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Final Report

STUDY OF THE MODE OF FORMATION OF MOLECULAR HYDROGEN IN NATURE

By: H. L. Brown
Physical Sciences Division

Prepared for:

OFFICE OF NAVAL RESEARCH
800 N. Quincy Street
Arlington, Virginia 22217

Contract Number N00014-75-C-1117
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P. A. Jorgensen
Vice President
Physical and Life Sciences
INTRODUCTION

This final report covers work performed from 1 June 1975 to 30 September 1977 for contract No. N00014-75-C-1117 between SRI International and the Office of Naval Research (ONR). The purpose of the contract was to study the modes of formation of molecular hydrogen in nature, particularly in the ocean. The objective of this program was to develop a special-purpose mass spectrometer that would make it possible to obtain the desired data.

TECHNICAL BACKGROUND

A complete description of the technical problem is given in SRI's proposal PYU 73-122 dated July 11, 1973 (Appendix A). Briefly, the problem is to determine the sources of planetary molecular hydrogen by (1) determining molecular hydrogen concentrations in seawater in the range of $10^{-7}$ to $10^{-11}$ M with a precision of 1% or better and (2) determining the isotopic composition of molecular hydrogen from the atmosphere or other origins with a precision of 0.01% or better. The proposed method for determining seawater hydrogen concentrations was to use isotope dilution analysis, with deuterium as the diluting gas, followed by a mass spectrometric determination of the $\text{H}_2^+$/D$_2^+$ ratio. The proposed method for determining the isotopic composition of atmospheric hydrogen was to extract the hydrogen from air as water and to make a mass spectrometric determination of the D$^-$/H$^-$ ratio produced from the resulting water sample. We planned to use the same instrument for the positive and negative ion determinations.
WORK ACCOMPLISHED

Instrumentation

A number of mass spectrometer manufacturers produce instruments capable of making D/H ratio measurements on pure hydrogen gas samples. These instruments as they are standardly produced do not incorporate the design features we considered necessary for our research, nor are they capable of negative ion operation. At the same time however, one must recognize that manufacturers possess a great deal of experience in producing standard spectrometers and that by purchasing a complete spectrometer system from a single source one can realize a considerable cost reduction compared with the cost of purchasing individual components from a number of different sources. Therefore we elected to purchase a main frame commercial isotope ratio mass spectrometer, constructed to our specifications, that could be modified to achieve our proposed objectives. Because of the limited funds provided for this purpose, only one manufacturer, Nuclide Corporation, responded to a request for bids to provide such an instrument. The specifications agreed upon by SRI and Nuclide Corporation are contained in Appendix B.

The instrument, a modified Nuclide Corporation type 3-60-RMS mass spectrometer system, is shown schematically in Figure 1. The ions formed in the ionization source are accelerated to a given energy, separated according to their momenta by the sector magnetic field, and collected at locations along the dispersion plane corresponding to the masses of interest. With this instrument, one can simultaneously collect any two ions with $e/m$ in the ratio of 1:2, for example, in the positive ion case $\frac{2^+}{4^+}(H^+:D^+)$ and in the negative ion case $1^-:2^-(H^--D^-)$. The collected ion currents are subsequently amplified and converted to voltages whose ratio can be determined with high precision using two alternate techniques. In either technique, a fraction of the more abundant ion signal can have its polarity inverted and be applied (via a
feedback loop) against the smaller signal to null out the majority of the smaller signal. Then the larger signal and the balance of the smaller signal, are measured simultaneously either from a strip chart recording or by a frequency cycle counting technique using a voltage to frequency convertor. By measuring the magnitude of the larger signal, the fraction that is applied against the smaller signal, and the remainder of the smaller signal, one can compute the detected ion current ratio of the two original signals with high precision.

Absolute isotope ratio measurements require extreme care and detailed corrections to account for instrumental mass discriminations, but measurements of relative differences of ratios (i.e., the difference between the isotopic ratio for a given sample and the isotopic ratio for some standard) are comparatively easy to perform and provide all the necessary information required for our purposes. For relative ratio measurements, the sample inlet system shown in Figure 2 is used in conjunction with the ratio mass spectrometer described above. One sample reservoir (or trap) on the inlet system (Figure 2) is filled with the standard gas and the other with the sample, whose relative isotopic composition is to be determined. After the gas flow in the viscous leaks has stabilized, the switching valves are actuated in diagonal pairs to alternately allow a gas to flow from its reservoir either to the waste pump (while the second flows into the spectrometer) or into the spectrometer (while the other flows into the waste pump) without disturbing the flow through the viscous leaks. When the ratio spectrometer described above is used in conjunction with such an inlet system, ion current ratios for the sample gas or for the standard gas can be alternately measured. If the operating conditions have remained the same (except that two different gases have been admitted to the ion source), it is possible to determine the relative difference of the two ratios with high precision. The form of this information as it is generally reported is the "del" value defined by

$$ \delta = \frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \times 1000 \ \% $$
SAMPLE TAPER JOINTS

Vent to Mechanical Pump

COLD TRAP

THERMOCOUPLE GAUGE

To Mercury Diffusion Pump

VARIABLE VOLUME SAMPLE RESERVOIR

MICRO TRAP

MERCURY MANOMETER

VISCOS LEAK

WASTE PUMP

AIR-ACTIVATED SWITCHING VALVES

To Spectrometer Ion Source

FIGURE 2 SAMPLE INLET SYSTEM
where R is the isotopic ratio determined for that particular gas. (The symbol \( \delta \) denotes parts per mil). Standards are typically chosen so that \( \delta \) values are a few \( \delta \). The advantages in this practice are:

1. gas flow characteristics are essentially the same from sample to standard; 
2. signal voltage characteristics are essentially unchanged from sample to standard (reducing concern about voltage coefficients and similar effects); 
3. instrumental mass discrimination effects are reduced, and 
4. in general, any differential effect is minimized.

**Negative Ion Measurements: Isotopic Composition of Atmospheric Hydrogen as Water**

A desirable technique for determining hydrogen isotopic compositions is to observe the negative ions of hydrogen rather than positive ions in the classical fashion. This is because the positive ion method requires measurement of \( 2^+ \) and \( 3^+ \), and \( 3^+ \) is ambiguous since this mass ion can be produced either by the HD\(^+\) one wishes to observe or by H\(_3^+\) produced from the reaction \( \text{H}_2^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H} \), which almost always occurs to a small extent in the ionization source. The negative ion spectrum is not subject to this uncertainty since the only assignments possible for \( 1^- \) and \( 2^- \) are \( \text{H}^- \) and \( \text{D}^- \) under normal operating conditions. Recently, the ion H\(_2^-\) has also been observed, but only in a dense plasma discharge ionization source, and even then the observed ion current of H\(_2^-\) is only \( 10^{-7} \) of the H\(^-\) current and is therefore negligible for our purposes.

There is however a difficulty connected with negative ion methodologies, which is producing sufficient numbers of ions. The direct production of H\(^-\) from H\(_2\) is particularly inefficient: its maximum cross section is \( 2 \times 10^4 \) times smaller than that for the direct production of positive ions in H\(_2\). Practical limitations in electron current and gas pressure thus preclude the use of H\(_2\) itself as a sample gas. However, H\(_2\)O appears to be a reasonable substitute for H\(_2\), and could be used after conversion of the H\(_2\) sample to H\(_2\)O. The maximum cross section for H\(^-\) production from H\(_2\)O is \( 6 \times 10^{-18} \text{ cm}^2 \), which is 350 times larger than that from H\(_2\). There are still some drawbacks in the use of H\(_2\)O, however.
First, the published cross sections show a maximum as a function of electron impart energy at \( \sim 7 \) eV. It is difficult to produce large electron currents at such low energies. Second, the \( \text{H}^- \) ion is produced by dissociative attachment and can have several eV of kinetic energy when it is formed and therefore presents special ion extraction problems. Third, water vapor is significantly more difficult to work with in a vacuum system and presents handling problems not encountered with "ideal" gases. While the manufacturer was constructing the mass spectrometer system, we proceeded to design, build, and test the ionization sources required for the instrument. Two ionization sources were constructed; one for producing positive ions (discussed later) and one for producing negative ions, taking into account the considerations given below.

In designing the negative ion source, the problem we considered most difficult was that of producing sufficiently large (\( 10^{-5} \) A) electron currents at low energies. The largest electron current that can be supplied to a given volume is obtained by operating in the space-charge-limited mode. Therefore, we investigated the theory of space-charge-limited electron guns and found that in principle, it is possible to achieve the goal of producing electron beams of \( \sim 50 \) \( \mu \)A at \( \sim 7 \) eV, the desired energy. A prototype of such a gun was tested in a bell jar vacuum station and incorporated into the ionization source shown in Figure 3. The figure shows that the electron gun is followed by a 127° electrostatic energy analyzer. The reasons for this are as follows: The linear dimensions of the gun are such that it cannot be placed transversely in the ionization source volume of the spectrometer without requiring redesign of the ionization source chamber. Further, the gun supplies electrons with a circular image whereas a ribbon of electrons would be preferable. The electrostatic sector has point-to-line focal properties that accomplish this. An added benefit of such focusing is that it minimizes space-charge effects after the beam exits the final aperture of the electron gun. In addition, the electrostatic sector allows positive control of the energy and the energy spread of the electron beam entering the ionizing region.
FIGURE 3 NEGATIVE ION SOURCE
This ionization source was tested in a bell jar system, because the Nuclide spectrometer had not yet been delivered. The electric sector performed well and in accordance with theory; however, at 6.5 eV, the maximum current of energy analyzed electrons was 7 µA rather than the 50 µA required. Development of this ionization source was suspended because of delivery of the mass spectrometer. Furthermore, subsequent findings (see below) obviated the need to continue this particular work. The mass spectrometer and most of the electronic components (except the dual inlet system) were delivered on February 23, 1976. At that time the negative ion sources development was at the stage mentioned above and the positive ion source, which had been developed simultaneously (see the positive ion discussion), was available to be tested on the spectrometer. When the positive ion source was checked for its ability to produce negative ions from H₂O, we observed two important results. First, as shown in Figure 4, we observed that although there was a maximum in the mass analyzed H⁻ current detected at low electron energies, after going through a minimum in the vicinity of 14 eV the H⁻ current again rose as a function of electron energy and became a slowly varying function of energy beyond ~35 eV. The data in Figure 5 were taken with the current to the electron trap held constant, however it is not known whether the high energy behavior is representative of the relative H⁻ production cross section, or is affected by the characteristics of the ion source. We are not aware of any H⁻/H₂O cross section data for energies above 20 eV. In any case, these results suggested the possibility of operating at higher electron energies without suffering a loss in ionization efficiency and with the ability to produce much higher ionizing electron currents than are achievable at low electron energies. The second important finding was that the source developed for positive ion work could produce a mass analyzed H⁻ ion current of 0.5 x 10⁻⁹ A at these higher energies. This was extremely encouraging since the statistical precision considered necessary for the experiments (1 part in 10⁶), requires H⁻ current ~1 x 10⁻⁹ A for current integration times of 100 seconds. Conversely, to attain this precision with 0.5 x 10⁻⁹ A of H⁻, current integration times of ~200 seconds are required. We considered
FIGURE 4  H⁺/H₂O VERSUS ELECTRON ENERGY
this acceptable and concluded that preliminary ratio measurements could be made as soon as the dual inlet system was delivered. However, this was too optimistic, for reasons that shall be explained using Figure 5.

Figure 5 is a strip chart recording showing the change in H\(^-\) current observed when water vapor admitted from the dual inlet system was suddenly interrupted by switching to the other sample volume which was empty for these experiments. In the recording, the H\(^-\) current appears noisy or unstable. This was attributed to unstable pumping of the water vapor admitted to the spectrometer. The recording also shows that when the H\(_2\)O flow into the spectrometer is interrupted, the H\(^-\) current does not drop to some negligibly small value as it would for other gases; instead the ion current exhibits an initial sharp decline followed by a subsequent very slow decrease. A similar response was observed in the analyzer pressure. This situation deteriorated to the extent that the base pressure of the system could not be reduced below \(\approx 2 \times 10^{-6}\) Torr and background H\(^-\) signal rose to \(\approx 6 \times 10^{-10}\) A, which obscured the signal due to the added H\(_2\)O.

There are several reasons for this high background problem. The first is that the mass spectrometer as supplied by the manufacturer was unable to handle the specified H\(_2\)O sample flow rate of 1 \(\times 10^{-4}\) Torr \(-1\) sec\(^{-1}\) and obtain a base pressure of \(10^{-8}\) Torr. The maximum total pumping speed available from the ion pumps included with the spectrometer was 36 liters/s (25 liters/s at the source and 11 liters/s at the detector) at the mouths of the pumps. The 11 liter/s pump was located close enough to the detector chamber to provide its full pumping speed there, but the 25 liter/s source pump was located \(\approx 60\) cm from the source chamber, thus reducing the pumping speed available at the source by 50%. Additionally, the final ion beam defining slits were mounted so as to provide differential pumping of the analyzer tube and detector region; hence, the 11 liter/s pump did not aid in the removal of sample gas admitted to the ionization region. Therefore, the total available pumping speed in the ion source housing was only 12 liter/s for H\(_2\)O. This proved to be inadequate.
A second reason for this high background is that the means provided by the manufacturer for baking the system (two heating tapes and a power-stat) were insufficient. We supplemented these by additional heater tapes, but since some regions could not be heated by this method while the spectrometer was in operation, some of the admitted sample was trapped on the walls, resulting in high background signals from outgasing.

Still another problem existed because the ion pumps supplied were not capable of extended operation at the maximum sample flow rate (specified at $1 \times 10^{-4}$ Torr liters/s) without overheating, outgasing, and eventually shutting off. Nevertheless, at lower sample flow rates it may still have been possible to distinguish the desired signal from the background by using the synchronous chopper/detector system specified on page 2 in Appendix B. However, Nuclide had not developed such a system by the stop-work date of this contract, (September 30, 1977).

Positive Ions Measurements: Hydrogen Concentrations in Seawater

The analytical method is described in detail in the original proposal, PYU 73-122 (Appendix A), and further elaborated in our renewal proposal, PYU 76-052 (Appendix C). The technique entails addition of a known amount of $D_2$ spike to the seawater sample, equilibration of $D_2$ with the sample, extraction of the total gas from the water, and determination of the $H_2/D_2$ ratio in the extracted gas as $H_2^+/D_2^+$ using the ratio spectrometer described earlier. From this ratio, the known amount of added $D_2$, and the volume of the water sample, the original $H_2$ concentration in the water may be calculated.

Since there are a number of standard extraction techniques used by other investigators, we concentrated on determining the $H_2/D_2$ ratio, using the isotope ratio mass spectrometer. We assumed that the typical sample introduced to the spectrometer would consist of 1 cm$^3$ STP $D_2$ in which $H_2$ would be present at a level of $\sim$2 parts in $10^8$. That concentration would require an ionization source capable of producing $1 \times 10^{-9}$ A of $D_2^+$ from a gas flow rate of $1 \times 10^{-4}$ torr - liters/s into the spectrometer. This would permit measurement of the $H_2$ concentration with a precision of 1% in a reasonable length of time ($\sim$4 min).
Furthermore, we assumed the ionization source needed to operate at 30 eV or below in order to avoid formation of D\(^+\), which would complicate our analysis since D\(^+\) has the same mass as H\(_2\)\(^+\). Commercially available ion sources known to us do not obtain that efficiency; therefore, we elected to construct our own ionization source. This work proceeded in parallel with the negative ion source work.

The positive ionization source developed is shown in Figure 6. Formation of unwanted ions produced by ion molecule reactions within the source was avoided by injecting the sample into the electron beam with a hypodermic syringe. The remainder of the source was kept open so that the gas was immediately pumped away. This approach minimized collisions of the H\(_2\)\(^+\) and D\(_2\)\(^+\) with H\(_2\), which could result in second order, pressure dependent production or loss mechanisms for H\(_2\)\(^+\). To verify the effectiveness of this method before the Nuclide instrument was delivered, we operated the source on another magnetic sector instrument and monitored ions 1\(^+\), 2\(^+\), and 3\(^+\) (corresponding to H\(^+\), H\(_2\)\(^+\), D\(^+\) and HD\(^+\)) as a function of sample flow rate. The ions were linearly dependent on flow, thereby confirming their direct production from the hydrogen introduced. Figure 7 shows this linearity for H\(_2\)\(^+\) produced by 70 eV and 100 eV electrons.

When the Nuclide instrument was received, this source was installed in it and found to achieve an ionization efficiency (including mass analysis) of \(\sim 1 \times 10^{-5}\) ion/molecule at 30 eV electron impact energy. This exceeds the efficiency of commercially available ion sources by \(\sim 10\), and also exceeds our minimum efficiency requirement.

In our original proposal we had assumed that if we operated at electron energies below the dissociative ionization threshold there would be no interference at mass 2 by the possibility of simultaneously observing D\(^+\) and H\(_2\)\(^+\). However, the ability of the ratio instrument to simultaneously monitor two ions lead to the observation that D\(^+\) (or H\(^+\)) was produced along with D\(_2\)\(^+\) (or H\(_2\)\(^+\)), even at electron energies well below 18 eV as shown in Figure 8. Further, the number of ions produced by the dissociative process, varies rapidly with electron energy until the energy reaches \(\sim 35\) eV after which it changes slowly as the electron energy is increased. Since the dissociatively ionized fraction remains approximately constant beyond 50 eV and also, as shown in Figure 9, the
FIGURE 6  POSITIVE ION SOURCE
FIGURE 7  TOTAL ION CURRENT COLLECTED VERSUS H₂ BACKING PRESSURE
FIGURE 8 \( \frac{H^+}{H^+ + H_2^+} \) VERSUS ELECTRON ENERGY
FIGURE 9  H$_2^+$ PRODUCED VERSUS ELECTRON ENERGY
ionization efficiency for producing the molecular ion remains high and varies only slowly beyond 35 eV, we elected to perform future work at 70 eV.

The existence of ions produced by dissociative ionization required corresponding revision of the intended analytical procedure, namely the extent of the dilution by D₂ as shown below. After receiving the dual inlet system in June 1976, we were able to verify the internal precision of the mass spectrometric system (≈ 1 part in 10⁶), using pure H₂ as the sample and standard gas. Stated differently, the smallest detectable difference in isotopic composition between the sample and standard was 1 x 10⁻⁴ for H⁺/H₂⁺ ∝ 10⁻², so that, in principle, one could detect 1 part in 10⁶ H₂ in D₂. Subsequent mechanical improvements to the low mass ion collector produced internal precisions measured on the D⁺/D₂⁺ system of ≈ 2 x 10⁻⁵ or a smallest detectable ratio difference of ≈ 2 parts in 10⁷. Because of the existence of D⁺/D₂ (or H⁺/H₂), one is forced to measure the ratio (D⁺ + H₂⁺)/D₂⁺ instead of H₂⁺/D₂⁺ as planned; and, since one can measure the D⁺ contribution to a precision of 2 parts in 10⁷, the H₂-D₂ sample supplied to the spectrometer must have H₂ present in concentrations greater than 2 parts in 10⁷ in order to be distinguished from D⁺. Therefore, the largest permissible dilution ratio is ≈ 2 x 10⁻⁵ = H₂/D₂ if we are to determine the H₂ contribution with ±1% error. This does not represent any serious practical problem except for sample size. Recall that in the original proposal we had assumed 10 cm³ of seawater to which 1 cm³ STP D₂ was added, with the result that the assumed H₂/D₂ ratio in the extracted gas sample was 2 parts in 10⁸. The above finding simply changes the size of the required water sample to 1 liter. This work was performed prior to introduction of H₂O into the system. After H₂O had been introduced in order to perform the negative ion work described earlier, the background ion currents were too high to proceed further until the H₂O sample retention problem was solved.

We began construction of a bakeout oven that would allow a complete high temperature bakeout. While this was in progress, the pumping system was changed. The 11 liter/s pump was returned to Nuclide Corp. for a warranty repair of a leak. In its place, we added an ionization gauge
for pressure measurements. We removed the 25 liter/s ion pump from the source and replaced it with a 2-in. diffusion pump filled with polyphenyl ether and trapped by a freon refrigerated cryotrap. This combination provided an estimated 100 liter/s pumping speed at the mouth of the trap and approximately 25 liter/s at the source chamber. Pressure read on the ionization gauge could not be reduced below \( \sim 2 \times 10^{-5} \) Torr and the background \( \text{H}_2^+ \) ion current rose to \( \sim 10^{-12} \) A. We subsequently removed the diffusion pump and dismantled the entire spectrometer for cleaning. When the instrument was reassembled, the 25 liter/s ion pump, which had previously been used on the source chamber, was installed at the detector chamber. A liquid nitrogen cooled sorption pump was also added to the detector chamber for providing rough vacuum during the initial pump down. At the ionization source chamber, we installed a 60 liter/s ion pump with a titanium sublimation pump appendage and a second liquid-nitrogen-cooled sorption pump to provide rough vacuum. By this time, the bakeout oven was also completed so that the entire system could be processed at high temperature after initial pump down.

The system was baked for a period of 3 days with the maximum temperature at \( \sim 300^\circ \), after which the pressure throughout the entire instrument was in the low \( 10^{-9} \) Torr range. After the oven was removed, the instrument exhibited a number of internal failures that could only be repaired by breaking vacuum, requiring the bakeout cycle to be repeated. Again, the ultimate base pressure throughout the system was in the low \( 10^{-9} \) Torr range and the measured background ion currents for both \( \text{H}_2^+ \) (\( \text{H}_2^+, \text{D}^+ \)) and \( \text{D}^+ \) (\( \text{D}_2^+, \text{He}^+ \)) were \( \sim 6 \times 10^{-14} \) A. There was no detectable negative ion current and \( \text{H}_2\text{O} \) was not admitted to the system since we did not want to risk contamination until the positive ion work was concluded. We then resumed work on the positive ion methodology by making measurements on artificial mixes of \( \text{D}_2 \) and \( \text{H}_2 \) to experimentally confirm the maximum dilution possible and to check for any unexpected instrumental behavior. The results of these experiments are presented in Figure 10.

Detailed analysis of the data in Figure 10 led us to conclude that within pressure measurement errors, the mass spectrometric response appears to reproduce the ratio determined by pressure measurements, and that the maximum allowable dilution is \( \text{H}_2/\text{D}_2 \sim 10^{-5} \). The latter con-
clusion is based on several pieces of information. First, by making repeated measurements on the same sample mixture, we found the internal precision of the instrument to be $\sim 2 \times 10^{-7}$ of the D$_2^+$ current, just as was found earlier for D$^+$/D$_2^+$. Hence, the minimum abundance ratio allowable for a 1% measurement is $\sim 2 \times 10^{-5} = \text{H}_2$/D$_2$. Secondly, recall that the background ion current is $\sim 6 \times 10^{-14}$ A and that we normally make measurements with $\sim 10^{-9}$ A, which might lead one to conclude that the minimum ratio should be $\sim 10^{-4}$. However, ratio measurements are always made by comparing the sample with a standard. The instrument is designed to switch back and forth, making alternate measurements of the sample and standard so that if the background fluctuates no more than $\sim 10\%$ during a measurement, dilutions of $10^{-5}$ can be used, as verified by the internal precision measurement mentioned above. The third piece of information is the standard error determined for the ratio measurements presented on the dilution graph in Figure 10. For example, the mass spectrometric error associated with the H$_2^+$/D$_2^+$ ratio plotted on that graph at $\sim 3.5 \times 10^{-5}$ was determined to be $\sim 1\%$ by making repeated measurements and calculating the standard deviation for these measurements.

With this information in hand, we proceeded to attempt measurements of the quantity of dissolved hydrogen in three fresh water samples (two of tap water, one of distilled water equilibrated with the atmosphere). A 450-cc stainless steel lecture bottle was evacuated and then filled with D$_2$ to a pressure of $\sim 2$ Torr. Approximately 400 cc H$_2$O was drawn into the vessel, after which the vessel was slightly pressurized with CO$_2$. After thorough shaking, the vessel was attached to the sample inlet system of the spectrometer and opened to release the excess pressure into a previously evacuated liquid-nitrogen-cooled trap. This causes the dissolved CO$_2$ to effervesce and strip out other dissolved gas as well. The balance of the gas (since the CO$_2$ freezes out in the cold trap) was then transferred to the sample side of the inlet system for admission to the spectrometer. The H$_2$/D$_2$ ratio was determined by alternately admitting to the spectrometer either this extracted sample...
FIGURE 10  DILUTION CURVE
or some of the same H₂ that was originally used to fill the sample vessel. In this manner, the excess 2⁺ signal determined was attributed to H₂ previously dissolved in the H₂O sample.

The results of these measurements indicated the amount of dissolved H₂ to be ~ 3(-5) liters per liter H₂O, which is significantly higher than the expected equilibrium concentrations of 1-2(-9) liters per liter H₂O. Analysis of the mass spectra made at the time of each measurement showed that the 2⁺ signal observed was not due to H₂⁺/CH₄ or H₂⁺/H₂O and therefore must be ascribed to H₂ only, which we first believed originated from the metal container. When we repeated the experiment with glass vessels, the results were essentially unchanged. A spectral scan revealed that the most abundant ions were 28⁺ and 14⁺. The 14⁺ intensity was about equal in intensity to the D₂⁺ signal, and the 28⁺ signal was about five times as large as the 14⁺ intensity, corresponding to the intensities due to ionization of N₂. We verified that the 28⁺ ion could not also be ascribed to CO⁺ from the CO₂ used in the gas extraction and concluded that the gas sample contains large amounts of N₂, and that the N₂ was not quantitatively removed by the liquid nitrogen trap. In addition, when CO₂ was admitted to the instrument we observed a 2⁺ signal, which we at first ascribed to a hydrogen impurity in the CO₂ used for extraction. However, we also observed this same phenomenon when other assayed reagents were admitted to the instrument. The source of the difficulty was found to be in the ion pump.

The ion pump manufacturer informed us that diode ion pumps normally will outgas some of the previously pumped sample due to the sputtering process inherent in the pumping mechanism, which uncovers previously pumped gas. This corroborated our observations since we had by this time pumped large quantities of D₂ and H₂ with our diode-type ion pumps. When we introduced the extracted gas sample, we of necessity introduced N₂ along with the D₂-H₂, and the N₂ was present in sufficient quantities to cause the evolved hydrogen from the pumps to completely obscure the H₂ in the sample. We had not detected this problem earlier because we had dealt with samples that were essentially identical as far as the pumping system was concerned, so that the background produced by the pumps was
stable and unchanged by switching from sample to standard. With the extracted sample however, this did not apply. We therefore needed to either eliminate the evolution of the pump background or to negate its existence.

The synchronous chopper/detector system described in the mass spectrometer specifications (Appendix B, p.2) would have provided the means of automatically subtracting out the background emitted by the pump and other mass spectrometer components. However, because this item was never developed by Nuclide, we were left only the possibility of attempting to eliminate the evolution of previously pumped sample gases.

One way to accomplish this would be to preseparate the $\text{D}_2$-$\text{H}_2$ gases from the other gases in the sample. This task would have required considerably more time to accomplish than remained in the contract. This approach was also unsatisfactory because the pumping system would still be capable of producing spurious effects. Therefore, we elected to modify the pumping system itself.

Varian Associates advised us that triode ion pumps have a considerable lower and more stable background than diode pumps. Therefore, we borrowed from Varian a 20 liter/s triode pump, which we installed on the detector chamber, and a 110 liter/s triode pump, which we installed at the source chamber. This pumping system was evaluated by introducing $\text{D}_2$ and $\text{N}_2$-$\text{D}_2$ mixtures to the spectrometer while measuring the apparent $\text{H}_2^+/\text{D}_2^+$ ratio.

The experimental procedure was to first fill both sides of the dual inlet system with $\text{D}_2$ to detect any side-to-side differences in the inlet system (which existed by this time since we had consistently used one chamber as the standard and the other as the sample so that there was a small but detectable $\text{H}_2$ background from the sample side). Next, $\text{D}_2$-$\text{N}_2$ mixtures with varying amounts of $\text{N}_2$ were prepared and let into the sample and standard volumes. Our intent was to find how small an amount of $\text{N}_2$ was tolerable in the sample and how small a difference in $\text{N}_2$ mixing ratio from side to side could be detected in the $\text{H}_2^+/\text{D}_2^+$ ratio.
Our conclusions were that only very small amounts of N\textsubscript{2} were tolerable. The apparent H\textsubscript{2}/D\textsubscript{2} ratio was found to change by $4 \times 10^{-6}$ per \% difference in N\textsubscript{2} concentration. This should be compared with $2 \times 10^{-5}$ per \% difference in N\textsubscript{2} concentration found for the diode pumps. (It should be noted that these changes had different algebraic signs since the diode pumped system had previously pumped great amounts of H\textsubscript{2}, while the triode system had only pumped D\textsubscript{2} in our laboratory). Since one would have to prepare different standards for each extracted sample and have the D\textsubscript{2}/N\textsubscript{2} ratio precise to 1\% or better to use this system for H\textsubscript{2} concentration studies, this pumping scheme was not considered appropriate.
SUMMARY AND CONCLUSIONS

Based on our experience with D/H determinations using negative ion mass spectrometry, it appears possible to make precision isotope ratio measurements with the H$_2$O technique discussed, providing the spectrometer is specifically designed for fast pumping of the H$_2$O after it exits the ionization source. In addition, the spectrometer should be designed to operate at sufficiently high temperatures that the instrument does not trap water vapor on any cool components. A phase-sensitive detection technique (such as the synchronous chopper/detector system promised by Nuclide) would also be an invaluable aid for suppressing any additional background. We recommend continuation of this work in the future.

For H$_2$ concentration measurements in seawater, there appear to be alternate more satisfactory analytical techniques available to ONR. Another change in the pumping system might also make these measurements possible on the ratio spectrometer. Technology has advanced rapidly in the area of turbo molecular pumps, which are now available with high pumping speeds for H$_2$. Since there is no pump memory with turbo molecular pumps (the pumped gas is exhausted), such a change may benefit this portion of the project. The use of phase-sensitive detection to provide automatic background subtraction would also be beneficial.
REFERENCES


APPENDIX A

July 11, 1973

Proposal for Research

SRI No. PYU 73-122

STUDY OF THE MODE OF FORMATION OF MOLECULAR HYDROGEN IN NATURE

PHASE I: CONSTRUCTION OF A HIGH PRECISION DUAL PURPOSE

MASS SPECTROMETER

Part I: Technical Program and Qualifications

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Approved:

C. J. Cook, Executive Director
Physical Sciences Division
INTRODUCTION

The objective of this proposal submitted by Stanford Research Institute (SRI) to the Oceanographic Section of the Office of Naval Research (ONR) is to initiate a research program to study the modes of formation of molecular hydrogen in nature, particularly in the ocean. In this study, we propose to use several novel concepts in mass spectrometry that should facilitate obtaining reliable data on the abundance and isotopic composition of molecular hydrogen. In the first phase of this program we intend to construct a special purpose mass spectrometer that will make it possible to obtain the desired data.
TECHNICAL BACKGROUND

Hydrogen is practically the only element that escapes this planet in significant quantities in molecular form. It is of interest, therefore, to examine all the sources that produce \( \text{H}_2 \) and to determine their relative contributions. Unlike the relatively extensive information available on the formation, distribution, and turnover of oxygen, nitrogen, and the rare gases in the ocean, there is practically no information on the fate of molecular hydrogen in nature. The main reason is the extremely low concentration of molecular hydrogen in air and in seawater. No analytical method has been available to determine hydrogen at such low concentrations. A new methodology is being proposed, based on isotope dilution analysis and novel mass spectrometry, that will allow the determination of \( \text{H}_2 \) in water at concentrations down to \( 10^{-13} \text{ M} \). A related experimental approach will allow the precision determination of \( \text{D}/\text{H} \) ratios in water samples. This ratio may provide additional important information on the mode of formation of molecular hydrogen.

Atmospheric molecular hydrogen, which is continuously generated to compensate for the losses in the upper atmosphere, originates from volcanic sources, from biological processes, from extraterrestrial protons, and from the photolysis of water in the atmosphere and in the ocean. There is little information on the relative contributions of each of these sources and there is correspondingly little information on the rate of escape of \( \text{H}_2 \) from the upper atmosphere. If the photolytic process is the major source of \( \text{H}_2 \) in the atmosphere, then the hydrogen in the ocean originates primarily from the atmosphere. On the other hand, it is conceivable that the hydrogen in the ocean is generated in it and released from it into the atmosphere.

Little is known about the concentrations of molecular hydrogen in the ocean. A recent book, Horne's *Marine Chemistry,* does not even mention the subject. Like most other gases that do not interact strongly

*References are listed on pages 17 and 18.*
with the ocean (e.g., nitrogen and the rare gases), we may assume that hydrogen near the ocean surface is more or less in equilibrium with the atmosphere. The atmospheric concentration of free hydrogen is $5 \times 10^{-6}$% or about $2 \times 10^{-8}$ M. The solubility of hydrogen in seawater at 20°C is about 2 volume %, so that the basic background concentration in seawater might be expected to be about $4 \times 10^{-10}$ M. However, this number could be changed by the existence of oceanic sources and sinks.

Hydrogen in fairly large amounts probably enters the ocean through volcanoes in the ocean floor. There are four possible mechanisms for underwater volcanic hydrogen formation: (1) primary magmatic molecular hydrogen, escaping from vents just as it does from terrestrial volcanoes, (2) hydrogen formed by the reaction of molten metals with seawater, (3) hydrogen formed by the thermal dissociation of water, and (4) hydrogen formed in the cavitation occurring when superheated steam impinges on seawater containing dissolved gases. The sonochemical generation of hydrogen in seawater may also occur in cavitation processes that take place by wave action. Cavitation processes in water induce its decomposition to yield molecular hydrogen. The mechanism of this reaction involves the adiabatic compression of permanent gases in the collapsing cavities, resulting in the formation of H atoms and OH residuals as intermediates. Another possible source is the radiolytic action of dissolved radioactive materials and cosmic rays. Finally, it is possible, though not highly probable, that the living organisms in the ocean produce or consume hydrogen.

The local or seasonal variations in molecular hydrogen concentration in seawater could provide us with substantial information on its modes of formation and distribution. Thus, we would expect higher H$_2$ concentrations over volcanic regions, in straits (cavitation of fast moving water), following storms (enhanced wave action), and so on. The differences in concentration and concentration gradients would provide information on the relative contribution of the different potential sources.
Another approach to the origin of hydrogen is via the D/H isotopic fractionation factors associated with the different modes of hydrogen formation. Molecular hydrogen formed by photolysis of water in the gas phase has a different isotopic composition from that formed by the photolysis of liquid water. Radiolytic hydrogen has a substantially different isotopic effect than sonolytic hydrogen. \( \text{H}_2 \) formed by thermal dissociation of \( \text{H}_2\text{O} \) will have a different D/H ratio than hydrogen formed by the reaction of water with metals. It is also very likely that molecular hydrogen formed by biological processes will have a different isotopic composition. If the ocean is the major source for molecular hydrogen, we would expect the isotopic composition of hydrogen in the air above the sea to vary locally in parallel to the local variations of the modes of formation of hydrogen.

The analytical problems we are confronted with are: (1) the determination of molecular hydrogen concentrations in seawater in the range \( 10^{-7} \) to \( 10^{-11} \) M with a precision of 1% or better, and (2) the determination of the isotopic composition of molecular hydrogen in the atmosphere with a precision of 0.01% or better. The first problem can be solved by an isotope dilution methodology using ultrapure molecular deuterium as carrier followed by mass spectrometric determination of the \( \text{H}_2^+ / \text{D}_2^+ \) ratio, while eliminating the HD\(^+ \) artifact. The second problem can be solved by extracting the atmospheric molecular hydrogen as water and analyzing the latter for its isotopic composition using the \( \text{D}^- / \text{H}^- \) ratio. One single, special-purpose instrument is capable of measuring both parameters with the required precision, just by changing its operating conditions.

**Measurement of Hydrogen Concentrations in Seawater**

An analytical method is required that can measure hydrogen concentrations in seawater at a level of \( 1 \times 10^{-10} \) M with a precision
and reproducibility of 1% or better. This capability will enable the researcher to record variances of $1 \times 10^{-12} \text{ M}$ from sample to sample.

Isotope dilution analysis facilitates the quantitative determination of molecular hydrogen dissolved in water down to concentrations of $10^{-13} \text{ M}$. This high sensitivity of detection is attained by shaking a sample of water (say, 10 ml) with a known amount (say, 1 ml NTP) of pure deuterium gas (preferably 99.999% D). This degree of purity of D$_2$ can be attained by thermal diffusion isotope separation. At isotopic equilibrium practically all protium (H) contamination in the deuterium will be in the form of HD and will not interfere with the determination of H$_2$.

Thus, if the deuterium contains 10 ppm protium, the molar fraction of H$_2$ will be only $10^{-10}$. Following isotopic equilibration attained by shaking, an aliquot of the hydrogen gas is readily separated from the water, completely dried by passing through a trap at liquid N$_2$ temperature, and the ratio H$_2^+$/D$_2^+$ is determined by mass spectrometry. From this ratio and the known amounts of deuterium gas and of the water sample, the H$_2$ concentration in the water may be readily calculated.

For determining the H$_2$/D$_2$ ratio without interference from the HD impurity, positive molecular ions will be formed by electron impact on the hydrogen. The sample gas will be introduced at a low pressure ($\sim 10^{-3}$ torr) into the ionization source. The pressure must be kept low enough to prevent depletion of D$_2^+$ and H$_2^+$ by ion molecule reactions and the consequent appearance of undesirable atomic hydrogen and triatomic ions. The formation of D$_2^+$ would obscure the small signal of H$_2^+$ and the formation of H$_2$D$^+$ from the H$_2$ would remove undetermined amounts of H from being determined as H$_2^+$. To avoid the formation of D$_2^+$, the electron energy must be reasonably well defined and kept below the dissociative ionization threshold, i.e., below $\sim 30$ eV. Electron energy can be controlled by using a low resolution electrostatic energy selector operated at $\sim 25$ eV with a width of $\sim 1$ eV.
In this manner one can produce a usable molecular ion current > 1 x 10^{-6} ampere. The total ionization cross sections for H\(_2\) and D\(_2\) are known to be identical so that below the dissociative threshold, the ratio of H\(_2^+\)/D\(_2^+\) will be practically identical to the H\(_2\)/D\(_2\) ratio in the gaseous sample.

The following is a quantitative illustration of the dilution analysis. Let us start with 10 ml seawater with a concentration of 10^{-10} M H\(_2\), i.e., 6 x 10^{11} molecules of H\(_2\), to which we add 1 ml NTP, i.e., 2.7 x 10^{19} molecules of 99.999% D\(_2\) (containing 3 x 10^{9} molecules of H\(_2\) as impurity; also 3 x 10^{14} molecules HD, which do not influence the analysis). The H\(_2^+\)/D\(_2^+\) ratio after equilibration will, therefore, be

\[
\frac{6 \times 10^{11} + 3 \times 10^{9}}{2.7 \times 10^{19}} \approx 2 \times 10^{-6}
\]

The ionization would result in the formation of molecular ions emitted at a rate of \(\sim 2 \times 10^{10}\) ions/sec. The H\(_2^+\) current emitted from the ionization source will thus be about 4 x 10^{2} ions/sec. With an overall transmission efficiency of \(\sim 10\%\), a total of 0.1 x 4 x 10^{2} = 40 counts/sec will be detected by the H\(_2^+\) detector, yielding a precision of better than 1% in 4 min. Variations in concentration of 3 x 10^{-13} M can thus be detected. This degree of precision makes counting errors small compared with other limiting factors. Following the same reasoning, 10^{-11} M hydrogen in water can be determined with the same precision by taking a 100-ml sample and counting for 4 min. Further, the given precision allows the determination of less than 1% variation in the background concentration of H\(_2\) in seawater for an ambient concentration as low as 10^{-11} M.

The precision of the dilution analysis is actually determined by the precision of pressure measurement of the deuterium gas added to the water and by the precision of volumetric sampling of the water; thus the overall
precision of the routine analytical method is estimated at 1%. It should be emphasized that our procedure is not affected by solutes other than hydrogen in the water and is thus directly applicable to samples of seawater.

The use of dilution analysis of D₂ as isotopic carrier must be compared with the possibility of using an inert gas (say, helium or argon) to wash out the hydrogen from the seawater sample. The separated gas may then be subjected to gas chromatography–mass spectrometry analysis. Using this technique, we would be relying solely on the partition coefficient of H₂ between water and vacuum, or on the partial pressure of dissolved H₂ in water. This method seems attractive because it avoids the complications of D¹ in assessing the H₂, but it has serious experimental pitfalls and intrinsic inaccuracies. One drawback is the possibility that a major fraction of the hydrogen, especially under nonequilibrium conditions, would be adsorbed on particulate matter or even on the walls of the sampling vessel, and would not be readily released when the water is subjected to vacuum or to an inert washing gas. Adsorbed H₂ will, however, readily exchange with D₂ in the isotopic dilution process. The rate of molecular exchange is also much faster than the rate of total removal. Furthermore, in the mass spectrometric analysis, the ion-molecule reactions between the carrier gas ions (such as Ar⁺) and H₂ could interfere considerably with the measurement. These reactions are strongly dependent on the pressure in the ion source and will not allow the assessment of the H₂ content with a precision better than about 5% irrespective of the counting time. Finally, H₂ may be specifically adsorbed to metal surfaces in the
ionization source or oxidized by traces of oxygen—critical complications that are avoided in the presence of an overwhelming excess of molecular deuterium. For all these reasons, it seems that our unique isotope dilution mass spectrometry offers a more reliable and precise solution than using an inert gas as carrier.

**Determination of Isotopic Composition of Atmospheric Hydrogen**

Determination of H/D in atmospheric hydrogen requires a somewhat different analytical method. First, one must eliminate the ambient H_2O, which might contribute interfering ions to any mass spectrometric determination of H/D. This can be accomplished by freezing out the water contained in the air sample with liquid N_2. At 77°K the vapor pressure of ice is ~ 1.5 x 10^{-9} torr, which reduces the partial pressure of H_2O to < 4 parts in 10^{8} of H_2. The same treatment would remove quantitatively most hydrocarbons and other organic compounds present in air as trace impurities with the exception of methane and ethane. The dried air sample is then passed over heated palladium asbestos, which catalyzes the oxidation of molecular hydrogen into water. The temperature of the catalyst will be kept low enough to avoid oxidation of hydrocarbons. The water is in turn frozen out and the remaining air is pumped off, leaving all the oxidized hydrogen in the sample as H_2O and HDO. If one begins with 1 liter of air, this final sample contains 10^3 x 2.69 x 10^{19} x 5 x 10^{-7} = 1.35 x 10^{16} molecules of water. This water must be analyzed mass spectrometrically directly without any further treatment. This amount of water (~ 20 nmol or about 0.4 µg) is too small to be reconverted into molecular hydrogen without losses, memory and irreproducible isotopic fractionation.

Production of positive ions from the water cannot be used for precision assessment of the isotopic composition of the hydrogen. The appearance potential for H_2O^+ is 12.6 eV and those for producing H^+, OH^+, and O^+ from water all lie in the range 18.7 to 19.5 eV. Under practical
conditions most of the H⁺ will appear in the analyzer as H₃O⁺ and some even as H₂O₂⁺. The variation in the isotopic composition of O¹⁷ in air and the variation in the distribution of hydrogen between the different species in the mass spectrum, which involves different isotopic fractionation factors, limit the precision of determination of the H/D ratio by positive ion mass spectrometry. However, if one produces negative ions, the only ion produced from H₂O below ~18 eV is H⁻ with no contribution from competing channels.

One must, however, ensure that source pressures are kept low enough to inhibit OH⁻ formation by ion molecule reaction. Furthermore, one can expect a large isotope effect for the process

\[ e + \text{HDO} \rightarrow \text{H}^- + \text{OD} \]

\[ \text{D}^- + \text{OH} \]

based on studies of electron impact on H₂, HD, or D₂. The branching ratio for this process would have to be determined in a separate measurement before the H/D ratio could be determined. Such a measurement could be made by preparing and observing a number of samples of known isotopic composition and extrapolating the results to zero H₂O pressure.

With an electron energy of ~6.5 eV, the cross section for producing H⁻ (D⁻) from H₂O (HDO) is comparable to the cross section for producing H⁺ (D₂⁺) from H₂(D₂). Therefore, one again expects a useable ion current in the negative ion mode of ~1 x 10⁻⁹ ampere. Since the H/D ratio is ~1.5 x 10⁻⁴, the upper limit for the D⁻ current (including overall transmission efficiency of ~10%) is ~1.5 x 10⁸ counts/sec. Even if the isotope effect resulted in a loss of an order of magnitude in the D⁻ signal, the H/D ratio could be measured with a precision of 1 part in 10⁴ in 3 minutes.
The determination of D/H ratio has a significant advantage over the measurement of the HD+/H2+ ratio in molecular hydrogen, even if we could isolate the molecular hydrogen from the air without converting it into water. The precision measurement of the isotopic composition of molecular hydrogen as carried out today by mass spectrometers has a major limitation; as the measured masses are 3/2, i.e., HD+/H2+, significant error is introduced by the formation of H3+, which can be only partially eliminated by ion source design, control of electron energy, and extrapolation to zero H2 pressure. The determination of HD+/H2+ with a precision of 1:10^4 requires that the H3+/H2+ ratio be > 10^-8. (The formation of minute (> 10^-8) amounts of D3+ does not interfere with the precision determination of the H2+/D2+ ratio in our dilution analysis method discussed above.) Using the best technique hitherto applied, it is possible to attain a 1/1000 precision in isotopic composition assessment, but it is difficult or perhaps impossible to attain a precision of 1 in 10^4 or better. Negative ion mass spectrometry overcomes the shortcomings of precision determination of D/H isotope ratios. The advantages of the negative ion methodology are: (1) the assayed masses are mass 1 and 2 only because H2 is an unstable species, and thus no error is introduced as is the case with HD+ and H3+, and (2) H- and D- are produced directly from H2O. A certain isotope fractionation is involved in this process, but as it is measurable and reproducible, it does not cause a special problem.

Use may be made of a duoplasmatron negative ion source. This type of source operates with an intense hot plasma capable of fragmentation of the H2 or H2O molecules introduced into it, producing a beam of H- ions of up to 100 microamperes. Although duoplasmatron negative ion sources have a larger current output and possibly lower intrinsic isotope fractionation correction factor than our proposed controlled energy electron impact source, we prefer the latter because it allows us to
carry out the complete proposed research scheme with a single instrument. Furthermore, the duoplasmatron forms ions from a number of mechanisms and with a wide range of electron energies, i.e., it is very nonspecific and uncontrolled in the ionization mechanisms. This mode of ionization results, therefore, in an unreproducible isotopic fractionation factor and thus it is not suitable for cases where the isotopic fractionation involved in the ionization processes must be reproducible to the highest degree possible.

Our proposed instrumentation, because of its simplicity, seems to be more readily convertible to a transportable form that could be operated on board an oceanic research vessel. On the other hand, the lower current outputs of our source limit its applicability to hydrogen and deuterium monitoring, and it could not conceivably be used for the mass spectrometric determination of tritium if ever the necessity arises.

**Instrumentation**

A dual purpose instrument is well within the current technology and can be constructed largely from commercially available components. A schematic of the proposed isotope ratio spectrometer is shown in Figure 1.

Either positive or negative ions are generated in the electron impact source (see previous section) depending on the substrate (hydrogen or water) and on the electron energy. Ions extracted from the source are focused into a beam, which then enters a Wien type velocity filter where mass selection is accomplished by velocity analyzing the monoenergetic beam. This type of velocity filter consists of an electromagnet and a pair of electrostatic plates mounted to produce perpendicular \( \vec{B} \) and \( \vec{E} \) fields orthogonal to the beam axis. When an ion beam with
FIGURE 1 PRECISION H/D MASS SPECTROMETER
\( v = \sqrt{\frac{2eV}{m}} \) passes through the filter, the ions experience opposing forces due to the \( E \) and \( B \) fields, \( F_{\text{mag}} = qv \times B \), \( F_{\text{elec}} = qE \). When these forces are balanced \( E = B v_0 \), and ions with velocity \( v_0 \) are transmitted straight through the filter while ions with other velocities are deflected to either side. Since all ions entering the filter have the same energy, mass \( m_0 = 2eV(B/E)^2 \) is on axis at the exit of the filter, while ions with smaller or larger masses are dispersed to either side in a plane perpendicular to \( B \). At the detector the dispersion is given by \( D \approx \frac{L a}{4} \left( \frac{E}{V} \right) \frac{\Delta m}{m} \) where \( a \) is the length of the filter, \( L \) is the drift distance measured from the center of the filter to the collector, and \( \frac{\Delta m}{m} \) is the mass resolution.

The ion velocity filter was chosen as a mass selector in preference to a magnetic deflector for a number of reasons. First, the resolution of the ion velocity filter is not dependent on entrance and/or exit slits, allowing the analysis of broader beams for a given resolution. Second, the magnetic fields required to disperse ion beams to the same degree are much lower than in sector magnets so that for a given resolution the Wien filter is smaller and lighter and consumes less power. The dispersion is also adjustable independent of resolution, which simplifies the detector location for isotope ratio measurements. Furthermore, the velocity filter can simultaneously select \( v_0 \) for both negative and positive ions with the only difference in the mass selection being that the mass number increases from left to right in the one case and from right to left in the other. This has a special advantage for our instrument since the spectrometer can be converted for positive or negative ions by simply reversing the polarities on the supplies powering the extraction and focusing lenses and on the vertical deflection plates. No changes are necessary in either the velocity filter or the detectors.
The resolution required has been calculated by assuming a Gaussian beam profile. For a mass resolution $\Delta m/m = 1/500$, the contribution from mass $3^+$ to mass $2^+$ is still $10^{-4}$. Although this resolution, which is readily attainable with a commercial medium-sized mass filter, may be sufficient for crude dilution analysis, it is not sufficient for precision H/D determinations, where $D^-/H^-$ in ambient concentrations is about $2 \times 10^{-4}$. To overcome this shortcoming, we will insert an additional small ion velocity filter at the position of mass 2. This filter with a resolution of $\Delta m/m = 1/50$ or better reduces the overall contribution of masses 1 or 3 to mass 2 to one part in $10^{-7}$. This is an upper limit as the nominal resolution of each of the two ion velocity filters cited is about an order of magnitude higher than assumed in our calculations.

Let us assume that we use deuterium gas with a purity of 99.99% to extract a million times smaller quantity of hydrogen from seawater. In this case the background at mass 2 will be $10^{-4} \times 10^{-7} = 10^{-11}$ of the abundance of mass 4, i.e., $10^{-3}$ times less than the abundance of the original $H_2$ in the deuterium gas, which in turn constitutes 1% of the observed abundance of mass 2. When the instrument is used in the $D^-/H^-$ mode, the natural abundance of $D^-$ is $2 \times 10^{-4}$ of that of $H^-$, and the instrumental background at mass 2 will be, therefore, 3 orders of magnitude smaller than the measured signal. As this background is expected to remain constant within $\pm 10\%$, it allows the determination of the $D^-/H^-$ abundance ratio with a precision of one in $10^4$.

Since a small fraction of the beam may be neutralized by collision with background gas along the beam path, the mass analyzed beam is separated from the fast neutral beam by the electrostatic deflectors after exiting the velocity filter. The majority beam ($H^-$ or $D_2^+$) is detected by collecting the beam current in a Faraday cup grounded through an electrometer grade resistor, and the induced voltage signal is
amplified by an electrometer grade amplifier. The resistor and amplifier will be contained in a common thermal housing inside the vacuum envelope where the temperature will be regulated to within 0.001°C. This arrangement would maintain the amplifier stability to one part in $10^8$ so that the overall stability of the resistor—preamp combination is determined by the temperature coefficient of the resistor. This places the stability of the overall system at about one part in $10^8$.

The voltage signal is subsequently fed into a voltage—to—frequency convertor, and the number of cycles counted by the frequency counter yield an analog to time integral of the beam current, i.e., the number of ions detected. Voltage—to—frequency convertors are commercially available with linearity better than 5 part in $10^8$; thus the current integral can be readily determined with an accuracy better than 0.01%.

The minority ion ($H_2^+, D^-$) is detected by directing the beam onto the first dynode of an electron multiplier where the ions eject secondary electrons to "fire" the electron multiplier. The resulting pulse of electrons is collected, amplified, and registered on a counter as an individual ion count.

An isotope ratio measurement is obtained by integrating both signals for a preset time or number of counts until the desired statistical accuracy is obtained, giving the ratio of the number of counts in each detection channel. We are now using successfully exactly the same electronic arrangement on our $^{48}$Ca/$^{40}$Ca high temperature precision isotope ratio mass spectrometer. (The latter instrument has not only a different ionization source but a completely different geometry and cannot, therefore, be used for the isotopic determination of hydrogen).
The proposed program of research consists of four major phases:

- The construction, testing, and evaluation of the precision mass spectrometer followed by development of the methods of sampling handling.
- The measurement of a limited number of representative samples of seawater and air to establish the range of concentrations and isotopic abundances of hydrogen. This phase may require setting up a small thermal diffusion facility to produce ultrapure deuterium if it cannot be purchased commercially or custom-produced by another research institution.
- The design and construction of a transportable version of our mass spectrometric system for shipboard operation.
- Oceanographic surveys of hydrogen by research vessels.

This proposal is concerned with the first phase only. The following phases will be carried out in tight collaboration with leading oceanographic institutions. The first phase may be subdivided into two main tasks: (1) the design, construction, and testing of the mass spectrometer, which is expected to take 12 months (an overall 2 man-year effort, including technicians), and (2) the development of the sample handling techniques and the evaluation of the operation of the whole analytical system, which is expected to take 6 months (an overall 1 man-year effort).

The second phase will be carried out in close collaboration with Dr. Louis I. Gordon of the School of Oceanography, Oregon State University at Corvallis and with Dr. Ted R. Folsom of the Scripps Institute of Oceanography at LaJolla. These scientists will provide us with samples of seawater to allow critical testing and evaluation of our methodology. In fact our proposed program of research is complementary to that currently carried out at Oregon State University under the sponsorship of ONR.
REFERENCES


QUALIFICATIONS OF STANFORD RESEARCH INSTITUTE

General Qualifications

Stanford Research Institute is a nonprofit corporation conducting basic and applied research in physical and life sciences, engineering, social and systems sciences, and economics. The emphasis on interdisciplinary research enables the Institute, with its 1300 professional scientists, to assemble specially qualified research teams tailored to the requirements of a given research problem. The research operations of the Institute are coordinated by the Office of Research Operations, Dr. D. R. Scheuch, Vice President. The organization of the Institute is shown in Figure 2. The entire program of research will be performed in laboratories and by personnel located in the Menlo Park facilities of SRI.

The Institute comprises nine divisions. The Physical Sciences Division, Dr. C. J. Cook, Executive Director, is composed of four laboratories, each with its own director: Chemistry Laboratory, Poulter Laboratory (for engineering mechanics), Applied Physics Laboratory, and Materials Laboratory. The experimental phase of the proposed project will be carried out by the Mass Spectrometry Development Group of the Applied Physics Laboratory.

Within the Institute are many specialized service groups that provide support as required to the projects being carried out. The Institute has many machine shops, electronic shops, model shops, and glass blowers for the fabrication of the specialized instrumentation that might be required.

Mass Spectrometry Development Group

The Mass Spectrometry Development Group carries out an extensive program of development of novel types of mass spectrometers and new methodologies using mass spectrometry. The Group has developed numerous novel types
of mass spectrometers, including field ionization mass spectrometers applied to isotope dilution analysis and to wide range "fingerprint" mass analysis; a high temperature sustained discharge mass spectrometer, designed for high precision isotope ratio mass spectrometry of calcium ions; a surface ionization negative ion mass spectrometer for measuring halogen isotopes; and a plasma ionization negative ion mass spectrometer for the assay of $^{14}$C at very low concentrations.

The range of applications of mass spectrometry actively pursued by the Group includes drug detection, identification of oil slicks, determination of subpicogram quantities of metabolites, epidemiological survey of nitric oxide in humans, diagnosis of osteoporosis, detection of explosives, determination of the viability of tissue cultures, radiocarbon dating, and geochemical studies using the $^{48}$Ca/$^{40}$Ca isotope effect.
The project will be carried out under the supervision of Dr. Michael Anbar, Director, Mass Spectrometry Development Group, Physical Sciences Division, who has over 20 years of experience in mass spectrometry for biomedical and geochemical purposes. Dr. Anbar has carried out pioneering work in the field of sonochemistry and is the initiator of the ideas on the role of sonolytic processes in geochemistry. Dr. H. Lewis Brown, a physicist with over 6 years of experience in mass spectrometry and related fields, will be project leader. Dr. Brown has constructed and is conducting research on a high precision isotope ratio mass spectrometer designed to determine $^{48}\text{Ca}/^{40}\text{Ca}$ ratios. These scientists will be assisted by Dr. William Aberth, senior physicist, with over 10 years of experience in mass spectrometry and molecular physics, by Dr. Rafael Schnitzer, physical chemist, with over 5 years of experience in the same fields, and by Mr. Ferdinand C. Engesser, a physicist who has over 15 years of experience in the construction of high vacuum instrumentation, ion accelerators, and mass spectrometers in particular.

Biographies of these scientists are attached.
MICHAEL ANBAR, DIRECTOR
TECHNICAL PROGRAM DEVELOPMENT
PHYSICAL SCIENCES DIVISION

Specialized professional competence

- Physical inorganic chemistry; mechanisms of redox reactions; stable isotope methodology and mass spectrometry; radiation chemistry of aqueous systems; sonochemistry; radioisotope tracer applications; nuclear chemistry; inorganic biochemistry and physiology; molecular radiobiology

Representative research assignments at SRI (since 1968)

- Mass spectrometry and mass spectrometric applications
- Chemical behavior of hydrated electrons
- Oxidation and electrochemical processes in molten salts
- Mechanism of sonochemical reactions
- Isotope geochemistry
- Tooth and bone physiology
- Dental restorative materials
- Biomedical applications of stable isotopes

Other professional experience

- Senior research chemist, the Weizmann Institute of Science, Rehovoth, Israel
- Director, Chemistry Division, Israel Atomic Energy Research Laboratories
- Head, Department of Radiation Research, Soreq Nuclear Research Establishment, Yavne, Israel
- Professor of inorganic and radiation chemistry, the Feinberg Graduate School, the Weizmann Institute of Science
- Visiting professor of inorganic chemistry, Tel Aviv University
- Visiting professor of chemistry, Stanford University
- Director, Radiisotope Training Center, Rehovoth, Israel (sponsored by the Weizmann Institute of Science and the Israel AEC)
- Senior research associate and consultant to the Argonne National Laboratory on problems in radiation chemistry
- Senior research associate, National Research Council, National Academy of Science at the NASA Ames Research Center, Moffett Field, California

Academic background

- M.S. in physical chemistry (1950) and Ph.D. in physical organic chemistry (1953), the Hebrew University, Jerusalem; postdoctoral fellow (1953-55), Department of Chemistry, University of Chicago

Publications

- More than 150 publications in professional journals

Professional associations and honors

- American Association for the Advancement of Science; American Chemical Society; Chemical Society, London; Faraday Society; New York Academy of Science; Radiation Research Society; Meyer Award (1959); Sigma Xi; Zondek Award (1962)
HAROLD L. BROWN, PHYSICIST
MASS SPECTROMETRY DEVELOPMENT GROUP
PHYSICAL SCIENCES DIVISION

Specialized professional competence

- Positive and negative ion research; design, construction, and testing of drift tube mass spectrometry apparatus; electron bombardment ion sources; Kunzman ion sources; reaction rate studies

Representative research assignments at SRI (since 1972)

- Interfacing a multipoint field ionization source with a quadrupole mass spectrometer
- Construction and operation of a high precision isotope ratio mass spectrometer for the measurement of $^{48}$Ca/$^{40}$Ca isotope ratios

Other professional experience

- Graduate student researcher, Physics Department, University of Pittsburgh
- Graduate teaching assistant, University of Pittsburgh

Academic background

- B.S. in engineering (1962), U.S. Military Academy; Ph.D. in physics (1972), University of Pittsburgh

Publications

- Author of five published articles

Professional associations

- American Physical Society
- American Geophysical Union
- Sigma Xi
REFERENCES


APPENDIX B

April 2, 1975

PRECISION H/D ISOTOPE RATIO MASS SPECTROMETER SPECIFICATIONS
APPENDIX B

PRECISION H/D ISOTOPE RATIO MASS SPECTROMETER SPECIFICATIONS

2 Apr '75

General

A complete spectrometer system, except for the ionization source, is to be provided. The electron impact source (ionizer and electron emission controller) is to be provided by the user. The ratios to be determined are $H_2^*/D_2^+$ and $H^-/D^-$ utilizing as sample gas $H_2$ and $H_2O$, respectively. The ratios of $H_2/D_2$ and $H/D$ in the samples introduced will be $2 \times 10^{-8}$ (minimum) and near $6 \times 10^3$, respectively. These relative abundances are to be determined with a precision of better than 1% and 1 part in 104, respectively, which defines the overall abundance sensitivity and precision required.

The instrument is to be performance tested before shipment, and installed by Nuclide representatives at the Mass Spectrometry Research Center, Stanford Research Institute in Menlo Park, California. For the in-plant tests Nuclide will provide a standard ionizer. The purpose of the tests will be to demonstrate that the transmission, stability, regulation, detector noise level, etc. of the instrument are adequate to permit achieving the precision goals stated above. Installation will not include ratio determinations with the mentioned samples and the SRI ionizer.

Specific requirements are included below.

Inlet System

The proposed inlet system must be capable of providing steady viscous flow of sample gas to the ionization source at a rate of $1(-4)$ torr-1-sec-1 ($3 \times 10^{-1}$ mol/s) for a period of at least 10 min from total samples of either $5 \times 10^{-2}$ cm$^3$ STP $H_2O$ or 1 cm$^3$ STP $H_2$. This inlet system must be designed for isotope ratio studies of water, i.e., it must be capable of being used at a temperature at which the entire sample will be vaporized, and of alternate sample switching through matched viscous leaks from unknown to reference samples, and must have a sample capacity of at least six samples. Inlet system pumping is to be accomplished by means other than by hydrogen bearing fluid pumps, and sample pressure and/or flow measuring capability is required. (It is recognized that this system may not be optimal for all $H_2$ in $D_2$ samples, and that later additions or modifications may be necessary for those with the highest $D_2/H_2$ ratio or if it is decided to use smaller samples with greater $H_2/D_2$ ratios.)
Collector System

A dual collector system is to be provided which will permit simultaneous collection of either negative ions of mass 1 and 2 or positive ions of mass 2 and 4. Provision is to be made for the signal detected by the collectors to be presented to the spectrometer operator as digital output in both a visible display and a permanent "hard copy" record. Any power supplies required by the collection/data handling system are to be supplied by the manufacturer.

Vacuum System

A bakeable metal system is to be provided which assembles with standard Varian Conflat flanges and copper gaskets. A bakeout system is to be included. The system base pressure is to be in the low 10^-8 torr range when sample is not being admitted, with sufficient pumping speed available to maintain the analyzer pressure during operation below the point where scattering from background gas affects the minor collected ion at a level of 5 x 10^-5 of the minority ion signal of the water sample. Pumping is to be accomplished by means other than by hydrogen-bearing fluid pumps. A means for monitoring the system pressures is to be provided.

Analyzer System

Mass analysis is to be accomplished by a 90° or 60° sector, direction-focusing electromagnet system capable of analyzing an ion beam of 1 x 10^-9 A (or greater) total intensity consisting of either H_2^+ and D_2^+ in a ratio H_2/D_2 \approx 2 \times 10^-8 or greater, with a precision, including data handling of better than 1%, or H^- and D^- in a ratio of H/D \approx 6 \times 10^3 with a precision including data handling of better than 1 part in 10^4. Appropriate ion optics are to be provided to extract and focus the beam given that the exit aperture of the electron impact ionizer to be provided by the user is an appropriate slit having the same area as a 0.5 mm radius circle (e.g., a 0.25 mm wide slit 3 mm long). It is recognized that hydrogen gas being released from the mass spectrometer vacuum system and inlet system presents a problem to the analysis of the D_2 samples with the smallest relative H_2 concentration, and that measuring H_2/D_2 ratios with the precision cited, for the samples with smallest relative H_2 concentration, may require presently unknown techniques. However, as a beginning Nuclide will provide a synchronous chopper/detector system which can be used to automatically subtract out MS background H_2.

Frame

Suitable support is to be provided for the sample inlet, vacuum and analyzer components.
Electronics Systems

Electronic Control. A system is to be provided which includes controls for ion acceleration, source focusing, and ion current measurement.

(a) Ion acceleration—provide 0-10 keV positive or negative polarity.

(b) Source lens—provide beam draw out and focus potential for positive or negative ions.

(c) Ion current—provide means of detecting either majority or minority currents with the ability to output on an X-Y recorder.

Magnet Supply and Regulator. A regulated current supply is to be provided which will permit either mass scanning or static operation. Field regulation is to be provided, as well as coil current regulation, and in the ratio mode, short term drift shall be sufficiently small that the overall instrumental precision is maintained for at least 0.5 hr. In the presence of ambient temperature fluctuations of 1.0 °C.

Vacuum Protection Circuit. It is required that the instrument fails safe in the event of water or power outage or loss of vacuum. A control panel is to be provided for turn off and turn on of the pumping system.

Electronics Console. Appropriate cabinetry is to be provided to contain the electronic components and controls.

Other Information

The user will make all reasonable provision for power, water, and environment. Space requirements are not a restriction.
APPENDIX C

February 27, 1976

Proposal for Research

SRI No. PYU 76-052

STUDY OF THE MODE OF FORMATION OF MOLECULAR HYDROGEN IN NATURE
PHASE IB DEVELOPMENT OF ANALYTICAL PROCEDURES

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(Code 485)
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Attention: Dr. John B. Gregory
Director, Ocean Technology Program

Approved:

C. J. Cook, Executive Director
Physical Sciences Division
This is a proposal for research submitted by Stanford Research
Institute (SRI) to the Oceanographic Section of the Office of Naval
Research (ONR) to continue and complete the first phase of a research
program to study the modes of formation of molecular hydrogen in nature,
particularly in the ocean. The performance of the mass spectrometric
system that has been designed and constructed during the first year of
this program will now be evaluated and the analytical methodologies for
the measurement of the abundance and isotopic composition of hydrogen
will be developed, tested, and evaluated. At the completion of the
second year of this program, we will be in a position to start the
second phase of the program, namely, to perform routine measurements of
hydrogen in sea water samples on a batch basis. We hope also to be in a
position at that time to initiate the third phase (which may proceed in
parallel) to design and construct shipboard instrumentation for batch
or continuous monitoring of $H_2$ abundance and/or the ratio of $HD/H_2$ of
molecular hydrogen in sea water.

The technical background of the proposed program was presented in
our original proposal dated July 1973. To avoid repetition of this
information, we will comment only on two studies on this topic that have
been published since that time. Following this short revised background
section, we will describe the instrument development and the planned
development of analytical methodologies.
TECHNICAL BACKGROUND

Since the submission of our original proposal, two papers have appeared in the oceanographic literature which are relevant to our study. The first one, by Williams and Bainbridge of the Scripps Institute, claims to be the first reported measurement of molecular hydrogen concentrations in the open ocean. The second, by Seiler and Schmidt, summarizes a series of measurements by European oceanographers in 1971-1972. The first study tried to measure molecular H₂ in sea water by gas chromatography, using pure nitrogen as a stripping and carrier gas. The results were highly disappointing in their lack of reproducibility (uncertainties by factors of 2 to 10) indicating only that the sea water analyzed was supersaturated with H₂, or that some artifactual H₂ was produced in the analyzing system. The second paper contains much more dependable results. The hydrogen concentrations measured ranged between 8 to 50 x 10⁻⁶ ml NTP/lit or 3.5 x 10⁻¹⁰ to 2.2 x 10⁻⁹ M in excellent agreement with our prediction in the original proposal that the base line concentration of molecular hydrogen will be 4 x 10⁻¹⁰ M. Furthermore, the finding of increased concentration of molecular hydrogen at depths of about 2500 m and 3500 m may indicate stratification of H₂ from volcanic origin. The study of Seiler and Schmidt also indicates a very substantial contribution of hydrogen from biological sources, which they believe accounts for most of the increased concentrations of molecular hydrogen at shallower depths. However, their measurement technique was of limited precision though not necessarily of insufficient sensitivity.

In any case, this first study indicated that the ocean may very well be a major source of molecular hydrogen in nature, and that certainly the molecular hydrogen in the ocean does not originate from atmospheric
The variation in the isotopic composition of $^0\text{O}^{17}$ in air and the variation in the distribution of hydrogen between the different species in the mass spectrum, which involves different isotopic fractionation factors, limits the precision of determining the H/D ratio by positive ion mass spectrometry. However, if one produces negative ions, the only ion produced from $\text{H}_2\text{O}$ below ~18 eV is $\text{H}^-$ with no contribution from competing channels.

The determination of $^3\text{D}^-/\text{H}^-$ ratio has a significant advantage over the measurement of the $\text{HD}^+/\text{H}_2^+$ ratio in molecular hydrogen, even if we could isolate the molecular hydrogen from the air without converting it into water. The precision measurement of the isotopic composition of molecular hydrogen as carried out today by mass spectrometers has a major limitation; as the measured masses are $\bar{3}/2$, i.e., $\text{HD}^+/\text{H}_2^+$, significant error is introduced by the formation of $\text{H}_3^+$, which can be only partially eliminated by ion source design, control of electron energy, and extrapolation to zero $\text{H}_2$ pressure. The determination of $\text{HD}^+/\text{H}_2^+$ with a precision of $1:10^4$ requires that the $\text{H}_3^+/\text{H}_2^+$ ratio be $< 10^{-8}$. (The formation of minute ($< 10^{-6}$) amounts of $\text{D}_3^+$ does not interfere with the precision determination of the $\text{H}_2^+/\text{D}_2^+$ ratio in our dilution analysis method discussed above.) Using the best technique hitherto applied, it is possible to attain a 1/1000 precision in isotopic composition assessment, but it is difficult or perhaps impossible to attain a precision of 1 in $10^4$ or better. Negative ion mass spectrometry overcomes the shortcomings of precision determination of D/H isotope ratios. The advantages of the negative ion methodology are: (1) the assayed masses are mass 1 and 2 only because $\text{H}_2^-$ is produced in negligible amounts, and thus no error is introduced as is the case with $\text{HD}^+$ and $\text{H}_3^+$, and (2) $\text{H}^-$ and $\text{D}^-$ are produced directly from $\text{H}_2\text{O}$. A certain isotope fractionation is involved in this process, but since it is measurable and reproducible, it does not cause a special problem.
hydrogen. These findings strengthen our conviction of the importance of obtaining additional reliable data on hydrogen distribution in the ocean. Moreover, the variety of possible sources of hydrogen makes it even more interesting to measure the H/D isotope effects of marine molecular hydrogen in order to identify its sources and to determine their relative contributions. Without this powerful tool, it will be difficult to interpret the concentration data. As we shall see in a later section, it seems to be feasible to measure these isotope effects with our new instrumentation, and it will be possible to construct instrumentation to monitor these effects on a continuous basis.

The analytical problems we are confronted with are: The determination of molecular hydrogen concentrations in seawater in the range $10^{-8}$ to $10^{-11}$ M with a precision of 1% or better, and the determination of the isotopic composition of molecular hydrogen in the atmosphere and in seawater with an adequate precision. The first problem can be solved by an isotope dilution methodology using ultrapure molecular deuterium as a carrier followed by mass spectrometric determination of the $\text{H}_2^+/\text{D}_2^+$ ratio, while eliminating the $\text{HD}^+$ artifact. The second problem can be solved by extracting the molecular hydrogen in air as water and analyzing the latter for its isotopic composition using the $\text{D}^-/\text{H}^-$ ratio. There exists the possibility that the $\text{HD}/\text{H}_2$ ratio could be measured directly in relatively small samples of seawater (1 liter) with sufficient precision. This could be achieved by washing the water sample with pure (helium free) argon, and analyzing $\text{HD}^+/\text{H}_2^+$ following complete removal of the water. This methodology will be discussed later in detail. Our single, special-purpose instrument should be capable of measuring both the abundance and isotopic composition of molecular hydrogen with the required precision.
Measurement of Hydrogen Concentrations in Seawater

The analytical method is intended to measure hydrogen concentrations in seawater down to a level of $1 \times 10^{-11}$ M with a precision and reproducibility of 1% or better. This capability will enable the researcher to record variances of $1 \times 10^{-13}$ M from sample to sample. Alternatively, one could determine $H_2$ at $10^{-13}$ M concentrations with 10% precision. This technique is expected, therefore, to be over 100 times more sensitive than the hot mercuric oxide method of Robbins et al. modified by Sieler et al., which is limited to $10^{-10}$ M with only 10% precision.

Isotope dilution analysis facilitates the quantitative determination of molecular hydrogen dissolved in water down to concentrations of $10^{-13}$ M. This high sensitivity of detection is attained by equilibrating a sample of water (say, 10 ml) with a known amount (say, 1 ml NTP) of pure deuterium gas (preferably 99.999% D). This degree of purity of D₂ can be attained by thermal diffusion isotope separation and could be custom ordered from the Monsanto Mound Laboratories. At isotopic equilibrium practically all protium (H) contamination in the deuterium will be in the form of HD and will not interfere with the determination of $H_2$. Thus, if the deuterium contains 10 ppm protium, the molar fraction of $H_2$ will be only $10^{-10}$. Following isotopic equilibration attained by shaking, an aliquot of the hydrogen gas is readily separated from the water, completely dried by passing through a trap at liquid N₂ temperature, and the ratio $H_2^+/D_2^+$ is determined by mass spectrometry. From this ratio and the known amounts of deuterium gas the volume and of the water sample, the $H_2$ concentration in the water may be readily calculated.

For determining the $H_2/D_2$ ratio without interference from the HD impurity, positive molecular ions are formed by electron impact on the hydrogen. There are three principle requirements for such an ionization source. First, the pressure must be kept low enough to prevent depletion...
of \( D_2^+ \) and \( H_2^+ \) by ion molecule reactions and the consequent appearance of undesirable atomic hydrogen and triatomic ions. Second, the electron energy must be reasonably well defined and kept below the dissociative ionization threshold, i.e., below \( \sim 30 \) eV to avoid the formation of \( D^+ \). The total ionization cross sections for \( H_2 \) and \( D_2 \) are known to be identical so that below the dissociative threshold, the ratio of \( H_2^+/D_2^+ \) will be practically identical to the \( H_2/D_2 \) ratio in the gaseous sample.

Third, the efficiency of the source must be sufficiently high that measurements can be made in reasonably short times without requiring unreasonably large samples.

The ionization source developed for this purpose is shown in Figure 1. The first requirement above is met by utilizing a hypodermic syringe for injecting the sample into the electron beam. The remainder of the source is kept open so that the gas is immediately pumped away, thereby minimizing collisions of the \( H_2^+ \) and \( D_2^+ \) with \( H_2 \), which could result in pressure dependent production or loss mechanisms for \( H_2^+ \). To partially verify this claim, the source was operated on a magnetic sector instrument and ions \( 1^+, 2^+, \) and \( 3^+ \), corresponding to \( H^+, (H_2^+, D^+) \) and \( HD^+ \) were monitored as a function of sample flow rate and found to be linearly dependent on flow, thereby confirming their direct production from the hydrogen introduced. Figure 2 shows the linearity for \( H_2^+ \) produced by \( 70 \) eV and \( 100 \) eV electrons.

The effect of electron energy on the production of the ion \( 2^- \) \( (H_2^+ \) or \( D^+) \) could not be determined on the instrument utilized for testing this source, since the instrumental dispersion is far too large to permit simultaneous monitoring of \( 2^+ \) and \( 4^+ \). However, the source was checked for the possibility of operating at low electron energies and with reasonably small energy spread. The electron energy spread was found to be approximately constant and \( \leq 1 \) eV. Evidently the majority of this spread is due to the voltage drop across the filament which for
FIGURE 2 BALLAST VOLUME PRESSURE VERSUS TIME
AFTER GAS SHUT OFF

\[ r^{-1} = 2.39 \times 10^{-3} \text{ sec}^{-1} \]
the heating currents utilized was ~ 1.6 volts. This is an acceptable energy spread for our purposes. There was concern about the electron current which could be extracted at lower electron energies, but as can be seen from Table I, the source can readily operate at 20 eV, where the trap current obtained was ~ 65% of its value at 100 eV.

Source efficiency was measured using the apparatus shown in Figure 3. The ballast chamber pressure can be precisely controlled by a Baratron automatic pressure controller combination. Likewise, the fall in ballast chamber pressure can be precisely measured after the servo-controlled valve is shut off and sample gas is allowed to leak out through the source only. This information allows us to determine and control the rate at which sample gas is introduced to the source by the following technique: If one assumes molecular flow through the hypodermic needle (the capillary is .010" in diameter by 0.10" long), then the conductance of the leak can be determined by monitoring the ballast volume pressure drop after the input is cut off from the relationship

\[ \frac{-V}{dt} = FP \]

where P is the pressure, F is the conductance, and V is the volume. This expression can be integrated to yield

\[ P = P_0 e^{-t/\tau} \]

where \( \tau = V/F \), so that we can determine F from a semilog plot of the pressure in the ballast volume versus elapsed time, as shown in Figure 4. The characteristic time \( \tau \) is determined from the slope of the plot and F is computed from this time and the known volume of the system. Once F has been determined, the volumetric flow rate through the hypodermic needle can be determined by

\[ Q = F(P_1 - P_2) \]
Table I. TRAP CURRENT VERSUS ELECTRON ENERGY

<table>
<thead>
<tr>
<th>Electron Energy (eV)</th>
<th>Trap Current ($x10^9$ Amps)</th>
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<tr>
<td>10</td>
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<td>20</td>
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<td>110</td>
<td>71</td>
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<td>120</td>
<td>71</td>
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</table>
FIGURE 3  TOTAL ION CURRENT COLLECTED VERSUS H₂ BACKING PRESSURE
FIGURE 4  POSITIVE ION SOURCE
$P_1$ is the entrance pressure and $P_2$ is the exit pressure. As one sees in Figures 2 and 4, the entrance pressures are in the range of tenth of a Torr so that the exit pressure is negligible, allowing the flow rate of sample gas to be determined by

$$Q = FP.$$ 

From Figure 2 then we determine the source efficiency, defined by

$$\epsilon = \frac{\text{number of ions detected}}{\text{number of molecules introduced}}.$$ 

For example, at 0.5 Torr backing pressure and 100 eV electron energy, the measured ion current due to $H_2^+$ is $\sim 1.4 \times 10^{-8}$ A. The source efficiency is found to be

$$1.4 \times 10^{-8} \frac{\text{coulomb/sec}}{1.6 \times 10^{-19} \text{coloumb/ion}} = 5.5 \times 10^{-6} \text{ions/neutral} \frac{3 \text{ Torr cm}^3/\text{sec}}{0.5 \text{ neutral} \frac{3.22 \times 10^{16}}{\text{Torr cm}^3}}$$

This is somewhat better than what one obtains from a good commercial electron impact source, e.g., the EAI model Bl908, which according to the manufacturer's specifications has a maximum efficiency of $\geq 1.7 \times 10^{-6}$ ions/neutral. Moreover, such commercially available sources are the "enclosed" type and therefore are unacceptable for our purposes from the standpoint of ion molecule reaction contributions.

The source developed satisfies, therefore, our project requirements as can be seen in the following example: Let us start with 10 ml of seawater with a concentration of $10^{-10} M \, H_2^+$, i.e., $6 \times 10^{11}$ molecules of $H_2$, to which we add 1 ml NTP $D_2$, i.e., $2.7 \times 10^{19}$ molecules of 99.999% $D_2$ (containing $3 \times 10^9$ molecules of $H_2$ as impurity; also $3 \times 10^{14}$ molecules $H_D$, which do not influence the analysis). The $H_2/D_2$ ratio after equilibration will, therefore, be

$$\frac{6 \times 10^{11} + 3 \times 10^9}{2.7 \times 10^{19}} \approx 2 \times 10^{-8}$$
For 20 eV electrons and 0.5 Torr backing pressure, ionization results in the formation of molecular ions emitted at a rate of $\sim 6.25 \times 10^{10}$ ions/sec. The $H_2^+$ current emitted from the ionization source will thus be about $1.25 \times 10^3$ ions/sec. With an overall transmission efficiency of $\sim 10\%$, a total of $0.1 \times 1.25 \times 10^3 = 125$ counts/sec will be detected by the $H_2^+$ detector, yielding a precision of better than $1\%$ in 3 min. Variations in concentrations of $\sim 10^{-13}$ M can thus be detected. This degree of precision makes counting errors small compared with other limiting factors. Following the same reasoning, $10^{-11}$ M hydrogen in water can be determined with the same precision by taking a 100 ml sample and counting for 3 min. It should be noted that the ionization efficiency achieved is higher by a factor of 3 than that estimated in the original proposal.

The sample size required for 3 min of integration is given by

$$1.61 \times 10^{16} \text{ molecules/sec} \times 180 \text{ sec} = 2.9 \times 10^{18} \text{ molecules}$$

or about $10\%$ of the total sample assuming we began with 10 ml seawater and 1 ml NTP $D_2$.

It should be pointed out that the estimate above may be based on an unnecessarily small sample, and that the ultimate sample size will need to be determined experimentally during the development of the analytic and sample handling methodology phase of the project.

The overall precision of the dilution analysis is ultimately determined by the precision of the pressure measurement of the deuterium gas added to the water and by the precision of volumetric sampling of the water; thus the overall precision of the routine analytical method is estimated at $1\%$. It should be emphasized that our procedure is not affected by solutes other than hydrogen in the water and is thus directly
applicable to samples of seawater. The advantages of using D₂ as dilutant-carrier over nonisotopic carriers, e.g., He, Ar, for the quantitative assessment of dissolved H₂ in seawater have been discussed in the original proposal and will not be elaborated here.

Measurement of the Isotopic Composition of Atmospheric Hydrogen

Determination of H/D in atmospheric hydrogen requires a somewhat different analytical method. First, one must eliminate the ambient H₂O, which might contribute interfering ions to any mass spectrometric determination of H/D. This can be accomplished by freezing out the water contained in the air sample with liquid N₂. At 77°K the vapor pressure of ice is ~ 1.5 x 10⁻⁹ Torr, which reduces the partial pressure of H₂O to < 4 parts in 10⁶ of H₂. The same treatment would remove quantitatively most hydrocarbons and other organic compounds present in air as trace impurities with the exception of methane and ethane. The dried air sample is then passed over heated palladium asbestos, which catalyzes the oxidation of molecular hydrogen into water. The temperature of the catalyst will be kept low enough to avoid oxidation of hydrocarbons. The water is in turn frozen out and the remaining air is pumped off, leaving all the oxidized hydrogen in the sample as H₂O and HDO. If one begins with 1 liter of air, this final sample contains 3 x 2.69 x 10⁻¹⁹ x 5 x 10⁻⁷ = 1.35 x 10⁻⁻¹⁶ molecules of water. This water must be analyzed mass spectrometrically directly without any further treatment. This amount of water (~ 20 nmol or about 0.4 µg) is too small to be reconverted into molecular hydrogen without losses, memory and irreproducible isotopic fractionation.

Production of positive ions from the water cannot be used for precision assessment of the isotopic composition of the hydrogen. The appearance potential for H₂O⁺ is 12.6 eV and those for production of H⁺, OH⁺, and O⁺ from water all lie in the range 18.7 to 19.5 eV.
One must, however, ensure that source pressures are kept low enough to inhibit OH⁻ formation by ion molecule reaction. Furthermore, one can expect a large isotope effect for the process

\[ e + \text{HDO} \rightarrow \text{H}^- + \text{OD} \]
\[ \text{D}^- + \text{OH} \]

based on studies of electron impact on H₂, HD, or D₂. The branching ratio for this process would have to be determined in a separate measurement before the H/D ratio could be determined. Such a measurement could be made by preparing and observing a number of samples of known isotopic composition and extrapolating the results to zero H₂O pressure.

With an electron energy of \( \sim 6.5 \text{ eV} \), the cross section for producing \( \text{H}^- \) (D⁻) from H₂O (HDO) is comparable to the cross section for producing \( \text{H}_2^+ \) (D₂⁺) from H₂ (D₂). Therefore, one again expects a useable ion current in the negative ion mode of \( \sim 1 \times 10^{-9} \) amperes. Since the H/D ratio is \( \sim 1.5 \times 10^{-4} \), the upper limit for the D⁻ current (including overall transmission efficiency of \( \sim 10\% \)) is \( \sim 1.5 \times 10^6 \) counts/sec. Even if the isotope effect resulted in a loss of an order of magnitude in the D⁻ signal, the H/D ratio could be measured with a precision of 1 part in \( 10^4 \) in 3 minutes.

The positive ion source developed for this project has also been checked for its ability to produce negative ions from H₂O. At 100 eV it is possible to produce \( \sim 0.5 \times 10^{-9} \) mass analyzed H⁻, however, this drops by an order of magnitude at 10 eV electron energy. This leaves us with two possible ways to proceed. One approach is to utilize the higher energy electrons and accept the additional fractionation due to competing ionization channels, as well as inherent isotopic fractionation in the formation of H⁻. This may be a viable approach if the source conditions are very well controlled and reproducible, but in principle
the simplest solution is to increase the ion current produced (i.e., the efficiency) at low electron energies. There are at least two possible ways of increasing the source efficiency. One way is to increase the electron current available at these low energies. The other is to improve the extraction geometry of the ionizer, recognizing that the H is formed by dissociative attachment and that the H is therefore formed with a certain amount of energy.

The largest electron current which can be supplied to a given volume is obtained by operating in the space charge limited mode. Therefore, we began experimentation with space charge limited electron guns and found that it is possible to obtain reasonably well-defined electron beams of \( \sim 50 \, \mu\text{A} \) at \( \sim 7 \, \text{eV} \) desired energy. A prototype of such a gun was tested in a bell jar vacuum station and incorporated into the ionization source shown in Figure 5. In the figure, it can also be seen that the electron gun is followed by a 127° electrostatic energy analyzer. The reasons for this are as follows: The gun requires sufficient length so it cannot be placed transversely in the ionization source volume of the spectrometer without redesigning the standard source chamber, requiring that the electrons be deflected into the ionizing volume after exiting the gun. Further, the gun supplies electrons with a circular image and ideally we want to have a ribbon of electrons. The electrostatic sector has point-to-line focal properties which accomplish this. An added benefit of such focusing is that it minimizes space charge effects after the final aperture of the electron gun. Most important, however, is that the electrostatic sector gives us positive control of the energy and the energy spread of the electron beam entering the ionizing region.

This ionization source has been tested in a bell jar system, but not on a spectrometer. The electric sector performs well and in accordance with theory however, we have had unresolved difficulties with the electron current, and have not as yet been able to produce \( 50 \, \mu\text{A} \) of energy analyzed.
FIGURE 5 NEGATIVE ION SOURCE
electron current. The problem has been isolated to the extent that it is known that the fault lies in the electron gun. This is encouraging because the understanding of the electron gun design is well-advanced, and we hope to overcome this problem in the near future.

Improving the extraction geometry is strongly dependent upon having the spectrometer on hand. Since the instrument was delivered to our laboratory February 23 and is presently being installed, we have not been able to pursue this aspect of the negative ion problem. Work will therefore continue on the negative ion source during the remaining quarter of the contract.

Measurement of the HD/H₂ Ratio in Hydrogen Extracted from Sea Water

The determination of the isotopic composition of the molecular hydrogen in seawater, which may become a major objective in the proposed program, can be carried out by a procedure different from that for H₂ in air. The water may be washed with pure Ar and the gases extracted passed over appropriately sized molecular sieves at 77°K (liq N₂) to remove the water quantitatively (partial pressure < 10⁻¹¹ torr), as well as part of the O₂ and all the CO₂, and hydrocarbons (except CH₄). The O₂ is then quantitatively removed by passing through a 1% sodium amalgam which would also remove the last residue of H₂O without conversion to H₂. The reason for this is that under conditions where the O₂/H₂O ratio is > 10⁶, the reactions occurring in Na amalgam would be Na + O₂ → NaO₂;

\[ \text{NaO}_2 + \text{Na} \rightarrow 2\text{NaO} \]

\[ \text{NaO}_2 + \text{Na} \rightarrow \text{Na}_2\text{O} \]

\[ \text{Na}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{NaOH} \]

\[ \text{Na} + \text{H}_2\text{O} = \text{NaOH} + \text{H} \]

\[ \text{H} + \text{O}_2 \rightarrow \text{HO}_2 \]

\[ \text{HO}_2 + \text{Na} \rightarrow \text{NaO}_2 \]

\[ \text{Na}_2\text{O} + \text{Na} \rightarrow \text{Na}_2\text{O}_2 \]

The reaction \( \text{OH}^- + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}^- \) cannot take place in concentrated aqueous solutions, cannot take place in Na amalgam, and evidently H₂ will not react with Na₂O or NaOH. The gas containing predominantly Ar (the partial pressure of Ar at 77°K 156 Torr) is then introduced into the positive ion source and the mass ratio \( 3/2 \) determined. Owing to the slightly higher ionization potentials of Ar compared with H₂,
(15.76 eV for Ar compared with 15.43 and 15.46 eV for H₂ and HD respectively) effective charge transfer reactions in a "closed" type ion source (10⁻³ torr) are expected to give at low electron energies (< 20V) an ionization efficiency of > 10⁻⁴ for hydrogen molecules in the sample. The H₂⁺ + H₂ → H₃⁺ + H reaction is extremely unlikely at the low partial pressures of hydrogen available. This technique of diluting hydrogen with argon to augment the ionization efficiency and diminish the contribution of H₃⁺ has been used in the study of H/D isotope effects in the radiolysis of water.

Let us now illustrate the effectiveness of this technique by an example. Let us wash with one ml Ar (NTP) a sample of 1000 ml water containing about 2 x 10⁻⁵ ml hydrogen, i.e., about 10⁻⁹ moles or 6 x 10⁻¹⁴ molecules of hydrogen. The HD content will be therefore 10⁻¹¹ molecules, which would produce 10⁷ ions, ending with 10⁶ counts at the mass 3 detector. The interference of He with the determination would be negligible. First, the concentration of He in seawater is comparable with that of H₂, namely about 4 x 10⁻⁵ ml NTP/lit containing just 5 x 10⁻¹¹ ml He³ compared with 3 x 10⁻⁹ ml HD. On the other hand, the Ar, if unpurified, might contain 5 x 10⁻⁴ ml He⁴ or 6 x 10⁻¹⁰ ml He³ per ml Ar. Ar containing < 10⁻⁸ He is, however, readily available commercially. Furthermore, the ionization efficiency of He (IP = 24.59 eV) with electrons of ≤ 20 eV in the presence of overwhelming amounts of Ar is expected to be extremely small (≤ 10⁻¹⁰) thus altogether eliminating He³ as a source of interference.

In short, it seems to be feasible to measure the HD/H₂ ratio of ambient hydrogen in seawater with a precision of 0.1%. We intend to test these assumptions during this proposed second half of the first phase of this program. This precision ought to be sufficient to distinguish between molecular hydrogen formed by different processes, since the H/D isotopes expected are of the orders of hundreds of percents.
The monitoring of H/D ratio on a continuous basis by this approach using continuous stripping with Ar, followed by appropriate pretreatment is feasible in principal. At a sample feed rate of 1 ml NTP/min, the desired precision could be achieved in 10 minutes or changes in the H/D isotopic ratio on the order of 1% could be observed in less than 10 seconds.

**Mass Spectrometric System**

The mass analyser purchased for the project is in essence a highly modified version of the Nuclide Corporation 3-60-RMS spectrometer, which is widely used for precision isotope ratio work. The instrument which was built to our specifications as outlined below, was delivered to our laboratory very recently.

**General** - The abundance sensitivity required is such that with $H_2$ gas introduced in the ratio $H_2/D_2$ (H/D) of $2 \times 10^{-8}$ the relative abundance can be determined with a precision of better than 1% (1 part in $10^4$).

**Inlet System**

The proposed inlet system must be capable of providing steady viscous flow of sample gas to the ionization source at a rate of $1 \times (4 \text{ torr} \cdot 1\text{-sec}^{-1}) \cdot (3 \times 10^{15} \text{ mol/s})$ for a period of at least 10 min from total samples of either $5 \times 10^{-2} \text{ cm}^3 \text{ NTP H}_2 \text{O}$ or $1 \text{ cm}^3 \text{ NTP H}_2$. This inlet system must be designed for isotope ratio studies of water, i.e., it must be capable of being used at a temperature at which the entire sample will be vaporized, and of alternate sample switching through matched viscous leaks from unknown to reference samples, and must have a sample capacity of at least six samples. Inlet system pumping is to be accomplished by means other than by hydrogen bearing fluid pumps, and sample pressure and/or flow measuring capability is required.
Collector System - A dual collector system is utilized which permits simultaneous collection of either negative ions of mass 1 and 2 or positive ions of mass 2 and 4. Provision is made for the signal detected by the collectors to be presented to the spectrometer operator as digital output in both a visible display and a permanent "hard copy" record.

Vacuum System - A bakeable metal system is assembled with standard Varian Conflat flanges and copper gaskets. A bakeout system is included. The system base pressure is to be maintained in the low $10^{-8}$ torr range when a sample is not being admitted, with sufficient pumping speed available to maintain the analyzer pressure during operation below the point where scattering from background gas affects the minor collected ion at a level of $5 \times 10^{-5}$ of the minority ion signal of the water sample. Pumping is accomplished by an ion pump to avoid possible contamination by hydrogen bearing fluid pumps.

Analyzer System - Mass analysis is accomplished by a 60° sector, direction-focusing electromagnet system capable of analyzing an ion beam of $1 \times 10^{-9}$ A (or greater) total intensity consisting of either H$_2^+$ and D$_2^+$ in a ratio $H_2/D_2 \approx 2 \times 10^{-8}$ or greater, with a precision, including data handling, of better than 1%, or H$^-$ and D$^-$ in a ratio of $H/D \approx 6 \times 10^3$ with a precision including data handling of better than 1 part in $10^4$.

This instrument was received at SRI on February 23, and is being installed at present.
Program of Research

As stated in the original proposal, the proposed program of research consists of four major phases:

- The construction, testing, and evaluation of the precision mass spectrometer followed by development of methods of sampling handling.
- The measurement of a limited number of representative samples of seawater and air to establish the range of concentrations and isotopic abundances of hydrogen. This phase may require setting up a small thermal diffusion facility to produce ultrapure deuterium if it cannot be purchased commercially or custom-produced by another research institution.
- The design and construction of a transportable version of our mass spectrometric system for shipboard operation.
- Oceanographic surveys of hydrogen by research vessels.

This proposal is concerned with the second year of the research program in which we hope to complete the second half of the first phase. By now the mass spectrometric instrumentation including the ionization sources and the mass analyzers has been constructed and will be performance tested before the end of this first year. The second year of the program will be devoted to methodology development. The following tasks are envisaged.

1. Determination of accuracy, reproducibility, precision, and memory of mass spectrometric instrumentation.
   a. For positive ions $H_2^+/D_2^+$ measurement on hydrogen samples.
   b. For $H^-/D^-$ measurement on water samples.
   c. For $HD^+/H_2^+$ measurement on hydrogen samples highly diluted with argon.

Task 1 is expected to take about 3 months at a level of effort of 1 man month/month.
2. Development of an extraction procedure for $\text{H}_2$ from water with $\text{D}_2$ as carrier. This will include apparatus design, construction, and calibration by dilution curves in the predicted concentration range.

Task 2 which will proceed partly in parallel with Task 1, will take 3 months at a level of effort of 0.75 man months/month.

3. Development of an extraction and purification procedure for determination of the isotopic composition of dissolved hydrogen in seawater using pure argon as carrier. Part of the procedure will be identical with that developed under Task 2, only that the purification stage will include the sodium amalgam clean-up step.

Task 3 is expected to be completed 1 month after completion of Task 2 at a level of effort of 1 man month/month.

4. Development of extraction procedure for atmospheric hydrogen to facilitate its collection as water for ultimate $\text{H}/\text{D}$ determination.

Task 4 is expected to take 3 months at a level of effort of 0.75 man months/month.

5. Measurement of hydrogen concentrations in a limited number of samples of seawater.

Task 5 is expected to take 2 months at a level of effort of 1 man month/month.

6. Design and construction of sampling vessel for deep seawater sampling. This task will be carried out with appropriate inputs from chemical oceanographers, (including Charles Keiling of the Scripps Institution and Louis Gordon from Oregon State University).

Task 6 is expected to take 2 months at a level of effort of 0.5 man months/month.

Task 7 is expected to take 2 months at a level of effort of 0.75 man months/month.

8. Design and construction of a portable air sampling system.

Task 8 is expected to take 3 months at a level of effort of 1 man month/month.

9. Measurement of the isotopic composition of atmospheric hydrogen in seawater at a number of locations.

Task 9 is expected to take 3 months at a level of effort of 0.75 man months/month.

10. Evaluation of the methodologies to allow a decision on the most rewarding experimental approach.

Task 10, including report writing and supervision, is expected to take 1-1/2 man-months at a level of effort of 0.1 to 0.2 man month/month.

The financial constraints imposed on us at this point may not allow us to complete all these tasks in the second year of the program. Only if the first 7 tasks can be accomplished faster than predicted will we be able to proceed and possibly accomplish tasks 8 and 9. We prefer to defer these two tasks, if necessary, to the third year of the program, since the determination of the concentration and isotopic composition of dissolved hydrogen seems to us to be of greater immediate interest.
The schedule of the second year's program is outlined as follows:

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<th>Task</th>
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</table>

*aMay have to be deferred for the third year of the program - see above.*
QUALIFICATIONS

The qualifications of the Stanford Research Institute and of the Mass Spectrometry Research Center have been presented in the original proposal.

PROJECT MANAGEMENT

The project will be carried out under the supervision of Dr. Michael Anbar, Director, Mass Spectrometry Research Center, Physical Sciences Division, who has over 20 years of experience in mass spectrometry for biomedical and geochemical purposes. Dr. Anbar has carried out pioneering work in the field of sonochemistry and is the initiator of the ideas on the role of sonolytic processes in geochemistry. Dr. H. Lewis Brown, a physicist with over 8 years of experience in mass spectrometry and related fields, will be project leader. Dr. Brown has constructed and is conducting research on a high precision isotope ratio mass spectrometer designed to determine \(^{48}\text{Ca} /^{40}\text{Ca}\) ratios. These scientists will be assisted by Dr. Rafael Schnitzer, physical chemist, with over 7 years of experience in mass spectrometry and molecular physics, and by Mr. Arthur C. Scott, inorganic physical chemist, with over 10 years of experience in different aspects of analytical chemistry.

Biographies of these scientists are attached.
References

CONTRACTUAL PROVISIONS

Statement of Work

SRI proposes to exert its best efforts in developing analytical techniques and instrumentation to determine the concentration and isotopic composition of molecular hydrogen dissolved in seawater. After appropriate calibration, the instrument developed will be ready to measure the $H_2$ content in $D_2$ samples, as well as the $D/H$ ratios in water samples, with the highest possible precision. Following this, appropriate extraction and purification techniques will be developed to allow the above-stated measurements.

Project Management

The project leader for the proposed work will be Dr. H. L. Brown under the supervision of Dr. Michael Anbar, with assistance from Dr. R. Schnitzer and Mr. A. C. Scott.

Biographies of these professional personnel are included in this proposal.

Reporting

Informal letter progress reports will be submitted upon request, and an annual report will be submitted at the conclusion of the contract period.

Estimated Time and Costs

The time required to complete the proposed project is 12 months. Charges for the research are estimated to be $80,117. A detailed cost breakdown is attached.

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Contract Form

It is requested that any contract resulting from this proposal be awarded on a cost-plus-fixed-fee basis.

Acceptance Period

This proposal will remain in effect until May 30, 1976; however, the Institute will be pleased to consider an extension if requested.

Attachment: Cost Breakdown
### Salaries and Wages

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<th>Category</th>
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**Total Direct Labor**: $25,294

**Payroll Burden at 31%**: 7,841

**Total Salaries and Wages**: $33,135

### Overhead at 110% of Salaries and Wages

36,449

### Direct Costs

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**Total Direct Costs**: $5,643

### Total Estimated Cost

$75,227

### Fixed Fee

4,890

**Total Estimated Cost Plus Fixed Fee**: $80,117
STANFORD RESEARCH INSTITUTE

SRI PROPOSAL NO. PYU 76-052

SCHEDULE A - DIRECT LABOR

Direct labor charges are based on the actual salaries for the staff members expected to do the project work, plus a judgmental factor added to the current base salaries for merit increases during the proposal contract period. Frequency of salary reviews and level of merit increases are in accordance with SRI's salary and wage payment policy as published in Topic No. 505 of the SRI Administration Manual and as reviewed by the Defense Contract Administration Services Region.

SCHEDULE B - OVERHEAD AND PAYROLL BURDEN RATES

These provisional rates have been submitted to the Department of Defense as bidding and billing rates for the year 1976. We request that these rates not be specifically included in the contract, but rather that the contract provide for reimbursement at billing rates acceptable to the Contracting Officer, subject to retroactive adjustment to fixed rates negotiated on the basis of historical cost data. Included in payroll burden are such costs as vacation, holiday and sick leave pay, social security taxes, and contributions to employee benefit plans.
SCHEDULE C - TRAVEL COSTS

Air fares are based on the current issue of the Official Airline Guide Quick Reference. Subsistence daily rates are based on SRI's rate schedule approved by DCAA. Surface travel is based on an average of $15 per day for car rental, parking, fees, tolls, etc. Mileage rate for personal auto expense is currently established at 15¢ a mile.

Air Fares

1 RT Menlo Park, Calif. to Washington, D.C. @ $357/fare $ 357
4 RT Menlo Park, Calif. to San Diego, Calif. @ $59.74/fare 239
2 RT Menlo Park, Calif. to Corvalis, Ore. @ $124/fare 124

Subsistence *

2 days at Washington, D.C. @ $42.50/day 85
10 days at Corvalis, San Diego @ $30/day 300

Surface Travel

12 days at $15/day 180

Total Estimated Travel Costs $1,285

*SRI policy provides for reimbursement to the travel on an actual reasonable basis, as detailed in an expense claim and supporting documentation. The rates represent composite cost data from our own accounts and from trade publications. The average rate includes lodging at a quality but not a premium hotel, three meals, and gratuity.
SCHEDULE D - MATERIALS AND SUPPLIES

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<td>Glassware</td>
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SCHEDULE E - SHIPPING AND COMMUNICATIONS

The communications estimate of $100 is based on our past experience for a contract of this size; it includes the cost of telephone tolls and wire messages.
SCHEDULE F - REPORT COSTS

Report costs are based on the following rates per page. Allowance is made for the reduction of rough draft material to a finished report form.

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MONTHLY REPORTS (8)

REPORT PRODUCTION: 16 pp text x 1.33 = pp

Report Pages: 21 @ $4.06 = 85.26
Press & Bindery: 16 pp x 5 cys = 80 pp x 1.92 = $87.18

QUARTERLY REPORTS (3)

REPORT PRODUCTION: 18 pp text x 1.33 = 24 pp

Illustrations: 3 @ $21.96 = 65.88
Report Pages: 24 @ $4.06 = 97.44
Pages & Bindery: 21 pp x 5 cys = pp x 2.52 = $165.84

FINAL REPORT

REPORT PRODUCTION: 25 pp text x 1.33 = pp

Illustrations: 5 @ $21.96 = 109.80
Report Pages: 33 @ $4.06 = 133.98
Press & Bindery: 30 pp x 50 cys = 1500 pp x 36.00 = $279.78

TOTAL ESTIMATED REPORT COSTS

Publications: 3 pp @ $75.00/p = $225.00
$757.80
MICHAEL ANBAR, DIRECTOR
MASS SPECTROMETRY RESEARCH CENTER
PHYSICAL SCIENCES DIVISION

Specialized professional competence

• Physical inorganic chemistry; mechanisms of redox reactions; stable isotope methodology and mass spectrometry; radiation chemistry of aqueous systems; sonochemistry; radioisotope tracer applications; nuclear chemistry; inorganic biochemistry and physiology; molecular radiobiology

Representative research assignments at SRI (since 1968)

• Mass spectrometry and mass spectrometric applications
• Chemical behavior of hydrated electrons
• Oxidation and electrochemical processes in molten salts
• Mechanism of sonochemical reactions
• Isotope geochemistry
• Tooth and bone physiology
• Dental restorative materials
• Biomedical applications of isotopes and radiation

Other professional experience

• Director, Chemistry Division, Israel Atomic Energy Research Laboratories
• Head, Department of Radiation Research, Soreq Nuclear Research Establishment (Yavne, Israel)
• Professor of inorganic and radiation chemistry, Feinberg Graduate School, Weizmann Institute of Science
• Visiting professor of inorganic chemistry, Tel Aviv University
• Visiting professor of chemistry, Stanford University
• Director, Radioisotope Training Center (Rehovoth, Israel)
• Senior research associate and consultant to the Argonne National Laboratory on problems in radiation chemistry
• Senior research associate, National Research Council, National Academy of Science at the NASA Ames Research Center

Academic background

• M.S. in physical chemistry (1950) and Ph.D. in physical organic chemistry (1953), Hebrew University (Jerusalem); postdoctoral fellow (1953-55), Department of Chemistry, University of Chicago

Publications

• Author of more than 160 publications in professional journals; editor of Multicomponent Analysis (Wiley, 1977); coauthor of The Hydrated Electron (Wiley, 1970)

Professional associations and honors

• American Association for the Advancement of Science; American Chemical Society; American Society for Mass Spectrometry; Chemical Society (London); Faraday Society; Israel Chemical Society; New York Academy of Sciences; Radiation Research Society; Meyer Award (1959); Sigma Xi; Zondek Award (1962)

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HAROLD L. BROWN, PHYSICIST
MASS SPECTROMETRY RESEARCH CENTER
PHYSICAL SCIENCES DIVISION

Specialized professional competence

• Experimental physics; mass spectrometry; positive and negative ion research; design, construction, and testing of drift tube mass spectrometry apparatus; electron impact ion sources; Kunsman ion sources; reaction rate studies; precision isotope ratio mass spectrometry; plasma ionization sources; field ionization sources; ion optics

Representative research assignments at SRI (since 1972)

• Research and development of field ionization sources
• Interfacing a multipoint field ionization source with a quadrupole mass spectrometer
• Construction and operation of a high precision isotope ratio mass spectrometer for the measurement of $^{48}\text{Ca}/^{40}\text{Ca}$ isotope ratios
• Construction of negative carbon dating spectrometer
• Postdoctoral physicist

Other professional experience

• Graduate student researcher, Physics Department, University of Pittsburgh
• Graduate teaching assistant, University of Pittsburgh

Academic background

• B.S. in engineering (1962), U.S. Military Academy; Ph.D. in physics (1975), University of Pittsburgh

Publications

• Ten publications

Professional associations and honors

• American Geophysical Union
• American Physical Society
• American Society for Mass Spectrometry
• Sigma Xi
• NASA predoctoral trainee
RAFAEL SCHNITZER, CHEMIST
MACS (RESEARCH CENTER
PHYSICAL SCIENCES DIVISION

Specialized professional competence
- Mass spectrometry; ion molecule reactions; data systems; sonochemistry; physical analytical methodology

Representative research assignments at SRI
- Development of duoplasmatron negative ion source
- Development of carbon dating mass spectrometer

Other professional experience
- Graduate student researcher, Isotope Department, Weizmann Institute (Israel)
- Research chemist, supervisor, physical analytical methods, Research Laboratories (Israel)

Academic background
- B.S. in physical chemistry (1962), Technion (Haifa, Israel); M.S. in physical chemistry/sonochemistry (1967), Weizmann Institute (Israel);
  Ph.D. in mass spectrometry/ion molecule reactions (1972), Weizmann Institute

Publications
- Author of three published articles; three more articles in preparation

Professional associations
- Israel Chemical Society
- Israel Society for Vacuum Technology
APTHUR SCOTT, CHEMIST
MASS SPECTROMETRY RESEARCH CENTER
PHYSICAL SCIENCES DIVISION

Specialized professional competence

- Physical inorganic chemistry; field ionization in mass spectrometry;
  isotope synthesis; kinetics of inorganic systems; polyelectrolytes;
  irradiation of polymers; metal plating; biophysical chemistry of nerve
  and bone; rheology of glass

Representative research assignments at SRI (since 1970)

- Biodegradability of oil shale
- New water-softening chemicals
- Polyphosphonates in caries prevention
- Electrochemical energy conversion
- Drug detection
- Identification of weathered oil spills
- Synthesis of labeled explosives
- Analysis of particles at low levels

Other professional experience

- Associate staff member, Exploratory Development, Raychem Corporation
- Summer research fellow, Westinghouse Research and Development

Academic background

- B.S. in chemistry (1968), Case Western Reserve University; M.S. in
  inorganic chemistry (1970), Stanford University

Publications

- Five publications

Professional associations and honors

- American Chemical Society
- Tau Beta Pi