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L'ÉNERGIE ATOMIQUE DU CANADA LIMITÉE

A DISCRIMINATING BUBBLER SYSTEM FOR HTO AND HT MEASUREMENT

UN SYSTÈME D'ÉCHANTILLONNEURS "MESURE-BULLES" À POUVOIR DE SÉPARATION POUR LA MESURE D'HTO ET HT

M.J. WOOD and R.G.C. McELROY

This work was co-sponsored by Canadian Fusion Fuels Technology Project

Chalk River Nuclear Laboratories Laboratoires nucléaires de Chalk River

Chalk River, Ontario

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RÉSUMÉ

On a construit et éprouvé un système simple d'échantillonneurs "mesure-bulles" à pouvoir de séparation. Ce système comprend deux échantillonneurs "mesure-bulles" pour piéger l'HTO, un réacteur pour oxyder l'HT, une deuxième séries d'échantillonneurs "mesure-bulles" pour collecter l'HT nouvellement oxydé, une pompe et un débitmètre. Le réacteur utilise un catalyseur commercial basé sur la technologie du catalyseur étanche à l'eau des LNCR. L'échantillonneur convient à l'utilisation comme échantillonneur de cheminée. Son utilisation pour la surveillance locale à de faibles niveaux de tritium est moins satisfaisante en raison de la retenue d'eau par le lit catalytique.

Recherche en dosimétrie
Laboratoires Nucléaires de Chalk River
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ABSTRACT

A simple discriminating bubbler system was built and tested. The system consisted of a pair of bubblers to trap HTO, a reactor for oxidizing the HT, a second set of bubblers to collect the newly oxidized HT, a pump and flow meter. The reactor uses a proprietary catalyst based on CRNL wetproof catalyst technology. The sampler is appropriate for use as a stack sampler. Its use for area monitoring at low tritium levels is less satisfactory due to water holdup in the catalyst bed.

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INTRODUCTION

A common method of measuring HTO concentrations is through the use of gas washing bottles (bubblers). Air is pumped through a pair of bubblers, filled with water (or other appropriate solvent) for a known period of time at a known flow rate and then the average HTO-in-air concentration is calculated from the total activity collected in the bubblers. This method gives a measure of the HTO-in-air concentration, but not the HT-in-air concentration, because only the HTO is absorbed in the water to any appreciable extent.

In many cases, such as around heavy water reactor sites, most of the tritium released is in the oxide form. In other environments, such as tritium extraction and handling facilities, or accelerator facilities in which tritium targets are being used, elemental tritium could be a significant fraction of the total tritium released. For these latter facilities, at least, both HT and HTO should be measured.

A common approach is to add a second stage to the basic sampling system. The second stage consists of a reactor for oxidizing the elemental tritium and a second set of bubblers to collect the newly oxidized tritium. The reactor is usually a heated catalyst bed and often requires the addition of hydrogen to improve recombination efficiency.

This report describes the use of a proprietary catalyst, based on CRNL wetproof catalyst technology, in the reactor or oxidizer. The CRNL catalyst should be capable of operating at room temperature without supplemental heating, in the moist atmosphere at the output of the initial bubblers, and without the addition of hydrogen carrier gas. The investigation being reported was to determine if these advantages are, in fact, realized.

DESIGN

There have been several discriminating tritium samplers designed over the years [1],[2],[3],[4]. Most of these have been designed for monitoring environmental levels of tritium. Sensitive systems for environmental monitoring do not use bubblers, since any water originally in the bubbler dilutes the tritium being collected, which in turn reduces the sensitivity. Most environmental samplers use moisture traps to collect HTO, usually molecular sieves or silica gels. When a drier is used, more complicated laboratory procedures are necessary to retrieve the water collected in the traps. Using bubblers to collect the sample eliminates the need for a water retrieval system.

The design investigated was simple; it consisted of two bubblers in series, followed by the reactor, two more collecting bubblers in series, a pump, and a flow meter (fig. 1). The reactor was made from a 60 cm length of 2.54 cm o.d. stainless steel tube with Swagelok fittings on either end. The pipe contained 100 g of catalyst, with a porous stainless steel fit at either end.

The catalyst is proprietary and was prepared to meet our specifications by the Chemical Engineering Branch of the Chalk River Nuclear Laboratories. Our specifications were for a catalyst capable of greater than 90% oxidation at

temperatures between 10°C and 40°C, at relative humidities approaching 100%, at environmental hydrogen levels and at a nominal flow rate of 1.5 L/min.

The primary design intention was to build and test a sampler system appropriate for compliance monitoring on effluent stacks. For this application, 25% accuracy is usually sufficient. Therefore an HT to HTO conversion efficiency of greater than 90% is more than sufficient. However, higher conversion efficiencies are desirable to avoid a biased underestimation of the HT concentration. The overall sampling accuracy is usually limited by flow measurements and uncertainties in the "stack factor".

Another application where discriminating sampling is desirable is area monitoring in the work place. Bubblers are appropriate for those situations where the concentrations are above environmental, but below those requiring real time monitoring. Although the catalyst was found to be effective, it was clear that it had not been optimized for this application.

EXPERIMENTAL RESULTS

Water holdup in catalyst

The first series of experiments were designed to determine the water holdup in the reactor. HTO was used as a tracer. A known concentration of HTO at a controlled dew point was pumped through the reactor until the HTO concentration at the reactor output was the same as the concentration at the input. The reactor was then flushed with air at the controlled dewpoint until all the HTO was flushed from the catalyst. The total HTO removed from the reactor was thus measured. From this measurement the total water holdup in the reactor could be calculated. This procedure was repeated for several different dew points and the relationship between dew point and the water holdup was determined. Experiments at high humidities were not carried out since ion chambers were used to measure the input and output tritium concentrations. Flow-through ion chambers of sensitivities appropriate to measure tritium become inoperative in very humid conditions.

The water content of the reactor at high dew points was extrapolated from the experiments at lower dew points. Figure 2 shows the measured relationship and shows that the amount of water held up in the catalyst is in the order of a few grams per 100 grams of catalyst at high humidities.

Time response of reactor to T_2

The time response of the reactor was measured at room temperature at a flow rate of 2.3 L/min. A T_2 in nitrogen mixture (at about 10 mCi/m^3) was drawn from a glass mixing chamber in which it had been diluted with room air. The sample was pumped through a bubbler to humidify it and to remove any HTO that might be present. The sample was then routed through the catalyst. Since the air stream coming out of the catalyst was very humid an ion chamber could not be used to measure the tritium coming out of the catalyst. A flow cell and scintillation counter were used to monitor the tritium at the catalyst output. The sample flow then went through a wet test meter, before being exhausted.

The time constant was found to be 1.5 hours.

This value is consistent with the time required to exchange the water held up in the catalyst. Within the accuracy of the experiment, the approach to equilibrium was exponential. There is no evidence for a significant extra time constant. The experiment was performed at a HT concentration of 3 mCi/m^3. The time constant associated with the water exchange should not be concentration dependent. In spite of these results and comments, when we attempted very low level measurements, we did observe long memory times. See section 3.5 below.

Efficiency of Catalyst

The flow system used for determining the conversion efficiency of the reactor is shown in fig. 3. After several preliminary experiments it became obvious that to test the system at different ambient temperatures, it was necessary to have the entire system in an environmental chamber. A large incubator was modified to accommodate the reactor efficiency experiments.

The system (fig.3) was left running overnight at each temperature to ensure that the catalyst was in equilibrium at the appropriate dew point. The following day, the efficiency of the catalyst was measured at different flow rates, starting at the higher flow rates and going down. A mixture of T_2 in argon (about 7 mCi/m^3) was diluted with room air. It was drawn from the glass mixing chamber, through a drying cartridge, an ion chamber, a bubbler, the reactor, a second drying cartridge, a second ion chamber, and a wet test meter before being exhausted into a fume hood. The T_2 concentration in the sample flow was between 50 and 200 $\mu Ci/m^3$, depending on the flow rate. The flow was controlled by varying the voltage on the d.c. pump. The first drier removed any HTO that may have been in the T_2 supply. The first ion chamber measured the T_2 concentration entering the reactor. The bubbler humidified the air stream to simulate the conditions in the discriminating bubbler system. A drier was then used at the output to remove the water vapour (HTO and H_2O) coming out of the catalyst. The second ion chamber then measured the T_2 that came through the system unoxidized. The wet test meter was used to measure the flow through the reactor. In the initial experiments, a bubbler was also installed prior to the wet test meter as a check on the efficiency of the final drier.

The efficiency of the catalyst was calculated from the T_2 input and output measurements. Efficiency measurements were made at flow rates in the range of 1 to 2 L/min. Linear regressions were performed on the efficiency measurements with the y intercept forced to (1 - Eff)=1.0. Figure 4 shows the results of these measurements.

Effect of hydrogen carrier on catalyst efficiency

A single test was conducted to determine the effect on the efficiency of the catalyst when a hydrogen carrier was added to the sample flow. The same experimental arrangement used in the efficiency experiments (fig. 3) was used, except for the addition of a hydrogen flow into the mixing chamber. The total flow rate was 1.9 L/min.

This experiment was not explicitly temperature controlled. It was performed in the laboratory at an ambient temperature of approximately 23°C.

The sampling pump was turned on with the T_2 and H2 supplies turned off. After several minutes the T_2 supply was turned on, resulting in a T_2 concentration at the input to the catalyst of about 9.6 MBq/m^3 (260 μCi/m^3). The T_2 measured at the output of the catalyst was about 930 kBq/m^3 (25 μCi/m^3), that is, about 10% of the input concentration. The conversion efficiency was therefore about 90%. Hydrogen carrier was then introduced to increase the hydrogen content of the sample stream from ambient levels of approximately 0.5 ppm up to approximately 2 500 ppm (0.25%). The T_2 concentration at the output dropped to less than the 3.7 kBq/m^3 (1.0 μCi/m^3), which indicates a conversion efficiency of greater than 99%. The introduction of a hydrogen carrier definitely improved the performance of the catalyst.

Field Test Results

An attempt to field test the bubbler system was made in the Dosimetric Research Branch's FINS (Fast Intense Neutron Source) accelerator room. The HTO levels were ~6 kBq/m^3 (1.6 μCi/m^3) and the HT levels were ~200 Bq/m^3 (0.05 μCi/m^3) at the time our measurements were being made, as determined by Brown and Workman using an environmental sampler incorporating a molecular sieve column, a custom palladium sponge catalyst and a hydrogen carrier gas. Our system had no difficulty detecting the HTO concentrations at this level. While our HT measurements were of the same order of magnitude as those measured by Brown and Workman, only poor correlation was observed between the two sets of HT measurements. We feel the reason for this was HT contamination of the catalyst, as we had previously been using significantly higher levels of HT in our efficiency experiments. We did not observe consistent results. As the HT levels were so low it was not a fair test of the sampling system. No other appropriate areas in which to conduct field tests were identified.

DISCUSSION

The ability of the bubbler system to discriminate between HT and HTO is characterized by two parameters: 1) the amount of HT trapped in the first set of bubbler and thus counted as HTO and 2) the amount of HTO not trapped in the first set of bubblers but subsequently trapped in the second set of bubblers and thus counted as HT.

The amount of HT trapped in the bubblers is limited by the solubility of hydrogen in water. Further, any HT that does dissolve in the first bubblers

can be removed by purging with clean air prior to counting. Thus the counting of HT as HTO is not a serious problem.

The amount of HTO not trapped in the first bubblers and thus subsequently counted as HT is determined by the efficiency of the bubblers. It is quite reasonable to expect greater than 95% of the HTO in a sample stream at 1 L/m to be trapped in a pair of series bubblers, using a 24 hour sampling period [5]. (For very short sampling periods trapping efficiencies of greater than 99% can be expected for a pair of series bubblers at 1 L/min.) The humidity of the air being sampled, however, must be considered when long sampling periods are used. That is, the collection efficiency is impaired if the bubblers begin to dry out. If greater discrimination is needed, either more bubblers in series or a shorter sampling period should be used.

Even though there is an appreciable time constant associated with the sampler, this is not likely to be a problem with most stack monitoring applications. Also, for many, but not all, area sampling applications, long time constants are acceptable.

The time constant can be decreased by increasing the flow rate. For small increases in flow rate, the time constant will be inversely proportional to the flow rate. For very large increases, the decrease in time constant will be less than predicted because of the drop off in efficiency of the input bubblers. This may also affect the discrimination. The other problem with operating the system at a higher flow rate follows from the data presented in figure 4; the reactor's efficiency drops off with increased flow rate. There are two ways to overcome this difficulty:

1. Heat the reactor directly. Extrapolating from the measurements shown in fig. 4, heating the reactor to 40^{o} C or more would ensure conversion efficiencies of greater than 95% at 2 L/min. The heat could be supplied by an electrical heating jacket.

2. Add a hydrogen carrier. From our single experiment it is evident that a hydrogen carrier, bringing the hydrogen content of the sample flow up to 0.25 %, results in a marked improvement in the reactor's conversion efficiency. Further experiments would be necessary to determine more quantitatively the effect of the hydrogen carrier.

However, the primary advantage of using the wetproof catalyst is to avoid the use of furnaces or carrier gases.

Another approach would be to use more catalyst to allow operation at higher flow rates. However, we expect the time constant to vary proportionately with the amount of catalyst because the amount of water absorbed should vary proportionately with the amount of catalyst. Thus, it seems that no significant improvement is possible via this route.

The sensitivity of this sampler is limited by the use of bubblers which dilute the sample collected. The use of bubblers was a fundamental decision which influenced the design of the particular catalyst used. It was not within the scope of this work to test this particular catalyst with other collection

methods such as silica gel or molecular sieve. However, it is clear that water retention would have to be carefully considered in choosing this catalyst for such an application.

CONCLUSIONS

Overall, the discriminating bubbler system worked as designed. For the amount of catalyst contained in our reactor, the oxidation efficiency was a little less than desired. However, acceptable performance at the $\pm$ 10% level could be obtained for flow rates less than 1 L/min at ambient temperatures between 10°C and 40°C and at ambient hydrogen levels. The oxidation efficiency could be increased by the use of more catalyst. The resulting system would be expected to have a somewhat longer time constant.

The original design was for a differentiating tritium sampler for compliance monitoring on a stack. The system described is appropriate for this use. It is less appropriate for area monitoring because of the long time constant and memory effects. However, the described system was not optimized for this use.

Other discriminating sampling systems are available that are more sensitive. But the increased sensitivity is achieved by foregoing the use of bubblers in favour of a nondiluting collector. These systems involve a more complicated analysis procedure, and often require the use of a carrier gas.

Samplers using heated catalyst beds are often used for compliance monitoring on stacks. These samplers require a furnace for their operation and may also require a carrier gas. Their sensitivities are determined by the collection method used.

The selection of a sampling system for mixtures of HT and HTO will depend upon the particular application. For many applications, a sampling system based on the CRNL wetproof catalyst would be appropriate.

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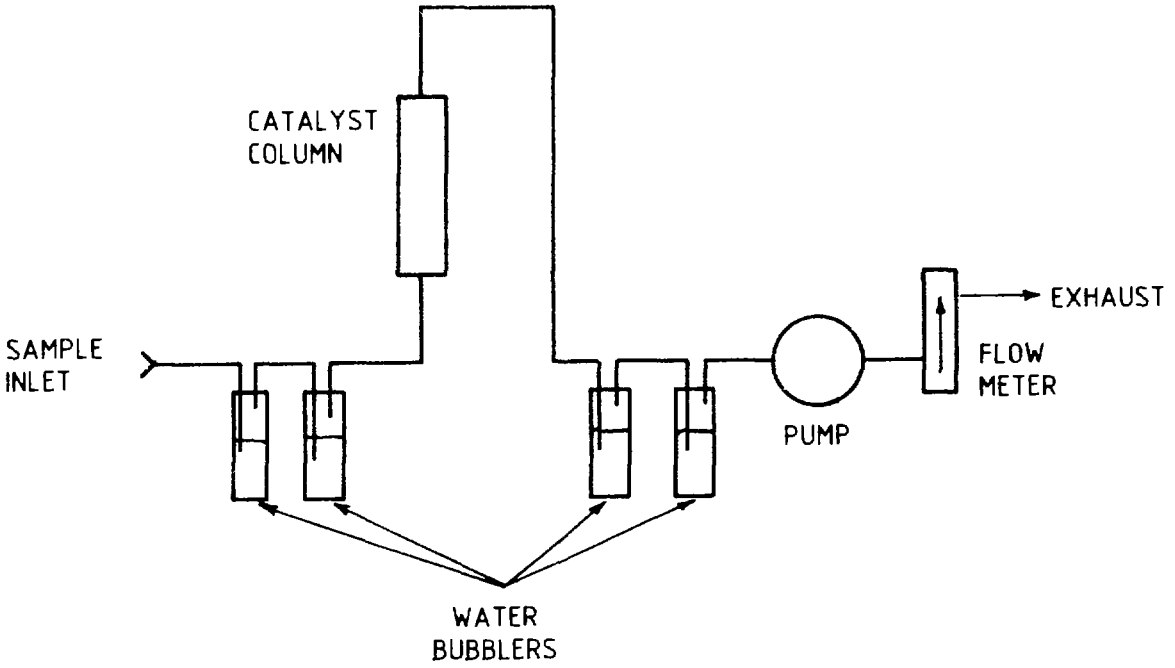

FIGURE 1. Simple discriminating bubbler system.

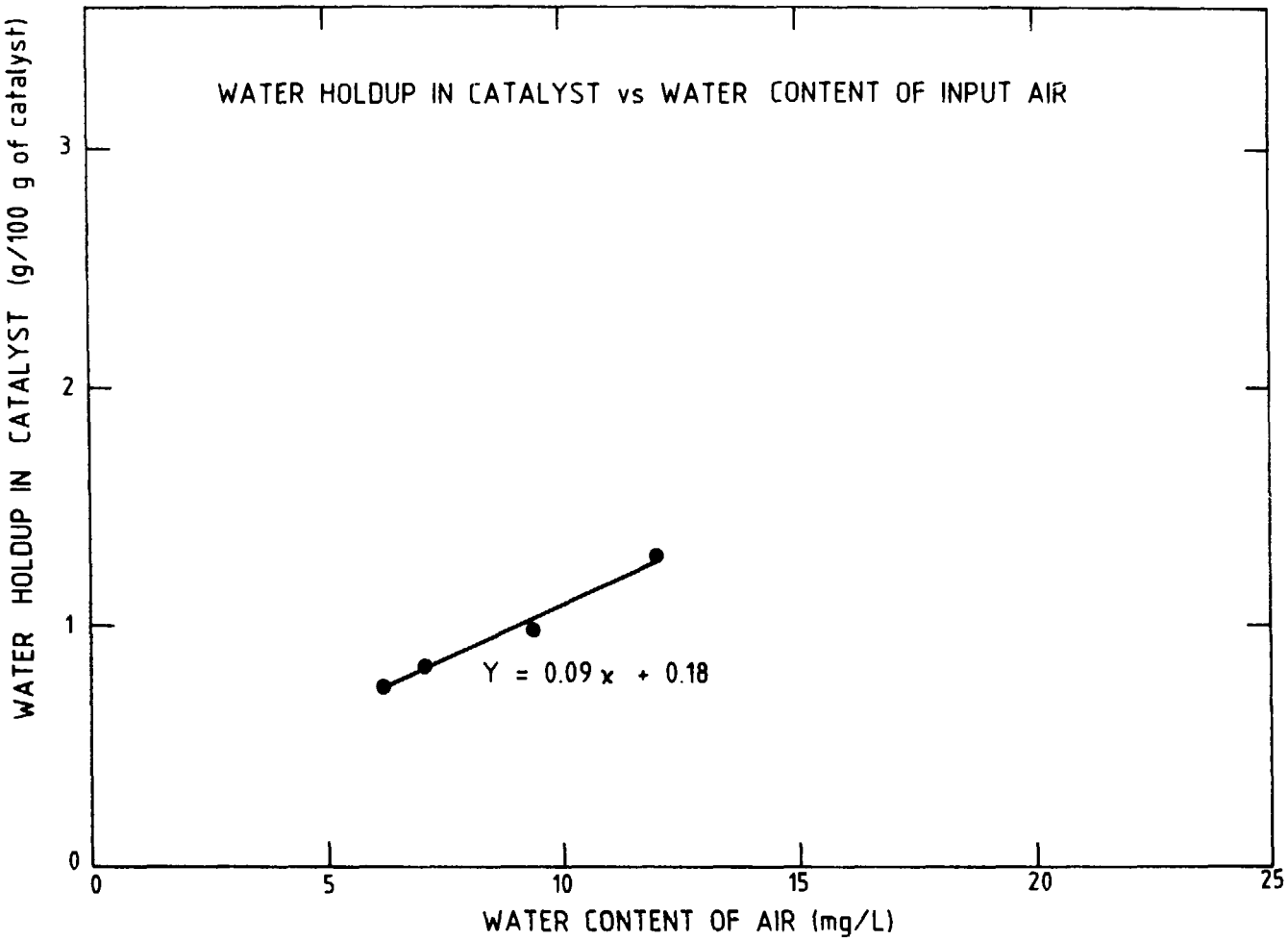

FIGURE 2. Water retention of catalyst as a function of dew point.

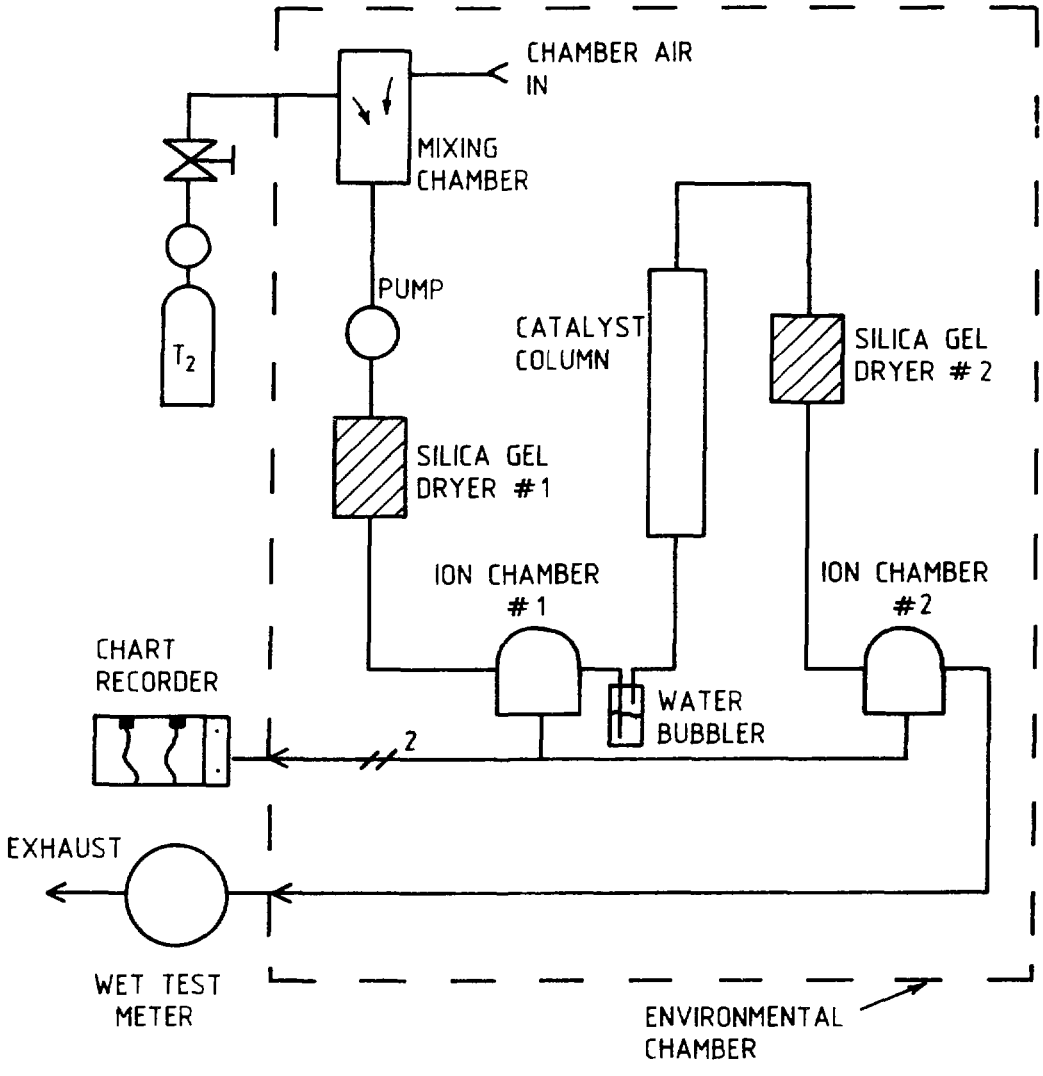

FIGURE 3. Flow system for determining efficiency of catalyst column.

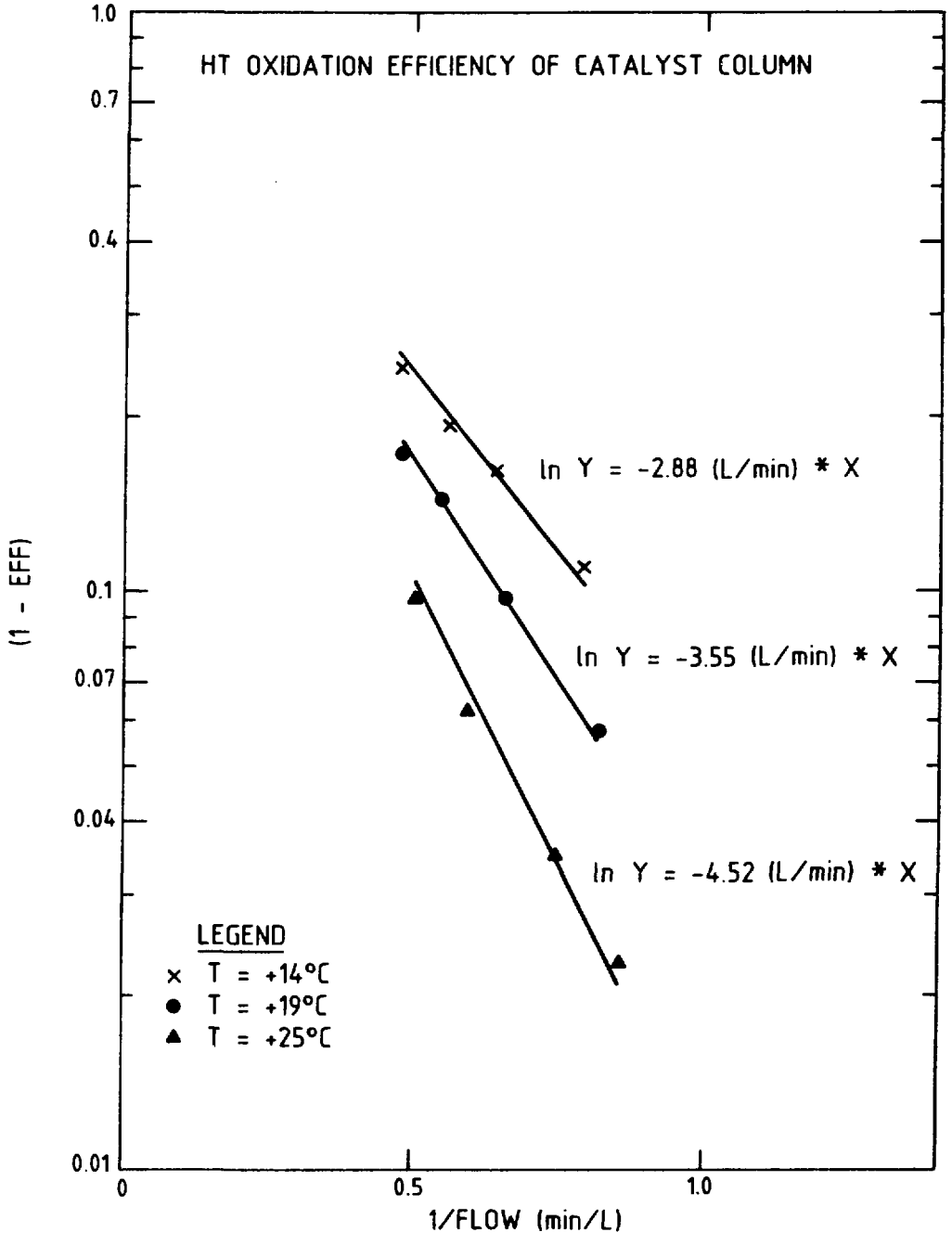

FIGURE 4. Reactor inefficiency vrs. 1/flow rate.

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