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Review

Advances in preparative gas chromatography for hydrogen isotope separation

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ABSTRACT

Early and recent developments of preparative gas chromatography for hydrogen isotope separation are briefly reviewed. Advanced gas chromatography techniques including peak cutting and temperature programming are discussed in detail. A novel position temperature programming technique which allows the column to be overloaded so that a surprisingly large amount of mixture can be processed in a relatively small column is introduced. This technique may have wide applications in gas chromatography other than hydrogen isotope separation.

CONTENTS

1. INTRODUCTION

While cryogenic distillation has been known and used for the purpose of separating isotope mixtures of hydrogen, this technique is mainly suitable for use on a large scale. Distillation suffers from the disadvantages of providing a low separating efficiency as well as requiring the retention of a fairly large inventory of material in the distillation system. On the other hand, gas chromatography provides a high separation efficiency and leaves very little inventory of desired material in the system. Gas chromatography has several other advantages over cryogenic distillation for relatively small tritium facilities. For example, it is simple, reliable, inexpensive, and easy to operate with low tritium inventory.

Gas chromatography is one of the outstanding

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scientific developments of the 1950s and the 1960s. However, the success of the gas chromatography technique during this time was largely associated with chemical analysis but not preparative gas chromatography. The problem of preparative chromatography is essentially that of the scale-up of the analytical procedures to a desired production level. The difficulties associated with the scale-up are mainly due to the fact that the efficiency with which compounds can be separated (resolution), the time needed for the separation (speed, retention time), and the quantity of material that can be handled (capacity) are linked and that any one of these can only be enhanced at the expense of at least one of the others. Only after the process underlying chromatographic separation became better understood, development of "production" or "plant scale" or preparative gas chromatography as it had become known gradually took place. The development of preparative gas chromatography for hydrogen isotope separation is no exception.

In the late 1950s and 1960s hydrogen isotopes were successfully separated by gas chromatography and large-scale separation was attempted. Only in the 1980s, significant advances were made for large-scale preparative gas chromatography for hydrogen isotope separation. The recent interest in hydrogen isotope separation is mostly related to recovery or purification of tritium for fusion applications as discussed by Bartlit [1] and to a lesser extent for fission applications as in heavy water reactors where tritium is produced as a byproduct. In this review, the historical developments will be discussed briefly while the emphasis will be on the recent progress in this area.

In the design of a column, several factors such as packing material, column diameter, and column length must be considered. For a selected column, the important operating parameters are carrier flow-rate, column temperature, method of sample injection and sample volume. The effect of some of these parameters is relatively obvious while others require more investigation and careful selection. In this review, parameters such as packing material, carrier gas, column temperature, and novel gas chromatographic techniques will be discussed.

2. LITERATURE REVIEW OF EARLIER DEVELOPMENTS

Hydrogen isotopes were successfully separated by gas chromatography in the 1950s and 1960s mostly for analytical purpose although attempts were made to separate larger quantities. A comprehensive review of these early developments was provided by Akhtar and Smith [2]. Developments on this subject in the 1970s were relatively slow. The column packing material can be divided into three different classes based on the mechanism of separation of hydrogen isotopes. These are molecular sieves used for size-exclusion chromatography, alumina used for gas–solid adsorption chromatography, and palladium as palladium dispersed on alumina used for catalytic or chemisorption chromatography.

Chromatographic separation of hydrogen isotopes on palladium has been reported for a mixture of H_2 and $^2H_2$ by the following techniques (i) breakthrough chromatography, (ii) displacement chromatography (by adding pure hydrogen to the column) by Glueckauf and Kitt [3] and Chadwick [4], (iii) self-displacement chromatography (by heating the column) by Glueckauf and Kitt [3], (iv) elution chromatography (using argon as carrier gas) by Thomas and Smith [5] and Smith and Carter [6]. The chromatographic columns are usually operated at moderately high temperatures above ambient and as high as 150–190°C. During the chromatographic process, palladium hydride was continuously formed and decomposed. The migration of the heavier isotope species through the column is faster than the lighter ones and as such the elution order of the hydrogen isotopes is in reverse order of molecular mass. However, the separation efficiency was reported to be poor by these early workers [2–6].

Efficient separation of hydrogen isotope on charcoal, silica gel, alumina or iron oxide-coated alumina, has been reported by a number of researchers. The mechanism of separation is based mainly on the varying degrees of physical adsorption on the packing material of the different hydrogen isotope species. The operating temperatures for these materials are relatively low in the range of 20–90 K. Packing materials

tested, carrier gas used, operating temperature, and degree of separation achieved were summarized by Akhtar and Smith [2].

In contrast to the physical or chemical adsorption type of chromatography inherent in the use of alumina or palladium, chromatography on molecular sieves proceeds mainly on the basis of molecular size. Molecular sieves are synthetic materials usually prepared from sodium or calcium aluminium silicates. The crystal structure of molecular sieves contains fine pores, ranging from of 3 to 10 Å in diameter. These forms a series of interconnecting "tunnels" throughout the particle, as suggested by Thompson [7]. Small molecules entering these pores pass through easily; larger ones pass through with more difficulty and therefore more slowly [7]. Thus, elution is usually in order of increasing molecular size as in the case of other non-metallic sorbents as charcoal, silica gel or alumina. (On the other hand, very large molecules may be excluded from the pores entirely and as a result, may be eluted without retention [7].) The sorption capacity of molecular sieves is relatively high in the range of 100 ml/g [8]. These packings were used in many of the earlier works [2,9].

The carrier gas for conducting the gas chromatographic separation of hydrogen isotope species on charcoal, silica gel, alumina or molecular sieves must not interact strongly with the column packing so as to adversely modify the retention of the hydrogen species. This rules out argon or nitrogen which adsorb very strongly on molecular sieves and may even condense at low temperatures. A suitable carrier gas must also be easily separated from the separated components, relatively low in cost and it must be compatible with the detector used to monitor the effluent from the column. From a consideration of these criteria, helium is the preferred carrier gas for hydrogen isotope separation using these non-metallic adsorbents at low temperatures.

3. RECENT DEVELOPMENTS WITH DIFFERENT COLUMN PACKINGS

Several large hydrogen isotope separation systems have been developed using palladium as the packing material. A hydrogen isotope system based on displacement gas chromatography using palladium deposited on small particles of porous alumina was designed to process up to 20 mol of hydrogen isotopes per day with four 3.36 cm and 5 m long columns for the Joint European Torus (JET) active gas handling plant [10]. The efficient palladium isotope chromatograph (EPIC) system was developed by EG&G Mound Applied Technologies [11]. The system was also based on palladium displacement chromatography. A 91×0.68 cm I.D. column operating under vacuum was tested at 78°C to minimize the length of the cycle time and to maximize the recovery fractions of the feed components. Westinghouse Savannah River developed a thermal cycling absorption process (TCAP) which was a semi-continuous gas chromatographic separation process using palladium coated on kieselguhr as the packing material in a 2.54 cm diameter stainless steel coil with hot or cold nitrogen as the carrier gas [12]. High purity hydrogen isotopes could be produced but the capacity of the system was not reported.

Notable developments using pretreated alumina were carried out by the Max Planck Institute [13,14]. They scaled up their analytical column packed with activated alumina to 8 cm diameter and constructed a pilot plant with two columns immersed in liquid nitrogen. Both columns can be operated simultaneously. It was projected that about 2 l [standard temperature (0°C) and pressure (1 atm), STP] of hydrogen isotopes could be processed per cycle and the time required per cycle of operation was in the range of 80 to 120 min.

Several studies have shown that among the various molecular sieves including 3A, 4A, 5A and 13X, molecular sieve 5A was found to be superior with respect to hydrogen isotope separation [15,16]. Molecular sieve 5A (supplied by Supelco Canada, Oakville, Canada) was used in the pilot testing and large-scale demonstration plant at the Ontario Hydro Research Division [17,18]. Details of the pilot and large-scale testing will be discussed later. The retention times of hydrogen isotope species in a column packed with molecular sieves 5A are highly dependent on the operating temperature of the column. Fig. 1 shows the retention time of H^2H,

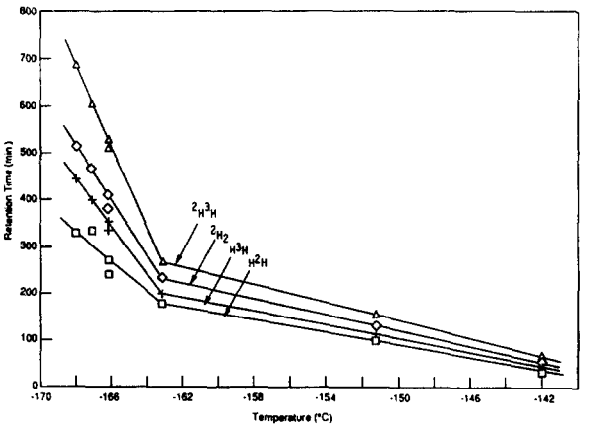

Fig. 1. Retention time of various isotope species as a function of operating temperature in a 7.6 m × 2 cm I.D. column [17].

H^3H, $^2H_2$, and $^2H^3H$ as a function temperature in a 2 cm I.D. and 7.6 m long column [17]. The retention time of the hydrogen isotope species increased as the temperature was decreased. The difference in retention times for the various isotope species also increased as the temperature was decreased. Hence, at lower temperature the throughput of sample decreased due to the increase in sample processing time, but the separation of the species was improved due to the increase of differences in retention time of the species.

JRC Establishment of Ispra (Italy) has been developing a hydrogen isotope separation system using (Ca, Na) mordenite as the substrate tested in a 2.5 m × 2.1 mm I.D. column operating in a temperature range of 130 to 160 K [19]. Further scale-up or development of the displacement chromatography technique using this packing material was planned.

In the above discussion, different packing materials tested and systems for each of these materials scaled up to separate large quantities of hydrogen isotopes mainly by increasing the column diameter were discussed. In the following, recent developments of processes that employ a plurality of columns to achieve peak cutting or utilizes temperature programming will be discussed in detail. These techniques enable the throughput of a gas chromatography system to be much greater than that previously achievable without sacrificing the high separation efficiency obtainable by a given column, and therefore, allow much more material to be processed without increasing the diameter and length of the column used.

4. RECENT DEVELOPMENTS IN PREPARATIVE GAS CHROMATOGRAPHIC TECHNIQUES

In addition to selecting the most appropriate packing material and increasing the column diameter and length, special chromatographic techniques can be used to achieve a higher column capacity. Fujie *et al.* [20] developed a two dimensional gas chromatography system that can separate hydrogen isotopes continuously. However, the system required a large number of inlet and outlet valves and a relatively complicated mechanical rotating system. Two other relatively simple preparative gas chromatography techniques developed for hydrogen isotope separation, namely, peak cutting and temperature programming will be discussed in detail in this section.

4.1. Peak cutting

Using the peak cutting technique, two or more columns are plumbed in series with a three-way valve in-between columns to allow diversion of the effluent from the first column either to vent or onto the second column. The high efficiency peak cutting technique is most beneficial when minor components are to be separated from a major component such as recovering traces of tritium from a large stream of H, ^2H, and ^3H in the cases of fusion fuel clean-up, tritium waste treatment, or recovered gas from an emergency tritium clean-up system. When two or more major gas components are to be separated, either much larger and longer columns must be employed or the separation scheme may be carried out by other techniques such as temperature programming.

The peak cutting technique was demonstrated in a pilot scale system for the fusion fuel clean-up application [17]. A schematic diagram of a typical gas chromatography system for hydrogen isotope separation is shown in Fig. 2 and the flow switching scheme for peak cutting operation is

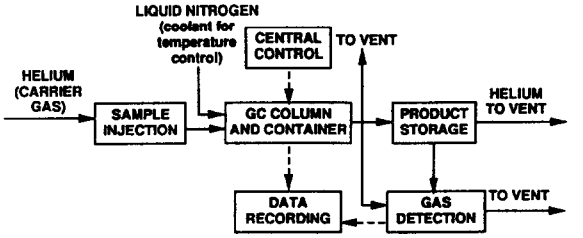

Fig. 2. Schematic flow diagram of a typical GC system for hydrogen isotope separation [18].

shown in Fig. 3. The decontamination factor of protium containing species was increased significantly while improving the throughput at the same time, by applying the peak cutting technique. In a 8-mm column, a throughput of 1.8 normal litre (NL)/h and a decontamination factor of 40 for protium containing isotopes were reached. The column pair was operating at 118 K with a 0.74 NL sample and a sample processing time of 25 min.

This technique may also be combined with the temperature programming technique discussed

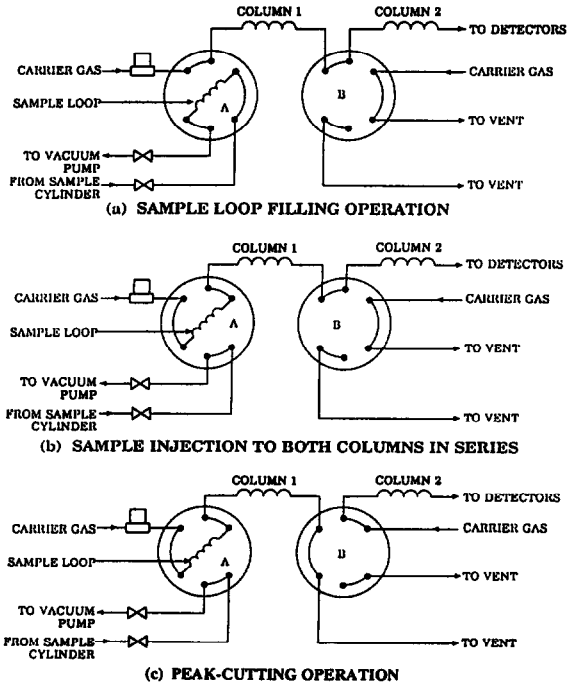

Fig. 3. Flow switching scheme for peak cutting operation [17].

below to improve the separation and capacity of a gas chromatography system.

4.2. Temperature programming

For the resolution or separation of any two substances, there is always an optimum temperature in a given separation system. When a mixture consists more than two substances as in the case of hydrogen isotope separation, more than on optimum temperature is required for optimum separation. The column temperature should, therefore, be increased during the separation from the lowest to the highest temperature required. Then any two of the hydrogen species are separated in the best possible way at optimum temperature for a given column. In the following, the conventional technique and a novel temperature programming technique will be discussed separately.

4.2.1. Conventional temperature programming

Conventionally, temperature programming is achieved by increasing the temperature of the entire column over a specified temperature range at a specified rate, *i.e.*, the temperature of the entire column varied as a function of time.

$$T = f(t) \quad \text{for all } L$$

where T is the temperature of the column, t is time, and L is the position along the column.

Applying this conventional temperature programming technique in a 2 cm column packed with molecular sieve 5A [17], the number of theoretical plates for most of the isotope species was increased by a factor of five compared with the number of theoretical plates achieved with the same column operating at a constant temperature. The sample processing time was reduced by a factor of two to three for the same degree of separation, hence the throughput was increased by the same factor to 0.6 NL/h in a 2 cm I.D., 8 m long column [17].

There are many difficulties in the implementation of this technique in a large system. Several innovative design features had to be incorporated in a recent large-scale demonstration system [18]. In this large demonstration system, uniform cooling of the column was effected by

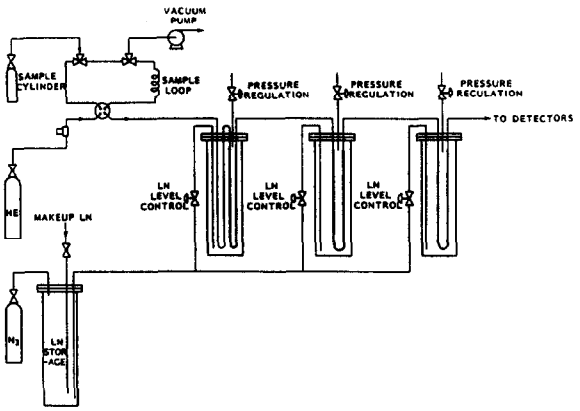

Fig. 4. Schematic diagram of a large-scale demonstration plant [18].

providing the column with a central tube through which the coolant could flow to cool the column centrally while at the same time coolant was contacting the exterior surface of the column. Thus a column having a central tube was immersed in a bath of liquified nitrogen to provide rapid and even cooling of the adsorbent, molecular sieve 5A, in the column. The temperature of the column was regulated by placing the column in a pressurized container and maintaining the liquid nitrogen at its boiling point which would vary with the pressure in the container. The total length of the column was contained in several pressurized containers which could be maintained at different temperatures. This arrangement allowed successive gas mixtures to be injected into the column without waiting for the previous sample to be completely eluted. A schematic diagram of the large-scale demonstration system showing the piping and control system is depicted in Fig. 4. Chromatograms of a typical experiment obtained in the demonstration system are shown in Fig. 5. The containers were typically operating at 77 K and then increased to 115 K. Good separation of all six hydrogen isotopes were obtained with this 68 NL sample. Samples up to 138 NL have been processed in this system.

4.2.2. *Advanced temperature programming*

As discussed above, typically, whole column temperature programming is frequently adequate for use in analytical gas chromatographic applications where column overloading is not an issue. However, when a gas chromatographic system is required to separate molar quantities of mixtures, the whole column temperature programming technique may be unsatisfactory since all advantages of temperature programming are quickly lost or even reversed when the heating of the column does not take place quasi-homogeneously in a large diameter column. Almost any, even the smallest, temporary change in temperature causes a temperature gradient in the column

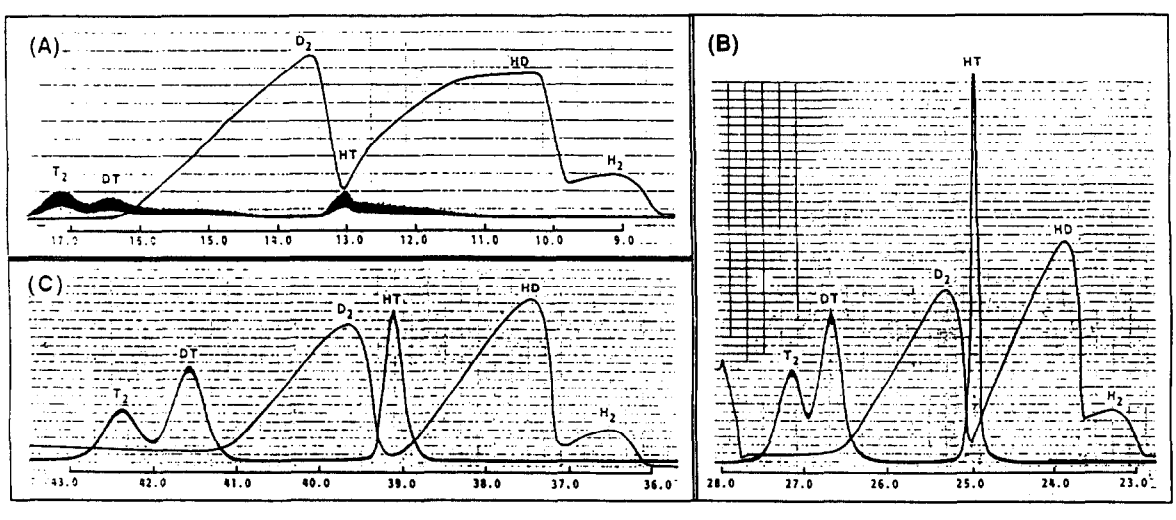

Fig. 5. Chromatogram of a 68 nl H–^{2}H (50:50) sample with 0.25 Ci ^{3}H from (A) the first, (B) second and (C) third container [18].

(local temperature change). When this radial temperature gradient is greater than the longitudinal or time-dependent temperature gradient, the separation of the adjacent two hydrogen isotope species is not improved but worsened which could easily happen when large diameter columns are used in preparative gas chromatography. Only the maximum elution time is reduced by this conventional temperature programming.

In a latest approach [21], rather than increasing the temperature of the entire column over time to effect a separation, this procedure utilizes a constant temperature profile along the length of the column, thereby affecting the rate of elution of each mixture component in each temperature zone, *i.e.*,

$$T = f(L) \quad \text{for all } t$$

where T is the temperature of the column, t is time, and L is the position along the column.

This technique may be called position temperature programming. In a column having an ascending temperature profile, (that is the temperature increases from the inlet to the outlet of the column, see Fig. 6a), the temperature effect causing the more volatile components to move along the column faster than the less volatile components is enhanced when compared with whole column programming heating. Ascending temperature profile chromatography also allowed the column to be overloaded so that a surprisingly large amount of mixture can be processed in a relatively small column. In some cases, this overloading of the column results in broadening of the elution of the less volatile components, but it has been found that by coupling an ascending temperature profile column with a descending temperature profile column, (that is the temperature decreases from the inlet of the column to the outlet of the column, see Fig. 6b), that this broadening or tailing effect is greatly reduced.

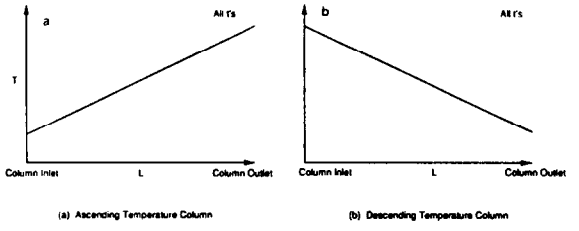

Fig. 6. Temperature profiles in columns operating in the position temperature programming mode. (a) Ascending temperature column; (b) descending temperature column.

This novel technique has been applied to hydrogen isotope separation. In addition to columns with ascending or descending temperature profile, a column immersed in liquid nitrogen in a Dewar jar on a retractable platform was found to be very useful as an injection column. Large samples could be loaded onto this column and then the platform was gradually lowered to expose the column to ambient temperatures. This column allowed for a rough ordering of mixture components by volatility prior to their entry into the primary separation columns. A schematic diagram of a system with an injection column, and columns having an ascending and a descending temperature profile are shown in Fig. 7. Each column is 5 m × 1 cm I.D. A typical chromatogram for a 4 NL sample with all six hydrogen isotope species obtained in this system is shown in Fig. 8. The processing time is relatively short in the order of 2 h, hence the throughput is very high. Applying the peak cutting and position temperature programming simultaneously in this system, up to 40 NL samples of hydrogen isotopes were separated in two hours.

It is believed that this position temperature

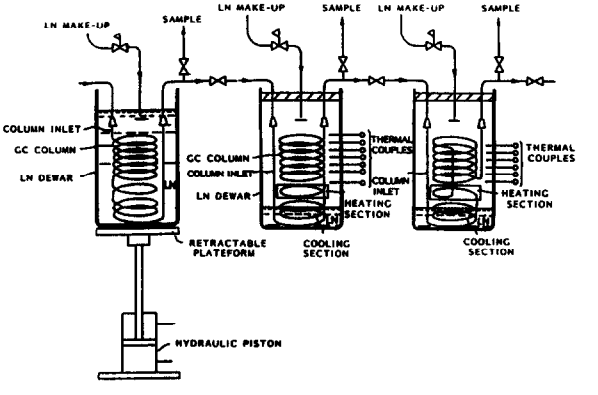

Fig. 7. Schematic diagram of a position temperature programming gas chromatographic system.

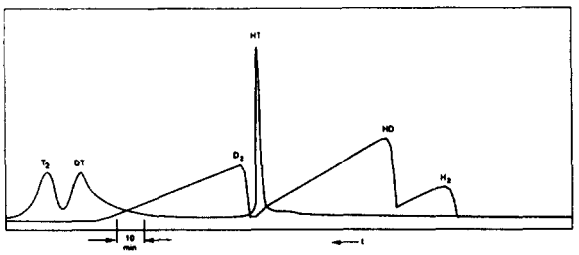

Fig. 8. typical chromatogram for a 4 NL sample from the position temperature programming system. (Three 5 m × 1 cm I.D. columns.)

programming technique will have wide applications in preparative gas chromatography separations other than hydrogen isotopes. This technique may also be beneficial to the field of analytical gas chromatography for some very difficult separations. Furthermore, it is conceivable that the position temperature programming technique can be combined with the conventional technique by adjusting the temperature of column as a function of both time and position, *i.e.*,

$$T = f(L,t)$$

where T is the temperature of the column, t is time, and L is the position along the column.

The benefits of this generalized temperature programming or time dependant position temperature programming technique has not been explored.

5. CONCLUSIONS

The recent increased interest in hydrogen and its isotopes is mainly due to their role is fusion energy and in heavy water nuclear reactors. The main objective in separating hydrogen isotopes is to recover the radioactive species, tritium. Although cryogenic distillation will still be used for large-scale tritium recovery facilities, recent advancements in preparative gas chromatography for hydrogen isotope separation has revolutionized this technology making it applicable and indeed more suitable for many tritium laboratory and small fusion devices than cryogenic distillation. The many researchers in this field have made significant progress in increasing the throughput of these systems while improving the operational flexibility and further reducing the inventory of tritium in these systems. It is the author's belief that the potential of these advanced preparative gas chromatography hydrogen isotope systems has not been fully explored and that in some cases, cryogenic distillation system may be effectively replaced by one of these systems or a hybrid cryogenic distillation/advanced gas chromatography system.

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