MLM-2376

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Albert Attalla, Carl T. Bishop, Donald R. Bohl, Terrence L. Buxton, Ronald E. Sprague, and David K. Warner

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U. S. Government Contract No. EY-76-C-04-0053

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Available from
National Technical Information Service
U. S. Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22161
Price: Printed Copy $3.50; Microfiche $2.25

MLM-2376
Distribution Categories UC-4, UC-22

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Abstract

Mass spectrographic methods have served well in the past to analyze gaseous mixtures of the hydrogen isotopes. Alternate methods of analyses are reviewed which offer wider ranges and variety of isotopic determinations. This report describes possible improvements of the mass spectrographic determinations, gas chromatography, anti-Stokes Raman spectroscopy, microwave-induced optical emission spectroscopy, and methods of measuring tritium using radiation detection devices. Precision, accuracy, limitations, and costs are included for some of the methods mentioned. Costs range from $70,000 for the anti-Stokes Raman spectroscopy equipment, which can determine hydrogen isotopes but not helium, to less than $10,000 for the gas chromatographic equipment, which can determine hydrogen isotopes and helium with precision and accuracy comparable to those of the mass spectrometer.

Introduction

This report reviews some of the more promising methods for the determination of H_2, HD, D_2, DT, HT, T_2, and ^3He in mixtures of the hydrogen isotopes. The techniques described in this report apply to gas mixtures only. Compounds containing the isotopes of hydrogen must be decomposed to collect the gases in a form suitable for analysis.

The time-honored mass spectrographic method has served well in these analyses, but technological advances now require a wider range and a greater variety of isotopic determinations, and with greater precision and accuracy than can be feasibly accomodated by mass spectrography. A critical review was made of alternate technologies for analyzing hydrogen isotopic mixtures. This review is presented in three parts with a contribution by each of three groups of technically qualified personnel. The mass spectrographic capability and possible alternatives for its improvement are discussed in Part 1. Hydrogen isotope analyses by gas chromatography, anti-Stokes Raman spectroscopy, and microwave-induced optical emission spectroscopy are also reviewed. Part 2 is concerned only with the radioactive properties of tritium and methods of measuring tritium using radiation detection devices are discussed. Part 3 reviews a laboratory feasibility study of the gas chromatographic determination of the hydrogen isotopes and helium in mixtures.

PART 1

CURRENT AND ALTERNATE TECHNOLOGIES FOR THE DETERMINATION OF HYDROGEN ISOTOPIC MIXTURES

A. Attalla and T. L. Buxton

Current Technology

The method currently used at Mound Laboratory to determine hydrogen isotopic ratios and helium is mass spectrometry coupled with a titanium sublimation pump (TSP). The mass spectrometer is accurate to within 0.5% relative standard deviation when at least one mole percent of the constituent is present, but this instrument has its limitations in accurately determining helium content. To improve the analysis of this constituent the titanium sublimation pump has been added to the mass spectrometer. The accuracy of the determination utilizing both instruments is within 0.2%. Although these accuracies are sufficient for most purposes, analytical capabilities need improvements. Therefore, new developments are followed closely. The titanium sublimation pump is the most accurate technique known for the determination of inert gases. However, other gases interfere and these are identified and corrected for by mass spectrometric measurement. Any method that would improve the selectivity of the TSP would be valuable.

The determination of hydrogen isotopic ratios is dependent on the accurate measurement of each isotopic species formed and the equilibria constants among these species at the time of measurement. Techniques yielding improved formation and equilibria constants are extremely important. Any improvement in instrument stability or in the resolution of the mass spectrum of these isotopes also improves the accuracy of the determination by decreasing the overlap of the mass peaks. One promising technique is magnetic-sweep mass spectrometry.[1] Instruments of this type reportedly achieve resolutions of one part per thousand. This resolution is good enough to spectrographically separate all hydrogen isotopes.

Alternate Technologies

Gentry and Schott[2] have demonstrated the use of gas chromatography (GC) to determine hydrogen isotopic ratios. All isotopic species and helium may be detected in 30 minutes. Gas chromatography is used at Mound Laboratory for trace impurity determinations. Experiments indicate the feasibility of determining major components. The precision of GC is normally determined by the injection technique and modern automatic injection systems reduce this imprecision to a negligible quantity. Although Gentry and Schott give no precision or accuracy figures, they show that GC and mass spectrometric values are in close agreement. Equipment for the gas chromatograph should cost less than $10,000. The technique would help confirm mass spectrometric results, even if it does not improve upon them.

Anti-Stokes Raman spectroscopy can determine isotopic hydrogen species, but not helium. Thus it would have to be linked with a TSP system. Large separations with no overlap can be obtained with hydrogen isotopic mixtures. Sample fluorescence should be considerably reduced by using the anti-Stokes technique as opposed to the more normal Stokes lines. Precision as good as mass spectrometry has been claimed for conventional Raman analyses.[3] Instrumentation for anti-Stokes Raman spectroscopy costs about $70,000, but a laser Raman spectrometer is currently available at Mound. The only disadvantage of the latter instrument is that it yields an emission spectrum, which means that the emissivity may not be linear with species concentration. The inability to measure helium or other monatomic species is also a disadvantage.

Stump[4] had developed a partial pressure meter for the direct determination of tritium. The instrument is reportedly accurate to 0.2% relative standard deviation. Since the total tritium concentration is measured independently, the value is not dependent on sample equilibrium. An independent determination of tritium could then be used to refine the mass spectrometric results.

Microwave-induced optical emission spectroscopy has been used to determine impurities in argon gas.[5] Because of the high electron temperature of the plasma, nonmetallic species such as oxygen and nitrogen give strong emission signals. Broida and Moyer[6] have used similar species to determine the isotopic ratio of hydrogen and deuterium mixtures. Since the emission line is determined by the species present, interferences are minimized and sensitivities in parts per million are achieved. The instrumentation necessary for a simple spectrometer would cost about $20,000. If the techniques previously mentioned fail to give significant improvement in the accuracy of the isotopic determinations, this technique might be pursued.

Several other techniques - deuterium gamma neutron interaction to measure deuterium, inelastic electron scattering, and energy dispersive analysis - have been considered, but they seem to be research tools rather than analytical instruments. Development in these areas may lead to new techniques that are superior to those mentioned earlier. At the present time, however, they do not seem to be readily applicable to routine analysis.

PART 2

DETERMINATION OF HIGH CONCENTRATIONS OF TRITIUM IN GASES BY RADIATION DETECTION METHODS

C. T. Bishop

Introduction

The purpose of this section is to describe briefly the radioactive properties of tritium and the method of measuring it using radiation detection methods. The use of an ionization chamber or a scintillation crystal to measure high concentrations of tritium in gases is discussed.

At high concentration in gases, tritium is ordinarily measured by mass spectroscopy. However, at low tritium concentrations the accuracy of the mass spectroscopic determination is poor. At 10 mole % tritium or less, the absolute accuracy is about 0.2 mole %. The relative accuracy at 10 mole % tritium would be 2%, but at 5, 3, and 1 mole % tritium, the relative accuracies would be 4%, 7%, and 20%, respectively. The lower tritium concentrations are still high concentrations as far as radiation detection methods are concerned. Accuracies down to 1% or less would be expected using radiation detection methods in the determination of tritium at the lower concentrations where the mass spectroscopic values are poor.

Radioactive Properties of Tritium

Tritium is a weak beta emitter with a maximum energy of 18 keV and an average energy of 5.7 keV. Even though the energy is extremely low, tritium can be determined by many of the common radiation detection techniques. Ionization chambers, internal gas counters, and scintillation counters are used in the determination of tritium. At concentrations greater than about 1% tritium, the beta disintegration rate is too high to allow counting techniques where individual beta particles are detected.

The disintegration rate, -dN/dt, or particle emission rate for one mole of tritium can be calculated as follows:

$$-\frac{dN}{dt} = \frac{0.69315wA}{Mt_{\frac{1}{2}}}$$

where

$0.69315 = \ln 2$

w = weight of one mole in grams = 6.032 for tritium

A = Avogadro's number = 6.022×10^{23}

M = atomic weight = 3.016 for tritium

$t_{\frac{1}{2}}$ = half-life = 12.34 yr for tritium = 525,600 min.

then

$$-\frac{dN}{dt} = \frac{(0.69315)(6.032)(6.022 \times 10^{23})}{(3.016)(525600)}$$

$$= 1.287 \times 10^{17} \text{ beta particles per minute.}$$

This rate is very high for radiation detection systems.

The disintegration rate per unit volume can also be calculated using the fact that one mole of gas at 0°C and 760 torr = 22,414 cm^3:

$$-dN/dt/V = \frac{1.287 \times 10^{17} \text{ min}^{-1}}{22{,}414 \text{ cm}^3}$$

$$= 5.724 \times 10^{12} \text{ min}^{-1}/\text{cm}^3$$

or, at 25°C, 760 torr,

$$-dN/dt/V = 5.26 \times 10^{12} \text{ min}^{-1}/\text{cm}^3.$$

This is equivalent to 2.37 Ci/cm^3 since 1 Ci = 2.22 x 10^{12} dis/min.

Thus, even at tritium concentrations of 1 mole %, a disintegration rate of 5.26 x 10^{10} min^{-1}/cm^3 would be too high to be detected by techniques such as internal gas proportional counting or scintillation counting. At concentrations greater than about 1% tritium ionization chambers or scintillation detectors coupled to photomultiplier tubes with an analog current output must be used.

A few references of general interest on tritium and its determination are of interest because of their extensive coverage. One of these is Tritium, a compilation of papers presented at a Tritium Symposium held in Las Vegas, Nevada in 1971.[7] Another is a report from the AEC Critical Review series, Sources of Tritium and Its Behavior Upon Release to the Environment.[8] The volume on radiation[9] in the extensive Survey of Instrumentation for Environmental Monitoring has a section on tritium.

Ionization Chambers

Three classes of gas-filled detectors - ionization chambers, proportional counters, and Geiger counters - are capable of detecting alpha, beta, and gamma radiation. A good explanation of the differences between these three kinds of detectors is given by Price.[10]

The ionization chamber is the only gas-filled detector of interest in determining tritium at concentrations of the order of 10^{12} dis/min/cm^3. In an ionization chamber the radiation ionizes the gas in the chamber, and the voltage between the electrodes is such that only the ions produced by the radiation itself are collected. This is in contrast to proportional and Geiger tubes, where the phenomenon of gas multiplication occurs at higher electrode voltages. Gas multiplication is the effect of producing a large number of ion pairs from the acceleration of a primary ion pair produced in the electric field by the interaction of a single particle or photon in a gas-filled detector. A good discussion of ionization chambers can be found in Price[10] (pp. 70-114).

Tritium is a gas and is introduced directly into an ionization chamber for measurement. An early study of the determination of tritium in an ionization chamber was made by Wilzbach, et al.[11] These authors pointed out that the number of ion pairs produced per unit of energy expended varied with the nature of the gas being used. Table 1 shows this effect with a number of gases when tritium is being detected. Thus, if tritium is being measured in a mixture of gases, the current output of the ionization chamber would depend to some extent on the composition of the gas mixture. One possible way of avoiding this problem when measuring tritium at high concentrations is to dilute a small aliquot of the sample gas with a large volume of the chamber gas. There would be a dilution error but this error could be reduced to less than 0.2%. Methane may be a good gas, since Wilzbach, et al,[11] state that "In this gas (methane), loss of ions by recombination is much less serious than in propane and the effects of pressure and of impurities are less than in hydrogen".

Several references[7-9] to the determination of tritium with an ionization chamber are given at the end of this report. However, references 8 and 9 are concerned with trace concentrations of tritium in gases. While discussing the measurement of tritium in an ionization chamber, Gentry, et al[12] state that "After a series of twelve measurements carried out on the same gas mixture, a tritium value of 19.95 ± 0.08% at the 99% confidence level was obtained." No details were given of the ionization chamber used.

Table 1

IONIZATION COLLECTED FROM TRITIUM RADIATION IN SEVERAL GASES

Gases	Relative Ionization	Ion Pairs/ Disintegration
Hydrogen	0.685	132
Nitrogen	0.82	158
Helium	0.84	162
Carbon Dioxide	0.84	162
Methane	1.00	193
Argon	1.06	205
Propane	1.13	218

In checking Analytical Chemistry's 1975-1976 Lab Guide[13], 20 manufacturers are listed which make ionization chambers and 9 are listed which make tritium monitors.

Instruments for measuring tritium gases were made by some of the listed manufacturers. One of them recently supplied Mound Laboratory with an ionization chamber which can measure tritium concentrations between 0.1 and 200,000 Ci/m^3. The chamber and the associated equipment cost $4,000. Although most commercial instruments have been made for low-level (<<1 mole %) tritium measurements, there seems to be no reason why instruments could not be made available at a cost under $10,000 which could accurately measure tritium in concentrations of the order of 1 to 10 mole %.

Tritium Determination by a Scintillation Crystal

A second type of radiation detection system for measuring tritium at concentrations approaching 100% is a scintillation crystal-photomultiplier tube combination using a current measuring device to measure the output. In a scintillation counting system, the radiation releases its energy in a scintillation material (which can be solid or liquid), producing light which is subsequently collected and amplified by means of a photomultiplier tube. A good description of scintillation detectors can be found in Price[10](pp. 159-211).

Anthracene as a crystal is used extensively in the determination of beta emitters. However, isotopic exchange of the tritium with the hydrogen in the anthracene could contaminate the detector. A scintillator material that has been used recently in tritium detection is europium-doped calcium fluoride [CaF_2(Eu)]. This material is commercially available and has been used in a few different applications.[4,14,15]

In Stump's application[4], it was stated that tritium in gases can be measured over a range from 1 ppm to 100%. At 4.90% tritium, the CaF_2(Eu) scintillation detector system gave a relative standard deviation of 0.2%, while the same gas sample analyzed by mass spectrometer analysis gave a relative standard deviation of 0.9%. It was pointed out, however, that to obtain maximum precision with the CaF_2(Eu) detector, recalibration with a standard was necessary every two hours. Another requirement for maximum accuracy is the elimination of polar gases such as T_2O and NT_3, which absorb on the surface of the detector and cause drift problems. In conclusion, however, it appears that the CaF_2(Eu) scintillation system for the determination of high concentrations of tritium in gases may give results which are as accurate as those obtained with the ionization chamber.

PART 3

THE POTENTIAL APPLICATION OF GAS CHROMATOGRAPHY TO THE DETERMINATION OF MAJOR HYDROGEN ISOTOPE GAS COMPONENTS

D. K. Warner, R. E. Sprague, and D. R. Bohl

Introduction

Gas chromatography (GC) has been used at Mound Laboratory since 1973 for the determination of isotopic impurities in hydrogen isotopic gas mixtures.[16] Examples of impurity analyses are given in Table 2. A chromatogram of a highly impure tritium sample is shown in Figure 1. Although the present use of GC at Mound Laboratory is only in the analytical range from about 40 ppm to 0.5%, there are strong indications that GC techniques could be extended to the determination of the major isotopic components in such mixtures. This section of this report is a feasibility study of the potential use of GC for the determination of the major components of H-D-T mixtures. Any component present at a concentration greater than 0.2 mole % is defined as a major component. Chromatograms are presented to illustrate the current status of GC separation technology, and the conclusions are based primarily on recent experiments.

Experimental

The chromatograms shown in this report were obtained from three D-T mixtures whose approximate concentrations are shown in Table 3. The absolute accuracy of the compositions in Table 3 is not critical since the purpose of these experiments was to observe the effective separation of the D_2-DT-T_2 mixtures at various isotopic ratios. The sampled mixtures contain a high T_2 mix (A),

an equal D_2-T_2 mix (B), and a high D_2 mix (C). ^3He and/or neon gases present in the mixtures were corrected for to give the net isotopic compositions shown. The mixtures were sampled using standard GC operating procedures, but the sample pressures were varied to avoid overloading the column with the D-T isotopes. Large recorder attenuations (to 50X) were required to maintain the larger peaks on the recorder scale. One chromatogram is included here for each mixture sampled (Figures 2, 3, and 5) and a chromatogram for a "combination" analysis of major and minor isotopes is shown in Figure 6.

Discussion

Mixture A, the high T_2-low D_2 composition, is shown in Figure 2 and has an HT impurity of roughly the same magnitude as the combined ortho-para D_2 components (~0.2%). HD and HT are well separated from the initial D_2-DT-T_2 mixture, and from the standpoint of assessing the general quality of the separation of GC analysis, the individual isotopes are considered to be completely separated. Note that for recorder presentation the DT and T_2 are attenuated by 50X, and also that the nuclear spin isomers of D_2 are separated. This spin isomer separation can be eliminated by coating the column alumina with Fe_2O_3 which catalyzes a rapid interconversion of the nuclear spins among D_2 molecules.[2] Thus a single mean-value D_2 peak will appear where the two ortho and para forms are located in the chromatogram.

This process is illustrated by the chromatogram shown in Figure 3 for the equal D_2-T_2 mixture B. The ortho and para forms of D_2 are incompletely separated from each other and from the DT for this mixture, as evidenced by the failure of the peak "valleys" (the arrows in Figure 3) to return to the normal baseline. The trace of a single D_2 peak caused by spin interconversion is shown in Figure 4 for the same mixture B. The mean value of the single peak's retention time has been demonstrated for H_2 spin isomers. The actual D_2 spin isomers are the broken lines seen in Figure 4.

A similar D_2-T_2 separation problem is present in the high D_2-low T_2 mixture C of Figure 5. The ortho-D_2 and para-D_2 trailing edges do not return to the baseline and an error is introduced into the calibration of these incompletely separated species. Although integration techniques, such as dropping vertical lines to the baseline, can partially compensate for the peak overlap, it would be preferable to try to achieve a full separation by the merging of the two D_2 spin isomers as discussed previously.

The last chromatogram (Figure 6) is an attempt to demonstrate a combination of major component and impurity analysis for mixture C that also contains ^3He as a major component. The attenuation is required only for recorder presentation since any modern electronic integrator will accomodate the disparate peak sizes. The limiting factor in attaining a complete analysis would clearly be the separation of the D_2 isomers and DT as previously discussed.

The discussion so far has considered only D_2-DT-T_2 and ^3He as the major components. The inclusion of H_2 as a major component adds a totally new dimension to the problem, and experiments have not been performed that realistically show its influence upon the separations. One can conjecture, however, about the effects of adding H_2 to these mixtures.

An H_2-HT-T_2 mixture would not pose an analytical problem since the three are well separated, and H_2 elutes before HD (to the right of HD in Figure 2). If, however, all isotopic species are present as major components (H_2, HD, HT, D_2, DT, T_2), and using the premise that an Fe_2O_3 column coating prevents ortho-para separation of the D_2 or H_2, then the most likely pair to cause

Table 2

EXAMPLES OF ANALYSES PERFORMED BY GAS CHROMATOGRAPHY

Components Determined	Sample Matrix
Ar, N_2	Purified T_2 H_2, D_2, T_2, ^3He Mixtures
^3He, HT, DT	Purified T_2
HD	D_2
HD, HT	Isotopic Mixtures of ^3He, D_2, T_2

Table 3

NET ISOTOPIC COMPOSITIONS (MOLE %) OF SAMPLED MIXTURES

	D_2	DT	T_2
Mixture A	0.2	9.2	90.6
Mixture B	25.2	49.5	25.2
Mixture C	74.1	21.5	4.4

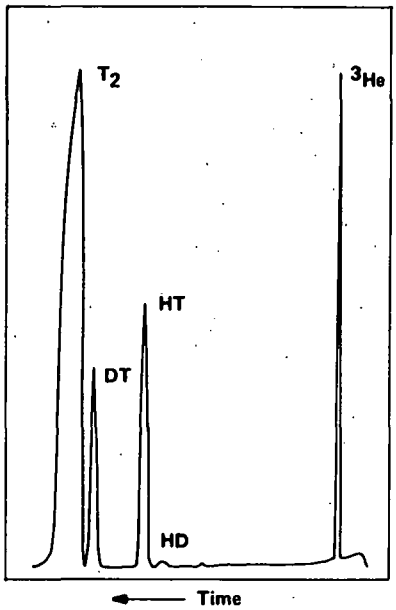

FIGURE 1 - Chromatogram of high level impurities in T_2.

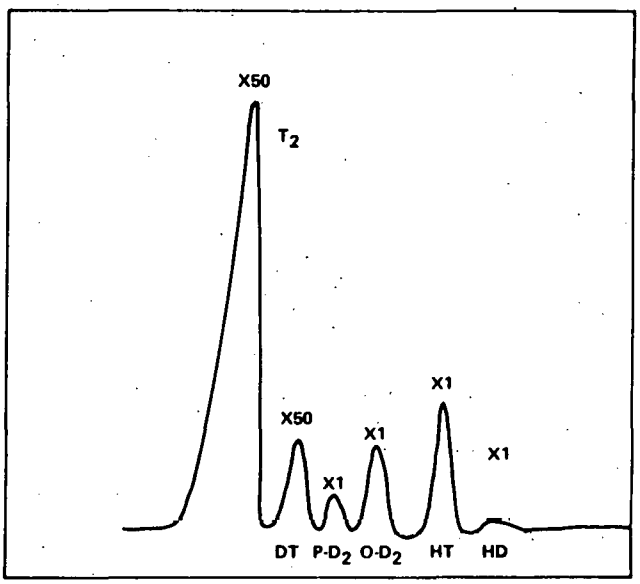

FIGURE 2 - Chromatogram of Mixture A.

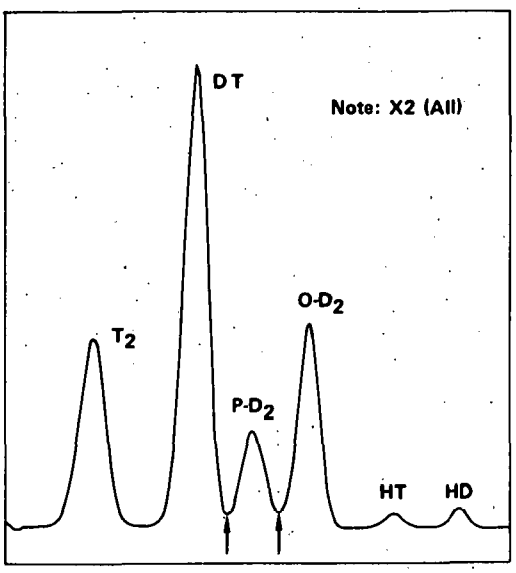

FIGURE 3 - Chromatogram of Mixture B.

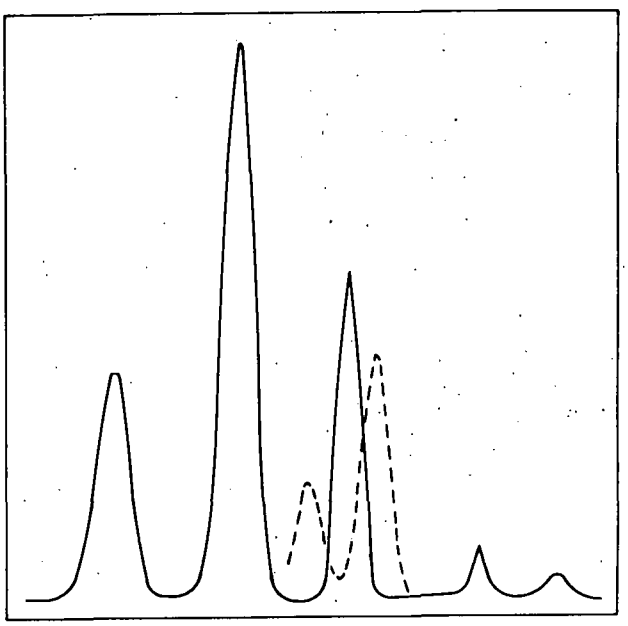

FIGURE 4 - Representation of a single D_2 peak for Mixture B.

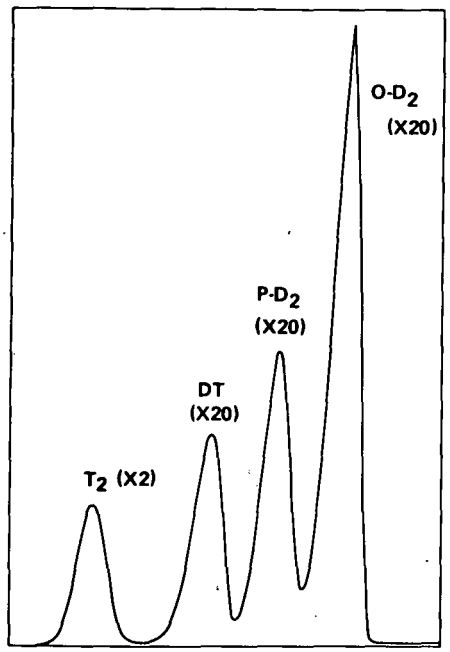

FIGURE 5 - Chromatogram of Mixture C.

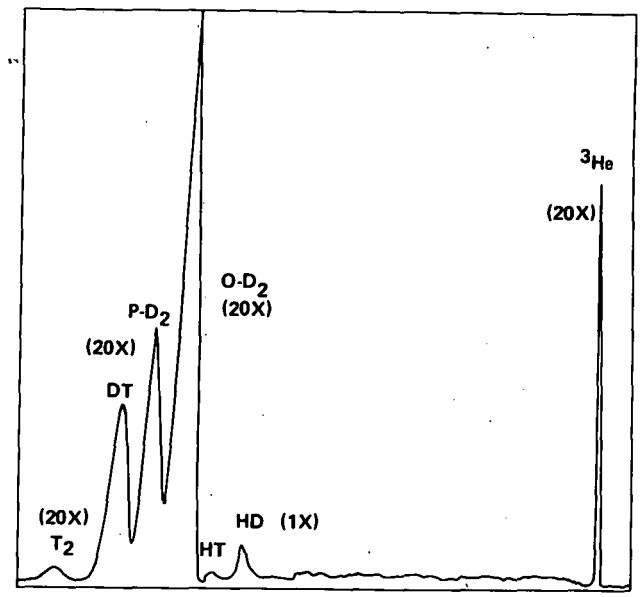

FIGURE 6 - Chromatogram of Mixture C: major and minor components.

problems would be HD-HT because their separation factor is smaller than that of other adjacent pairs. The problem does not occur with HD and HT as impurities; however, with the wider bases of larger peaks, an incomplete separation would cause analytical problems. The HT-D_2 and H_2-HD peaks would probably be adequately separated, and would cause no problems.

Sample size has an extraordinary influence upon GC isotopic separations, and an increase in sample volume can cause a deterioration in separation by changing the retention times of the species and by simple diffusion spreading. Since this separation parameter was not investigated, one can only speculate that a slight improvement in the general separation could be effected by reducing the sample size. This reduction, however, would be limited by the necessity of providing a measurable peak size of the component at the smallest concentration.

An important aspect of this evaluation is how well the GC method would compare with mass spectrometry, the conventionally used method for major component analysis. Some data are given in Table 4 that compare GC and MS results at a few selected low concentrations, but the error estimates should be examined with the knowledge that the table does not represent a complete statistical data base. The most revealing comparison in Table 4 is at T_2 where the precision estimates suggest that the GC precision is superior in the 0.5-1.5% concentration range. The MS precision (0.9%) for the analysis of 0.2% D_2 is unusually low for this concentration and is not considered to be too representative of the MS method for the purpose of this comparison. A better assessment of major component precision for the GC method is shown in Table 5. An isotopic mixture containing about 40% D_2, 41% DT, 11% T_2, and 8% ^3He was sampled five times in one day in order to establish reasonable values for GC within-day variations for major component determinations. The conclusions of this experiment are that the within-day variations are primarily a function of the peak area integration process, and that the error for major components (concentrations >2%) is about 0.25% - 0.50% (two times the relative standard deviation). The D_2-DT peaks are not entirely separated due to the nuclear spin isomer separation problem, but nevertheless, the reproducibility of all the isotopes is good. The ^3He and T_2 peaks are completely separated, so their errors may be used with confidence as representative of the within-day variation expected with the GC method.

Table 4

COMPARISON OF MS AND GC PRECISION ERRORS

Component	Concentration	Precision Error Estimate (2s)[a] GC	MS[b]
HT	1.0%	1.0%[c]	-
D_2	0.2%	-	0.9%
DT	1.0%	1.4%[c]	-
T_2	0.5%	-	6.9%
	1.0%	1.6%	-
	1.6%	-	1.9%

[a] 2s = two times estimated relative standard deviation.

[b] Variability of triplicate samples on three days (9 samples).

[c] Analysis of variance results for within-day variability.[2]

Conclusions

The analysis of major components in hydrogen isotopic mixtures is judged to be feasible with the qualification that the ortho-para spin forms of D_2 and H_2 should be eliminated through the use of Fe_2O_3-coated column packings. Also, it is concluded that it is possible to determine both major components and impurities in a single sample, but the advantage of using one sample might be offset by the necessity of reducing the pressure to improve the overall separation, and thus raising the detection limits of the impurities. More experimentation will be required to fully assess the impact of the presence of H_2 in the mixtures and the effects of sample size. However, gas chromatography appears to be a viable analytical method for major isotopes determinations. Based on the variation of data demonstrated in this study (Table 5), the overall error of the GC method should be competitive with other techniques for hydrogen isotopic analysis.

Table 5

MAJOR ISOTOPIC COMPONENT ANALYSIS BY GC

Component	Peak Area							Total Counts
	^3He	HD	HT	$o\text{-}D_2$	$p\text{-}D_2$	DT	T_2	
Approximate Concentration(%)	7.8	0.7	0.2	39.6		40.7	10.9	
Run #1 Counts*	48270	3282	1125	122500	43170	142400	36570	397400
Run #2 Counts	48220	3258	1142	122300	42970	142100	36490	396600
Run #3 Counts	48130	3213	1120	122200	43030	142000	36520	396300
Run #4 Counts	48250	3224	1132	122500	42910	142300	36590	396900
Run #5 Counts	48260	3231	1126	122600	42950	142500	36620	397300
Mean Counts	48226	3241.6	1129	122420	43006	142260	36558	396900
σ	56.8	28.0	8.4	164.3	101.4	207.4	52.6	436.7
Relative Standard Deviation (%)	0.12	0.86	0.75	0.13	0.24	0.15	0.14	0.12
2(R.S.D.) (%)	0.24	1.72	1.50	0.26	0.48	0.30	0.28	0.24

*Counts = mV-sec

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