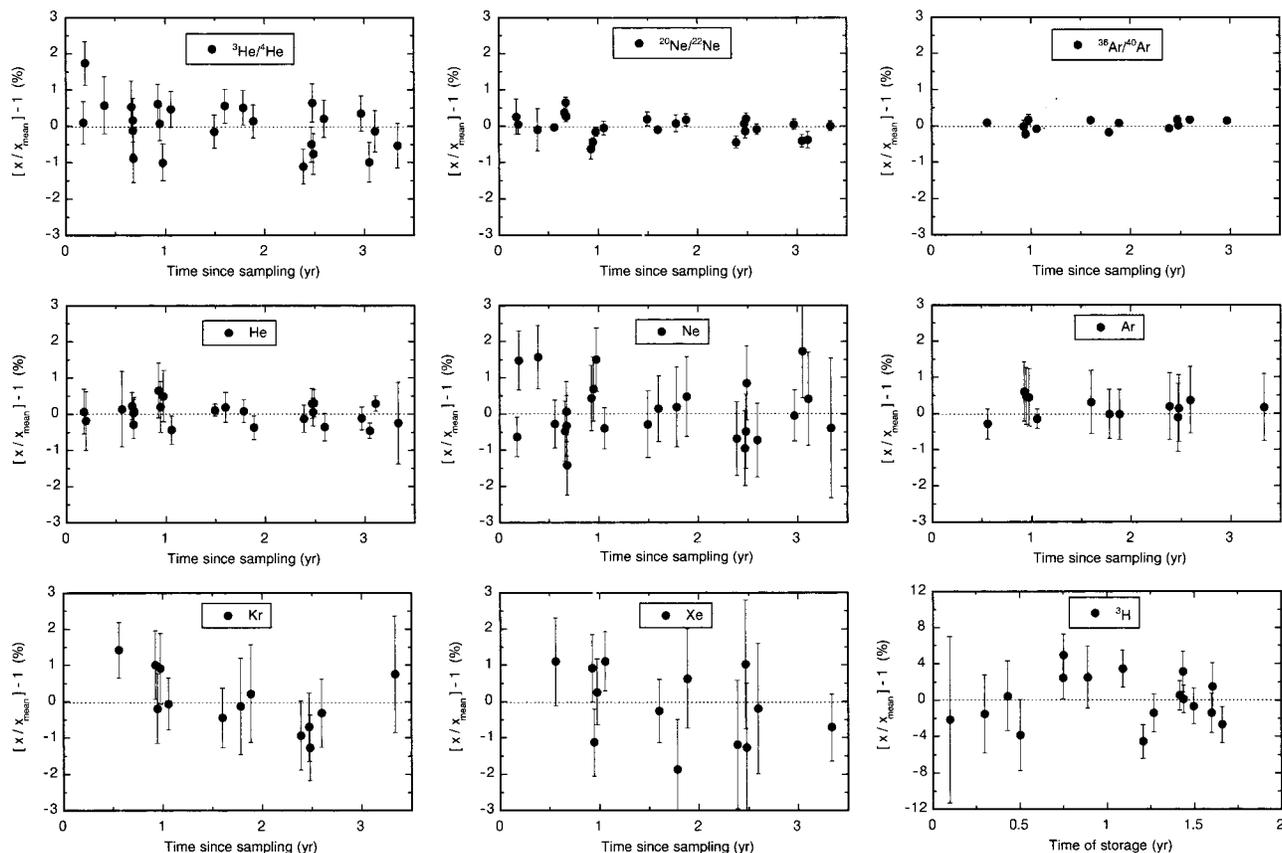
FIGURE 3. Isotopic ratios and concentrations of noble gases measured in aliquots of the lab-internal freshwater standard normalized to the respective mean values plotted versus the time since sampling. Tritium (^{3}H) concentrations are plotted against the storage time of the extracted sample. The aliquots were collected on July 18, 1995 in Lake Alpnach at a depth of 29 m. The error bars correspond to 1σ errors of the individual measurements. The ^{3}He/^{4}He ratios are corrected to time of sampling.

TABLE 3. Lab-Internal Freshwater Standard: Mean Results and Corresponding Standard Deviations Compared to Mean Errors of the Individual Measurements

element or ratio	mean value ($\pm$ SD) (cm^{3}STP/g, TU)	SD (%)	mean individual error (%)	calculated equilibrium temperature			
				Weiss (°C)	Clever (°C)	Benson (°C)	error (°C)
He[a]	$(4.594 \pm 0.035)\cdot 10^{-8}$	0.75	0.63				
He[b]	$(4.575 \pm 0.023)\cdot 10^{-8}$	0.50	0.54				
He[c]	$(4.585 \pm 0.013)\cdot 10^{-8}$	0.29	0.48	2.7	3.5	5.0	± 0.5
Ne	$(2.005 \pm 0.017)\cdot 10^{-7}$	0.84	0.95	5.6	6.5	6.9	± 0.8
Ar	$(4.080 \pm 0.011)\cdot 10^{-4}$	0.27	0.77	5.6	5.5	5.4	± 0.2
Kr	$(9.826 \pm 0.079)\cdot 10^{-8}$	0.81	1.01	5.7	5.7	5.9	± 0.3
Xe	$(1.456 \pm 0.015)\cdot 10^{-8}$	1.04	1.26		5.8	5.8	± 0.3
^{3}He/^{4}He	$(1.383 \pm 0.009)\cdot 10^{-6}$ [d]	0.68	0.55				
^{20}Ne/^{22}Ne	9.792 ± 0.029 [e]	0.30	0.19				
^{40}Ar/^{36}Ar	295.93 ± 0.44 [f]	0.15	0.09				
^{3}H	18.2 ± 0.5	2.7	2.9				

[a] Measured in spectrometer MS1. [b] Measured in spectrometer MS2. [c] Weighted average and weighted error of the two He concentrations measured on MS1 and MS2. [d] ^{3}He/^{4}He ratios are corrected to time of sampling. Note that in Lake Alpnach they are influenced by radiogenic ^{4}He and tritiogenic ^{3}He. Atmospheric ratio: $1.384\cdot 10^{-6}$ (15); ratio in air-equilibrated water: $\approx 1.36\cdot 10^{-6}$ (36). [e] Atmospheric ratio: 9.80 (27). [f] Atmospheric ratio: 295.5 (27).

prior to sampling were averaged for further calculations (standard deviation < 3‰). A few measurements of electrical conductivity showed salinity to be 0.36 ± 0.1‰, a small value hardly affecting the noble gas equilibrium concentrations. The uncertainties regarding the conditions during gas exchange have only a small effect on the noble gas equilibrium concentrations, causing a variation of between 0.3% (He) and 0.5% (Xe). ^{3}He equilibrium concentrations were calculated for each of the three sets of solubility data using the temperature dependent ^{3}He/^{4}He ratio in water given by Benson and Krause (36).

Measured concentrations of the artificially equilibrated samples are listed in Table 4 and compared with the solubility data in Figure 4. Except for He, all noble gases are in agreement with the solubilities. He is supersaturated in all samples, but the measured ^{3}He/^{4}He ratios (Table 4) are lower than the expected value of $1.36\cdot 10^{-6}$ for air-equilibrated water (36). These observations lead us to believe that the He partial pressure in the climate controlled rooms, located below ground level and vented only artificially, was slightly enhanced relative to air, due to the presence of He with a lower than atmospheric (radiogenic) ^{3}He/^{4}He ratio. Indeed, the

TABLE 4. Measured Concentrations of Artificially Equilibrated Water Samples

	sampling conditions				concentrations (cm³STP/g)				
sample	temp (°C)	pressure (atm)	salinity (‰)	$^3He/^4He \cdot 10^6$	$He \cdot 10^8$	$Ne \cdot 10^7$	$Ar \cdot 10^4$	$Kr \cdot 10^8$	$Xe \cdot 10^8$
C1	3.8	0.948	0.36	1.331 ± 0.005	4.72 ± 0.02	2.05 ± 0.02	4.27 ± 0.04	10.36 ± 0.09	1.57 ± 0.03
C2	14.5	0.959	0.36	1.341 ± 0.006	4.54 ± 0.02	1.86 ± 0.02	3.36 ± 0.03	7.66 ± 0.10	1.07 ± 0.02
C3	29.4	0.956	0.36	1.353 ± 0.006	4.28 ± 0.02	1.65 ± 0.02	2.51 ± 0.02	5.33 ± 0.06	0.70 ± 0.01
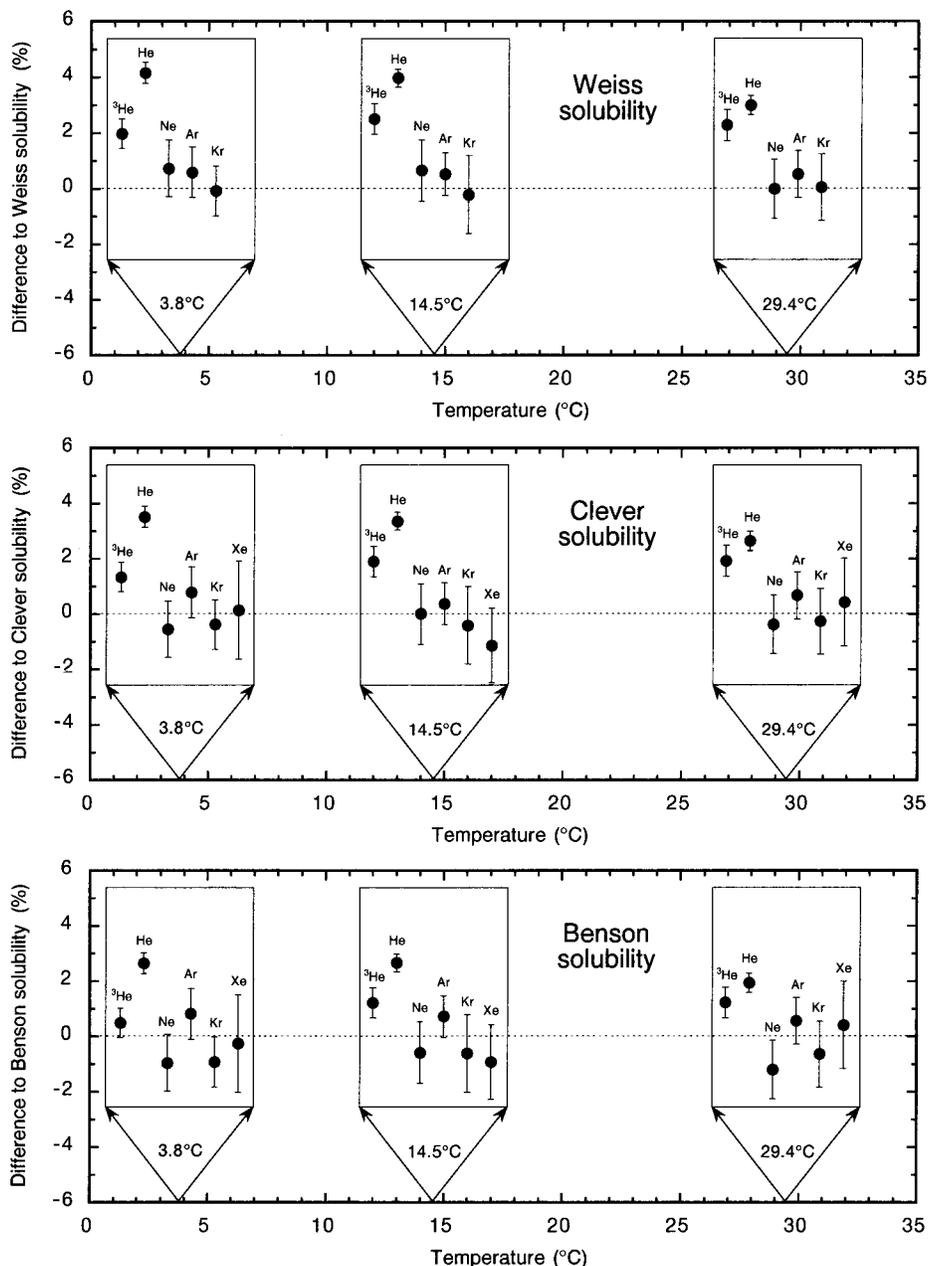
FIGURE 4. Measured noble gas concentrations of water samples artificially equilibrated with the atmosphere at 3.8, 14.5, and 29.4 °C, compared with three sets of solubility data (defined in text). The difference is plotted in percent relative to the solubility data.

observed supersaturations of ^3He are clearly lower than for ^4He. According to the Benson solubilities, the measured ^3He concentrations are close to equilibrium with the atmosphere.

Isotopic Fractionation during Solution. The solubility of noble gases is mainly dependent on their individual atomic mass. Light noble gases are less soluble than heavier noble gases. This fractionation also influences the solubility of the different isotopes of one noble gas. For He, the relative

difference between isotopic ratios in solution and air at equilibrium is defined as (36)

$$\delta^3He_{eq}(\%) = \delta(^3He/^4He)_{eq}(\%) = \frac{R_{eq} - R_{air}}{R_{air}} \cdot 100 \quad (3)$$

where R_{air} and R_{eq} are the $^3He/^4He$ ratios in air and in solution, respectively. The δ^3He values were first determined by Weiss
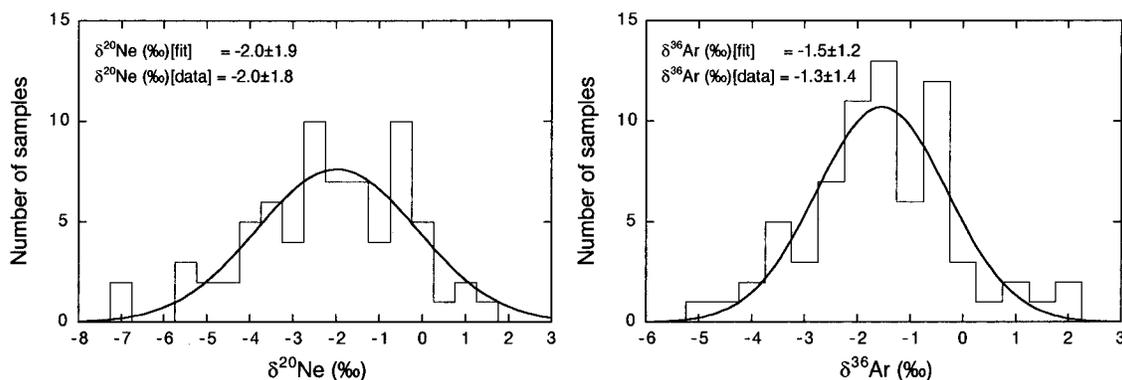
FIGURE 5. Stack histograms of the isotopic fractionation of $^{20}Ne/^{22}Ne$ and $^{36}Ar/^{40}Ar$ isotope ratios of 70 surface water samples relative-to-atmospheric ratios, fitted with Gaussian functions. The data are approximately normally distributed around mean values of −2.0‰ and −1.3‰, with standard deviations of 1.8‰ and 1.4‰, respectively. Since both distributions are entirely explained by statistical experimental errors (see Tables 2 and 3), their mean values are defined with uncertainties of only ±0.2‰.

(*37*) to be about −1.2%. Refined measurements by Benson and Krause (*36*) showed that δ^3He varies between −1.8 and −1.5% for water temperatures between 0 °C and 40 °C.

Aside from the helium isotopes ^3He and ^4He, hardly any information is available for noble gas isotope fractionation in equilibrated water. Up to now we have processed about 70 samples of surface waters (mainly of rivers and lakes). These data enable us to estimate the isotopic fractionation for Ne and Ar. The measured isotopic fractionations $\delta^{20}Ne = \delta(^{20}Ne/^{22}Ne)$ and $\delta^{36}Ar = \delta(^{36}Ar/^{40}Ar)$ are shown as a stack histogram plot in Figure 5. As indicated by our data, fractionation of Ne and Ar isotopes is much smaller than for He isotopes (per mill instead of percent). Yet, the observed values of −2.0‰ for $^{20}Ne/^{22}Ne$ and −1.3‰ for $^{36}Ar/^{40}Ar$ are in agreement with the fractionation of oxygen ($^{32}O_2/^{34}O_2$) of about −0.8‰ given by Benson and Krause (*38*). A slightly higher fractionation for Ne and Ar isotopes (compared to O_2 isotopes) can be explained by the larger relative mass difference of the two involved isotopes.

In conclusion, the system presented here for the measurement of noble gases and tritium in water samples yields coherent results and offers a powerful tool for the study of natural water systems. Soon, we plan to lower the detection limit of the mass spectrometer by higher sensitivity $^3He/^4He$ mass spectrometry. This improvement will reduce significantly the waiting period between the noble gas and tritium analysis, which is at the moment at least 3 months.

Acknowledgments

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