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An Efficient Palladium Isotope Chromatograph (EPIC) for Hydrogen

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Abstract

The efficient palladium isotope chromatograph (EPIC) system is based on a palladium displacement chromatograph developed and tested for the preparative scale separation of the isotopes of hydrogen. Rapid cycling and high efficiency are obtained by use of high-performance packing operating at an elevated temperature (80°C) and elevated pressure (1.5 atm). The process, which was tested with a 50/50 mixture of hydrogen and deuterium, depends on the exploitation of thermally driven pressure differences to recover and recycle the mixed transition zone between the bands of the pure components and also to recover and recycle the hydrogen gas used as the displacing agent. The purity of the product is significantly enhanced by partially backfilling the column with pure deuterium at the beginning of each displacement cycle. The computer-controlled system operates continuously, and it is capable of separating 2.2 std L/hr of feed at product assays of 99.86 at. % hydrogen and 99.992 at. % deuterium.

Introduction

In 1957 Glueckauf and Kitt [1] reported the first application of palladium hydride to the successful resolution of a hydrogen-deuterium mixture by displacement chromatography. Although the process is economically unattractive for large-scale applications, it is, nevertheless, quite useful for separations on a smaller scale. Some examples include the recovery of tritium for the analysis of natural samples [2] and the recycle of hydrogen isotopes in applications related to fusion energy [3].

In the Glueckauf experiments (Figure 1), the empty and evacuated palladium column was filled with a helium buffer gas. The column was loaded with feed mixture, and then the mixture was displaced either by the addition of pure hydrogen or by progressive heating from the inlet end of the column. As the mixture passed through the remainder of the column, it separated into bands of nearly pure deuterium and nearly pure hydrogen, separated by a short transition zone.

The Glueckauf process was manually controlled and relatively slow (several hours per cycle). At the end of each cycle there remained a quantity of mixed gas from the transition zone that had to be disposed of or stored for later recycle. When hydrogen was used instead of heat as the displacing agent, then there was also excess hydrogen that had to be handled.

This report describes the development and operation of a rapid cycling, computer-operated palladium displacement chromatograph. The design and operation of the new chromatograph incorporate several features that result in significantly higher product throughput

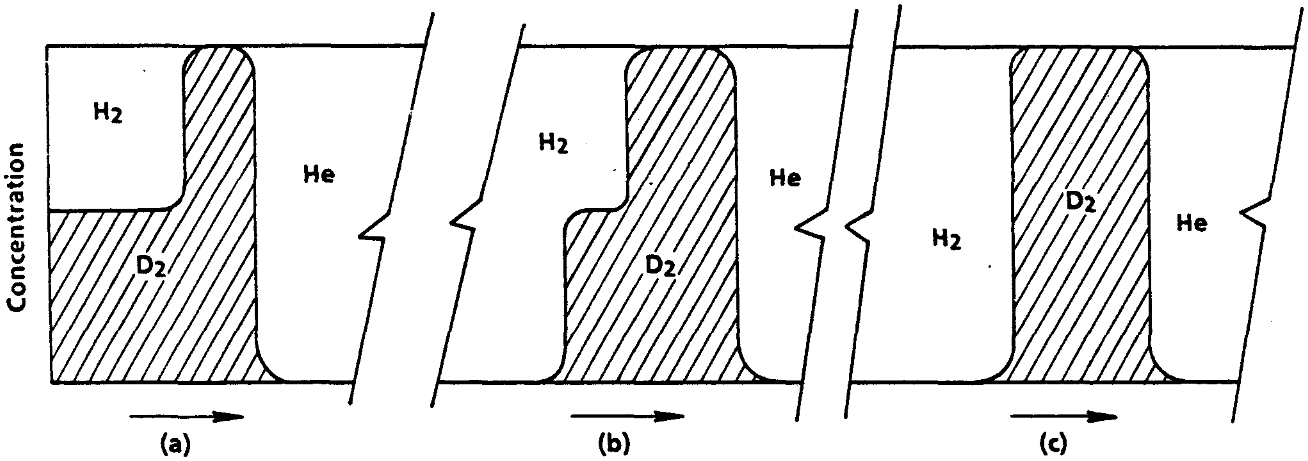


Figure 1 – Displacement chromatography of hydrogen isotopes.

and purity. These include (1) the use of high-efficiency, low surface area supported palladium packing, (2) the use of high-purity product gas as initial fill material instead of helium, (3) operation of the column at elevated temperature and pressure, (4) the use of thermally driven pressure differences to recycle the mixed zone between product bands, and (5) the use of thermally driven pressure differences to recover hydrogen used as the displacing gas.

The new chromatograph operates continuously without operator intervention. The only input stream to the process is the feed mixture, and the only output streams are the purified isotopes.

Theory

The theory of multicomponent displacement chromatography is well established. The basic principles of the method were established by Tiselius [4], and the equilibrium theory was developed by Hellfrich [5,6] and by Rhee et al [7]. The dynamic theory, including the effect of finite mass transfer rate, was developed by Bresler [8].

In the displacement technique, a column uniformly presaturated with a low affinity substance is used for separating a mixture of substances of intermediate affinities by development with a high affinity substance [4]. The Glueckauf and Kitt experiments had helium as the low affinity substance, deuterium as the intermediate affinity substance and hydrogen as the high affinity substance. The displacement process is shown schematically in Figure 1. As illustrated in the figure, development resolves the mixture into separate plateau zones of the individual components. Once the zones have been formed, the boundaries are self-sharpening and do not change with time as they move through the bed. The mixing length between the zones is related to the isotopic separation factor, the rate of axial diffusion and the rate of exchange of components between the absorbed and mobile phases. The latter two factors determine the equivalent stage height for the process [8].

The maximum amount of feed mixture that can be resolved in a single displacement depends on the separation factor between the components and on the concentration of the feed. According to Botter and coworkers, [9] the maximum feed load is given by

$$\frac{L_F}{L_T} = \frac{Q_s}{(Q_g + Q_s)\,[1/(\alpha - 1) + (1 - y_F)]} \qquad (1)$$

where α is the elementary separation factor, L_F is the equivalent length of column occupied by the feed mixture, L_T is the total length of the column, Q_s is the capacity of the solid phase, Q_s is the capacity of the gas phase, and y_F is the concentration of the heavier isotope in the feed mixture.

The derivation of this equation is based upon the assumption that the mixing length between zones is zero. In practice, some additional allowance must be made for nonzero mixing length, depending on the equivalent stage height for the column.

Design of the Apparatus

Objectives

It was considered essential or highly desirable that the new chromatographic system have the following characteristics:

1. palladium inventory small in relation to the rate at which feed is processed,
2. short time between displacement cycles,
3. capability to generate product streams with an isotopic purity >99.9 at. %,
4. capability for recycling the mixed transition zone between the pure components,
5. capability of unattended operation for extended periods, and
6. essential components compatible with and safe for operation with tritium mixtures.

System Description

The EPIC chromatographic system, as it was ultimately configured, is depicted schematically in Figure 2. The central element of the apparatus is the palladium separation column and its associated temperature control equipment. The other major elements of the apparatus are: (1) a thermal conductivity cell to monitor the composition of the column effluent, (2) a tank containing the hydrogen that is used as the displacing agent, (3) a tank that collects the mixed transition zone for recycle, and (4) a buffer/accumulator tank to provide a source of deuterium for backfilling the column at the start of each cycle. Other elements of the system are air operated valves, and pressure and flow controllers and transducers. Manual valves used for evacuation and initial filling of the apparatus are not shown in Figure 2.

Operation of the chromatograph is under the control of a microcomputer. Operation is continuous, and no intervention is required except to empty product tanks as they become filled and to replace the feed supply when it is depleted.

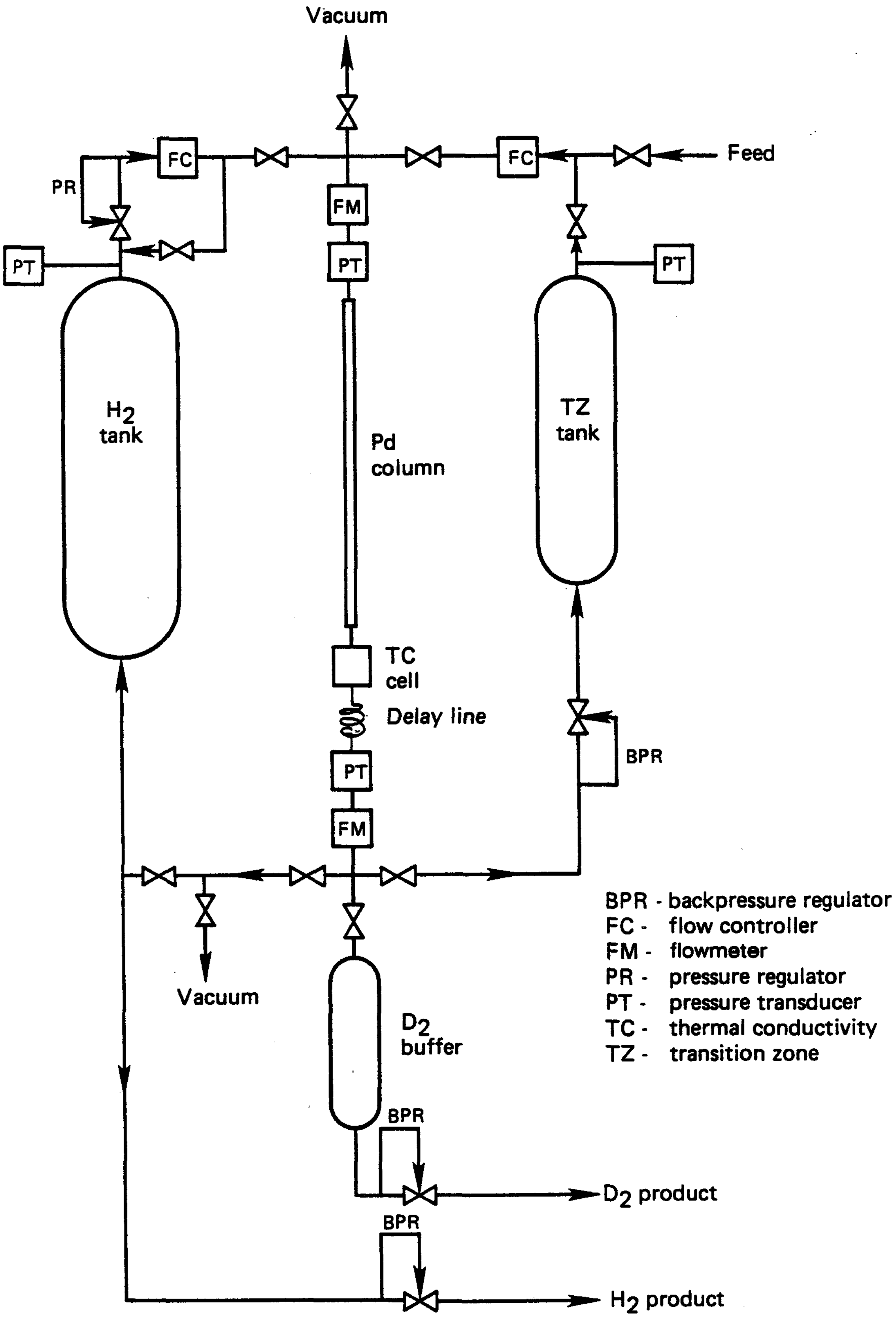


Figure 2 – The EPIC chromatograph. Manual valves are not shown.

Particular attention was given to avoiding components and design features that would lead to unnecessary degradation of the interfaces between zones of different composition. Thus, small diameter lines are used for external connections, and the switching valves at the ends of the column are specially designed for low holdup. The dead volume associated with the flow controllers and pressure regulation valves required that these components be duplicated and placed in separate lines connected to the switching valves. The pressure transducers are special, low-holdup components developed for analytical chromatography.

Operation

At the start of each cycle, the palladium column is empty, evacuated, and at the normal operating temperature. The deuterium buffer contains product gas from the previous cycle at the pressure set by the product backpressure regulator. Then the following steps take place in sequence:

1. The outlet of the column is opened to the D_2 buffer, and the pressure is allowed to equilibrate between the two. The volume of the buffer is chosen to contain approximately enough gas to saturate the α-phase of the palladium in the column. Thus, at the end of this step, the pressure is about equal to the absorption plateau pressure.

2. The inlet to the column is opened to the transition zone (TZ) tank, and an aliquot of mixed gas is allowed to flow into the column. The TZ tank contains gas at a pressure somewhat higher than the plateau pressure.

3. The TZ tank is closed, the feed line is opened, and an aliquot of feed mixture is allowed to flow into the column.

4. The feed line is closed, the hydrogen supply line is opened, and the displacement begins. After a time, the palladium in the column reaches β-phase saturation, and the system pressure increases beyond the absorption plateau pressure. When the pressure reaches the setpoint of the backpressure regulator, the excess gas flows out the D_2 product line.

5. As the transition zone arrives at the end of the column, the signal from the thermal conductivity cell begins to drop rapidly. At that time, the output of the column is switched, and the mixed gas is diverted to the TZ tank. A short delay line between the thermal conductivity cell and the valve cluster provides time for the valve switching to take place. As the transition zone accumulates, the pressure in the tank is restored to its original value, i.e., somewhere between the regulator setpoint and the absorption plateau pressure.

6. After the transition zone has passed, the two ends of the column are directly connected to the hydrogen tank, and the temperature of the column is increased to the bakeout level. Most of the hydrogen content of the column is thereby expelled back into the source tank. Excess hydrogen flows

out through the backpressure regulator in the H_2 product line. The gas that remains in the column is that which is required to fill the void volume at bakeout temperature and at the final pressure of the H_2 tank.

7. The gas that remains in the column is evacuated at bakeout temperature, and then the column is cooled to operating temperature in preparation for the next cycle.

System Details

Separation Column

The column is 6.8 mm i.d. and 91 cm long. It is packed with 48 wt % palladium on a 20 to 50 mesh alpha-alumina based catalyst support (Norton SA5*21). The hydrogen capacity of the column at 80°C is approximately 2400 std cm^3. The properties of the packing and the displacement behavior of the column are described in a previously published report [10]. The packing is referred to as REE4 in that report.

The stainless steel column is heated by passing an electrical current through it. A thermocouple is welded to the outside of the column, and the signal derived therefrom is used to control the temperature by proportional modulation of the power supplied to the column. At full power the column draws 152 A at 4.5 V. The column is mounted in front of a blower and air distributor. The blower is activated to accelerate cooling from bakeout temperature to operating temperature.

Switching Valves

The three-valve assemblies at the ends of the column are called cluster valves. Each assembly has one common port on the column side and three outlets (or inlets, depending on the end of the column that is in question). Valve bonnet assemblies were taken from standard Nupro bellows valves, adapted to a 2.75-in., 80 psig air operator, and fitted with a hardened stainless steel stem insert.

Thermal Conductivity Detector

Composition of the effluent gas is sensed by a four-element Gow-Mac cell, Model 10-952. Flow through the cell is limited to 50 cm^3/min; therefore, a flow splitter is used to permit most of the effluent to bypass the detector. The splitter is arranged so that the transit time through both paths is the same. Undesired mixing effects are thereby avoided. The reference side of the cell is attached to a 300 cm^3 cylinder filled with hydrogen at a pressure of 1.3 atm. At a supply current of 285 mA, the maximum output of the cell is about 500 mV in pure deuterium.

Tank Capacities

The hydrogen supply tank must be large enough to supply gas for a single displacement without undergoing an unacceptable drop in pressure. In this case a volume of 8150 cm^3, or 3.4 times the hydrogen capacity of the column, seems to work quite well. The holding tank for the transition zone must be large enough to discharge a volume equivalent to the volume of one transition zone. The discharge must take place within some reasonable fraction of the pressure difference between the displacement pressure and the absorption plateau pressure of the heavy isotope. A volume of 1100 cm^3 (or 0.4 of the hydrogen capacity) is satisfactory for this purpose.

The volume of the product buffer can vary from 0.1 to 0.4 of the column capacity. Purity of the product is sensitive to the volume chosen for the buffer. Larger buffer sizes yield higher product assays; therefore, the choice of buffer size depends on the specifications that the process must meet.

Operating Results

Useful operating data were acquired as the process evolved through several different configurations. At first there was no provision for recapture of the hydrogen displacement gas, nor was there any provision for recycle of the mixed zone. The process was run in this elementary mode through 330 cycles of separation and thermal regeneration.

The system was modified, and recovery of hydrogen during regeneration was started at cycle 331. Additional modifications, which were completed following cycle 457, made possible the recovery and recycle of the transition zone. At that point the system had reached its final configuration.

Feed for all of the experiments was a hydrogen–deuterium mixture containing approximately 50 at. % deuterium. Typical process parameters were as follows: displacement temperature, 80°C; displacement rate, 200 std cm^3/min; transition zone cut, 75 to 100 std cm^3; backpressure regulator, 1.5 atm; buffer volume, 1100 cm^3; regeneration temperature, 375°C. The feed quantity that was processed per cycle was in the range from 500 to 1000 std cm^3, and the cycles were completed in about 30 min.

Deuterium product purities in the range from 99.97 to 99.99% were routinely achieved during stable operation, and the gas in the transition zone cut was normally found to contain approximately equal amounts of hydrogen and deuterium, indicating that the size, timing, and switching of the cut were properly chosen.

Table 1 is a compilation of data acquired during one cycle of a typical experimental series that was run after the system had been fully developed. The operating parameters for the experiments are also given in Table 1. Feed was processed at a net rate of 1100 std cm^3 per 32-min cycle, or approximately 2100 cm^3/hr. The deuterium product assay at the end of the series of 24 cycles was 99.992 at. %, and the hydrogen product assay was 99.86 at. %, yielding an overall separation factor of 900,000.

Approximately 500 std cm^3 of gas flowed from the buffer into the empty column during the deuterium backfill portion of each cycle. This quantity was sufficient to reach an average atomic ratio of deuterium to palladium (D/Pd) equal to 0.13, thereby saturating the alpha phase. The average pressure at the end of the backfill step was 0.82 atm, consistent with the published value of 0.79 atm for the

Table 1 - OPERATING DATA FOR SEPARATION CYCLE NO. 657

	Pressure (atm)						
Step	Inlet	Outlet	Accumulator	H_2 Tank	Flow Rate (cm^3)	Column Temperature (°C)	Time (min)
1. Cooling	0.0	0.0	1.37	2.72	-	372 → 78	2.3
2. Backfill	0.73	0.92	1.37	2.72	-	78	2.1
3. TZ Recycle	0.94	0.86	1.19	2.72	122	78	1.4
4. Feed	1.24	0.89	1.20	2.72	205	78	5.4
5. D Production	1.78	1.50	1.20	2.48	207	78	8.6
6. Transition Zone	1.80	1.52	1.36	2.46	205	78	0.9
7. H Recover	2.72	2.74	1.37	2.75	-	78 → 372	2.1
8. Evacuate	0.00	0.00	1.37	2.75	-	372	9.0
						Total Time:	31.7

Operating Parameters (cm^3 STP)	
Feed Load:	1100
Transition Zone:	150
D_2 Buffer Volume:	1100
TZ Tank Volume:	1100
H_2 Tank Volume:	8200

absorption plateau pressure of the palladium–deuterium system at 80°C [11].

At the beginning of recycle step the steady state pressure in the transition zone accumulator was 1.36 atm. This pressure provided sufficient driving force to return to the column inlet the 150 cm3 of transition mixture that had been accumulated from the preceding cycle.

At the end of the recycle step, 1100 cm3 of feed mixture was introduced into the inlet end of the column, followed by hydrogen gas, both at a flow rate of 200 cm3/min. As this process proceeded, product grade deuterium flowed from the outlet of the column into the buffer, and the pressure in the column and in the buffer gradually increased. When the buffer reached the setting of the backpressure regulator, 1.5 atm, deuterium flowed into the product tank.

The onset of the transition zone was identified by the sharp change in slope of the output of the thermal conductivity cell. At that point, flow out of the column was diverted, and 150 cm3 of gas was allowed to flow into the transition zone accumulator. During this step, the pressure in the accumulator was restored from 1.18 atm to the initial value of 1.36 atm.

When the transition zone had passed, both ends of the column were connected directly to the hydrogen tank, and the temperature of the column was increased to 375°C. The pressure in the hydrogen tank was thereby restored to 2.8 atm, and excess gas was allowed to flow into a product tank. The hydrogen remaining in the column was evacuated to complete the separation cycle.

Effect of Buffer Size

Several experiments were conducted to determine the effect of the size of the deuterium buffer on the purity of the deuterium product. Results were obtained for buffer volumes of 0, 300, 500, and 1100 cm^3. At the end of the backfill step the corresponding column loadings, expressed as D/Pd ratios, were 0, 0.06, 0.09 and 0.13, respectively. The deuterium product assays that were obtained with the several buffer sizes are plotted in Figure 3. It is clear from this plot that there is a progressive increase in product purity as the buffer size is increased from 0 to 1100 cm^3. These results suggest that preloading the column with deuterium results in displacement of protium from some of the tightly bound states in the solid, and that the maximum purity of the product is obtained when the α-phase of the solid is fully saturated during the backfill step. There is also a possibility that improved deuterium purity is obtained at the expense of some decrease in the assay of the protium fraction, but the data are insufficient to establish such a relationship.

Effect of Displacement Rate

The effect of displacement rate on column performance had been evaluated previously in connection with the work on supported palladium materials [10]. An additional series of experiments was completed to determine the effect of increased displacement rate on the performance of the integrated system. The series was run at a nominal rate of 300 cm^3/min (11 cm/min linear velocity) instead of the usual rate of 200 cm^3/min (8 cm/min). The increased rate had no obvious effect on the purity of the products, and the time per cycle was reduced by about 4 min.

Effect of Regeneration Temperature

The standard temperature for regeneration of the palladium at the end of each cycle was 375°C. This temperature was selected to be as high as practical, given the electrical and thermal restraints imposed by the design of the system. In principle, high temperature should be effective in facilitating complete removal of residual hydrogen from the column during the evacuation step.

A series of experiments was conducted to determine whether a lower regeneration temperature would have an adverse effect on the process. At 275°, evacuation of the column was somewhat slower, and the overall cycle time increased to 34 min from the normal value of 32 min. There was no significant effect on purity of the separated products. The deuterium stream was 99.988% pure, whereas, in the immediately preceding series, it had been 99.992%. The hydrogen assay was

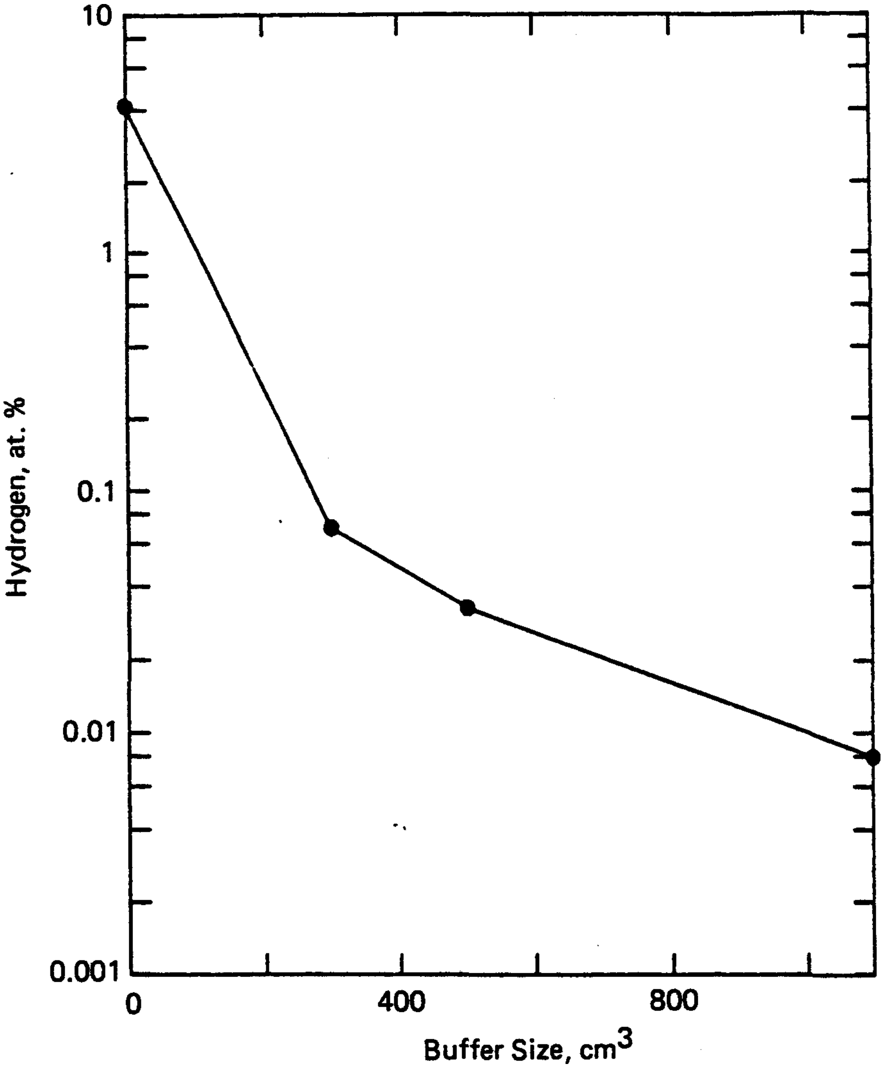


Figure 3 – The effect of buffer size on the hydrogen content of the deuterium product.

unchanged at 99.86%. Lower temperatures may also be useful, although at the expense of still longer cycle times.

Pressure Drop

Supported palladium packings tend to degrade as they are cycled between the dehydrided and hydrided states [10]. This can lead to deposition of fine particles in the interstices of the support material, thereby increasing the pressure drop required to sustain flow through the packing. When newly fabricated, the REE4 column had a pressure drop equivalent to 19 torr for hydrogen at 80°C and 200 cm3/min. After 11 cycles, the pressure drop had increased to 26 torr. The next measurement, after 267 cycles, yielded a value of 213 torr. The pressure drop stabilized at that value, and no further increase was observed after 680 cycles.

Application to Tritium Separation

There are several problems that must be addressed in adapting the EPIC system to tritium service. Some of these are the following: (1) component compatibility with radioactive service, (2) separation of ^3He, and (3) lower separation factor for the deuterium–tritium pair.

The essential components of the hydrogen–deuterium system were selected or constructed to be usable in tritium service. The column is 304 stainless steel with welded end closures. The cluster valves at the ends of the column are all–metal 304 stainless steel bellows valves with welded tubulations. The thermal conductivity detector is stainless steel with brazed ceramic electrical headers and brazed stainless steel tubulations, and the backpressure regulation valves are stainless steel bellows valves with welded tubulations.

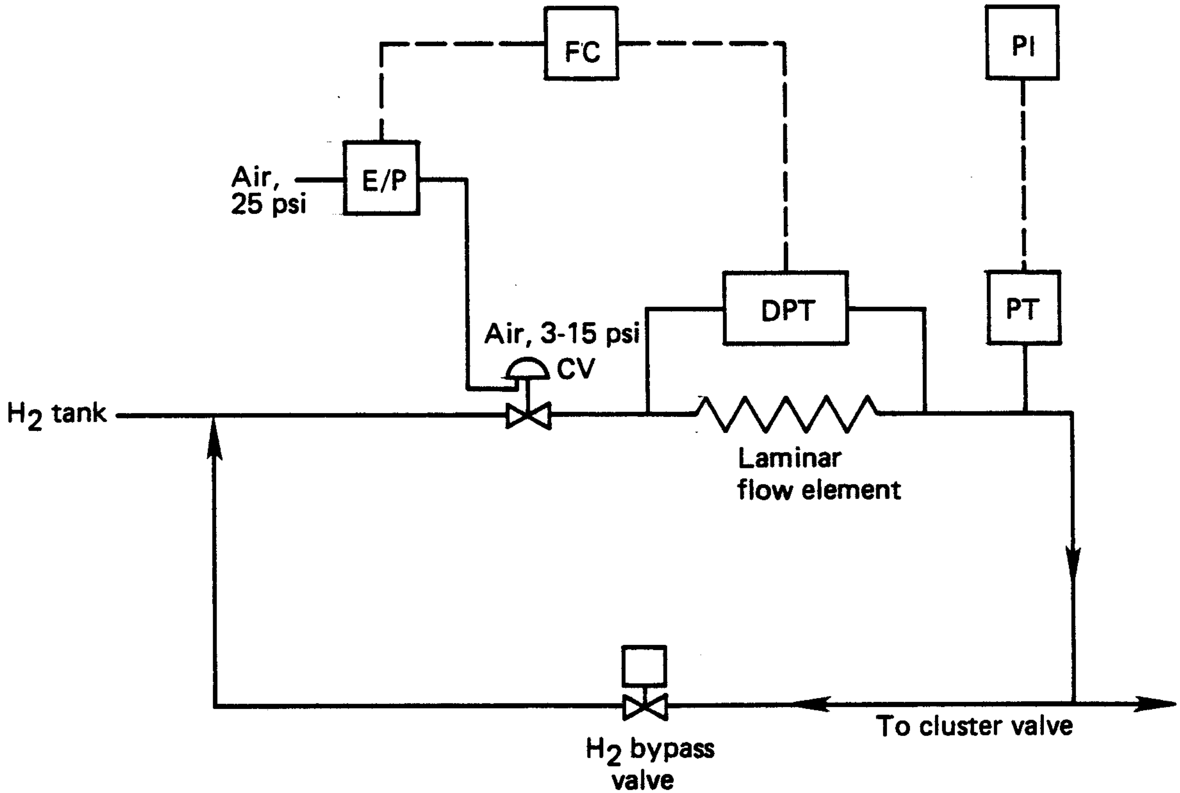
The remaining components of the system, as it is now constructed, are not satisfactory for tritium service. The most important of these are the pressure transducers at the inlet and outlet of the column, the flow meters, and the flow controllers in the feed and the hydrogen input lines.

The pressure transducers, which were manufactured by Senso–Metrics Inc., are special units with low holdup and dead volume. The diaphragm material, however, is 17–4 PH stainless steel, considered incompatible in tritium service. An equivalent, compatible unit is unavailable. Conventional transducers cannot be substituted in these locations. They have unacceptable holdup and dead volume, which cause undesirable mixing of otherwise sharp transitions in composition. To replace the units, therefore, it will be necessary to place transducers in feed and hydrogen input lines and in the product and transition zone output lines.

The Brooks flowmeters that were selected for this project were thought to be useful in tritium service; however, it seems that they contain an internal elastomer O–ring. The recommended fix is as follows: (1) Eliminate the flowmeter on the outflow end of the column; (2) Replace the inlet flowmeter with two flowmeters, one in the hydrogen input line and one in the feed input line; (3) Use the flowmeters as sensing elements for the corresponding flow control function, replacing the incompatible flow controllers now in the system.

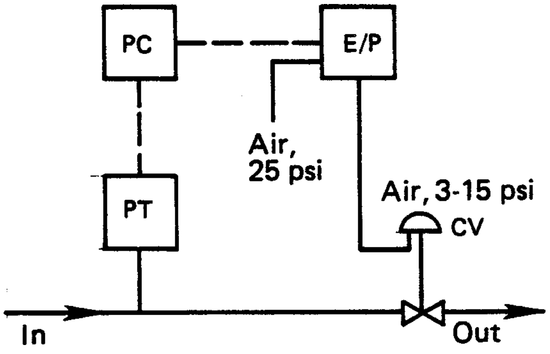
The recommended configuration for the input systems is illustrated in Figure 4. Figure 5 depicts the recommended arrangement of the backpressure control systems in the output lines. The control valves shown in the two figures are all metal bellows valves with welded tubulations (Research Control Valve, Badger Meter Inc., Tulsa, OK).

The hydrogen deuterium system is a two–component system with one transition between the two atomic species. Systems containing tritium, however, are generally four component systems, i.e., tritium, deuterium, protium, and helium–3. Instead of one transition zone, therefore, there will be three. Each of the four components has a unique thermal conductivity. Proper routing of the column output will require



CV - control valve
DPT - differential pressure transducer
E/P - voltage to air pressure
FC - flow controller
PI - pressure indicator
PT - pressure transducer

Figure 4 – Recommended configuration for tritium–compatible hydrogen inlet system. The feed inlet system is the same, but without the bypass valve.



CV - control valve
E/P - voltage to air pressure
PC - pressure controller
PT - pressure transducer

Figure 5 – Backpressure regulation of product and transition zone outlet lines.

that the output of the thermal conductivity cell be properly interpreted in the control software.

The productivity of a separation system is proportional to the square of the logarithm of the elementary separation factor. Under the conditions of this investigation, the hydrogen–deuterium separation factor is 1.8. The deuterium–tritium separation factor, however, is only about 1.4. Thus, everything else being equal, a deuterium–tritium separation system will have approximately one-third the productivity of a hydrogen–deuterium separation system.

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