

# *A system for accurate and fast measurement of the gas phase H/D ratio in electrolytic H/D separation factor experiments*

M. HAMMERLI AND W. J. OLMSTEAD

*General Chemistry Branch, Chalk River Nuclear Laboratories, Atomic Energy of Canada Limited, Chalk River, Ontario, Canada*

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Accurate and fast measurements of electrolytic hydrogen-deuterium separation factors are required to study short-term time effects and the effects of other variables, for example overpotential, before the cathode has suffered irreversible changes such as hydrogen embrittlement. A system for fast measurement of the hydrogen-deuterium ratio of the liberated hydrogen isotopes in argon as the sweep gas has been developed and is described in detail. Unique features include a modified Cartesian manostat and an automatic Toepler pump in the gas collection system, and an automatic mass spectrometer inlet system whose cycle time is about 4 min. Calibration procedures are outlined. The accuracy and reproducibility in the H/D ratio are  $\pm 1\%$  and  $\pm 0.5\%$  respectively, for the range 0.75 to 5.0 mol. % deuterium in mixtures containing 0 to 80 vol. % argon.

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## 1. Introduction

Measurements of electrolytic hydrogen-deuterium separation factors are important not only from the fundamental point of view regarding the well-known hydrogen evolution reaction [1-4], but also from the technical point of view regarding the reconcentration of downgraded heavy water from nuclear power reactors moderated by heavy water [5]. The electrolytic hydrogen-deuterium separation factor is defined by Equation (1):

$$S_{\text{HD}} = (\text{H/D})_{\text{gas}}/(\text{H/D})_{\text{liquid}} \quad (1)$$

Theoretical predictions as to the magnitude of  $S_{\text{HD}}$  are conflicting because of the complexity of the calculations and their inherent assumptions (e.g. see ref. [2]). Only in the limiting case of very high separation factors has there been good agreement between theory and experiment [6, 7].

Although Urey and Washburn [8] demonstrated the enrichment of deuterium in water by

the process of electrolysis as long ago as 1932, very few reliable experimental results for  $S_{\text{HD}}$  exist in the literature. In our opinion, the following two factors are mainly responsible for the poor quality of most of the data. Firstly, the separation factor is a function of many variables, some of which are hard to control, and include duration of electrolysis [9, 10], impurities in the electrolyte [11-13], nature of the cathode metal [14-16], overpotential [9, 14, 17] and temperature [6, 7, 18]. The effects of some of these have only recently been appreciated; for example,  $S_{\text{HD}}$  was first studied as a function of overpotential [19] in 1962. The second reason is that adequate instrumentation has not been available or was too costly until recently.

With the advent of suitable potentiostats and associated electronic equipment, the main instrumentation problem for accurate  $S_{\text{HD}}$  measurements reduces to measuring  $(\text{H/D})_{\text{gas}}$  rapidly and accurately. Evaluation of  $(\text{H/D})_{\text{liquid}}$  is not a serious problem for electrolyses liberating

about 1 or 2 cm<sup>3</sup> of hydrogen isotopes because the volume of catholyte can easily be made large enough so that (H/D)<sub>liquid</sub> remains virtually constant for a series of  $S_{HD}$  determinations. Therefore, measurement of (H/D)<sub>liquid</sub> described elsewhere [20], while important, is not time limiting. The measurement of (H/D)<sub>gas</sub> within a few minutes, however, is not an easy task if good reproducibility and accuracy are to be achieved.

Since the real surface area can change during and as a result of prolonged electrolysis [15], it is important to keep the duration of electrolysis as short as possible for each separation factor determination. At the same time it is desirable to study  $S_{HD}$  over as wide an overpotential range as possible, preferably on the same specimen of a given cathode material. Furthermore, from the theoretical point of view the deuterium concentration should not be greater than 10 Vol.% in the electrolyte [2, 3]. Otherwise, the simplifying assumptions that the H<sub>3</sub>O<sup>+</sup> and H<sub>2</sub>DO<sup>+</sup> ions, and H<sub>2</sub>O and HDO molecules are the only species undergoing discharge at the cathode in acidic and basic electrolytes respectively, are no longer valid.

The analysis system used to determine the H/D ratio of the liberated gases must therefore be capable of analysing about 1.5 cm<sup>3</sup> of hydrogen containing as little as 1% deuterium (mainly as HD) reproducibly and accurately in a few minutes. Good reproducibility requires more than one analysis on each 1.5 cm<sup>3</sup> of hydrogen isotopes. Good accuracy can only be achieved with reliable primary standards and gas handling operations which have been scrutinised for any tendency towards separation of the isotopes. It is the purpose of this paper to describe in detail

a system for measuring (H/D)<sub>gas</sub> which meets all of these requirements. Basically, the system consists of a gas collection system, which may be operated either in a batch or continuous collection mode, and an automatic mass spectrometer inlet system.

## 2. Gas collection system

### 2.1. Argon purge gas

The hydrogen isotopes produced electrolytically are swept out of the electrolysis cell by a purified stream of argon into the gas collection system shown schematically in Fig. 1. The amount of H<sub>2</sub> in the argon purge gas initially must be checked and should not be > 1 ppm. Matheson's ultra pure argon usually meets these requirements. The argon is further purified by passing it over a copper-copper oxide catalyst (BASF Canada, type R-3-11) at 120–150°C followed by a solid CO<sub>2</sub>-ethanol trap before it is humidified at the operating temperature with a solution of the same deuterium content as the electrolyte.

The argon-hydrogen isotope mixture leaving the electrolysis cell is dried by a water-cooled condenser on the cell itself and by means of a solid CO<sub>2</sub>-ethanol trap before it passes through the Cartesian manostat and into one of the evacuated collection lines. Between 3 and 5 litres of argon are used per collection.

### 2.2. Cartesian manostat

The sensitivity of the Cartesian manostat (Edwards High Vacuum Canada Ltd., Model 6) was greatly improved by replacing the original outlet orifice with a highly polished stainless steel

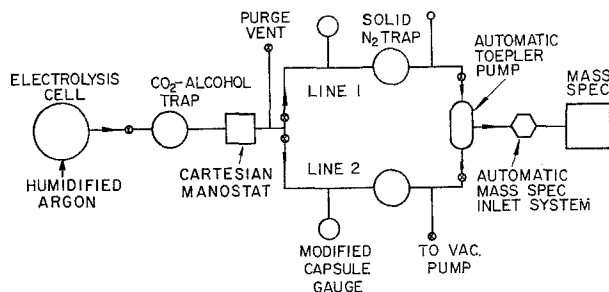


Fig. 1. Schematic diagram of electrolysis cell, gas collection system and H/D analysis system.

orifice (1.02 mm in diameter) and by replacing the neoprene gasket in the seat of the Cartesian diver with a silicone rubber gasket poured from a 1:2 mixture of benzene:Dow Corning silastic RTV 732. With these improvements, the manostat has operated on flow rates from 0 to 1.0 l min<sup>-1</sup> with the cell slightly above atmospheric pressure and the vacuum lines at 0.13 N m<sup>-2</sup> (10<sup>-3</sup> torr) with pressure fluctuations about the set point equivalent to no more than  $\pm 0.5$  cm of electrolyte. Also, the gas flow can be switched from the vacuum line at the end of a collection period (pressure about 13.3 kN m<sup>-2</sup>, or 100 Torr) to a vent to atmosphere with an initial fluctuation in liquid levels of only  $\pm 2$  cm. This degree of dynamic pressure control permits operation of the gas collection system either in a batch or continuous mode.

### 2.3. Solid nitrogen traps

To keep electrolysis times as short as possible, it is necessary to concentrate the hydrogen isotopes in the argon. This is accomplished by a solid-N<sub>2</sub> trap formed by pumping for 3 minutes on a liquid-N<sub>2</sub> trap with a 150 l min<sup>-1</sup> rotary vacuum pump. At the solid-N<sub>2</sub> temperature, 63° K, the vapour pressure of solid argon is about 0.4 kN m<sup>-2</sup> (3 torr). In practice, however, there is a maximum ratio of hydrogen (isotopes):argon above which the freezing down of the argon is partly diffusion controlled and hence slow. The system described here works well on samples containing no more than 3.5 cm<sup>3</sup> at S.T.P. of hydrogen and with argon content as high as 90%. Most samples are in the range 1–2 cm<sup>3</sup> but samples of 0.1 cm<sup>3</sup> have been analysed quantitatively. The average freeze-down time is about 10 min. and most samples will then contain in excess of 70% hydrogen isotopes. The freeze-down period is monitored on a 0–13.3 kN m<sup>-2</sup> (0–100 torr) capsule gauge [Edwards High Vacuum (Canada) Ltd., Model CG3] so modified that the aneroid of the gauge with its small volume forms part of the collection system.

### 2.4. Batch gas collection

When the gas collection system is operated in the batch mode, the electrolysis current is shut off

and the stopcock connecting the anode and cathode compartments [17] is closed between successive electrolyses. Hydrogen isotope samples from successive electrolyses are collected with argon at a flow rate of 1.0 l min<sup>-1</sup> for 3 min. and re-concentrated in collection lines 1 and 2 alternately (see Fig. 1) at a (maximum) rate of a sample every 20 min. for electrolysis times up to 5 min.

### 2.5. Continuous gas collection

When the gas collection system is operated in the continuous mode, the electrolysis current remains switched on for the duration of the experiment; this is definitely advantageous for observing time effects [9]. The argon flow rate is set at about 0.1 l min<sup>-1</sup> from the beginning of a collection period to the last 3 min. of this period when the flow rate is increased to 1.0 l min<sup>-1</sup>. At the end of a collection period, the gas stream is switched either to the other collection line or a vent to atmosphere. As in the batch mode, the maximum sampling rate is one sample every 20 min. for currents down to 50 mA.

It is important to collect *all* of the hydrogen isotopes from a given electrolysis to prevent significant separation [17] during collection, which would, of course, change  $S_{HD}$ . This fact has generally not been appreciated.

### 2.6. Automatic Toepler pump

An automatic Toepler pump (Eck and Krebs, 1 l capacity, Cat. No. 4105) is used to transfer a given gas sample from its collection line to the automatic mass spectrometer inlet system (see Fig. 2). A timer is used to delay the next pump cycle about 15 s. Five pump cycles are sufficient to transfer *all* of the hydrogen isotopes.

## 3. Automatic mass spectrometer inlet system

### 3.1. Inlet solenoid system

The inlet solenoid system connected to the Toepler pump (see Fig. 3) consists of a 1 mm glass capillary drawn down (by trial and error) to match the average sample inlet pressure, namely about 6.7 kN m<sup>-2</sup> (50 torr). The capillary

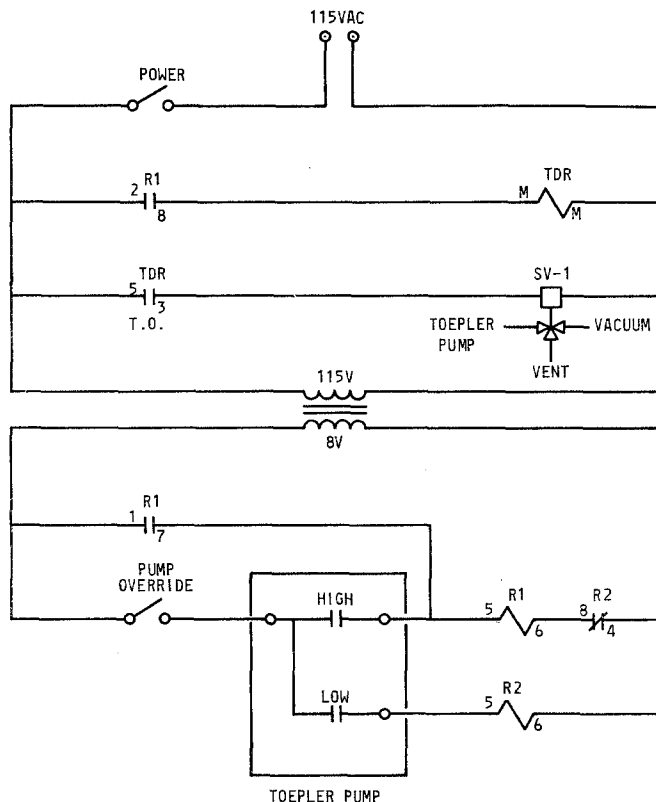


Fig. 2. Automatic Toepler pump circuit diagram. R1, R2-Strutters Dunn type B1XBX double-pole relays; TDR-Agastat model 2424 variable timer; SV-Ascoelectric three-way solenoid valve cat. no. 83143-B1.

is held in place by a double O-ring seal and can easily be changed to accommodate different inlet pressures. An iron rod with a silicone rubber seat is pressed against the tip of the capillary by a spring. When the inlet solenoid, consisting of the coil of an Ascoelectric valve (Cat. No. 8262C16) and the iron rod, is activated, gas is throttled through the capillary into the inlet manifold, which is of conventional design, of the mass spectrometer. A by-pass around the capillary allows rapid pump-out of the inlet solenoid system and the Toepler pump via the inlet manifold through the pump-out solenoid (see Fig. 4). The by-pass is also useful for manually analysing very small samples, for example  $0.05 \text{ cm}^3$  at S.T.P.

### 3.2. Mass spectrometer

A Bendix model MA-1 time-of-flight mass

spectrometer with two independent mass scanner units, so that masses 2 and 3 can be analysed simultaneously, is used. Modifications include an output integrator consisting of the electrometer amplifier, range multiplier and output amplifier sections of a mass scanner unit. This integrator gives a quantitative signal of all masses which *are not* gated by the two scanner units, that is all but masses 2 and 3 in the present case. For our samples, this signal corresponds to the amount of argon in the sample since the background signals for all other masses are orders of magnitude smaller unless air is present in the sample. Air is detected on the oscilloscope (Tektronix 453) readout of the mass spectrum; if the levels of oxygen and nitrogen are above background, signifying a leak, the sample is discarded. Since the apparent mass 2/mass 3 ratio is affected by both argon and air in this mass spectrometer, it is important to measure the former quantitatively and the latter qualitatively.

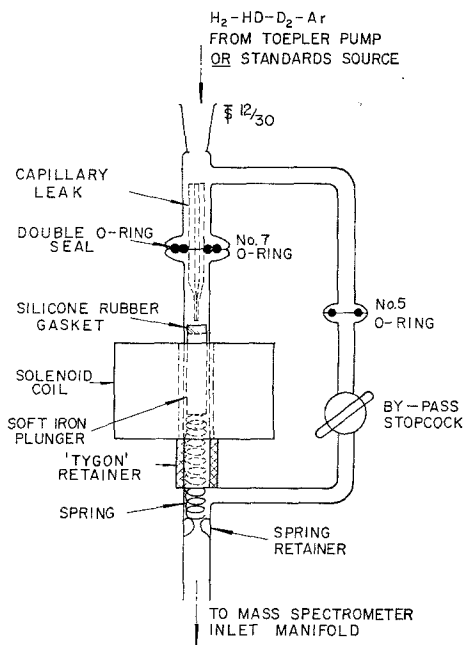


Fig. 3. Inlet solenoid system showing capillary throttle valve with double O-ring seal.

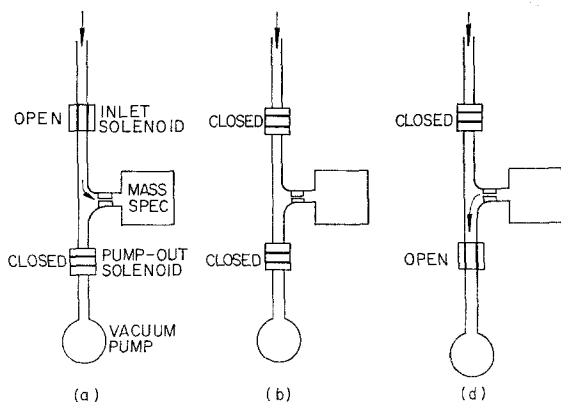


Fig. 4. Schematic of automatic cycle showing phases (a), (b) and (d) described in text.

### 3.3. Automatic cycle

Fig. 5 shows the circuit diagram for the automatic cycle. The circuit is designed to operate either automatically or manually. In the automatic mode, the peak decay time and the pump-out time are both variable from 0 to 120 s, but are normally pre-set at 30 s and 60 s respectively.

Before a cycle is initiated, the two mass scanners are pre-set on mass peaks 2 and 3 respectively. With the gate widths for each set at

maximum (variable from 10 to 100 ns), the peak tops are flat and the solid-state electronics are stable enough that the scanners sit on their respective peaks for days, requiring only minor adjustments periodically.

Fig. 4 shows a simple schematic of the cycle. The block labelled 'mass spec' includes a capillary leak. A cycle is initiated by activating the optical relay and setting S-1 and S-2 on 'automatic' from the 'override' positions (see Fig. 5).

In phase (a) of the cycle, the inlet solenoid is activated so that gas flows into the inlet manifold and the ion source of the mass spectrometer via the pre-selected capillary leak. Both mass 2 and mass 3 signals, recorded on a dual channel strip chart recorder (Moseley, Model 7100B-11-19 with two type 17501A plug-in modules), will start to grow. The mass 2 signal from the output of scanner 1 is also fed to the optical meter relay (A.P.I. Instruments, Canada, Model 502-L relay and type 903 control module). The cycle holds and the pressure rises until the mass 2 signal in the mass spectrometer reaches a pre-set value on the optical meter relay. Normally pressures vary over the range  $40 \mu\text{N m}^{-2}$  ( $3 \times 10^{-7}$  torr) to  $2.7 \mu\text{N m}^{-2}$  ( $2 \times 10^{-5}$  torr) for pure hydrogen isotope samples to 20% hydrogen isotope-80% argon samples. At this point, the inlet solenoid valve is closed [phase (b)] and the damped scanner output signals soon reach their maximum and start their natural decay (see Fig. 6). When the mass 2 signal has decayed to the same pre-set value as used for phase (b), the decay timer is activated [phase (c)], and the natural decay of each signal continues until the pre-set time on the decay timer has elapsed.

At a convenient point on the mass 2 decay curve, the output integrator signal is recorded and the H/D ratio calculated using the appropriate calibration factor.

At the end of the decay period the pump-out solenoid is activated [phase (d)] and the manifold pumped out for a pre-set time. The pump-out solenoid is then closed and the inlet solenoid opened simultaneously to start the next cycle. The cycle is completed in about 4 min. At least 3 cycles are run through for each sample. No memory effects are observed for samples whose deuterium content varies between 0.75 to 5.0 mol.%.

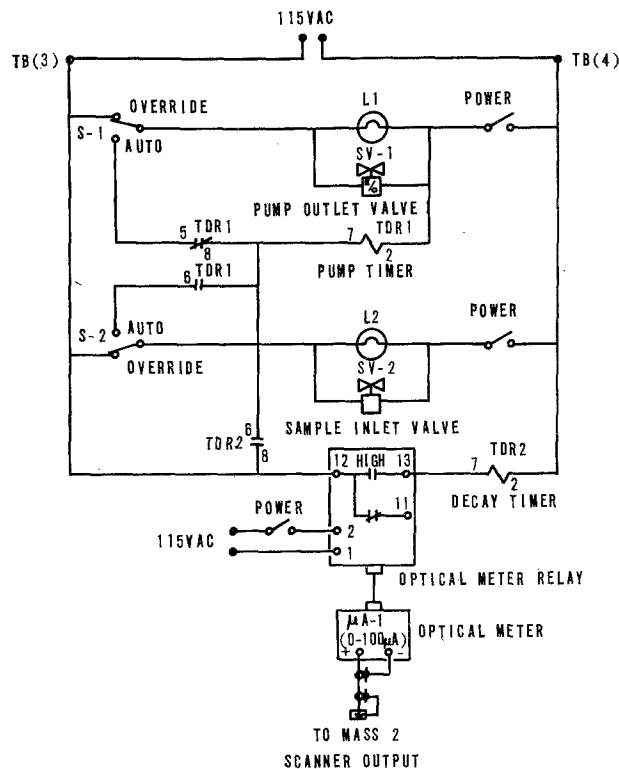


Fig. 5. Circuit diagram of the automatic mass spectrometer inlet system.

### 3.4. Calibration

As already mentioned, the observed H/D ratio is affected by the argon sweep gas. The mass spectrometer is therefore calibrated before each experiment with a secondary hydrogen isotope standard containing known amounts of argon using the automatic cycle just described. An electrolytic hydrogen generator (Milton Roy, Model Elhygen HI-P) is used to produce the secondary H/D standard. Each calibration gas mixture is analysed 5 or 6 times. The  $HD^+$  sensitivity factors relative to  $H_2^+$  are calculated for each analysis at the point where the H/D ratios of the samples will be determined. The corresponding output integrator signal, which is proportional to the argon content, is recorded. Alternatively, the pressure in the mass spectrometer has been used for this purpose but is not as accurate. Fig. 7 shows typical calibration curves as a function of percentage argon in the mixture. Only one H/D secondary standard is

required for the range 0.75 to 5.0 mol.% deuterium.

The primary H/D standard is produced by the total reduction of a  $D_2O-H_2O$  standard prepared gravimetrically, over hot uranium metal; the procedure is given in detail elsewhere [17].

### 3.5. Accuracy, stability and settling time

The accuracy of the H/D ratio depends on the accuracy of the primary standard and the calibration technique and is estimated at  $\pm 1\%$ . The reproducibility in the H/D ratio, which depends directly on the stability of the mass spectrometer, is  $\pm 0.5\%$  or better for a 12 h period.

Once the mass spectrometer has been calibrated, it remains so even for experiments lasting 36 h as long as all critical settings remain unchanged. This extraordinary stability is in part due to an external constant voltage regulator (Superior Electric Co., Model IES9103), and

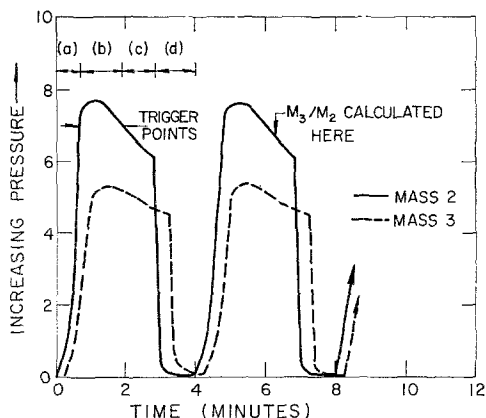


Fig. 6. Two cycles of the pressure (indicated as mass 2 voltage after amplification) versus time curves of the automatic increasing pressure sample introduction technique. The apparent time lag between the two curves is due to the physical separation of the two recorder pens.

an air conditioner which regulates the room temperature within  $\pm 2^\circ\text{C}$  of the set point and keeps the relative humidity at less than 45%.

The settling time of the mass spectrometer is here defined as the time necessary to obtain the first constant H/D ratio of a given standard when the mass spectrometer settings are changed from the stand-by to the operate mode. Experience has shown that if the filament (0.127 mm diameter tungsten wire) is left on at a temperature just below that required for thermionic electron emission, the settling time approaches 8 min, or two automatic cycles. This procedure does not shorten filament life.

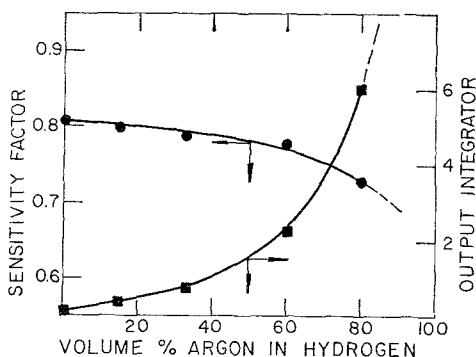


Fig. 7. Typical calibration curves (a) for the mass 3 sensitivity factor relative to unity for mass 2 and (b) the relative argon abundance (indicated as a voltage on the current integrator) for a preset value of the mass 2 abundance in the mass spectrometer versus the vol % argon in a 1% (nominal) deuterium secondary standard.

#### 4. Summary

(1) A gas collection system and an  $(\text{H}/\text{D})_{\text{gas}}$  analysis system have been developed for measuring electrolytic H/D separation factors accurately at a maximum rate of one determination every 20 min.

(2) The gas collection system incorporates a modified Cartesian manostat capable of handling flow rates from 0 to  $1.0 \text{ l min}^{-1}$  between the cell at  $0.1 \text{ MN m}^{-2}$  pressure and the collection line at  $0.13 \text{ N m}^{-2}$  pressure with pressure fluctuations about the set point equivalent to no more than  $\pm 0.5 \text{ cm}$  of electrolyte. This degree of control permits operation either in a batch or a continuous electrolysis mode.

(3) The gas collection system also incorporates solid- $\text{N}_2$  traps in which the hydrogen isotopes are concentrated by freezing out most of the argon sweep gas. This effectively reduces the electrolysis time so that short time effects in  $S_{\text{HD}}$  may be observed.

(4) Analysis of the  $(\text{H}/\text{D})_{\text{gas}}$  ratio is carried out on a Bendix MA-1 time-of-flight mass spectrometer equipped with an automatic inlet system whose cycle time is 4 min.

(5) The accuracy and the reproducibility of the  $(\text{H}/\text{D})_{\text{gas}}$  ratio are  $\pm 1\%$  and  $\pm 0.5\%$ , respectively, for hydrogen isotope samples of 1 to  $2 \text{ cm}^3$  at S.T.P. containing from 0 to 80% argon.

(6) Real changes as small as 2% in  $S_{\text{HD}}$  can be measured with the system described.

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