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**The Potential Application of Gas
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of Hydrogen Isotopes**

*David K. Warner, Ronald E. Sprague
and Donald R. Bohl*

September 20, 1976

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Abstract

Gas chromatography (GC) is used at Mound Laboratory for the analysis of hydrogen isotopic impurities in gas mixtures. This instrumentation was used to study the applicability of the GC technique to the determination of the major components of hydrogen isotopic gas mixtures. The results of this study, including chromatograms and precision data, are presented in this paper.

Introduction

Gas chromatography (GC) has been used at Mound Laboratory since 1973 for the analysis of isotopic impurities in hydrogen isotopic gas mixtures.¹ Examples of the impurity determinations are listed in Table 1, and a chromatogram of a highly impure T₂ sample is shown in Figure 1. Although the present use of GC at Mound is exclusively in the analytical range of 40 ppm to 0.5%, there are strong indications that GC techniques could be extended to the analysis of the major isotopic components in such mixtures. This

report is a feasibility study that examines the potential of GC for the analysis of major components of H-D-T mixtures, a major component being defined as greater than 0.2%. Chromatograms are presented to illustrate the current status of GC isotopic separation technology, and the conclusions are based on experiments performed on instrumentation designed for impurities analyses.¹

Table 1

EXAMPLES OF ANALYSES PERFORMED BY GAS CHROMATOGRAPHY

Components Determined	Sample Matrix
a) Ar, N ₂	Purified T ₂ H ₂ , D ₂ , T ₂ , ³ He Mixtures
b) ³ He, HT, DT	Purified T ₂
c) HD	D ₂
d) HD, HT	Isotopic Mixtures of ³ He, D ₂ , T ₂

FIGURE 1 - Chromatogram of high level impurities in T₂.

Experimental

The chromatograms shown in this report were obtained from three D-T mixtures whose approximate concentrations are shown in Table 2. The absolute accuracy of the compositions in Table 2 is not critical since the purpose of these experiments was to observe the effective separation of the D_2 -DT- T_2 isotopes with various isotopic ratios. Thus the sampled mixtures contain (1) a high T_2 mix, (2) a high D_2 mix, and (3) a 50-50 D_2 - T_2 mix. Helium-3 decomposition gas present in the mixtures was factored out to give the net isotopic compositions shown. The mixtures were sampled using standard GC operation procedures, but the sample pressures were varied to avoid overloading the column with the D-T isotopes. Large recorder attenuations (up to 50X) were also required to maintain the larger peaks on the recorder scale. A chromato-

Table 2

NET ISOTOPIC COMPOSITIONS
OF SAMPLED MIXTURES (in mole %)

	<u>D_2</u>	<u>DT</u>	<u>T_2</u>
Mix A	0.2	9.2	90.6
Mix B	25.3	49.5	25.2
Mix C	74.1	21.5	4.4

gram for each mixture sampled is shown in Figures 2, 3, and 5, and one "combination" analysis of major and minor isotopes is shown in Figure 6.

FIGURE 2 - Chromatogram of Mixture A. (HT and HD are present due to wall exchange phenomena.)

Discussion

Mixture A, the high T_2 -low D_2 composition, is shown in Figure 2, and is seen to have an HT impurity of roughly the same magnitude as the combined ortho-para D_2 components (~0.2%). The 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 for 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 causes a rapid interconversion of the nuclear spins among D_2 molecules;² thus a single mean-value D_2 peak would appear where the two (ortho and para) forms are located in the chromatogram.

The process is illustrated for the 50-50 D_2 - T_2 mix, whose chromatogram is shown in Figure 3. The ortho and para forms of D_2 are seen to be 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 50-50 D-T mixture. The mean value of the single peak's retention time has been demonstrated for H spin isomers. The actual D_2 spin isomers are the broken lines in Figure 4.

A similar D_2 -DT separation problem is present in the high D_2 -low T_2 mix of Figure 5. The o- D_2 and p- D_2 trailing edges do not return to the baseline, and errors would be introduced into a 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 species. The attenuation is

FIGURE 3 - Chromatogram of Mixture B.

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

required only for a recorder presentation since any modern electronic integrator will accommodate the disparate peak sizes. The limiting factor in attaining a complete analysis would clearly be the D_2 -DT separation problem that has previously been discussed.

The discussion so far has included only a consideration of D_2 -DT- T_2 and ^3He as major components. The inclusion of H_2 as a major species 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 problems would be HD-HT because their separation factor is smaller than for other adjacent pairs. The problem does not occur with HD and HT as impurities, but with the wider of larger peaks, an incomplete separation could

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 both (1) changing the retention times of species and (2) by simple diffusion spreading. Since this separation parameter was not investigated, one can 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 with the smallest concentration.

An important aspect of this evaluation is how well the GC method would compare with the conventionally used method for major component analysis, i.e., mass spectrometry. Some data are shown in Table 3 that compare GC and MS results at a few selected low concentrations, but these error estimates should be examined with the knowledge that the table does not represent a complete statistical data base. The most revealing comparison of Table 3 is for T_2 where the precision estimates suggest that the GC precision is superior in the 0.5-1.5% concentration range. The

FIGURE 5 - Chromatogram of Mixture C.

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

MS precision (0.9%) for the analysis of 0.2% D₂ 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 4. An isotopic mixture containing about 40% D₂, 41% DT, 11% T₂, and 8% ³He was sampled five times in one day in order to establish reasonable values for GC within-day variations for major components 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 of 2% concentration or greater is of the order of 0.2% to 0.5% (2 x relative standard deviation). The D₂-DT peaks are not entirely separated due to the nuclear spin isomer separation problem, but the reproducibility of all the isotopes is good. The ³He and T₂ peaks are completely separated, and their errors may be used with confidence as being representative of the within-day variation expected with the GC method.

Table 3

COMPARISON OF MASS SPECTROMETRY AND GAS CHROMATOGRAPHY PRECISION ERRORS

Component	Concentration	Precision Error Estimates (2s) ^a	
		GC	MS ^b
HT	1.0%	1.0% ^c	-
D ₂	0.2%	-	0.9%
DT	1.0%	1.4%	-
T ₂	0.5%	-	6.9%
	1.0%	1.6%	-
	1.6%	-	1.9%

^a2s = Two times estimated relative standard deviation.

^bVariability of triplicate samples of three days (9 samples).

^cAnalysis of variance results for within-day variability².

Table 4

MAJOR ISOTOPIC COMPONENT ANALYSIS BY GAS CHROMATOGRAPHY

Component	Peak Area							Total Counts
	³ He	HD	HT	O-D ₂	O-D ₂	DT	T ₂	
Approximate Concentration (%)	7.8	0.7	0.2	39.6	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	48226	3242	1129	122420	43006	142260	36558	396900
σ	56.8	18.0	8.3	163.2	101.3	207.4	52.6	463.7
Relative Standard Deviation (%)	0.12	0.86	0.75	0.13	0.24	0.15	0.14	0.12
2σ (%)	0.24	1.72	1.50	0.26	0.48	0.30	0.28	0.24

*Counts = Mv-sec.

Conclusions

From the chromatograms and discussion, 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 via 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 overall separation, and thus raising the

detection limits of the impurities. More experimentation will be required to fully assess the impact of H_2 presence in mixtures, and sample size effects, but overall, gas chromatography appears to be a viable analytical method for major isotopes determination.

Based on the variation of data demonstrated in this study (Table 4), the overall error of the method should be comparable to other techniques for hydrogen isotopes analysis.

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