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A CHROMATOGRAPHIC SYSTEM FOR THE
ENRICHMENT AND ANALYSIS OF LOW LEVEL TRITIUM SAMPLES

by

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ABSTRACT

An automated palladium gas chromatographic system was developed for measuring low activities of tritium in the 5 to 150 TR range (Tritium Ratio = one tritium atom/ 10^{18} hydrogen atoms). The system is used to routinely analyze water samples (40 ml) at the rate of 2 samples per day. Approximately 1.5 manhours per sample are required. The average recovery for the system is 81.2% with a procedural error of $\pm 6\%$. The counting time required for 10% relative precision on a sample of 89 TR processed by this system is approximately 45 minutes.

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INTRODUCTION

An analytical procedure was needed to measure routinely tritium in the 5 to 150 TR** range in a large number of water samples.

Florkowski et al¹ compared the results of analyses of tritium in natural waters in the range 10 to 250 TR by 35 laboratories and concluded that enrichment-gas counting was the more accurate method from 0 to 80 TR. Direct gas counting was more accurate for higher concentrations.

Electrolysis² and thermal diffusion³ have been used to enrich tritium in water samples, but are lengthy procedures that require considerable attention from the analyst. Hoy,⁴ Perschke,⁵ and Akhtar⁶ developed methods of tritium enrichment by chromatography.

Features and advantages of Hoy's gas-solid chromatograph include: relatively quick analysis of water samples containing

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** One tritium atom/10¹⁸ hydrogen atoms.

less than 10 TR; self-elution that eliminates the need of an inert carrier gas; a completely sealed system that reduces tritium contamination; and simple collection based on pressure measurements (tritium evolves first). The technique is specific for tritium, because most other gases likely to be associated with the sample either do not react with the palladium column or are tightly bound. The columns are regenerated simply by simultaneously heating and evacuating the columns.

In this paper I discuss the automation and optimization of Hoy's analytical system.

EXPERIMENTAL

A tritium enrichment system was designed with a palladium column capacity of about 50 liters (STP) of hydrogen (~ 40 ml water) per analysis preceded by a sample reduction furnace capable of producing up to 3 liters of hydrogen per minute from water. The assembly of the columns and magnesium furnace are shown in Figure A1 and A2 in the Appendix. The water sample size was determined by the sensitivity objective of 5 TR ($\pm 10\%$) and operational parameters of the columns. Radioassay of the enriched fraction by proportional counting requires an enriched recovery equivalent to ~ 1 cpm for a 5-TR water sample.

Previous experiments by Hoy⁷ showed that a palladium gas chromatograph could reproducibly enrich hydrogen samples of varying concentrations (50 to 440,000 TR). The recovery was not dependent on concentration but was dependent on sample volume

(56% recovery for a 50-ml sample; 80% for 10 ml). From a study of the effect of temperature on recovery, cooling the columns to -65°C would increase recovery (10 to 20%) above that at room temperature, but would complicate the design and operation of the columns. The distribution of tritium in the enriched sample was determined as the tritium left the last column. Approximately 50% of the tritium was in the first 50 cc which decreased to $\sim 0.6\%$ in the 600 to 700 cc fraction. A volume of 630 cc was selected for counting and represented $\sim 80\%$ recovery with a negligible error if slightly different enriched volumes were collected.

Briefly, the enrichment scheme is as follows: The water sample is reacted with magnesium chips at 650°C in an enclosed furnace. The hydrogen generated sorbs directly onto an evacuated palladium column at ambient temperature. When a sufficient volume of water has reacted, the furnace is isolated from the palladium column. No buffer gas or carrier gas is used; movement of hydrogen through the column is maintained by the initial pressure differential (vacuum at exit end and hydrogen partial pressure at feed end) and the additional pressure created by zonal heating of the feed end of the column that causes the palladium to release sorbed hydrogen.

Tritium exhibits the highest partial pressure over palladium and diffuses through the column faster than either deuterium or protium. The first gas evolved, the tritium-rich fraction, is

detected by a pressure increase in an evacuated proportional counter attached to the exit end of the column. After the tritium fraction is collected, the proportional counter is filled with propane gas and counted with a pulse-height analyzer to verify purity and electronic gain. The columns are regenerated by increasing the temperature of the entire system to 240°C and pumping out the residual hydrogen.

Details of the column and operational procedures are given in the Appendix.

Certain practical points should be noted with respect to operating the column. Recovery and enrichment are low if any trace of oxygen remains in the system. All leaks must be eliminated, and the columns are stored under inert gases or vacuum when not in use. Chemical vapors that react with palladium or catalytically combine with hydrogen must be avoided, that is, halogens, sulfides, and oxygen. One and one-half hours are required for the tritium to evolve from the column, but other gases inert to the column pass through in a few minutes. Gases dissolved in water or those released from magnesium upon heating may be pumped off the exit end of the column without affecting the final result.

RESULTS AND DISCUSSION

The conditions for the operation of the automated palladium-gas chromatograph are described in the Appendix. Average routine percentage recovery, disregarding first sample after column inactivity, was $81.2 \pm 1.6\%$. The first sample analyzed, after the

columns were dormant for two days or more, averaged 9.5% below samples analyzed subsequently. Therefore, the first sample (a blank) analyzed on the column after a dormant period of two days or more is disregarded.

To investigate the analytical behavior of the system, a series of standards (22 to 210 TR) prepared from low-tritium, deep-well water were analyzed and results are shown in Figure 1. The precision of the system is also indicated by the fact that duplicate samples usually agree within the procedural statistics of $\pm 6\%$ (2σ).

A procedural contamination level of 4.2 TR was established by routinely analyzing deep-well water samples. It is uncertain whether this level of tritium is present in the well water or is the result of exchange with air moisture during sample handling and processing. Contamination between consecutive samples was investigated by analyzing a high activity sample (8940 TR) and then immediately measuring a deep-well water sample in the system. An average residual tritium activity of 29 TR was found in the deep-well water sample. Approximately $0.34\% \pm 0.11$ of the tritium from one sample contaminates the next one processed.

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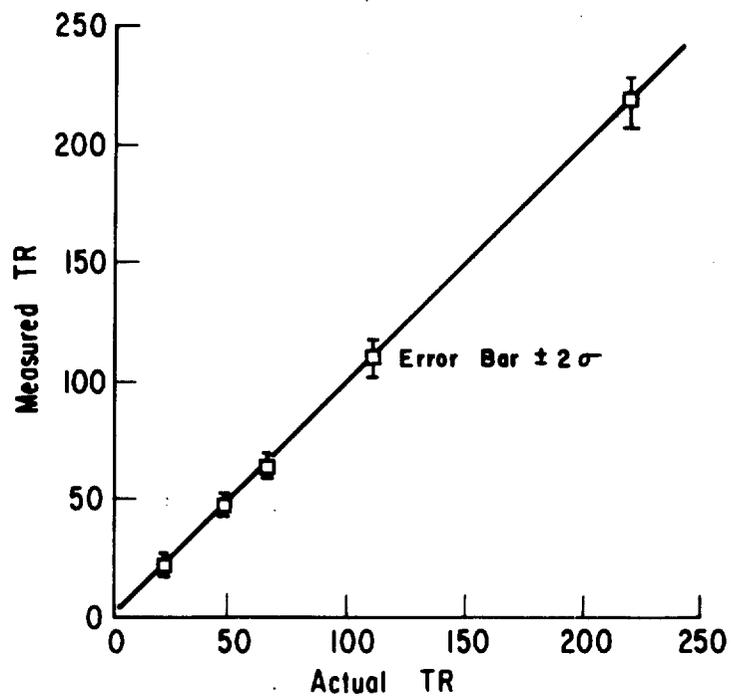


Figure 1 Column Analysis of Tritiated Water Standards

APPENDIX

Chromatographic Columns

The palladium-column system has a capacity of about 50 liters of hydrogen gas. The assembly of the chromatographic columns is shown in Figure A1. Column I contains 1 kg of palladium mixed with 100 grams of asbestos, and the mixture is supported in the column by stainless steel turnings. The column is wrapped with 1/4-inch-diameter copper water tubing for rapid cooling, three separate heating tapes (A, B, and C) for zonal heating, and insulation. The second and third columns contain lesser amounts of the palladium mixture (as indicated in Figure A1) and are wrapped with copper tubing, heating tapes, and insulation. All valves are bellows seal; connecting tubing is stainless. Swagelok* fittings are used for system couplings. The proportional counters, in a lead-water shield, are connected by stainless steel tubes to the exit of Column III.

Hydrogen Production Apparatus

A magnesium furnace capable of reducing a 40-ml water sample in less than 25 minutes and which could be evacuated to less than 50 μ was developed. The sample preparation system is shown in Figure A2.

The 650°C furnace (containing ~170 g of magnesium turnings supported on either end by stainless steel turnings) is sufficient for the reduction of two 40-ml water samples. The small

* Trademark of Crawford Fitting Company.

secondary furnace filled with 15 g of magnesium turnings is attached to the exit of the 650°C furnace. The furnace is positively fed by a small peristaltic pump at a rate of ~1.75 ml/min from a 50 ml buret. The intercoupled pressure switches are set such that the pump motor will shut off if the pressure reaches 10 inches of mercury (vacuum) and turn on when pressure drops below ~12 inches of mercury (vacuum). This technique allows uniform loading of the column and prevents pressure buildup in the glass manifold. The gas stream is passed through a liquid nitrogen trap, 200 cc of molecular sieves, and then to load Column I (Figure A1).

Operation

A buret is filled with the distilled water sample to be analyzed and attached to the inlet tube of the peristaltic pump. The prepared furnace (heated at 500°C overnight) and hydrogen purification apparatus are evacuated to 10 μ . Column I and sample preparation apparatus are isolated from vacuum and the sample is fed to the furnace at a rate of ~1.8 ml/min. Once the sample (40 ml) is reduced and load system pressure decreased to 20 inches of mercury (vacuum), Column I is isolated from the sample preparation apparatus. The elution sequencer is reset to automatic position, and elution of the tritium peak is initiated by turning on heater A.

When heater A reaches 240°C (~3 min), timer BT (Figure A3) is started, and at the end of seven minutes heater B is turned on.

When heater B reaches 240°C, timer CT (Figure A3) is started, and at the end of seven minutes heater C is turned on and automatic valve "a" (Figure A1) is closed. Approximately 20 minutes after heater A is turned on a positive pressure is shown on the gage between Columns I and II. Forty-two minutes after heater A is turned on, the pressure between Columns II and III has increased from 30 inches to 25 inches of mercury (vacuum), and automatic valve "b" is closed leaving the exit of Column III open to the proportional chamber. Nine minutes after valve "b" is closed, a pressure is registered at the exit of Column III, and 3 to 5 minutes later pressure switch 2 closes off the proportional chamber at 22 psi and reopens automatic valve "b" to vacuum. Total time of elution sequence is 55 to 60 minutes.

The columns are then opened to the vacuum manifold, elution sequencer set to manual, heaters to Columns II and III are turned on, and system pumped down to 200 μ (\sim 1.5 hours). After cooling to ambient temperature by passing air, water, then air again through the cooling coils, the pressure of the system is reduced to 20 to 30 μ . At this point a second sample may be analyzed.

The sample in the proportional chamber is increased to 30 psi with propane, high voltage applied, and counted with a pulse-height analyzer.

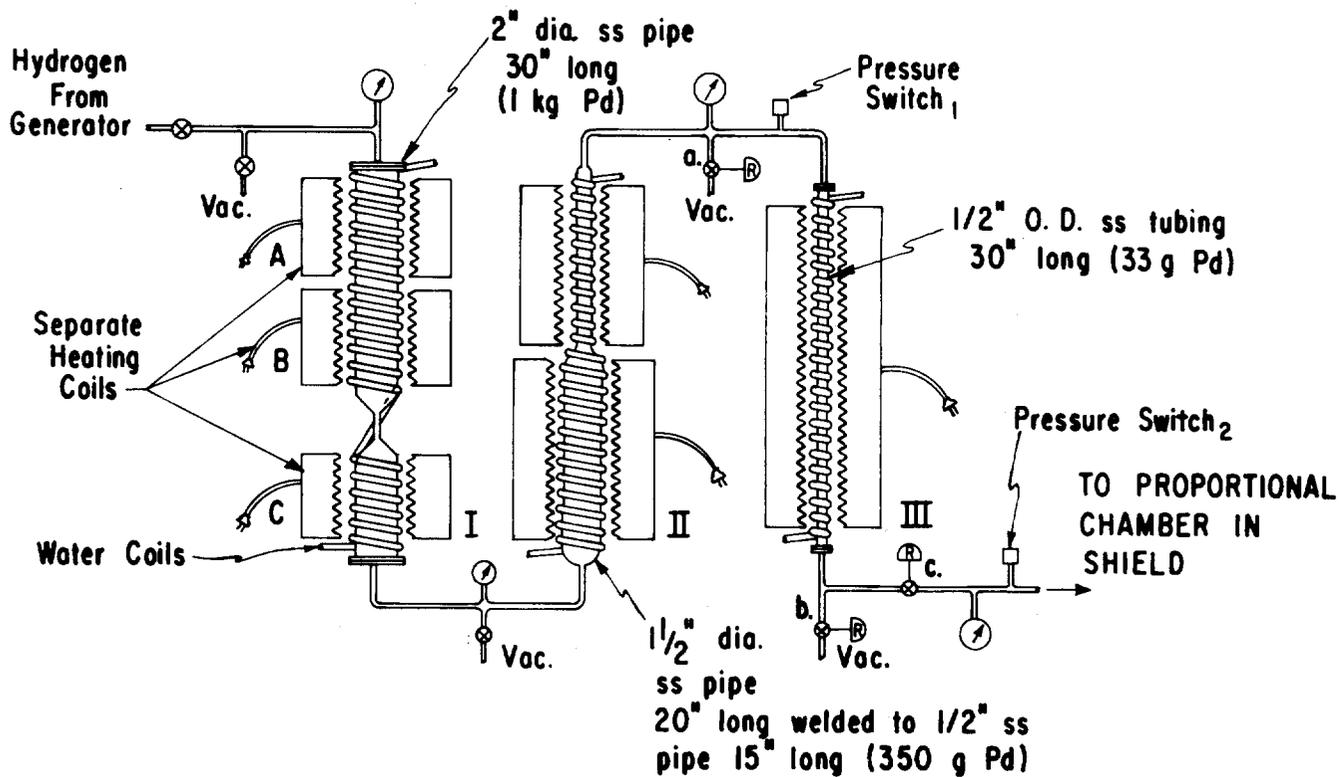


Figure A-1 Assembly of the Chromatographic Columns

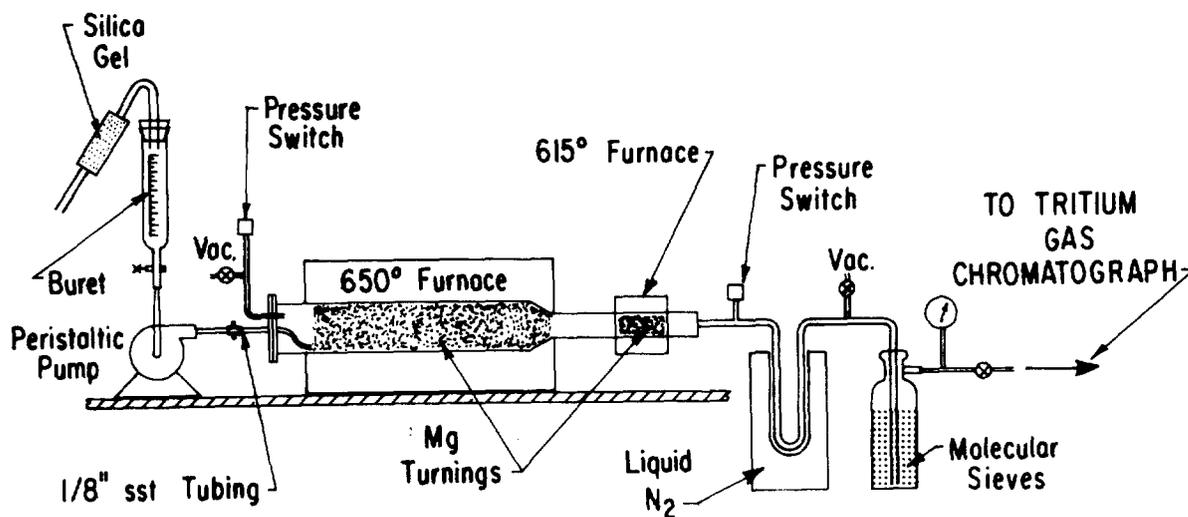


Figure A-2 Hydrogen Production Apparatus

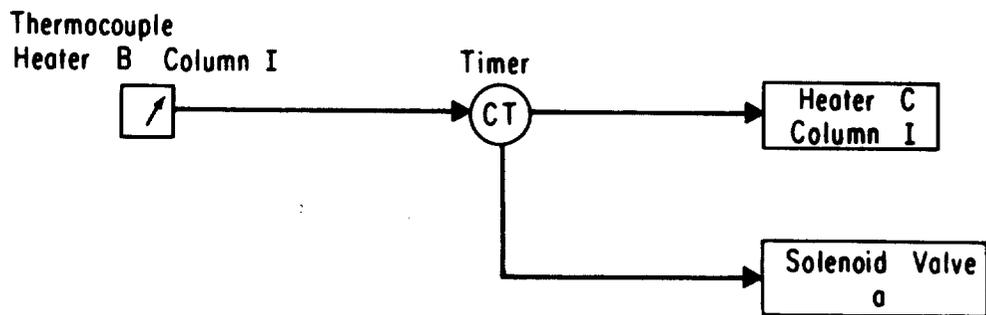
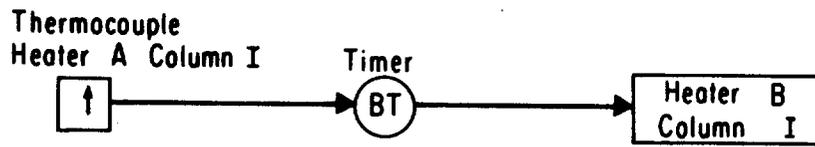


Figure A-3 Elution Sequencer

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