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Hydrogen-isotope analysis of potentially toxic organic materials employing manganese reduction and disposable nickel-pyrolysis tubes

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Abstract

Use of a simple, disposable apparatus allows the measurement of $^2H/^1H$ ratios in small quantities of potentially toxic organic materials without the release of hazardous compounds. The apparatus consists of welded nickel pyrolysis bombs encased in quartz breakseals. Samples are enclosed in the bombs with a manganese-reducing agent. Hydrogen diffuses through the nickel upon heating and is captured in the quartz envelope for analysis. Tests with standard polyethylene foil and cystine, as well as with water and several herbicides, show that this method produces good precision (typically between ±1.0‰ and ±4.0‰) and is equally applicable to solid and liquid materials. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Hydrogen-isotope analysis of potentially hazardous organic materials is problematic. Continuous-flow mass spectrometry has the advantage of simplicity, however, there is the potential danger of releasing toxic combustion products into the laboratory atmosphere. Off-line procedures have similar hazards, combined with time-consuming sample preparation. Here, we present a modification of an off-line nickel-pyrolysis method for hydrogen-isotope analysis (Motz et al., 1997), which uses simple, disposable materials that totally contain the analytical products, releasing only hydrogen into the mass spectrometer and laboratory atmosphere. We demonstrate good accuracy and reproducibility with a variety of solid and liquid materials. Furthermore, this system allows for the analysis of extremely small quantities of material, and presents the possibility of obtaining isotopic analyses of more than one element from a single sample.

All isotopic measurements are expressed in standard isotopic notation, such that

$$\delta^2\mathrm{H}_{\mathrm{sample}} = 1000\left[\left(R_{\mathrm{sample}}/R_{\mathrm{standard}}\right) - 1\right]‰,$$

where R is the $^2H/^1H$ ratio. The standard used is Vienna Standard Mean Ocean Water (VSMOW) normalized such that Standard Light Antarctic Precipita-

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tion (SLAP) $\delta^2H = -428‰$ and $\delta^2H_{VSMOW} = 0‰$ (see Coplen, 1996).

2. Materials and methods

The apparatus consists of pyrolysis bombs fashioned from 6-cm lengths of nickel gas–chromatograph tubing (nickel 200; 3.2-mm outside diameter; 0.5-mm wall thickness), which are sealed in evacuated 13-cm lengths of 9-mm quartz tubing (Fig. 1). To make pyrolysis vessels, the nickel tubing is cut to length, cleaned with acetone, then sealed at one end using a cold-welding tool (Pinch-off Systems: Team, Brookline, MA, 02146, USA) or TIG (tungsten inert gas) welding. The bombs are then baked at 1000°C under vacuum for 1 h to drive off any impurities. In all cases, 400 mg of manganese (Aldrich Chemical, −50 mesh, 99+%) is placed in the pyrolysis vessels as a reductant, prior to loading samples. This weight of manganese is used to ensure an excess. Solid samples are weighed into the bombs. Powdered materials are loaded using a funnel fashioned from a Pasteur pipette, while bulkier samples, such as polyethylene foil, are inserted with tweezers and pushed to the bottom with a stainless-steel rod. The bombs are placed in a vacuum dessicator overnight, then flooded with dry argon in a glove box and sealed using a cold-welding tool. For liquid samples, the manganese-containing bombs are placed under vacuum overnight, then flooded with argon. The liquids are introduced using a syringe while the vessels are in the glove box and the bombs are subsequently cold-welded.

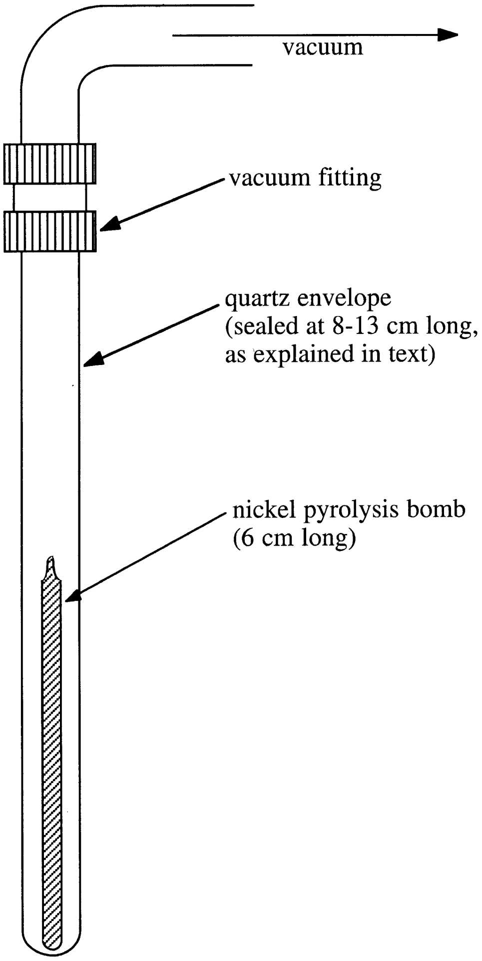

Fig. 1. Pyrolysis apparatus showing the sample-containing nickel bomb encased in a quartz envelope and connected to a vacuum line. The quartz tube is sealed at 8–13 cm in length and then heated at 975°C for 60 min, pyrolysing the sample and resulting in diffusion through the nickel of hydrogen, which is collected in the quartz envelope.

The sealed bombs are inserted in quartz breakseals on a vacuum manifold. For solid samples, the quartz envelopes are simply sealed. In the case of liquids, the portions of the tubes containing the nickel bombs are first inserted in liquid nitrogen and then sealed. This step is necessary to prevent premature reaction of volatile liquid samples under the heat of sealing the tubes. The quartz tubes are then heated at 975°C for 60 min. Speeds of heating and cooling appear to be irrelevant.

During pyrolysis, hydrogen is released from the sample (Thompson and Gray, 1977; Brenninkmeijer and Mook, 1981; Edwards et al., 1994; Motz et al., 1997), diffuses through the nickel and is trapped in the quartz envelope. A clean signal from the mass spectrometer confirms that only hydrogen is diffusing into the quartz tube. Other compounds are retained in the nickel tube. A 60-min reaction time was chosen based on experiments (Motz et al., 1997), which showed that shorter times resulted in depleted δ^2H values, possibly because of incomplete diffusion or reaction, leading to fractionation. A slightly lower reaction temperature of 975°C, versus 1050°C in earlier experiments (Motz et al., 1997), was deemed appropriate because the pyrolysis apparatus was much smaller than in the earlier work, and there were concerns that the cold welds would leak at the higher temperature. After pyrolysis, the samples are allowed to cool. A stainless-steel bellows tube breaker is then used to crack the quartz envelopes and introduce the hydrogen into the mass spectrometer (MicroMass 602C) for analysis.

3. Results and discussion

3.1. Calibration of apparatus

While the efficacy of pyrolysis for hydrogen analysis has been demonstrated, it has also been shown that systematic fractionating effects vary with the design of the pyrolysis bomb (i.e. variations in volume and wall thickness), necessitating calibration of any new apparatus (Motz et al., 1997). For the current design, calibration was first carried out using water of known δ^2H, then solid samples, which provide convenient working standards. Water samples with known δ^2H values of +11‰, −206‰ and −492‰ were prepared, using 5-μl aliquots, and reacted as described above, yielding the results shown in Table 1 and plotted in Fig. 2. Known δ^2H of water standards were determined using manganese reduction (Shouakar-Stash et al., 2000).

The perfect correlation of the regression in Fig. 2 indicates that the bomb- and machine-dependent fractionations are strictly linear and predictable over an approximately 500‰ range of true δ^2H values.

3.2. Solid standards

Because of the extra steps necessary to prepare liquid samples, solid standards are preferable for routine validation and recalibration of this technique. The materials chosen were polyethylene foil (IAEA CH-7) (Gonfiantini et al., 1995) and cystine (NIST 143C). The polyethylene has an accepted δ^2H of -100 ± 2.0‰, while the δ^2H of the cystine was unknown. Samples of 2.5-mg polyethylene foil and 3-mg cystine were loaded in nickel pyrolysis vessels with 400-mg manganese each, and processed as previously described. Results of these analyses are shown in Table 2.

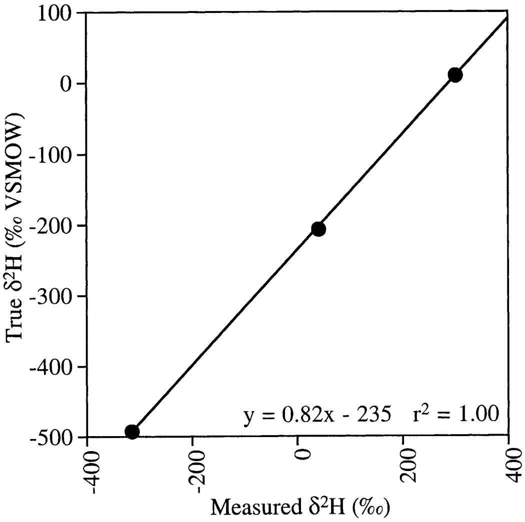

Fig. 2. Linear regression of water calibration data. Measured data are raw machine values with no corrections. Error bars are smaller than all data points.

Table 1
Actual and measured δ^2H values for water calibration standards

True δ^2H (‰VSMOW)	Measured δ^2H (‰)
+11	300 ± 5.1, $n = 4$
−206	39 ± 2.0, $n = 5$
−492	-315 ± 4.1, $n = 4$

Measured data are raw machine values with no corrections.

Average polyethylene foil corrected values of -97 ± 1.1‰ are slightly enriched by 3‰ over the accepted value of −100‰. An independent cross-check of the cystine by MicroMass UK Limited, using an on-line continuous-flow technique, yielded a δ^2H of 18 ± 2.7‰, which is close to the average

Table 2
Measured and corrected values for δ^2H of polyethylene foil and cystine

Polyethylene foil measured δ^2H (‰)	Polyethylene foil corrected δ^2H (‰VSMOW)	Cystine measured δ^2H (‰)	Cystine corrected δ^2H (‰VSMOW)
169	−98	314	21
168	−98	312	19
171	−96	313	20

Measured values are uncorrected machine values, while corrected values were derived by applying the regression equation from Fig. 2.

20 ± 0.7‰ figure obtained with this procedure. Subsequently, δ^2H values of −97‰ for polyethylene foil and 20‰ for cystine were employed as the known values when these standards were used to periodically recalibrate this method.

For further analyses, the length of the quartz envelope was reduced to 8 cm in order to conserve materials and increase the pressure of the hydrogen gas introduced into the mass spectrometer. Tests using polyethylene foil and cystine in the shorter tubes resulted in significant enrichments of approximately 25‰ for polyethylene foil and 8‰ for cystine when machine figures were corrected, using the original calibration equation (from Fig. 2) derived using water standards and 13-cm tubes. This is possibly because the lower pressure and greater length of travel in the longer quartz tubes favour the transfer of the more energetic light molecules to the mass spectrometer. While the calibration procedure automatically accounts for such systematic effects, this highlights the necessity of maintaining uniformity in the various components of the apparatus.

Precision with all samples analyzed for this paper was typically between ±1.0‰ and ±4.0‰. While this is somewhat less than the ±0.7‰ to ±1.8‰ obtained with manganese reduction (Shouakar-Stash et al., 2000), or the ±1.0‰ achieved with the continuous-flow IRMS equipment in the University of Waterloo Environmental Isotope Laboratory, it is certainly acceptable for most hydrogen isotopic analyses and may be improved with further refinement.

3.3. Other materials

To test the applicability of this procedure to materials which present a hazard if handled using conventional methods, a series of analyses was performed on seven common agricultural herbicides. Results of these tests are shown in Table 3. The 8-cm quartz tubes, 400 mg of manganese and 2.5–6 mg of sample were used in all cases. As can be seen from Table 3, this method provides good reproducibility with these compounds. It is unknown whether the variations in precision between the samples result from inconsistencies in the process or inhomogeneities within the samples, which are mixtures of several compounds, including filler material.

Table 3
δ^2H analyses of agricultural herbicides

Sample	Average corrected δ^2H (‰VSMOW)
A (Aatrex nine-O)	-170 ± 1.8, $n = 5$
B (Blandex nine-T)	-164 ± 3.8, $n = 3$
C (Classic)	-61 ± 1.0, $n = 3$
D (Fieldstar)	-102 ± 1.1, $n = 3$
E (Glean)	-120 ± 4.4, $n = 3$
F (Lorox DF)	-106 ± 2.9, $n = 3$
G (Striker)	-45 ± 3.7, $n = 3$

3.4. Other isotopes

Since the reaction products from pyrolysis are contained within the bombs, they can be recovered at a later time and analyzed for other isotopes. The nickel-pyrolysis method was originally developed to facilitate the analysis of oxygen isotopes from organic materials (Thompson and Gray, 1977; Brenninkmeijer and Mook, 1981; Edwards et al., 1994). The small pyrolysis vessels discussed in this paper have been successfully employed for oxygen isotopic analysis, using CO_2 extracted from the bombs with a puncturing device incorporated into a cryogenic separation line (Motz, 2000). Experimentation is also underway to recover chlorine from the bombs for determination of $^{37}Cl/^{35}Cl$ ratios, which may have important application in the study of chlorinated compounds, such as herbicides, pesticides and organo solvents. Such a system would provide an extension of environmental tracer research that currently relies on a variety of other complicated analytical methods for chlorine isotopic analyses (van Warmerdam et al., 1995).

4. Concluding comments

This method provides a simple means of accurately measuring δ^2H for a variety of materials for which other procedures would be difficult or hazardous. Furthermore, since combustion products are retained in the pyrolysis bombs after hydrogen is released, there is the potential to perform other analyses on these compounds, thus maximizing the information obtainable from each sample.

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