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Reduction of Water with Zinc for Hydrogen Isotope Analysis

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A 1–10 mg portion of water is reduced with Zn metal in a sealed tube at 450 °C to prepare hydrogen for isotopic analysis. After reaction the tube is attached directly to the mass spectrometer without further processing. Replicate analyses of water samples give reproducibility of 0.2–0.4‰ (1σ); fluid inclusion samples, 1.9‰; and water of hydration of gypsum, released and reduced in the sealed tube, 1.1‰. A batch of 10 samples can be prepared in 1 h.

A new technique for preparation of hydrogen gas from milligram quantities of water using zinc metal has been developed. It offers the advantages that it is more precise than conventional methods for small samples and, incidentally, results in much shorter preparation time. This project was initiated from an idea of T. J. Shepherd and was developed originally in order to make isotopic analyses of the very small amounts of water from fluid inclusions occurring in both natural and synthetic crystals. The method usually used (1, 2) involved the water sample being introduced to a high vacuum preparation line. The sample is vaporized and is moved through the line to a furnace containing uranium where reduction occurs. After a period of time to allow completion of the reaction, the resultant hydrogen is collected in a gas sample bottle, either by use of a Toepler pump or by adsorption on a large volume of charcoal. The movement of water in vapor form may cause problems of memory effects from previous samples and these will be exacerbated when small samples are prepared. The uranium used is usually in the form of turnings but fairly rapidly produces a fine powder which, in the absence of suitable precautions, can spread itself along the preparation line. The analysis of very small samples obviously is hindered by the possibility of memory effects, but equally it is important to present the sample to the mass spectrometer at a sufficiently high pressure, which militates against the use of large volumes of charcoal and is only solved by use of a Toepler pump, which is very time-consuming.

For the rapid preparation of small water samples, methods involving uranium reduction on-line to the mass spectrometer have been described by Hagemann and Lohez (3) and Hartley (4) but both have numerous disadvantages. The mass spectrometer must be dedicated to this form of analysis, whereas many laboratories need to analyze CO_2 on the same apparatus and must retain a conventional inlet system. These methods require the water to be introduced with a microsyringe which makes them inappropriate for fluid inclusions, water of hydration, products of oxidation of hydrocarbons, and the total hydrogen content of clay minerals and rock samples. Both suffer from very large memory effects for which a calibrated correction must be made. This means that only samples of similar isotopic composition can be measured and in the best case limits the isotopic difference between successive samples to 50‰ (4). The water quantities required by the two methods are 1–5 mg (3) and 9 mg (4), but in the first case, five successive samplings are required to correct for memory effects; extraction of fluid inclusions may produce only 1–2 mg of water.

In order to eliminate these disadvantages the present method was developed. The reaction occurs in a small-volume sealed vessel which can be connected directly to the mass spectrometer without further cleanup of the gas.

EXPERIMENTAL SECTION

Apparatus. The principal item of apparatus, shown in Figure 1, is a simple tube, 12.5 mm outside diameter, 9.2 mm internal diameter, and 70 mm long, made by sealing off a high vacuum, 90° pattern, high vacuum stopcock (Model 8195-47, Ace Glass Inc., Vineland, NJ) to which has been added a standard taper B14 socket to allow attachment to either a vacuum line or a mass spectrometer. The stopcock, which is sealed with elastomer "O" rings, has a plug and handle made only from Teflon which allows high-temperature operation.

Reagent. The agent used is Analar zinc shot (Hopkin and Williams, Chadwell Heath, Essex, England) sieved to produce a size range −30 to +60 mesh. This is washed in 30% nitric acid, washed in distilled water, dried, and outgassed under vacuum at approximately 300 °C. If a large batch of zinc is prepared, it is usually kept under vacuum.

Procedure. The plug of the vacuum stopcock is withdrawn and approximately 0.25 g of zinc shot is put into the reaction tube. After replacing the plug it is attached to a suitable vacuum line. (In our laboratory each of the sample preparation lines has a manifold of standard taper B14 cones with Viton "O" rings (J. Young (Scientific Glassware) Ltd., Acton, London, England) to accept gas sample bottles.) The vessel is evacuated to approximately 10^{-4} torr using rotary and diffusion pumps and outgassed by warming to about 100 °C using a hot air gun. On removal from the line the plug is removed again, the tube is filled with dry nitrogen from a cylinder, and the water sample (1–10 mg) is introduced to the bottom of the tube using a syringe. The plug is replaced immediately and the tube is shut before being reattached to the vacuum line. The tube is evacuated by twice freezing the water with liquid nitrogen and pumping quickly (usually less than 1 min) to about 10^{-4} torr.

The evacuated tube containing zinc and water is put into a heating block at 450 °C (Tecam Dri-Block, DB-4, Techne (Cambridge) Ltd., Duxford, Cambridge, England). The block is similar to an electrical hot plate but has three aluminum blocks each drilled with a 47 mm deep and 13.5 mm diameter hole. There is no temperature gradient from the block to the inside of the tube and thus the zinc is 30 °C above its melting point, 420 °C (5), and a small amount volatilizes to form a ring on the cooler part of the tube. Nevertheless, the shot does not fuse, possibly supported by a skin of oxide. Although the reaction tube protrudes considerably from the hole, the stopcock usually attains a temperature of about 75 °C; this is sufficient to prevent significant adsorption of sample water vapor but very much lower than the temperature at which the stopcock would be damaged. The reaction probably occurs almost instantaneously but the tubes are usually left for 30 min. After reaction the tube can be attached directly to the mass spectrometer inlet system for isotopic analysis without any further cleanup of the gas. The mass spectrometer used was a V.G.Micromass 602-C.

Obviously, it is not possible to measure the yield of hydrogen directly. However, it was thought advantageous to exclude this stage in favor of the simplicity and minimum volume of the method as described. By using a standard size tube, we were able to calibrate the mass spectrometer and thus determine the yield.

The usual procedure in the laboratory is to prepare two or three samples simultaneously at the begining of the day and to prepare subsequent samples while running the mass spectrometer. A batch
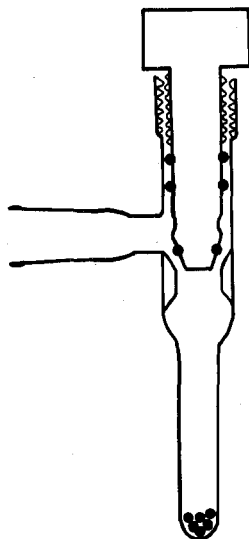
Figure 1. The water reduction tube. The zinc shot and water are introduced by completely removing the screwed Teflon plug.

Table I. Results (in Order of Running) of Separate Preparations of Water Samples Measured against Reference Gas Produced from SMOW

sample	δD, $^{0}/_{00}$
V-SMOW	−0.26, −0.43, −0.39, −0.22, −0.66

mean value with respect to reference −0.39 $^{0}/_{00}$; σ_5 = 0.17

New Preparation of Reference Gas

V-SMOW	+0.09, +0.38
V-SLAP	−426.24, −426.91
V-SMOW	+0.43, −0.54, +0.59, −0.06
V-SLAP	−426.85
V-SMOW	+0.05

mean value V-SMOW$_{reference}$ +0.13 $^{0}/_{00}$, σ_7 = 0.38
mean value V-SLAP$_{reference}$ −426.67 $^{0}/_{00}$
V-SLAP$_{SMOW}$ −426.74 $^{0}/_{00}$

of 10 samples can be prepared in about 1 h although a larger vacuum manifold would reduce the unit time.

RESULTS AND DISCUSSION

Water Analysis. The results of analyses of standard waters are given in Table I. For each data set the results are given in the order in which they were run as the values measured against a reference gas produced from Vienna SMOW (V-SMOW), but corrected for the valve mixing and H_3 contribution to the HD ion beam. The standard deviation on two sets of determination of SMOW, σ_5 = 0.17 and σ_7 = 0.38, are as good as, or better than, those from the uranium furnace methods. Early analyses of V-SLAP gave erratic heavy values around −420‰. It was suspected subsequently that the samples were contaminated with atmospheric water because the reaction tubes had not been outgassed sufficiently. The relatively few satisfactory analyses give a mean of −426.74‰ which compares very favorably with −426.1‰, the mean value (excluding deviant results) reported by Gonfiantini (6). There is no measurable memory effect in either the preparation or mass spectrometer.

Fluid Inclusion Analysis. The method was developed originally in order to make isotopic analyses of water from fluid inclusions. Because of the difficulty of preparing 4–5 g of sufficiently clean acid-washed quartz samples, the fluid inclusion water analyses were not run as large numbers of replicates. However, the results of duplicate analyses of seven quartz samples are given in Table II. The mean difference between duplicate analyses is 1.9‰ which is excellent for the fluid inclusion method. The slightly poorer reproducibility

Table II. Results for Duplicate Analyses of Fluid-Inclusion Water

sample no.	δD, $^{0}/_{00}$	difference, $^{0}/_{00}$
20	−65.1, −68.7	3.6
119	−52.4, −54.8	2.4
414	−35.7, −38.1	2.4
416	−28.3, −30.0	1.7
419	−33.4, −34.4	1.0
424	−27.1, −27.3	0.2
6476	−57.6, −59.3	1.7

mean difference 1.9$^{0}/_{00}$

Table III. Result (in Order of Running) of Separate Preparations of Water and Water of Hydration

sample	δD, $^{0}/_{00}$
V-SMOW	−0.04, −0.17
water distilled from gypsum GP1	−44.28, −50.29, −52.08, −52.76, −52.92, −49.26, −52.84, −51.10
V-SMOW	+0.20

mean value V-SMOW$_{reference}$ 0.00$^{0}/_{00}$
mean value GP1$_{SMOW}$ −50.69$^{0}/_{00}$; σ_8 = 2.91
excluding the first analysis of GP1 −51.61$^{0}/_{00}$; σ_7 = 1.43

V-SMOW	−0.04
direct reduction of GP1	−48.02, −50.06, −49.54, −47.52, −48.38
V-SMOW	+0.01

mean value GP1$_{reference}$ −48.70$^{0}/_{00}$; σ_5 = 1.06
V-SMOW$_{reference}$ −0.02$^{0}/_{00}$
GP1$_{SMOW}$ −48.69$^{0}/_{00}$

of these data compared with analysis of ordinary water may result from two causes: the inclusion population may not be isotopically homogeneous (despite careful selection of material) and the process of release and transfer of the fluid may not be absolutely complete in every case. This could lead to the observed variation.

Water of Hydration. The method was applied most successfully to the analysis of water of hydration in gypsum ($CaSO_4 \cdot 2H_2O$). The samples were treated in two ways. Firstly the gypsum was heated under vacuum and the evolved water frozen into a zinc reaction tube using liquid nitrogen. Subsequently, dehydration and direct reduction in the same tube were tried. For the latter technique, the solid sample and zinc shot were placed in an outgassed reaction tube which was evacuated. Obviously, the dry nitrogen and freezing as used for water samples were unnecessary in this case. On heating, the gypsum evolves its water which reacts with the zinc. The reproducibility of this latter method was better than that for the water samples produced from gypsum. A natural gypsum, used as a laboratory standard gave a δD value of −51.6‰, σ_7 = 1.4, compared with −48.7‰, σ_5 = 1.1 for direct reduction. The full results are given in Table III. The slightly better quality of data produced by direct reduction must be related to the process of transfer of water to the reaction tube, which may cause adsorption or loss of a small fraction of the water and thus isotopic fractionation. It is apparent that this method can be incorporated readily in other processes for isotopic analysis of hydrogen whenever water can be condensed into the reduction tube.

Choice of Apparatus and Reagent. It is important to note that the results given here have been obtained only by using the apparatus and reagent as detailed above. Early attempts to develop the method using flame-sealed borosilicate glass break-seal tubes gave less reproducible answers. At first it was thought that the hydrogen gas was diffusing through the thin glass of the seal. However, experiments using very thick-walled glass produced no improvement. We speculate

that the process of sealing the tube at high temperature produces an area of active glass which adsorbs, or exchanges with, either the water vapor or the hydrogen. This occurred despite the fact that the break-seal tube had been necked down to a narrow diameter and the area of hot glass was minimal.

Similarly, the choice of zinc reagent also seems to be important. The grain size is critical: use of coarser shot often produced incomplete reaction, while finer material was more difficult to handle. Attempts to use the zinc in other physical forms, wire, dust, or turnings, give incomplete yields of hydrogen and isotopically fractionate the sample (7). At one stage of the development of the technique, the water was introduced to the reaction tube in a sealed glass capillary which was broken by expansion of the water on heating. However, an inexperienced operator could not always produce reproducible results; this arose from two causes. If too long a time were taken to seal the capillary with a gas torch, some of the water evaporated, leading to large isotopic fractionation. The other difficulty occurred if the capillary tube was not completely full, since the presence of even a small amount of air may preferentially oxidize the zinc and result in isotopic fractionation from an incomplete reaction.

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CORRESPONDENCE

Integration of Differential Pulse Voltammograms for Concentration Measurements

Sir: Differential pulse techniques have been shown to be one of the most sensitive electroanalytical methods (1, 2) and because of this have been widely used since their inception by Barker (3, 4). The sensitivity of these methods arises because the potential wave form and data acquisition timing discriminate against charging current contributions. Although several variants now exist, the most commonly used potential wave form consists of a ramp with superimposed pulses and the output is a differential current (Δi). The current is sampled at a time where the residual current has decayed significantly relative to the faradaic current.

Quantitative analysis with differential pulse polarography or voltammetry is usually done by measuring the differential current at its maximum and comparing this to a calibration curve (5–7). However, in several reports it has been demonstrated that small perturbations in the resistance of the electrochemical cell, or in the degree of electrochemical or chemical reversibility, can greatly affect both the differential current amplitude and its location on the applied potential axis (5, 6, 8–10). All of these parameters are affected by the solution composition and therefore lead to a degree of uncertainty when samples are analyzed and compared to standards. To compensate for this shift on the potential axis, a commercial automated polarograph (Princeton Applied Research, Model 384) has incorporated a 100-mV potential window in its search routine to find the current maximum.

An alternate but little used method for evaluating differential pulse curves is to measure the area under the curve. In fact, the derivative of the current–voltage curve for a one-electron reversible system fits the differential pulse curve very well for pulse amplitudes (ΔE) less than 25 mV (11), and thus the area of the curve under these conditions is proportional to concentration. We have considered the equations for differential pulse voltammetry at larger pulse amplitudes for electrodes which show time-independent currents (i.e., disk electrodes with radii less than 1 μm). As will be shown, the area of the curves under these conditions is also proportional to concentration.

The current for the reduction of a reversible system at microelectrodes which shows time-independent behavior for a potential pulse (E) [assuming equal diffusion coefficients (D) for the oxidized and reduced species] is given by

$$i = i_d \left(\frac{1}{1 + \exp\left(\dfrac{nF}{RT}(E - E_{1/2})\right)} \right) \quad (1)$$

where $i_d = arnFDC$, n, F, R, and T have the usual electrochemical meaning, C is the bulk concentration of the oxidant, r is the radius of the electrode, and a is a coefficient which depends on the geometry of the electrode [$a = 4\pi$, 2π, or 4 for a sphere (12), hemisphere (13), or disk (14, 15), respectively]. The differential pulse current can be obtained by taking the difference of the currents (Δi) at the potential of the ramp (E_1) and at the potential of the pulse (E_2) (11). The result is

$$\Delta i = i_d \left[\frac{P - P\sigma^2}{P + \sigma + P\sigma^2 + P^2\sigma} \right] \quad (2)$$

where $P = \exp\{(nF/RT)[(E_2 + E_1)/2]\}$ and $\sigma = \exp\{(nF/RT)[(E_2 - E_1)/2]\}$. Similar equations have been derived for reversible systems at a dropping mercury electrode (11), rotated disk electrode (16), and stationary electrode which exhibit time-dependent chronoamperometric currents (8). In these cases i_d is simply the limiting current defined by the