

AN ELECTROLYTIC DEVICE FOR PREPARATION OF HYDROGEN AND OXYGEN FROM WATER FOR ISOTOPIC ANALYSIS

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Summary—An electrolytic device for decomposition of water has been developed which readily gives hydrogen and oxygen for isotopic measurement with a mass spectrometer. A 20- μ l sample can be decomposed quantitatively in 10 min with good reproducibility. The results produced are comparable with those obtained by reduction with uranium.

Production of hydrogen from water is vital in the mass spectrometric analysis of water for isotopic ratio determinations. The methods available in the literature¹ are: (a) reduction with heated metals such as uranium and zinc, (b) reduction on heated filaments, (c) reduction by compounds such as calcium hydride and lithium aluminium hydride, (d) equilibration of water with hydrogen of known composition and (e) electrolysis. The first method is usually used for routine work. The other methods are less frequently used owing to their lower efficiency or greater fractionation problems. All these methods except electrolysis involve the interaction of water with some other reagent, which may be a source of fractionation or memory effects to a variable degree. Electrolysis appears to be a neat method; the fractionation problems associated with it may be overcome if the sample is completely electrolysed. In the electrolysis of water, the electrolytic fractionation factor with respect to the ¹⁶O/¹⁸O isotopes is only about 1.01–1.03. Thus, electrolysing only 90% of the water introduces a maximum error of only 0.6% in oxygen isotope analysis. However, the fractionation factor with respect to the ¹H/²H isotopes has been reported to range from 3 to 10.¹ It can be shown that even with a fractionation factor of only 3, electrolysing 99.72% of a sample of natural water will result in a deuterium concentration in the gas that is 14% too low and even electrolysing all but 0.0085% of the

water will result in a 4% negative error in the deuterium determination.¹

Wright² developed a method in which water was fed continuously into a V-shaped electrolytic cell operated under constant volume, temperature and current conditions. At equilibrium, which was reached within seven days, the number of moles of deuterium put into the cell as feed water was equal to the number of moles of deuterium leaving the cell as electrolysed gas and water vapour. The average deviation from the mean was 0.0002 mole%. If we could avoid the long equilibration time and electrolyse water quantitatively the electrolytic method would be advantageous in that it provides oxygen for ¹⁸O and ¹⁷O analysis in the same sample without any additional work. In the present work we report an electrolytic device by which small amounts of water can be quantitatively electrolysed in about ten minutes, making this method rapid, efficient and hence acceptable for routine work.

EXPERIMENTAL

Construction of the electrolytic device

The device is shown in Figs. 1 and 2. The upper part is made of Perspex and consists of an injection port and one nozzle for connection to a vacuum line through a valve by the use of Swagelok fittings (with Teflon ferrules). The injection port is provided with a rubber septum capped with a screw-on nut. The lower part (called the cell) consists of two stainless-steel (SS 316L) blocks (28 × 15 × 15 mm) held together by two bolts. A thin (0.2 mm) sheet of Teflon is placed between the blocks for insulation. The

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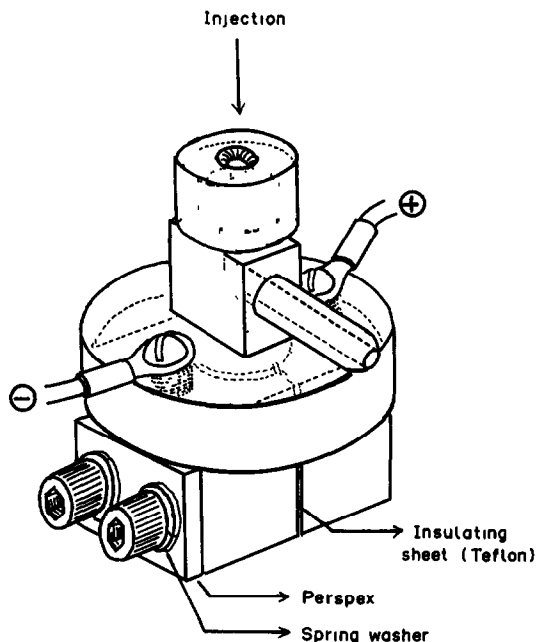


Fig 1 Perspective view of the electrolytic device

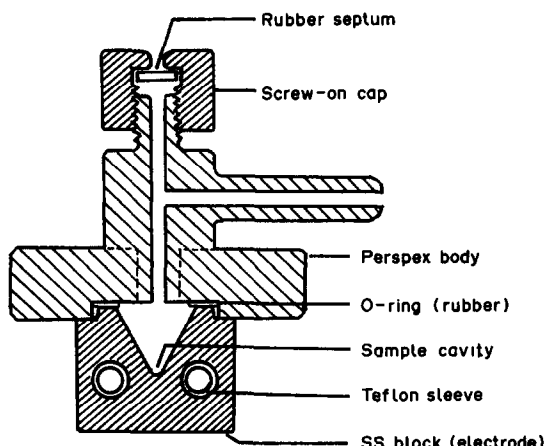


Fig 2 Cross-sectional view

bolts run through Teflon sleeves in one block (for insulation) and screw into the other. A Perspex sheet is provided between the heads of the bolts and the block for insulation. When joined together the blocks are well insulated and measure $30 \times 28 \times 15$ mm. One of the two 30×28 -mm surfaces of this piece, taken as the top, is machined to provide a 2-mm high circular platform about 20 mm in diameter. Each of the two blocks is machined at the top so that when they are joined together there is a conical cavity (about 5 mm deep and 8 mm in diameter) where the sample is placed for electrolysis. The injection port and the cell, with a rubber O-ring between them, are held together by two screws which also serve as connectors to a 6-V 10-A d.c. supply (or an ordinary car battery). Thus the two steel blocks act as the electrodes of the cell. A sample placed in the cavity is readily quantitatively electrolysed. The device is dismantled for cleaning by unscrewing the two screws joining the two parts. The dimensions are arbitrary and not critical except that the insulating Teflon sheet between the electrodes should be as thin as practicable to ensure contact of the liquid with both electrodes right up to the end, so that the maximum amount of water is electrolysed.

Sampling procedures

The device is connected to the inlet of the mass spectrometer by a Swagelok system and evacuated, after which the inlet valve is closed

and the metallic part of the device is immersed in liquid nitrogen so that the water vapour derived by evaporation of the sample into the evacuated system is condensed. When the sample is placed in the device it is put directly into the cavity, which is colder than the upper part. The water sample (around $20 \mu\text{l}$) is injected with a microsyringe through the rubber septum into the cavity. A small bead of a solid polymeric electrolyte (Nafion type, du Pont de Nemours), with a radius similar to that of the curvature at the bottom of the cone, is placed in the cavity, and no other electrolyte is required for the electrolysis. The liquid nitrogen bath is removed and as soon as defrosting at the outer surface starts, current is passed for about 10 min for electrolysis of a $15\text{--}20 \mu\text{l}$ sample. After this time the electrodes are again immersed in liquid nitrogen, with the current kept on so that any unelectrolysed water is trapped and electrolysed. Our experience indicates that 10 min is sufficient for complete electrolysis of $20 \mu\text{l}$ of water. The cell is allowed to warm to near ambient temperature and the valve to the inlet is opened to introduce the hydrogen-oxygen mixture thus obtained into the inlet for mass spectrometric measurements.

Analysis of tap water

A tap water sample ($20 \mu\text{l}$) was injected into the device and electrolysed for 10 min. The gaseous product was transferred to the "sample"

port of a Delta E (Finnigan MAT) mass spectrometer, which has a dual inlet system. The inlet is designed so that the gas enters pre-evacuated (5×10^{-5} bar) reservoirs of variable size (capacity 2–20 ml) through stainless-steel tubes (i.d. 3 mm, length 90 mm) on the “standard” and “sample” sides. Here the gas is kept for at least 1 min for equilibration, as the total volume of the system (reservoir cell and lines) is about 40 ml, the risk of overpressure and fractionation in the lines is covered. From the reservoir the gas is introduced into the mass spectrometer through capillaries by the use of pneumatically controlled valves. A working standard (20 μ l) is similarly electrolysed with the same device and transferred to the “standard” port of the mass spectrometer. Three sets of mass spectrometric measurements of the gaseous electrolysis product, each set consisting of twelve measurements for $\delta D/H$, were obtained with background measurement before and after each set. The $\delta D/H$ ratio is defined as:

$$\delta D/H = \frac{(D/H)_{\text{sample}} - (D/H)_{\text{std}}}{(D/H)_{\text{std}}} \times 1000\text{‰}$$

The mass spectrometer instrumental error thus evaluated was less than 0.2‰. The same procedure was repeated by taking ten more aliquots of the sample and the standard to determine the reproducibility of the electrolysis method. To compare the results with another method, ten aliquots of the sample and the standard were reduced over heated uranium according to the standard procedure^{3,4} and subjected to mass spectrometric analysis as before.

RESULTS AND DISCUSSION

The $\delta D/H$ values obtained for the tap water sample by the electrolytic and uranium-reduction techniques are listed in Table 1. The reproducibility of the electrolytic method is quite good (S.D. 0.135‰) and the results obtained by the two techniques are very close. In another experiment to demonstrate the “completeness” of electrolysis, the sample and the standard were taken from the same source, one being treated by electrolysis and the other by uranium-reduction. The mean $\delta D/H$ thus obtained was $-0.0258 \pm 0.005\text{‰}$ (see Table 2). The mean $\delta D/H$ value obtained by the uranium-reduction method in the experiment was $-0.0261 \pm 0.004\text{‰}$. Both values are statistically equivalent to zero and very close to each other, suggesting that the electrolysis is complete to

Table 1 Mean $\delta D/H$ values for 10 aliquots of tap water analysed by the electrolytic and uranium-reduction methods

Aliquot	Mean $\delta D/H$ (from three sets of 12 measurements each) \pm standard deviation, ‰	
	Electrolysis	Uranium-reduction
1	$-2\ 163 \pm 0\ 182$	$-2\ 256 \pm 0\ 191$
2	$-2\ 104 \pm 0\ 164$	$-2\ 531 \pm 0\ 135$
3	$-2\ 235 \pm 0\ 158$	$-2\ 467 \pm 0\ 177$
4	$-2\ 201 \pm 0\ 136$	$-2\ 438 \pm 0\ 160$
5	$-2\ 451 \pm 0\ 152$	$-2\ 300 \pm 0\ 163$
6	$-2\ 536 \pm 0\ 143$	$-2\ 315 \pm 0\ 158$
7	$-2\ 312 \pm 0\ 135$	$-2\ 281 \pm 0\ 131$
8	$-2\ 205 \pm 0\ 132$	$-2\ 320 \pm 0\ 152$
9	$-2\ 361 \pm 0\ 140$	$-2\ 256 \pm 0\ 141$
10	$-2\ 223 \pm 0\ 138$	$-2\ 111 \pm 0\ 125$
Mean \pm SD	$-2\ 279 \pm 0\ 135$	$-2\ 327 \pm 0\ 122$

Table 2 $\delta D/H$ values obtained by treating the sample by electrolysis and the standard by uranium-reduction, and by treating both by uranium-reduction

Aliquot	$\delta D/H$ (electrolysis and uranium- reduction), ‰	$\delta D/H$ (only uranium- reduction), ‰
	1	-0.032
2	-0.029	-0.032
3	-0.021	-0.025
4	-0.024	-0.023
5	-0.028	-0.030
6	-0.022	-0.031
7	-0.033	-0.027
8	-0.019	-0.021
9	-0.024	-0.025
10	-0.026	-0.027
Mean \pm SD	-0.0258 ± 0.005	-0.0261 ± 0.004

an acceptable extent. The sample preparation time for the uranium-reduction method was 20–30 min, which is about 2–3 times more than that for the electrolytic device. The new electrolytic device reported here therefore provides a rapid, efficient and precise decomposition method for water for subsequent mass spectrometric measurements.

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