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# A RUGGEDIZED ULTRASENSITIVE FIELD AIR SAMPLER FOR DIFFERENTIALLY DETERMINING TRITIUM OXIDE AND GAS IN AMBIENT AIR ATMOSPHERE

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## Abstract

The instrument described is an operational, practical, ruggedized, ultrasensitive, tritium field air sampler assembled for the simultaneous, differential sampling of the environmental air for tritium oxide and elemental tritium. The system uses hardware assembled and packaged in such manner as to facilitate use in the field as well as in the laboratory. The sampling system occupies relatively small space and is simple to operate. The detection sensitivity approaches tritium background levels and is achieved by high volume sampling, efficient removal of tritium oxide and elemental tritium ("tritium gas"), and counting the recovered fractions by liquid scintillation spectrometry.

## Introduction

The AEC standard for the maximum permissible concentration of tritium gas in uncontrolled areas is 200 times greater than for tritiated water vapor. Because of this difference, monitoring for tritium in the past at Mound, as well as at other locations, was for tritium as the oxide with the assumption that if the levels did not exceed the standard for the oxide, then the gas would be well within the standard.

When tritium in the environment or releases of tritium to the environment are measured, a measurement of oxide or even total tritium would not be sufficient to determine whether concentration guides have been exceeded; measurement of both tritium gas and tritiated water are necessary. Numerous methods for monitoring tritium oxide have been reported, but the literature is scant concerning tritium gas measurements. Mound Laboratory's goal is to determine background levels of tritium oxide and gas, both from natural and artificial sources, and to establish a baseline to provide a means of measuring any tritium that might be inadvertently added from operations at Mound.

## General Description

The Mound Laboratory total system designed by MRC, Dayton Laboratory, consists of a tritium field sampler and a separate laboratory sample recovery system.

Collection System A picture of the collection system is shown in Fig. 1. The collection system with sample inlet, sample outlet, and hydrogen inlet connections, mounted controls, and indicators occupies a space 44 in. wide, 16 in. deep, and 38 in. high. The

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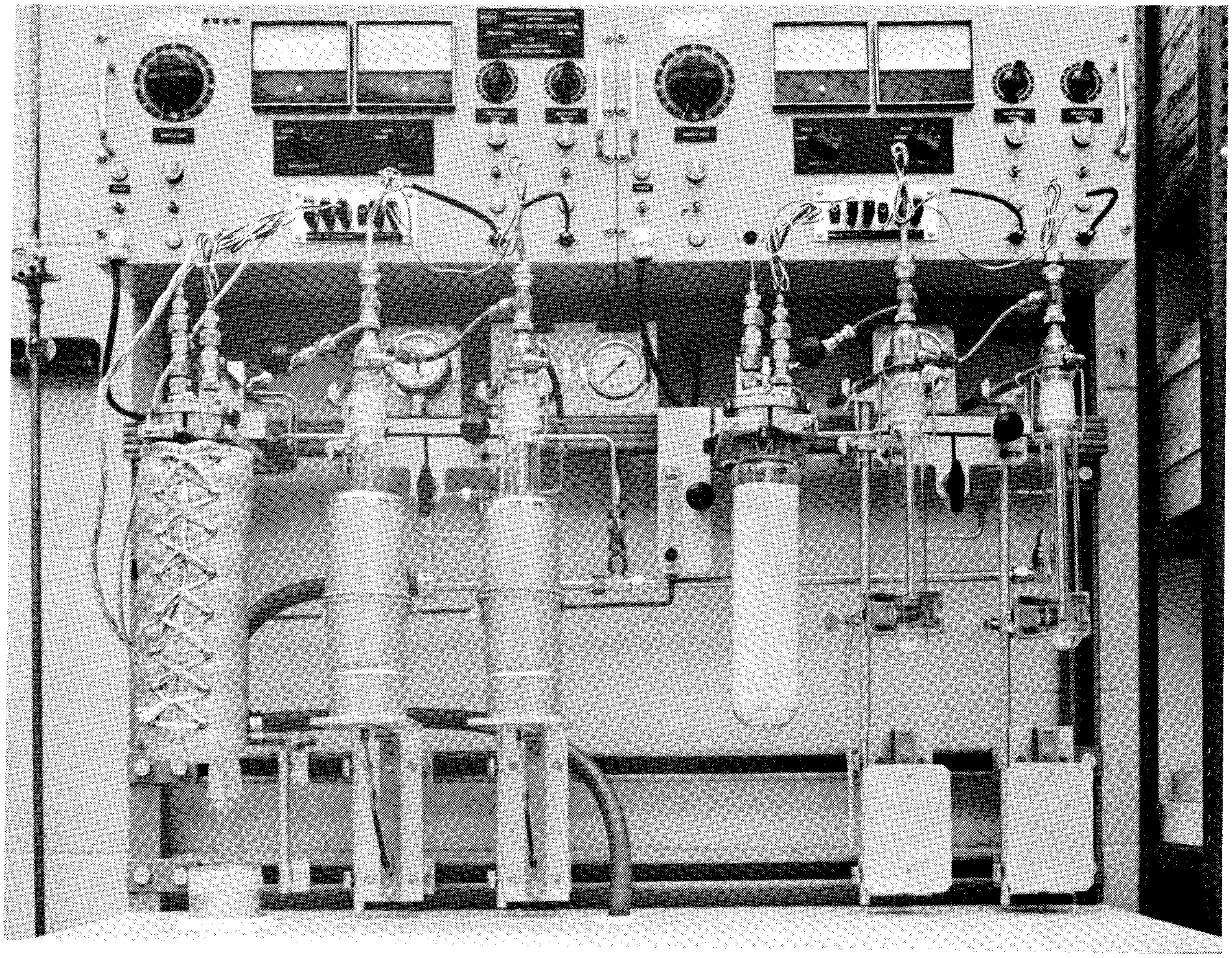

Fig. 1 - Tritium sample collection system.

sample collection/concentration bottles with protective wire-coated grid encasement are 3.88 in. in diameter and 17.55 in. overall length. The weight of the collection system, less bottles, is approximately 135 lb.

The collection system accommodates four sample collection bottles, the first two for the collection of tritium oxide and the other two for the collection of elemental tritium. The system valving permits a wide range of operating modes. Inadvertent introduction of hydrogen into the system (for the collection of elemental tritium) is averted by requiring air to flow past a sensor before a solenoid valve in the hydrogen line can be opened. Maintaining hydrogen supply within the limit of the flow meter provides assurance that the 4% lower explosive limit (L.E.L.), will not be exceeded. For normal air sample system flow rates of 30 to 75 liters/min with carrier hydrogen supplied at the rate of 100 cc/min, the mixture runs 0.2 to 0.4% of the L.E.L. The sensor and solenoid valve shut off the hydrogen inlet line in the event of low or no air flow during sampling.

Recovery System A two-station sample recovery system is shown in Fig. 2. This versatile, two-station system, was provided at Mound Laboratory to determine various operating parameters. The

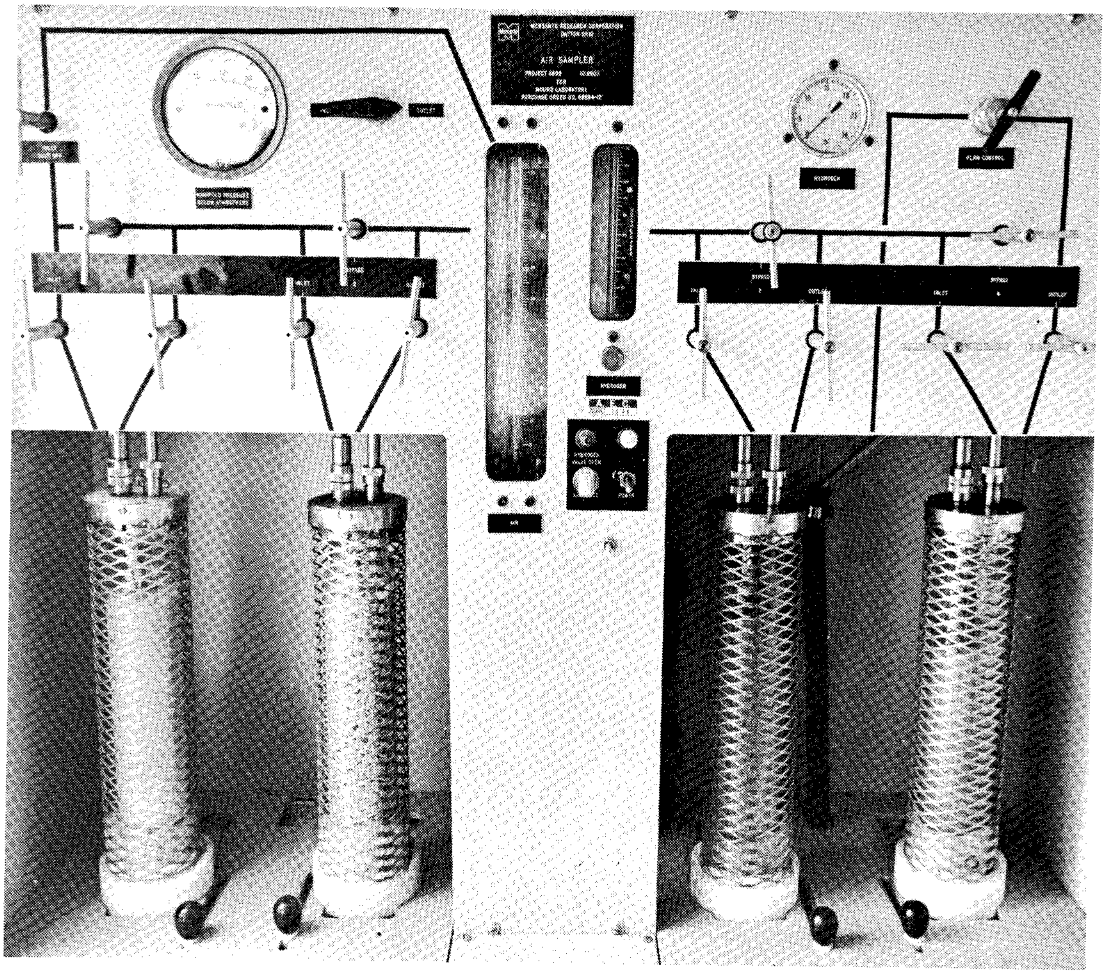

Fig. 2 - Two-station tritium sample recovery system.

recovery system provides a laboratory facility for dry gas displacement or low pressure desorption of a collected sample at selected temperature and pressure into two cold traps in series.

## Results and Discussion

Experience to-date with the system at Mound Laboratory indicates that the silica gel used in the sample collection bottles must be thoroughly dehydrated prior to use. Typical air flow rate used in sampling has been 50 liters/min. At this flow rate, 750 g of silica gel in the collection bottles is adequate for a large volume grab sample in the range of 1500 to 3000 liters even under unfavorable ambient conditions of high relative humidity and temperature. Preliminary results in calibration of the system indicate 97-99% of the water vapor in the sampled air is recovered using one oxide collection bottle.

Seven hundred fifty grams of silica gel is also placed in the elemental tritium or gas collection bottles. The silica gel is coated with palladium black by adding 2 g of palladium powder to the 750-g charge of silica gel and agitating the mixture thoroughly until the palladium powder is completely coated on the surfaces of the silica gel particles. As the ambient air stream passes through this collection bottle, hydrogen gaseous isotopes are reacted with the palladium to form oxides. The reaction is:

$$2H_2 + O_2 \xrightarrow{Pd} 2H_2O + \Delta$$

The resulting water is collected by the silica gel just as in the primary oxide collection bottles.

The cryogenic moisture recovery traps employed in the recovery system use liquid nitrogen. Essentially all of the water driven off the catalytic collector is captured in the first cold trap. No visible moisture has occurred in the second cold trap. Moisture is recovered in the system in a simple reverse of the method of collection. Recovery is completed in 30 min with the collection bottle at a temperature at 300°C. The heating mantle and its associated control variac are used to obtain the desired temperature. When the moisture has been driven off the sample, the exit temperature decreases. This temperature change can be monitored as the signal for desorption completion.

The use of palladium black is preferable to copper oxide since palladium reacts with hydrogen at ambient temperatures, whereas copper oxide must be heated before it will react. Since silica gel was found to be satisfactory, no other desiccant was evaluated.

Silica gel, as received from the manufacturer, contains residual moisture, so it must be thoroughly baked out before using at a temperature high enough to condition the silica gel for use in a reasonable period of time but not at a temperature high enough to destroy its sorption properties. Tests performed in the development of this monitoring system showed that a one-hour bakeout at 300°C adequately removed the moisture without affecting sorption properties. Normal residual moisture ranges from 0.03 to 0.07 g of water per gram of new silica gel.[1] To date, silica gel has been reused since there has been no indication that the bakeout reduced the collection efficiency in subsequent runs using known aqueous solutions of tritium oxide.[2]

The efficiency of the procedure for the determination of tritium oxide was tested using the set-up shown in Fig. 3. Known solutions of varying tritium oxide content, assayed by liquid scintillation counting and calibrated against a National Bureau of Standards (NBS) tritium oxide standard, were placed in the container marked "tritium oxide". Air was pulled through the drying trap at a flow rate of 50 liters/min, during which time the standardized tritium oxide was evaporated into the air stream and collected in the oxide collection bottle. Results indicate an overall recovery of 97-99%.

The efficiency of the procedure for the determination of elemental tritium was tested using the setup shown in Fig. 4. The flow rate of the calibration system was adjusted to 50 liters/min with valve #1 open and valves #2 and #3 closed. Hydrogen flow was adjusted to 150 cc/min. The system was operated in this configuration for 20 min after which time valves #2 and #3 were opened and valve #1 was closed. The tritium gas sample standard flask was flushed for 10 min. Gas samples used in calibration were standardized against an NBS gas standard prepared from the NBS tritium oxide standard.[3] At the end of 30 min the set-up was shut down, the

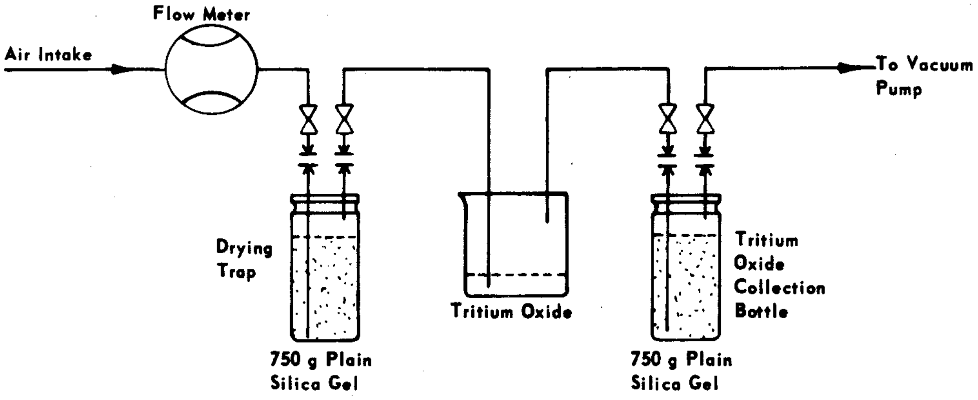

Fig. 3 - Setup used to test efficiency of tritium oxide collection.

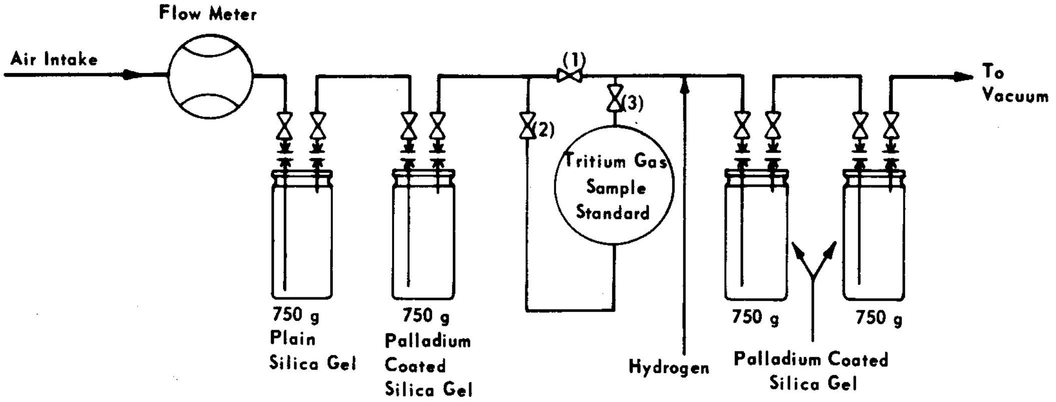

Fig. 4 - Setup used to test efficiency of elemental tritum collection.

collection flask containing the palladium-coated silica gel was removed, and the water was removed using the standard recovery procedure.

Two grams of palladium powder coated on the 750 g of silica gel are required to achieve recoveries in excess of 90% in the collection bottle. One gram of palladium powder achieved only 53 to 80.5% overall recovery in the collection bottle.

The theoretical sensitivity of this sampling system is 1.6 x $10^{-12}$ μCi/cc of air at the 95% confidence level for liquid scintillation counting with a 20 counts/min counter background, a 21% counter efficiency, and a 100 min sample counting time. A total of 1,223 liters of air sampled at a relative humidity of 50%, 68°F, and 760 mm barometric pressure would yield 10 ml of water which is the optimum amount that can be blended with a scintillation liquid for counting. A typical one-hour sample run at a flow rate of 50 liters/min would sample 3000 liters of air and yield some 25 ml of water. If all of the water could be counted as a single sample, the tritium oxide sensitivity would calculate to 0.6 x $10^{-12}$ μCi/cc. The limitation in the system sensitivity is, therefore, not in the air sampling/collecting apparatus but in the liquid scintillation counting since only 10 ml or less of collected moisture can be analyzed. The lower detection limit could be achieved by concentrating the tritium in moisture collected to 10 ml by electrolysis. A sensitivity of 1.6 x $10^{-12}$ μCi/cc of air at the 95% confidence level, however, is in the range of tritium oxide background levels at Miami, Florida[4] and is adequate for an effective environmental oxide monitoring program.

A sensitivity of 0.6 x $10^{-12}$ $\mu$Ci/cc of air is attainable for all samples containing elemental tritium since the total water in the collected gas sample can be controlled to a volume of 10 ml, all of which can be counted. The carrier hydrogen must be used to obtain sufficient water for analysis. Theoretically, 600 cc of hydrogen carrier gas produce 0.5 cc of water.

The use of silica gel, or other desiccants, for air sampling presents a "memory effect" that must be taken into consideration. The memory effect results from the fact that complete moisture desorption of silica gel is not attainable. The tritium content of the residual moisture will affect the results of each air sample collected. This factor has not been completely investigated with this sampling system, but based on limited data obtained to date, it appears that about 1% of the moisture from tritium oxide samples and from 3 to 10% of the moisture from tritium gas samples is not removed. In accurate sampling the memory effect can be corrected for by passing vapor of known tritium concentration through the sample collection bottle while it is being baked out under vacuum. Sufficient moisture is passed on to the silica gel to assure that all residual moisture is "pushed out" and replaced. When the sample collection bottle is used, the sample data are corrected to account for the controlled, known residual or background moisture and its tritium content.

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