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CHROMATOGRAPHIC SEPARATION OF HYDROGEN ISOTOPES**

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Modified Molecular Sieves - Stationary Phase for the Gas
Chromatographic Separation of Hydrogen Isotopes

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Abstract

Gas chromatographic separation of hydrogen isotopes on different molecular sieves at liquid nitrogen temperature has been investigated. Normal molecular sieves 5A, 13X and AW500 are not satisfactory for the purpose both in the partially dehydrated as well as totally dehydrated state. Molecular sieve 4A in the partially dehydrated state separated H_2 and D_2 while H_2 and HD are not well resolved. Iron exchanged or coated molecular sieves 4A, 5A, 13X and AW500 in the partially dehydrated state separated the isotopic mixtures H_2 , HD, D_2 and H_2 , HT, T_2 . The resolution varied depending on the amount of iron content and the residual moisture in the molecular sieves. Good separations were obtained on 15% "Fe" coated Molecular sieve 5A and 5% "Fe" coated Molecular Sieve 4A.

Introduction

Gas Chromatography has been used for the separation of hydrogen isotopes since about 30 years. Over the years this separation technique has gained importance and a number of papers (1-14) have been published. However, most of these relate to various pretreatment and conditioning procedures to improve the performance of the basic stationary phase Alumina(8), such as ferric hydroxide treatment(1-7), chromic oxide treatment(9), conditioning temperature effects(6,7), deactivation by CO₂ pretreatment (6,7) and so on. Other stationary phases such as molecular sieve, 4A(10,11), molecular sieve 5A(12), etched glass beads(13,14) have also been tried out. In the case of molecular sieve 4A, separation of these isotopes is reported in the temperature range of -140 to -160°C with the material preconditioned by heating at high temperature(10) for several hours under vacuum. In spite of all these, ferric hydroxide treated alumina remains the column of choice, with helium or neon as the carrier gas, though the column conditioning requires special care and normal analysis time varies from 30 to 40 minutes. Further, the precise reproducibility of retention time using this column over extended period of use has been difficult.

Molecular sieves 13X, 5A and to a lesser extent 4A have been used routinely for gas chromatographic separation of permanent

gases with excellent reproducibility. Hence, we attempted to investigate the feasibility of using them (as such and with pretreatment) as stationary phase for the separation of hydrogen isotopes and assess the critical parameters affecting resolution and reproducibility.

The effect of ferric hydroxide doping on alumina has been found to give better separation and symmetric peaks. Hence attempts were made to incorporate "ferric" hydroxide or exchanged "Fe" ions in the molecular sieve itself and study the hydrogen isotope separation characteristics of this material. These experiments were carried out with a view to obtain faster separation of hydrogen isotopes with long term stability of the column and reproducibility of retention times in order to facilitate routine analysis. The results of these experiments are reported in this communication.

Experimental

The gas chromatograph, used in these experiments, fabricated in this laboratory consists of a sample injection port, an appropriate column which can be cooled to -196°C by liquid N_2 , an on line copper oxide converter(3) maintained at 400°C and a four filament thermal conductivity detector (TCD) maintained at 150°C with its associated power supply and control as shown

schematically in fig.1. Helium was used as the carrier gas. Copper oxide converter was used to convert hydrogen into water, so that the sensitivity of detector is enhanced by the large difference in thermal conductivity between steam and helium as compared to H_2 and Helium. In the case of hydrogen/tritium isotope analysis a low volume flow through ionization detector (6,7) was connected in series between the column outlet and the copper oxide converter followed by TCD.

Since the objective was to compare the relative separation efficiency of different stationary phases, after preliminary experiments, a 3.8 meter long 2.2mm (I.D) copper column was selected and in all cases 30-60 mesh stationary phase was filled in under vacuum suction.

A mixture of D_2 and HD was obtained by sodium reaction with D_2O in a vacuum set up. A measured volume of this gas was mixed with known volume of hydrogen in a gas bulb and used as stock sample for all analyses. Independently $H_2/HD/D_2$ concentration was also ascertained by mass spectrometric analysis of the mixture. In the case of tritiated samples, known amount of H_2 was mixed with tritium containing HT in another gas bulb and used as the stock sample. (In this case the exact concentration of HT was not determined).

Stationary phase

The stationary phases tried out in this study are molecular

sieves 4A, 5A, 13X and AW500 from M/s Union Carbide. These were modified in two ways.

(i) Molecular sieves were partly converted into Fe^{++} exchanged system using the method reported by W.N. Delgass et al (15). The exchange of sodium ions in molecular sieves by Fe^{++} is somewhat difficult as the change in pH(>5) of the system results either in breaking down the molecular sieve structure or precipitation of Fe^{++} as hydroxide. The amount of Fe in the system after exchange was ascertained by elemental analysis. The material after exchange was washed thoroughly with distilled water, dried at $120^{\circ}C$ in an air oven, cooled, sieved and 30/60 mesh fraction was used for the experiments.

(ii) In the second set of experiments, the molecular sieves were coated with ferric chloride ($FeCl_3$, E Merck L.R.). The required quantity of $FeCl_3$ was taken to give 5%, 10% and 15% w/w iron with respect to molecular sieve (moisture saturated) using methanol(G.R.) as the solvent and coating the material in the usual way as in the case of liquid coating for GLC columns. After evaporation of methanol solvent at room temperature under air draft, the material was further dried in an air oven for 30 minutes at $120^{\circ}C$. It was then cooled to room temperature and washed with 3M ammonia solution to neutralize all residual acid and then thoroughly washed with distilled water to remove excess ammonia and dried in the oven at $120^{\circ}C$, cooled, sieved and 30/60

mesh fraction was used for the experiments.

Conditioning

In the case of molecular sieves preconditioning at 200°C to 300°C for six hours or more in a flowing stream of carrier gas is necessary for obtaining separation between permanent gases such as H₂, O₂ and N₂. In view of this, each of the normal and modified molecular sieves was packed in the chromatographic column and conditioned at 240°C in helium flow for six hours, then cooled to liquid N₂ temperature and used for the separation of hydrogen isotopes. In our study, the hydrogen isotopes were found to be strongly absorbed in both normal and modified molecular sieves, elution commencing only after 40 minutes or longer at carrier flow rate of 60 ml/minute. The peaks were broad, tailing and overlapping. However, it was observed that when the conditioning was done at lower temperature for shorter duration some of the modified molecular sieves separated the hydrogen isotopes. Also it was observed that the conditioning of packed column in situ was not satisfactory because of non-uniformity of the residual moisture content along the length of the column. In this context it is of relevance to note that the effect of partial dehydration of molecular sieve 5A with respect to gas chromatographic separation of gas mixtures containing H₂, O₂, N₂, CO, CH₄, Kr and Xe and changes in retention behaviour has been reported earlier by R. Aubeau et al.(16).

Thus in all the cases, following procedure for conditioning was adopted . The molecular sieve was allowed to absorb water vapour to saturation at room temperature. A weighed amount of the sieve was then taken in a shallow glass container , spread evenly and heated in an air oven at the desired temperature ($\pm 1^\circ \text{C}$) for the required duration. At the end of conditioning the sample was quickly transferred to a weighing bottle, stoppered, cooled to room temperature and weighed noting the percent water loss. This material was then packed in the column under vacuum suction with minimum exposure to room humidity, connected to the gas chromatograph, flushed with helium, cooled to liquid N_2 temperature under helium flow and used for analysis.

Results

The results obtained with normal, exchanged and coated molecular sieves (MS) are given in Table I along with relative retention for H_2 , D_2 and HT , T_2 with respect to H_2 . Some of the typical chromatograms are given in figures 2-6 . As seen from the table and chromatograms , MS 4A with 5% Fe^{3+} , MS 5A with 15% Fe^{3+} and Fe^{2+} (5.4%) exchanged MS 4A give good separation for H_2 , HD and D_2 . In most of the cases good separation between H_2 and D_2 is obtained whereas iron treated moisture saturated molecular sieves give a single unresolved peak for H_2 , HD and D_2 . These results

clearly indicate that the residual moisture in the sieves significantly affect the separation and resolution of H₂, HD and D₂ fractions. Partly dehydrated normal MS 5A and MS 13X do not separate H₂ and D₂ while in the case of normal MS 4A the resolution between H₂ and D₂ is not as good as in iron treated MS 4A.

Since partial moisture removal was found to be of utmost importance, attempts were made to coat the material with high boiling polar compounds like glycerol, triethanol amine, with a view that the substitution of voids created by the moisture removal with these high boiling compounds may facilitate reconditioning with ease leaving only required percentage of moisture. These were not successful for the following reasons.

(1) The material was picking up moisture more than the limited percentage (17-19%) required. (2) The separation was poor when the high boiling material percentage coating was increased (6 to 12 to 18%) as shown in table II.

The iron exchanged activated molecular sieve was treated with a titanate coupling agent (KRTTS) (17) with the hope that the active sites for moisture will be blocked by the titanate derivative and freeze the moisture level at the desired concentration. This method also failed as the titanate treatment did not inhibit moisture absorption by the sieve. The relative retention data of the original sample and the titanate treated

sample are given in Table III.

Mossbauer study of the iron coated and exchanged molecular sieves in fully hydrated and partly dehydrated (activated) conditions has not revealed any specific distinction. However, the iron on the sieves was found to be in Fe^{3+} state.

X-ray analysis of the modified molecular sieves show that the sieves are still crystalline though the crystallinity is relatively less in $FeCl_3$ coated sample and iron exchanged material in the following order.

Normal > Fe coated > Fe exchanged

The columns were pretreated with CO_2 injections to ascertain improvement in resolution between peaks as reported in the case of Alumina(6,7). However, these columns did not show any significant change after CO_2 injections in the peak shape or resolution.

Conclusion

The results indicate that partially dehydrated iron exchanged or coated molecular sieves 4A, 5A, AW 500 and 13X can be used as the stationary phase for the separation of H_2 , HD and D_2 ; H_2 , HT and T_2 . The separation efficiency depends on both the iron content and the residual moisture content.

The column material preparation by the coating method does

not need any special skill and the separation characteristics from batch to batch are easily reproduced. A column once prepared can be used for a long time without significant loss in resolution and can be easily reactivated. The analysis time required is less and the carrier gas flow rate required is also lower than that required for Alumina column. However, the peak shape is not as good as that obtained with properly treated Alumina column though routine analysis can be easily performed.

A part of this data has been published (18).

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Figure Captions

Figure.1

Schematic lay out of Gas-chromatography system.

Figure.2

Chromatograms of H₂, HD and D₂ mixture on 3.8m x 2.2mm copper column

- (a) 6.1% of Fe²⁺ exchanged MS 13X conditioned at 125°C/2 hrs
Helium flow 24 ml/mt.
- (b) 10% Fe³⁺ coated MS AW500 conditioned at 165°C/2 hrs. Helium
flow 25 ml/mt.
- (c) 3.7% Fe²⁺ exchanged MS 5A conditioned at 157°C/2 hrs. Helium
flow 23 ml/mt.
- (d) 10% Fe³⁺ coated MS 5A conditioned at 191°C/2 hrs . Helium
flow 27 ml/mt.

Figure.3

Chromatograms of H₂, HD & D₂ mixture

- (a) 2.8m x 2.16mm s.s. column, 15% Fe³⁺ coated MS 5A conditioned
at 180°C/2 hrs. Helium flow 54ml/mt.
- (b) 3.8m x 2.2mm copper column, normal MS 5A (without iron)
conditioned at 150°C/2 hrs. Helium flow 12ml/mt.

Figure.4

Chromatograms of H₂, HD & D₂ mixture on 5.3m x 2.5mm copper column.

(a) Normal MS 4A (without iron) conditioned at 186°C/2 hrs.
Helium flow 60 ml/mt.

(b) 5.4% Fe³⁺ exchanged MS 4A conditioned at 168°C/2 hrs. Helium
flow 60 ml/mt.

(c) 5% Fe³⁺ coated MS 4A conditioned at 180°C/2 hrs. Helium flow
60 ml/mt.

Figure.5

Chromatograms of H₂, HD & D₂/ H₂, HT & T₂ on 4.0m x 2.16mm s.s.
column 5% Fe³⁺ coated MS 4A conditioned at 175°C/2 hrs.

(a) Helium flow 60ml/mt. Separation of H₂, HT & T₂ recorded using
TCD and ionization detector (5ml volume).

(b) Helium flow 79 ml/mt. Separation of H₂, HT & T₂ recorded
using TCD and ionization detector (1ml volume).

(c) Same as (b) for H₂, HD & D₂ .

Figure.6

Chromatograms of H₂, HD & D₂ on 3.8m x 2.2mm copper column.

(a) 5% Fe³⁺ coated MS 4A conditioned at 192°C/2 hrs Helium flow
60 ml/mt.

(b) 10% Fe³⁺ coated MS 4A conditioned at 185°C/2 hrs . Helium
flow 24 ml/mt.

(c) 15% Fe³⁺ coated MS 4A conditioned at 185°C/2 hrs . Helium
flow 27 ml/mt.

FIG. 1

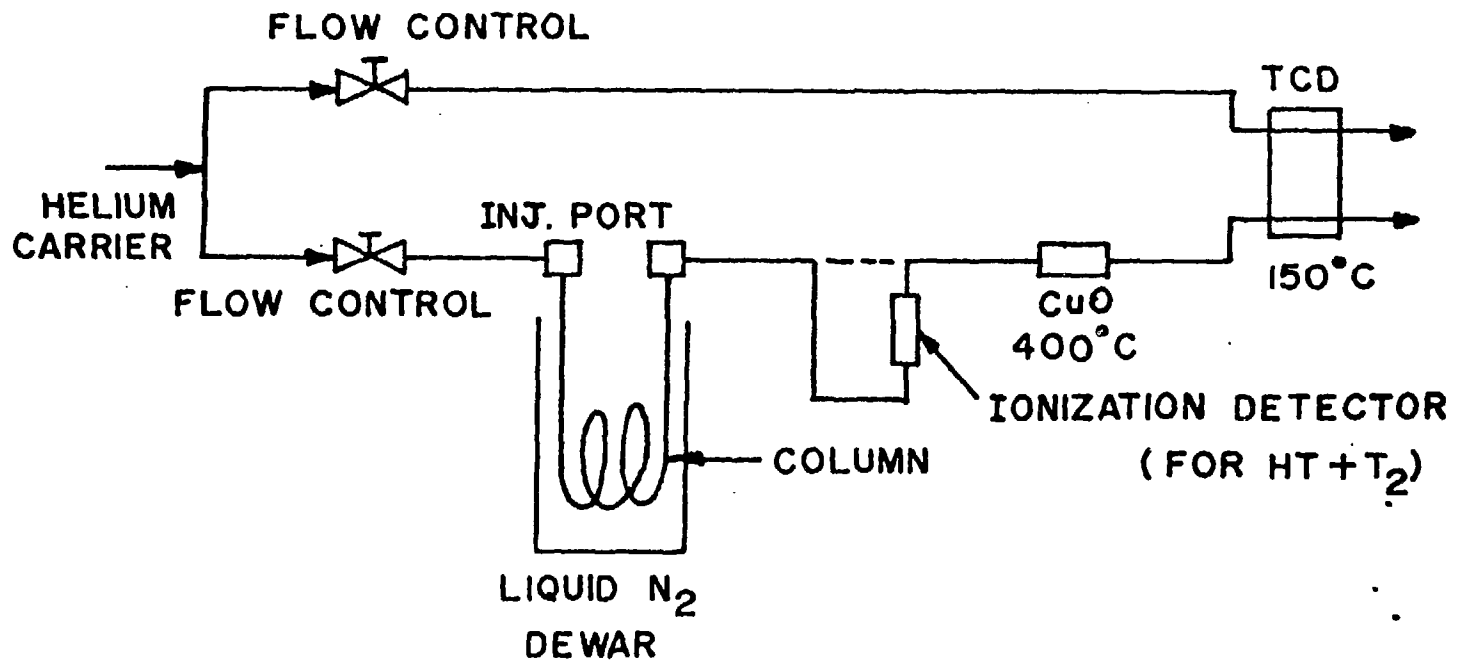


FIG. 2

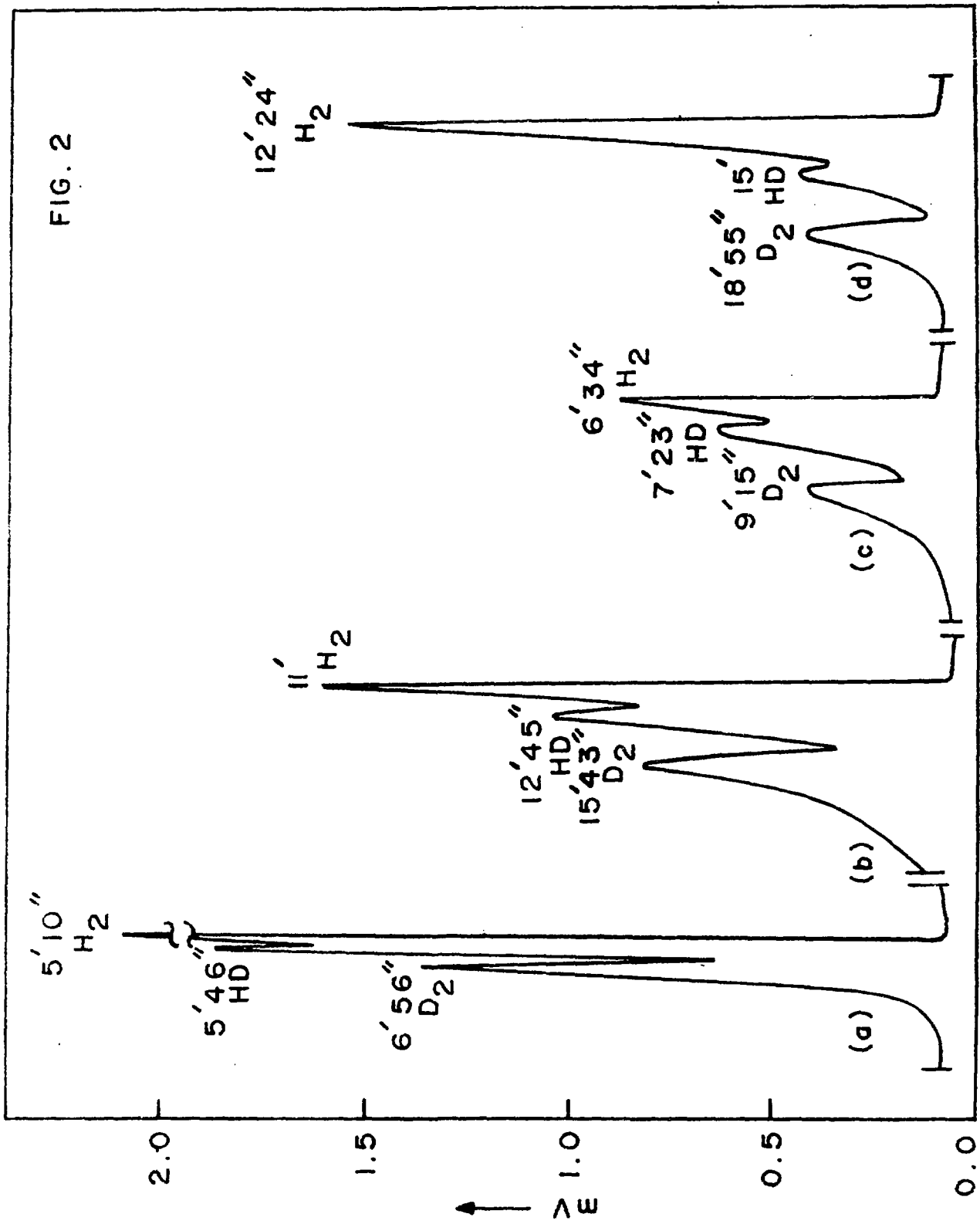


FIG. 3

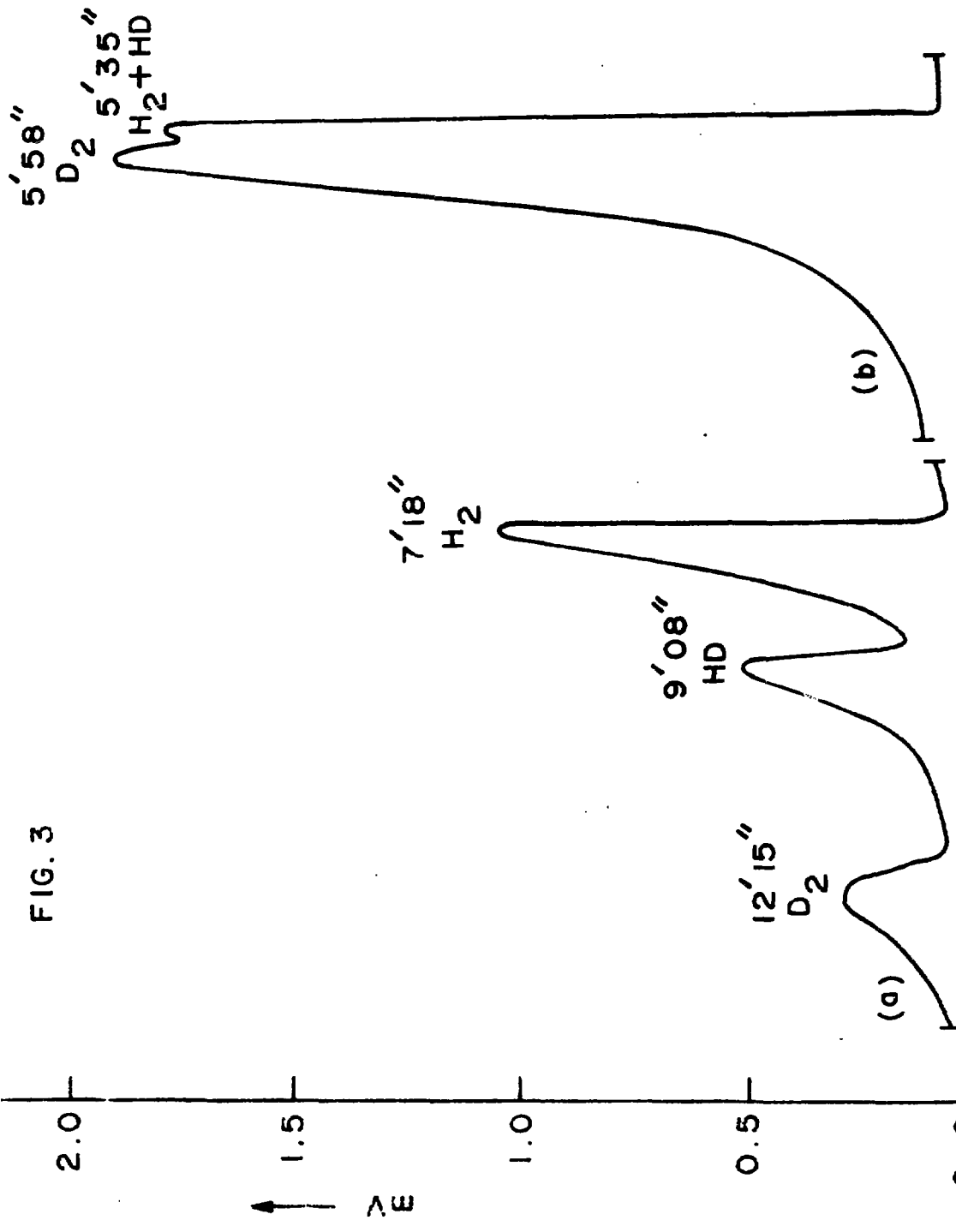


FIG. 4

2.5 —
2.0 —
1.5 —
1.0 —
0.5 —
0.0 —

↑ ΔE

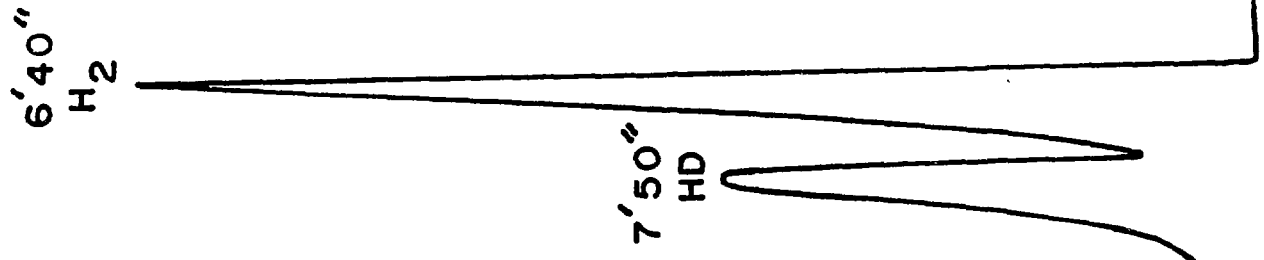
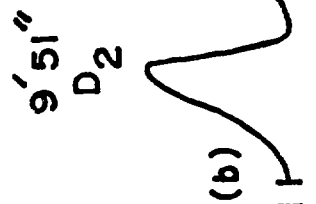
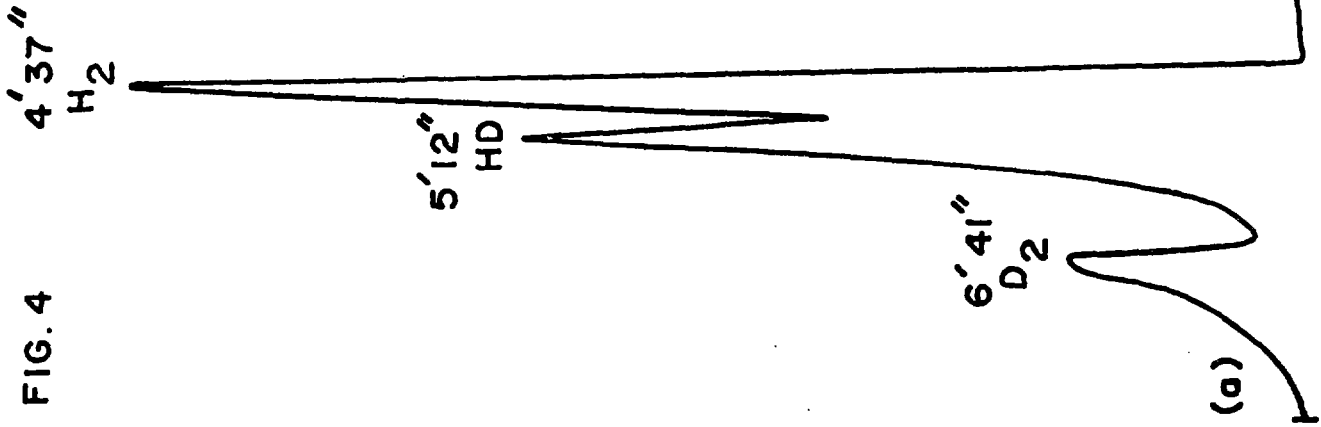


FIG. 5

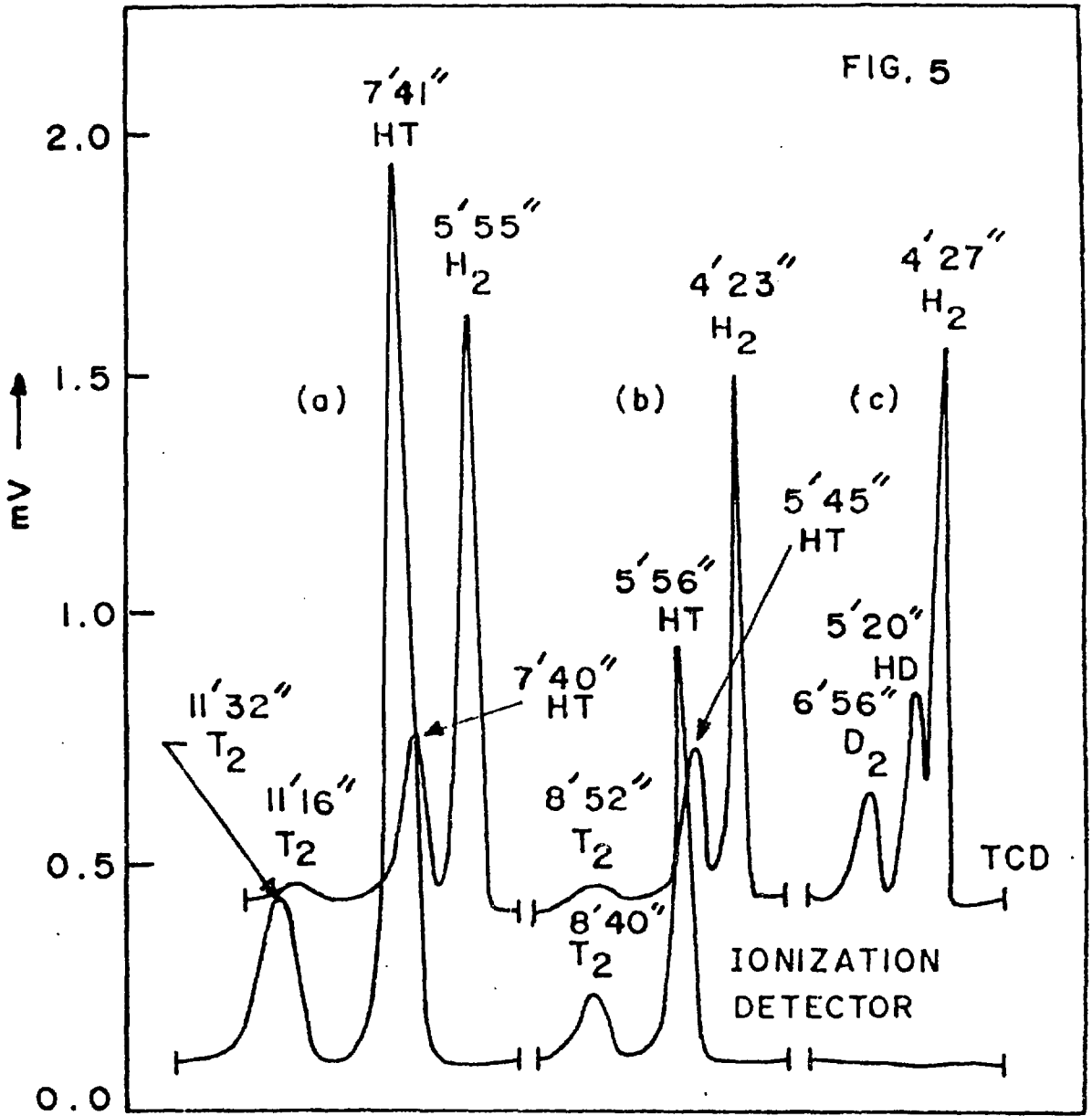


FIG. 6

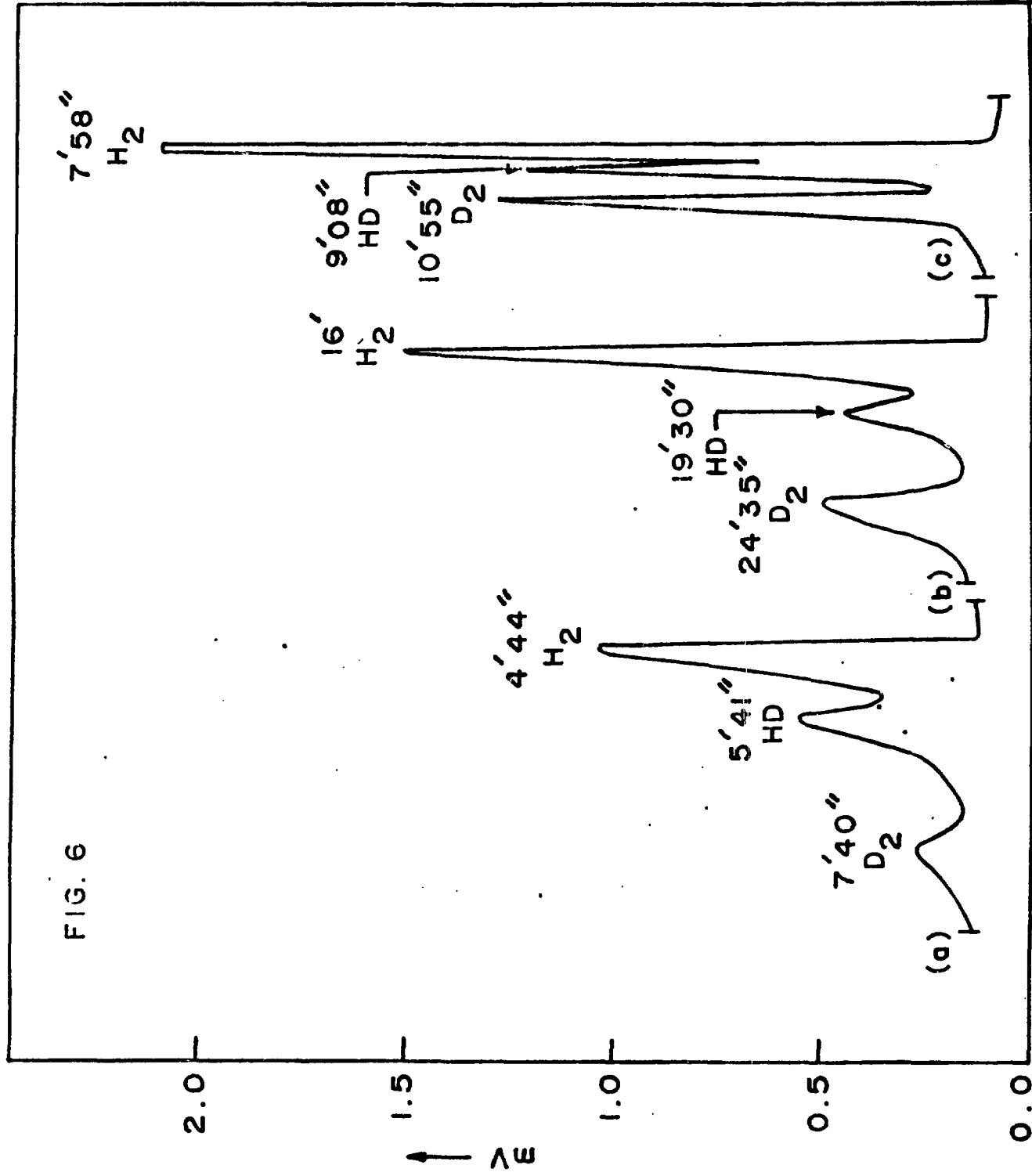


TABLE 1

Relative Retention Data for Hydrogen Isotopes for Different Molecular Sieves

Sr No	Type	Treatment	condi- tion- ing temp °C	Mois- ture loss %	Column length m	Carrier flow ml/mt	Reten- tion time for H ₂	Relative retention with respect to H ₂		Remark
								(H ₂ =1) HD	D ₂	
1.	13X	6.1% Fe ²⁺ exchanged	145	18.1	3.8	24.0	-	Broad tailing peak		
2.	13X	"	125	15.7	3.8	24.0	5'10"	1.116	1.342	Fig.2a
3.	13X	4.6% Fe ²⁺ exchanged	107	14.1	3.8	58.0	-	Broad tailing peak		
4.	13X	"	89	11.3	3.8	24.0	8'03"	1.149	1.449	
5.	13X	10% Fe ³⁺ coated	155	12.8	3.8	58.0	24'45"	1.199	1.535	
6.	13X	"	125	10.1	3.8	25.0	10'30"	-	1.429	
7.	13X	15% Fe ³⁺ coated	153	23.2	3.8	56.0	16'	merged with H ₂	1.5	
8.	13X	"	145	-	3.8	58.0	12'09"	Broad tailing peak		
9.	AW500	10% Fe ³⁺ coated	145	13.6	3.8	25.0	10'45"	1.14	1.38	
10.	AW500	"	165	-	3.8	25.0	11'	1.159	1.429	Fig.2b
11.	AW500	15% Fe ³⁺ coated	150	25.2	3.8	63.0	7'49"	merged with H ₂	1.50	
12.	AW500	"	130	23.4	3.8	26.0	10'31'	1.16	1.37	
13.	5A	NIL	160	14.6	3.8	63.0	20'	Broad peak		

table I contd.

14.	5A	NIL	150	14.1	3.8	12.0	5'35"	merged with H ₂	1.069	Fig.3b
15.	5A	1.9% Fe ²⁺ exchanged	165	14.3	3.8	56.0	2'57"	Broad tailing peak		
16.	5A	"	145	13.6	3.8	56.0	1'45"	merged with H ₂	1.143	
17.	5A	3.7% Fe ²⁺ exchanged	157	17.0	3.8	23.0	6'34"	1.124	1.409	Fig 2c
18.	5A	3.0% Fe ²⁺ exchanged	156	15.7	3.8	54.0	12'	Broad tailing peak		
19.	5A	"	147	12.6	3.8	25.0	4'02"	1.070	1.256	
20.	5A	1.7% Fe ²⁺ exchanged	162	16.5	3.8	58.0	>20'	No peak upto 20 minutes		
21.	5A	"	155	13.4	3.8	23.0	3'51"	1.04	1.27	
22.	5A	10% Fe ³⁺ coated	191	17.2	3.8	27.0	12'24"	1.203	1.51	Fig 2d
23.	5A	15% Fe ³⁺ coated	200	-	3.8	25.0	8'06"	Broad tailing peak		
24.	5A	"	180	19.4	2.8	54.0	7'18"	1.25	1.678	Fig 3a
25.	5A	"	142	-	3.8	60.0	7'02'	1.192	1.455	
26.	5A	"	100	14.9	3.8	25.0	8'08"	1.121	1.322	
27.	5A	"	175	-	2.8	58.0	5'19"	1.335(HT)	2.138(T ₂)	
28.	4A	NIL	190	21.0	3.8	58.0	2'15"	Broad tailing peak		
29.	4A	"	186	17.0	3.8	22.0	4'14"	1.024	1.409	

table I contd.

30.	4A	"	"	"	5.3	60.0	4'37"	1.126	1.448	Fig 4a
31.	4A	3.5% Fe ²⁺ exchanged	185	18.3	3.8	23.0	2'53"	merged with H ₂	1.173	
32.	4A	"	194	22.3	3.8	27.0	2'45"	1.06	1.21	
33.	4A	5.4% Fe ²⁺ exchanged	200	20.1	3.8	63.0	18'20"	Broad tailing peak		
34.	4A	"	182	17.7	3.8	25.0	7'42"	1.171	1.582	
35.	4A	"	168	16.0	5.3	60.0	6'40"	1.175	1.478	Fig 4b
36.	4A	5% Fe ³⁺ coated	192	19.1	3.8	60.0	4'44"	1.201	1.620	Fig 6a
37.	4A	"	180	17.0	5.3	60.0	10'36"	1.202	1.415	Fig 4c
38.	4A	"	175	17.0	4.0	79.0	4'23"	1.312(HT)	2.023(T ₂)	Fig 5b
39.	4A	"	142	15.3	3.8	24.0	6'46"	1.129	1.416	
40.	4A	10% Fe ³⁺ coated	185	16.8	3.8	24.0	16'	1.219	1.537	Fig 6b
41.	4A	15% Fe ³⁺ coated	185	16.6	3.8	27.0	7'58"	1.146	1.37	Fig 6c

TABLE 11

Relative Retention Data for Hydrogen Isotopes on Glycerol and Triethanol Amine loaded iron exchanged Molecular Sieves 5A and 13X

Sr No	Mol.Sieve type with Fe concn.	Chemical Treatment	Condi- tion- ing temp °C	Water loss %	Carrier flow ml/mt	Retention time for H ₂	Relative retention with respect to H ₂ (H ₂ =1)	
							H ₂	D ₂
1.	5A-3.0%	NIL	150	12.9	26	3'50"	1.065	1.300
2.	"	6%(w/w) glycerol coated	150	-	25	3'20"	N.S.	1.095
3.	"	"	162	14.8	24	3'54"	N.S.	1.137
4.	"	"	178	-	60	>30'	Very broad peak	
5.	"	18%(w/w) glycerol coated	157	10.8	54	~7'30"	Broad peak	
6.	"	"	146	-	25	4'04"	1.078	1.291
7.	5A-8.2%	NIL	140	15.1	24	6'31"	1.13	1.39
8.	"	6%(w/w)TEA coated	160	13.0	25	3'01"	N.S.	1.094
9.	"	"	198	-	56	3'11"	1.099*	1.490*
10.	"	12%(w/w)TEA coated	196	10.2	25	4'10"	N.S.	1.224

table II contd.

11.	"	"	222	-	24	5'	N.S.	1.307
12.	"	18%(w/w)TEA coated	198	8.7	63	3'50"	Broad peak	
13.	13X-4.6%	NIL	104	11.3	24	8'03"	1.149	1.449
14.	"	11% glycerol coated	104	12.7	23	5'34"	1.093	1.347
15.	"	"	160	-	58	>30'	No peak	
16.	"	NIL	104	13.2	23	8'32"	1.152	1.523
17.	"	13%(w/w)TEA coated	106	14.2	25	3'04"	No separation	
18.	"	"	158	17.7	60	6'18"	No separation	

* Peaks are tailing: N.S. Not separated from H₂
TEA-Triethanql amine

Column dimensions - 3.8m x 2.2mm

TABLE III

Relative Retention Data for Hydrogen Isotopes on Titanate Coupling Agent Treated Iron exchanged Molecular Sieve 4A

Sr No	Molecular Sieve type with Fe concn	Chemical Treatment	Conditioning temp ^o C	Water loss %	Carrier flow ml/mt	Retention time for H ₂	Relative Retention with respect to H ₂ (H ₂ = 1)	Retention with respect to D ₂
1.	4A-5.4%	NIL	182	17.7	25	7'42"	1.171	1.582
2.	"	~1% KRITS treated	181	17.0	24	7'03"	*1.163	*1.608
3.	"	"	140	-	24	5'22"	1.121	1.416
4.	"	Titanate treatment till saturation	182	13.8	23	5'22"	*1.102	*1.460
5.	"	"	142	13.5	24	5'53"	1.116	1.465

*Peaks are tailing

Column dimensions - 3.0m x 2.2mm.

