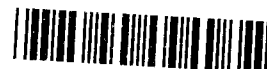64061

Multisample Conversion of Water to Hydrogen by Zinc for Stable Isotope Determination

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Two techniques for the conversion of water to hydrogen for stable isotope ratio determination have been developed that are especially suited for automated multisample analysis. Both procedures involve reaction of zinc shot with a water sample at 450 °C. In one method designed for water samples in bottles, the water is put in capillaries and is reduced by zinc in reaction vessels; overall savings in sample preparation labor of 75% have been realized over the standard uranium reduction technique. The second technique is for waters evolved under vacuum and is a sealed-tube method employing 9 mm o.d. quartz tubing. Problems inherent with zinc reduction include surface inhomogeneity of the zinc and exchange of hydrogen both with the zinc and with the glass walls of the vessels. For best results, water/zinc and water/glass surface area ratios of vessels should be kept as large as possible.

In the conventional method for the conversion of water to hydrogen for stable isotope determination, water is passed over hot uranium (1) or zinc (2), and the evolved hydrogen is collected with a Toepler pump (1) or sorbed on activated charcoal (3) or uranium metal (4). These preparation methods suffer from numerous disadvantages: (1) Memory effects due to nonquantitative transfer of water are difficult to eliminate without excessive heating of the vacuum line. (2) Saline waters leave salt deposits that may not easily be dehydrated, giving rise to memory effects and isotopically fractionated hydrogen. Distillation of the sample at temperatures over 350 °C prior to analysis dehydrates most salts but is time-consuming and is a potential source of error (5). (3) Uranium is easily contaminated with nitrogen and organic compounds. (4) Both mercury in Toepler pumps and uranium are toxic. (5) Conventional methods are labor intensive and slow.

Several procedures have been employed to eliminate some or all of the disadvantages with current hydrogen preparation techniques. Direct injection of water into a heated mass spectrometer (6, 7) looks promising but may suffer from memory effects when saline waters are analyzed. Coleman and others (8) have reported a multistep method for converting water to hydrogen using disposable aliquots of zinc in individual reaction vessels. Their technique was designed for use with fluid inclusion samples where water is frozen under vacuum into each vessel. Alternatively, water samples can be introduced into the vessels with a syringe. Their technique involves several heating and freezing steps for each sample vessel; this is time-consuming and would be difficult to automate. We have modified the method of Coleman and others (8) to eliminate freezing and preheating of sample vessels so that it can be used more easily for batch analysis of water samples with a multisample automated gas handling system.

Numerous investigators have attempted to modify the zinc preparation technique for use in sealed glass tubes because (1) tubes can be stockpiled for subsequent analysis, (2) only a small furnace is required for sample preparation, and (3) sealed glass tubes can be analyzed on a mass spectrometer

equipped with multiple automated tube crackers. We describe herein a quantitative method employing Vycor or quartz tubing.

EXPERIMENTAL SECTION

Apparatus. The 90-mL Pyrex reaction vessel shown in Figure 1 has a 10 mm bore Ace stopcock (no. 8195-63) with a glass plug. FETFE self-lubricating O-rings are used for ease in cleaning; there is no appreciable reaction or absorption of water or hydrogen with the FETFE. The shape of the vessel was selected for easy breaking of capillaries. The finger at the vessel base is designed to hold the hairpin-shaped capillary steady for easy cracking; the walls of the finger are thickened to withstand the impact of the capillary breaker bar. The vessels are connected to the vacuum manifold with Cajon fittings which permit quick removal of vessels and require no cleaning. Small wads of copper wool enclosed in copper wire are placed between the Cajon fittings and the pneumatically actuated valves of the gas handling manifold to prevent migration of glass chips.

Hairpin-shaped capillaries are easily fabricated from 75-mm-long capillary tubing with 1.0–1.4 mm o.d. and 0.17 ± 0.05 mm wall thickness on an asbestos-covered metal holder 4 mm wide which is flame heated to bend 12 capillaries at a time. Maximum width and length of hairpin-shaped capillaries are 7.5 mm and 35 mm, respectively. However, due to the large number of samples processed annually in this laboratory, we procured 100 000 hairpin-shaped capillaries from Ace Glass, Vineland, NJ. Capillaries are heated in air to 530 °C to remove all carbon prior to filling.

Two types of 8-mm-diameter magnetic capillary breaker bars have proved satisfactory. Pyrex-enclosed iron bars 4 cm in length are preferred although they require delicate handling. Nickel bars 2 cm long were used; however, they eventually corroded from cleaning in HNO_3 and needed repolishing. Glass bars cannot be used because they have insufficient mass to break the capillaries.

An aluminum-block furnace was fabricated with 16 3.2-cm diameter, 23-cm-deep holes. To reduce the cost of the block furnace by 50%, the block furnace was fabricated from 40 sheets of aluminum 15 × 45 × 0.6 cm welded together on both ends, rather than from a single block of aluminum. Sample vessel holes were punched in the sheets before they were welded. Flat heating elements were mounted on the sides and base of the furnace. Individual furnaces mounted on the vacuum manifold were not employed due to the difficulty in maintaining precise temperature regulation.

Reagents. Although several types of analytical grade zinc shot were cleaned and tested for their effectiveness, only BDH Hopkins and Williams AnalaR shot (available in the United States from Gallard-Schlesinger Chemical Manufacturing Corp., Long Island, NY) would reliably and quantitatively reduce water without further preparation of the zinc.

Zinc shot is sieved to collect the ≤1 mm fraction, cleaned in 3 M HNO_3 to remove surface oxidation, rinsed in water and then in acetone, outgassed under vacuum at 250 °C, and stored under vacuum until needed. Although care is taken to minimize air contact with cleaned zinc before use, zinc exposed for up to 3 months in an open beaker still performed satisfactorily. Additional heating and outgassing of the zinc and vessel surfaces to remove adsorbed water prior to reaction is unnecessary as shown below.

Procedure. By use of a microsyringe, water samples 15–35 μL in volume are introduced into the hairpin-shaped capillaries which are then sealed with a glassblowing torch with a 4-cm flame. Care is taken to suck out any water droplets remaining on the inside walls within 1 cm of the ends of the capillary to prevent

Table I. δD of Hydrogen Prepared from V-SMOW and SLAP Using Different Reducing Agents, Relative to the Working Standard in ‰[a]

	V-SMOW			SLAP		
reagent	no. of prepns	std dev 1σ	δD	no. of prepns	std dev 1σ	δD
uranium	9	0.9	+132.1	10	1.1	−343.8
AnalaR, batch 1	11	0.6	+130.8	15	1.1	−341.8
AnalaR, <1 mm, batch 4	6	1.1	+132.5	6	1.1	−338.0
AnalaR, >1 mm, batch 4	5	1.0	+129.7	5	1.2	−339.4
AnalaR, 0.7 g (>1 mm, batch 4) and 1.2 g of lead	5	0.8	+130.5	5	0.4	−341.9
AnalaR, reused, 1 g (>1 mm, batch 4) and 1.5 g of lead	7	0.9	+131.5	5	1.8	−338.5
Baker, 1 g and 1.5 g of lead	6	1.4	+132.9	5	0.8	−334.1

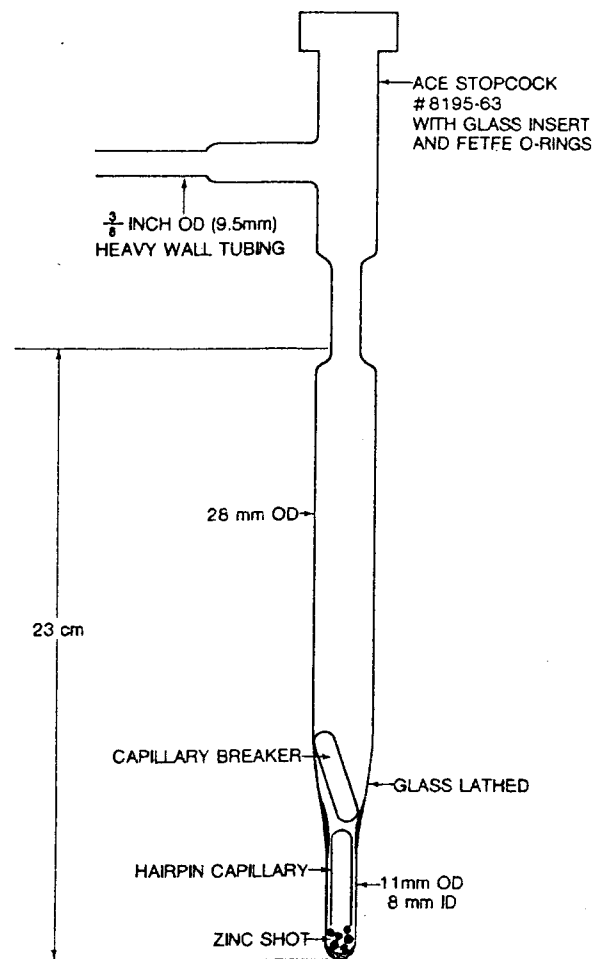[a] H_3^+ abundance is constant for all results.

Figure 1. Pyrex reaction vessel shown loaded with zinc shot, hairpin-shaped capillary, and capillary breaker. Walls are thicker below the glass-lathed area and at the tip to prevent breakage.

isotopic fractionation during flame sealing. Three capillaries are filled from each bottle in a batch of samples and are stored in plastic vials indefinitely prior to analysis. A leaking capillary is easily detected because its water moves when the vessel is evacuated. In contradiction to Coleman and others (8), we find that capillaries are not difficult to fill or seal properly because the capillaries are only 30% full, nor does trapped air have any effect upon the reaction or the mass spectrometric analysis.

A 0.5-g aliquot of zinc, a capillary (concave side down), and a breaker bar are carefully loaded into each vessel (Figure 1). With our preparation lines, vessels in multiples of 15 are evacuated simultaneously for 20 min and then are closed and removed from the vacuum line. Each capillary is broken by using a magnet to raise and lower the breaker bar; the vessels are then placed in the aluminum-block furnace at 450 ± 3 °C. The water is com-

pletely reduced after 1 h and the vessels are returned to the gas handling manifold for automated analysis. An incompletely reacted sample is identified with the moisture sensor installed on the mass spectrometer manifold (Panametrics model 500-S, Waltham, ME) or by vapor condensed on the stopcock plug. Convection from the furnace keeps the vessel stopcocks at approximately 70 °C, minimizing condensation during reaction. After extraction, the plug, breaker bar, capillary fragments, and oxidized zinc shot are removed and the vessels are cleaned with dilute nitric acid.

Capillaries placed concave side down in the vessels are readily cracked with breaker bars with much less strain to vessel bottoms than if straight capillaries are used. If capillaries are not broken mechanically but are allowed to explode during heating, the resulting glass dust is later transferred into the mass spectrometer gas handling system and damages the valve seats of the pneumatically actuated valves. Additionally, the glass dust is difficult to remove from vessels and the explosion usually fractures the vessel. In breaking the capillary, the operator occasionally breaks the Pyrex breaker bar or cracks the base of the vessel. Such accidents are the chief flaw we see in this procedure, and their frequency decreases with practice.

RESULTS AND DISCUSSION

Comparison with Other Reduction Techniques. The standard deviation of 30 V-SMOW water samples prepared with this zinc technique is 0.7‰, which compares favorably with that of the uranium reduction method. It is not clear whether this technique is less precise than that presented by Coleman and others (8) because those investigators presented few data on reference waters. An advantage of this zinc technique is that saline samples are completely dehydrated at 450 °C. It is also much faster; 45 samples can be completely prepared in about 1.5 h, and the reduction reaction requires an additional hour for each 15 samples.

After use of our zinc technique for over 15 000 analyses since 1980, it is clear that hydrogen produced by zinc and uranium reduction from the same water may differ in D/H abundance by a few permil. Table I lists values for the reference waters V-SMOW and SLAP prepared with a variety of reagents. Since 1980 we have received four different batches of AnalaR zinc and have cleaned and outgassed hundreds of zinc preparations for use in reaction vessels. The data in Table I are representative of the variations we have observed over this period. In general, the values of SLAP relative to V-SMOW are a few permil heavier for zinc than for uranium. We have analyzed a number of waters of intermediate D/H composition and conclude that the bias in the zinc technique is linear. Because all data are routinely normalized to a value of −428‰ for SLAP relative to V-SMOW (9), the bias in the zinc technique has no effect on the values calculated for waters. Each new preparation of zinc is calibrated prior to use.

Coleman and others (8) reported erratically heavy δD values for SLAP and only a few values which agreed with their uranium reduction results. Hence, a slight bias relative to the

Table II. δD of Hydrogen Heated in Vessels and Tubes, Relative to SMOW in ‰[a]

sample description	reaction time at 430 °C initial H₂ δD = −121.5		reaction time at 430 °C initial H₂ δD = −688.5	
	2 h	24 h	2 h	24 h
Pyrex vessel	−122.0	−129.0	−685.0	−665.0
quartz vessel	−121.5		−688.0	−682.0
Pyrex, 6.3 mm o.d., 9 cm long	−130.0		−671.5	
Pyrex, 9 mm o.d., 9 cm long	−126.5		−676.0	
Vycor, 6.3 mm o.d., 9 cm long	−123.5		−683.5	
Vycor, 9 mm o.d., 9 cm long	−122.0	−125.0	−687.5	−684.5

[a] The standard deviation of the replicate analyses is 2‰.

uranium reduction technique may be inherent to zinc techniques. Causes of the bias are discussed below.

Sensitivity of Method to Choice of Apparatus. The extent of exchange between hydrogen or water in glass vessel walls and hydrogen produced by reduction of water was determined by introducing hydrogen gas of known isotopic composition at various pressures into freshly washed vessels and tubes which had been heated with a torch for 1 min to 100 to 200 °C under vacuum to remove any adsorbed water. They were then heated to 430 °C or 450 °C for different periods of time. Results at a hydrogen pressure of 33 kPa (25 cmHg), the normal gas pressure at 25 °C in our reaction vessels during sample preparation, indicate that 2 h of heating is sufficient to change the D/H composition of gaseous hydrogen in a Pyrex vessel by 0.5 to 3‰ depending on the δD of the initial gas (Table II). After the sample was heated for 24 h, the δD value changed by 7.5 to 20‰. Vessels filled with hydrogen with an initial composition of −688.5‰ prior to 2 h of baking were found to contain gas with a δD of −686‰ regardless of whether the vessels were previously baked for 2 h with hydrogen whose δD was −688.5 or −121.5‰. This suggests that exchangeable hydrogen is not simply adsorbed on vessel surfaces. Yields after 72 h of heating are 100 ± 2%; hence, diffusion of hydrogen through vessel walls can be discounted. Pyrex reaction vessels filled with hydrogen with a δD of −121.5‰ to a pressure of 33 kPa required 8 days of continuous heating at 430 °C to reach a steady-state composition of approximately −175‰. Thus, there appears to be a significant reservoir of hydrogen in borosilicate glass that can exchange with gaseous hydrogen during heating. The effect of hydrogen exchange with glass is to decrease the difference between the δD values of samples (i.e., "shrink the permil scale").

Table II shows that the degree of exchange is directly correlated to the surface to volume ratio; hydrogen in small tubes or vessels is more exchanged than that in large ones at a constant pressure. Experiments at higher and lower hydrogen pressures confirmed that the higher the hydrogen pressure, the less the δD value was affected. At a hydrogen pressure of 6 kPa, the δD of hydrogen changed from −121.5 to −125.0‰ in Pyrex vessels after 2 h at 450 °C. Therefore, to minimize changes in δD due to exchange of hydrogen with the glass, the size and shape of the sample vessel should be selected carefully to maximize the ratio of hydrogen to vessel surface area.

Vycor and quartz behaved identically and showed much less exchange than Pyrex. Either would make ideal reaction vessels except that such vessels are quite fragile and expensive for routine use.

Sensitivity of Method to Choice of Reagent. One major contribution of Coleman and others (8) was identifying a brand of zinc shot which would satisfactorily reduce water in a disposable-shot technique. We were unable to find any other

Table III. δD of Laboratory Reference Water Using Zinc That Has Been Melted and Lathed, Relative to SMOW in ‰

BDH Chemicals zinc metal shot 0.5–2 mm	J. T. Baker Chem. granular zinc 20 mesh	Fisher Sci zinc metal shot Z-12
−321.4	−319.0	−321.3
−321.3	−318.8	−320.3
−321.4	−321.3	−320.3
−318.4		
−321.0		

type of analytical grade zinc shot which, without requiring any additional preparation, would reduce water. The only significant compositional difference among the zinc brands we analyzed was that AnalaR contained at least five times more lead (36 ppm).

SEM photographs of thoroughly cleaned zinc grains showed that AnalaR has a much smoother and homogeneous surface than the other brands. The rougher surfaces of the other zincs might impede the removal of oxides or other contaminants during cleaning, resulting in less zinc available for water reduction. In an attempt to produce zincs with identical surface configurations, several types of zinc were cleaned and melted under vacuum in long Vycor tubes. When cooled, impurities and oxides were concentrated at one end and had also reacted with the glass. Solid zinc cylinders were lathed to produce fine turnings which were cleaned and outgassed by the method discussed above. About 1–1.5 g zinc was required for complete reduction of 15 µL of water in 1 h at 450 °C. As shown in Table III, two other brands of zinc performed satisfactorily. These experiments show that other types of zinc are potentially usable, but re-forming the zinc requires a great deal of effort. Sublimation of 0.5 g of a non-AnalaR zinc on the walls of the vessel prior to reaction with water can produce complete reaction, but is also too time-consuming. Successful reductions using several re-formed brands of zinc suggest that the zinc oxidation is highly dependent on surficial casting-produced features and not on chemical composition.

To test whether addition of lead would improve the surficial oxidation of zinc, lead shot was added to AnalaR zinc. This lead had little or no effect on the reaction rate or isotopic composition, but it apparently improved the precision of the isotopic measurements (Table I). Addition of lead to other brands of zinc, either by subliming the lead onto zinc or by adding lead shot, resulted in complete reaction in 3 h. However, the isotopic compositions of the hydrogen formed showed considerable scatter and the hydrogen produced from SLAP was too heavy by several permil (Table I). Replacing lead by 0.5–1 g of tin or cadmium resulted in incomplete conversion of water to hydrogen. Although lead is apparently not necessary for quantitative reduction of water, it does improve oxidation of the zinc. We theorize that the lead effectively increases the available surface area of the zinc grains by preventing armoring by zinc oxides. AnalaR zinc may be reused indefinitely if about 50% lead shot by weight is added to the zinc shot after thorough recleaning and outgassing at 250 °C.

The four different batches of AnalaR received do not produce isotopically identical hydrogen. The first batch produced values for V-SMOW and SLAP which were within 1 to 2‰ of the values obtained by uranium reduction. Later shipments here and in other laboratories yielded hydrogen from V-SMOW whose isotopic composition showed considerable scatter and was 2 to 10‰ depleted in D relative to that obtained by uranium reduction. Incomplete reduction of water produces a similar effect, but hydrogen yields at both 430 °C and 450 °C were quantitative (100 ± 2%); thus, no appreciable hydrogen was gained or lost. Preheating the zinc and vessels

Table IV. δD of Hydrogen Prepared from V-SMOW Water in 9-mm Vycor Tubes, Relative to SMOW in ‰

treatment	no. of prepns	std dev 1σ	δD
analyzed immediately	32	1.7	−0.1
stored unreacted for 1.5 y	5	1.7	−1.2
stored reacted for 1.5 y before anal.	6	1.9	+0.3

under vacuum prior to use to remove any adsorbed water had no effect.

There appears to be a reservoir of some hydrogen-bearing contaminant within the zinc or on its surface which exchanges with hydrogen gas in the vessel. Neither cleaning with acid nor outgassing at up to 375 °C seem to have any effect on the availability of exchangeable hydrogen. Because zinc shot is generally cast by quenching molten zinc in water, the zinc probably acquires its exchangeable hydrogen during this step, possibly as a hydroxide. The amount of exchangeable hydrogen in the zinc seems to vary both among grain sizes and shipments. Due to the inhomogeneity observed between different zinc preparations and shipments, each preparation should be calibrated by reference standards prior to use. To minimize the effects of this hydrogen on the isotopic composition of samples, the ratio of water to zinc should be kept as high and constant as possible.

The variable results shown in Table I reflect the combined effects of exchangeable hydrogen in glass and in zinc. In an attempt to separate the effects due to these two sources of exchangeable hydrogen, two experiments were conducted using quartz and Vycor instead of Pyrex to minimize exchange with glass walls. In the first, aliquots of two different batches of zinc were placed in Vycor tubes which were then heated during evacuation for 2 min with a glassblowing torch to remove adsorbed water. Two tubes were filled with isotopically light hydrogen (−688.5‰) and two with isotopically heavy hydrogen (−121.5‰) to a pressure of 33 kPa. The tubes were sealed and heated at 430 °C for 2 h. A 0.5-g aliquot of a batch 1 zinc (Table I) did not change the D/H ratio of the hydrogen appreciably, but a 1-g aliquot caused a 5‰ enrichment in D in the light hydrogen and a 4‰ depletion in the heavy hydrogen. A 0.5-g aliquot of batch 4 zinc caused a surprising 21‰ enrichment in D in the composition of the light hydrogen. However, this same zinc when used in Pyrex reaction vessels produced results only a few permil different than results using batch 1 zinc (Table I). The decreased sensitivity to zinc amount and batch number seen with vessels is due to the much larger ratio of gaseous hydrogen to zinc in the vessels which substantially dilutes the hydrogen derived from reaction with the zinc.

In the second experiment SLAP was reacted in quartz vessels using zinc from two different shipments that had yielded distinctly different values for SLAP when reacted in Pyrex vessels. The δD of the hydrogen produced by the two zincs differed by the same amount as found with Pyrex vessels; however, both δD values from the experiments in the quartz vessels were more negative and nearer the value found with the uranium technique.

The above experiments indicate that AnalaR zinc contains a significant amount of hydrogen, with more hydrogen in batch 4 than in batch 1. Small amounts of hydrogen and water and considerable quantities of oxides can be removed by melting and re-forming the zinc. Before melting, use of even 1 g of batch 4 zinc in a vessel was sufficient to shift δD values up to 7‰. After the zinc was melted and re-formed, up to 1.5 g of zinc showed no adverse effect on the δD values of water or gases (Table III).

Our experiments illustrate that most of the "permil scale shrinkage" is due to exchange with some source of hydrogen

in the zinc. Under the conditions we now use routinely, this exchange affects both V-SMOW and SLAP by 1 to 3‰. Exchange in Pyrex seems to affect waters and gaseous hydrogen which are depleted in D more so than waters or gases enriched in D; hence, such exchange probably causes an additional 2 to 3‰ shift in δD values of SLAP.

SEALED TUBE TECHNIQUE

Coleman and others (8) speculated that they failed to develop a sealed tube technique using borosilicate glass because adsorption or exchange occurred with water or hydrogen in areas of "active glass" (which they did not define) produced during sealing of the tubes. Table II indicates that hydrogen exchange occurs even in vessels which have no active glass zones and appears to be a function of both the type of glass and the glass surface to hydrogen ratio. Early efforts to use borosilicate glass tubes for the reduction of V-SMOW resulted in values consistently isotopically too light by several permil.

Vycor shows little exchange with hydrogen (Table II) and is an obvious choice for a sealed-tube technique. Quantitative conversions are obtained using 9-mm o.d., 20- to 40-cm-long Vycor or quartz sealed tubes, 0.12–0.5 g of a batch 1 zinc, 3–20 μL water, and reaction times of 1–3 h at 430–450 °C. To eliminate adsorbed water, the tubes are heated with a torch for 2 min before water is introduced under vacuum. Table IV shows δD values of V-SMOW generated over several months with the large range in conditions above. With larger water samples the standard deviations decrease to about 1‰. Optimum amounts of water and zinc appear to be 15 μL and 0.25 g, respectively.

If water samples are extracted from bottles, the vessel technique is unquestionably easier and more precise than the sealed tube technique. However, for water samples evolved under vacuum from fluid inclusions or hydrocarbon oxidation, or for laboratories that analyze water only occasionally, freezing the samples into Vycor or quartz tubes eliminates the need for expensive reaction vessels and furnaces. In addition, because storage of either reacted or unreacted samples for 18 months (Table IV) does not affect the isotopic composition of the gas, the technique is ideal for researchers who must stockpile samples because they lack direct access to a hydrogen mass spectrometer.

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