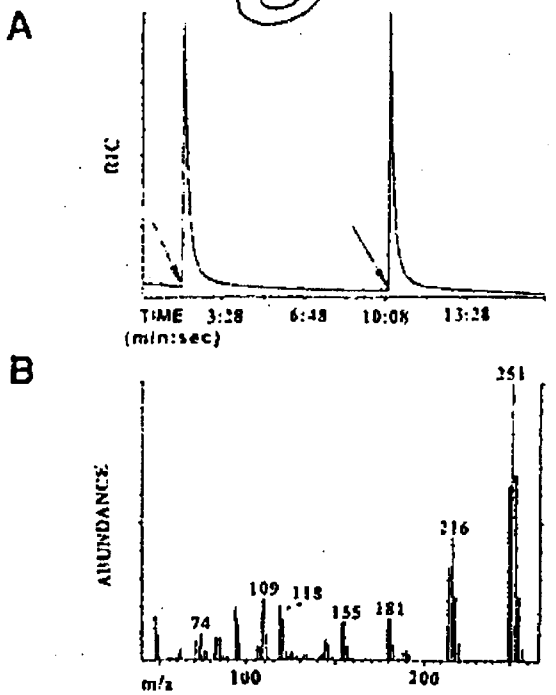

Figure 5. (A) Time vs ion intensity profile of duplicate injections of PCP in a quadrupole mass spectrometer (arrows indicate injection points). (B) Mass spectrum of PCP.

scribed in the Experimental Section. Pentachloropyridine passes rapidly through the interface and demonstrates little tailing, as seen in Figure 5A. Duplicate injections show reproducible profiles. The acquired mass spectrum, shown in Figure 5B, matches the known spectrum of PCP.

CONCLUSIONS

The simplicity of this novel sampling interface and adaptability to on-line monitoring make it an attractive alternative to membrane devices for industrial process analysis. Moreover, the mechanics of the valve make it suitable for operation in a fully automated system, and this type of interface essentially eliminates the need for sample preconditioning or dilution. Finally, an inverse valve offers several advantages over pulsed electromagnetic valves for gas sampling. First, the inverse sampling valve described in this report does not require a stable or defined back-pressure (of the process stream being monitored), as is typically necessary for operation of a pulsed valve. Additionally, the inverse sampling valve is more rugged and is easier to clean than a pulsed valve.

ACKNOWLEDGMENT

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Registry No. Benzene, 71-43-2; pentachloropyridine, 2176-62-7.

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Extraction Technique for the Determination of Oxygen-18 in Water Using Preevacuated Glass Vials

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INTRODUCTION

The need for a rapid, inexpensive technique for routine $^{18}O/^{16}O$ extraction from water has arisen recently through applications in the medical sciences[1] and in hydrology. The traditional experimental technique for determining the oxygen isotope composition of water, the CO_2–H_2O equilibration method,[2] is tedious, time consuming, and involves the use of custom-made glass apparatus. Furthermore, because of potential memory effects from one sample to the next, the glassware needs to be thoroughly cleaned between runs. A few attempts have been made to improve upon the method.[3,4] Attempts to analyze water directly in the source of the mass

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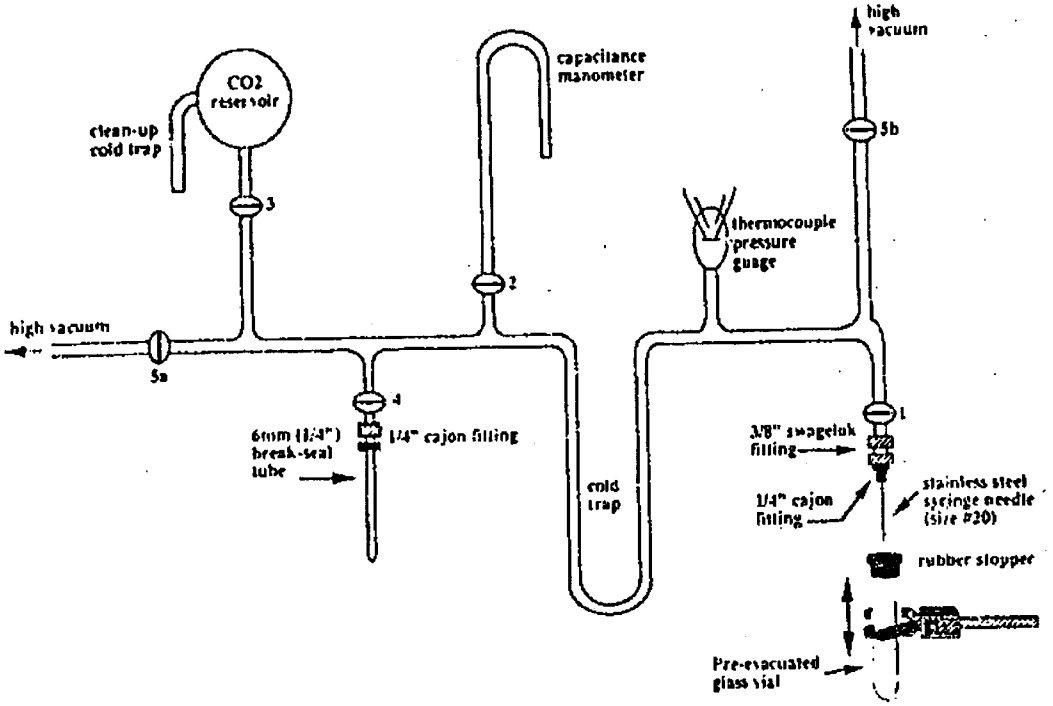

Figure 1. Diagram of the extraction line showing the position of the preevacuated vial.

spectrometer[5,6] produced large memory effects and questionable results. Commercially available apparatus for automated extraction of $^{18}O/^{16}O$ from water is generally prohibitively expensive and often is designed to interface only with the manufacturer's own mass spectrometer. The method described in this paper utilizes inexpensive, off-the-shelf, preevacuated, glass vials. Preevacuated vials have been used by others for the isotopic analysis of breath CO_2 and are well tested.[7] The vials can be purchased in bulk from scientific apparatus suppliers at a relatively low cost. These are coupled with a simplified extraction line consisting of a stainless steel syringe needle and a glass cold trap. Vials are filled with CO_2 and H_2O and shaken in a constant-temperature water bath for at least 90 min. Since the vials are discarded after use, no cleaning is necessary, essentially eliminating any memory effect. Reproducibility is generally better than ±0.05‰. The only reagents required are gaseous CO_2 for equilibration, a dry ice/alcohol mixture for trapping water, and liquid nitrogen for transferring the CO_2.

EXPERIMENTAL SECTION

Experimental Details. A diagram of the preparation line is shown in Figure 1. A preevacuated vial is placed in the sample holder clamp, as shown in Figure 1. Care should be taken when choosing commercially available vacuum vials since some have rubber stoppers lubricated with silicone gel. The silicone gel lubricant has been known to produce an array of volatile components which may interfere with the isotopic analysis.[8] We use Venoject brand, 7-cm³ vials with a nonsiliconé coating, available from Terumo Medical Supply, Elkton, MD 21921. The holder is a small-size steel glassware clamp with the plastic sleeves on the jaws removed. This provides a "snug" fit and prevents the vial from moving sideways while freely allowing upward movement. Vial and holder are positioned directly beneath the syringe needle on the extraction line with the vial resting on a lab jack. The jack is raised far enough so the syringe needle is embedded into the top of the vial's rubber stopper. The needle is evacuated through valve 1. The vial is then raised further so the needle punctures the rubber stopper. After pumping for a few seconds, the valves to the vacuum (valves 5a,b) are closed and 150 μmol of CO_2 is expanded into the vial by opening the CO_2 reservoir (valve 3) and opening valve 2 (manometer). The CO_2 pressure inside the vial is about 0.52 atm. Valve 1 is then closed, and the vial is removed from the syringe needle. Off-line the vial is injected with 1.4–1.5 cm³ of water via a 5-cm³ glass syringe. Care should be taken when filling the vials with water to ensure that not too much air is let in. Since the pressure in the vial is lower than atmospheric pressure, the water sample from the glass syringe will be drawn directly into the vial.

The rubber stopper on top of the vial is designed to have 1 atm of pressure "pushing" it in. Care must be taken, however, not to force the lip on the rubber stopper from side to side, as this would result in a leak across the stopper seal. Samples should not be stored in the CO_2-charged vials for more than a few weeks due to the probability of leaks occurring.

Once filled, the CO_2–H_2O vessels are placed in a 25 ± 0.1 °C constant-temperature bath. The containers are clamped sideways in a wrist action shaker and completely immersed in the bath water. Complete immersion of the vials is necessary if ambient laboratory air temperatures are significantly less than 25 °C. Cool air temperatures will cause the water in the vial to condense at the portion sticking above the level of the water bath. We use a relatively low-cost oscillating motion shaker turned on its side to produce a wrist-action movement. Stroke amplitude can be adjusted on the shaker to produce the desired degree of agitation of water in the vial. Sufficient agitation breaks the surface of the water sample and facilitates quick isotopic equilibration.

After equilibration is complete, the vials are placed back in the holder on the line and the syringe needle is again pumped out as described in the filling procedure. However, this time the bottom of the vial is immersed in a dewar of liquid nitrogen. Since some of the water tends to "stick" to the bottom of the rubber stopper, the top of the vial is lightly heated with a flameless heat gun to condense all of the water to the bottom of the vial. The noncondensibles are then pumped out by raising the tube so the needle punctures the stopper. Any water vapor caught inside the syringe needle will immediately freeze and may later block the flow of CO_2. To eliminate blockage, the syringe needle is also lightly heated with the heat gun. After sufficient pumping, valve 5 is closed and the liquid nitrogen dewar is replaced with a dry ice/alcohol dewar to keep the water frozen at the bottom of the vial. Released CO_2 is then frozen into the cold trap with liquid nitrogen, dried again by exchanging the liquid nitrogen dewar with one containing dry ice/alcohol, and transferred to a 6-mm Pyrex break-seal tube (valve 4) where it can be stored for analysis later.

Analytical Details. All CO_2 in this study was analyzed for oxygen and carbon isotopes on a triple-collecting Finnigan MAT 251 stable-isotope mass spectrometer at NASA-JSC. All oxygen

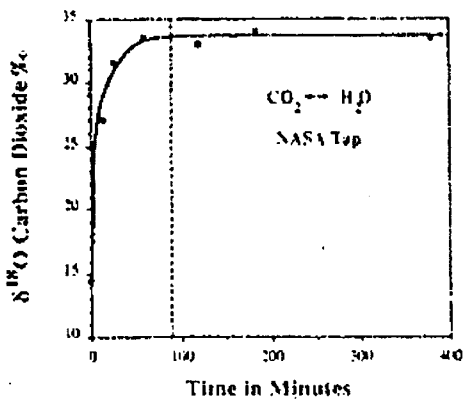

Figure 2. Variation with time of the $\delta^{18}O$ composition of CO_2 equilibrated with our laboratory working standard (NASA tap water). Oxygen isotope exchange equilibration is complete in about 1.5 h (broken line).

Table I. $\delta^{18}O$ Results for Three International Water Standards and Three Laboratory Standards

sample name	no. of preparations	std dev 1σ, ‰	measd[a] $\delta^{18}O$ SMOW, ‰	normalized[b] $\delta^{18}O$ SMOW, ‰
		International Standards		
V-SMOW	5	±0.08	+0.04	0.00
GISP	6	±0.02	-24.85	-24.83
SLAP	5	±0.03	-55.59	-55.50
		Laboratory Standards		
GOMS	24	±0.05	+0.36	
NASA tap	33	±0.02	-6.63	
ADAM	20	±0.05	-41.34	

[a] These data were calculated using the CO_2-H_2O fractionation factor of 1.041 20 recommended by Friedman and O'Neil (1977).[10] [b] These data were normalized to Δ(V-SMOW - SLAP) = -55.50‰.

isotopic ratio results are reported relative to SMOW.[3]

RESULTS AND DISCUSSION

Equilibration Time. Figure 2 is a plot of $\delta^{18}O$ of our laboratory working standard water (NASA tap) versus time and indicates the time needed to reach isotopic equilibrium between CO_2 and H_2O. Seven vials were filled with 1.5 cm^3 of NASA tap and 150 μmol of CO_2. These were shaken in a 25 °C water bath for up to 380 min. The $\delta^{18}O$ value at time = 0 is the initial oxygen isotope composition of the injected CO_2. With increasing time, the $\delta^{18}O$ composition of the CO_2 approaches an equilibrium value with that of the water in the vial. Data indicate that equilibration is completed in at least 90 min if the vials are placed sideways and shaken. The process of shaking the vials sideways breaks the surface of the water sample and facilitates more rapid oxygen isotope exchange.

Accuracy and Precision. Data for the oxygen isotope composition of six different water standards using the technique described in this paper are reported in Table I. Our three laboratory standards consist of an isotopically light water (ADAM, acronym for average depleted Antarctic meltwater) prepared by filtering a block of Antarctic ice, a water of intermediate isotopic composition (NASA tap, distilled Houston tap water), and a water relatively enriched in $\delta^{18}O$ (GOMS, acronym for Gulf of Mexico sea water, distilled sea water taken from the south shore of Galveston Island, TX). International standards provided by the IAEA, Vienna, that were analyzed include V-SMOW, SLAP, and GISP.

On the basis of the number of analyses, reproducibility of all six standards using our technique is generally better than ±0.05‰ at the 1σ level of confidence. Furthermore, the oxygen isotope composition of the international standards V-SMOW, SLAP, and GISP are well within the mean of reported values.[11]

CONCLUSIONS

The method described in this paper satisfies the need for a rapid and inexpensive $^{18}O/^{16}O$ water extraction technique. Since the preevacuated vials are discarded after use, the potential for memory effects during extraction is eliminated. Furthermore, good sample reproducibility makes our method acceptable for routine $^{18}O/^{16}O$ water extractions.

ACKNOWLEDGMENT

We thank Dale Schoeller for drawing our attention to the use of preevacuated vials. This research was supported by the NASA Planetary Biology Program. Use of trade names and manufacturers/suppliers in this publication is for descriptive purposes only and does not constitute endorsement by Lockheed Engineering and Sciences Co. or NASA.

Registry No. ^{18}O, 14797-71-8; water, 7732-18-5.

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CORRECTION

Enzymatic Flow Injection Analysis in Nonaqueous Media

Lorenzo Braco, José A. Darós, Miguel de la Guardia (*Anal. Chem.* **1992**, *64*, 129–133).

On page 129, on the first line under the Experimental Section, the word *spiralis* should be species.