

MASTER

**A CONTINUOUS REALTIME RADIOIODINE MONITOR EMPLOYING
ON-LINE METHYL IODIDE CONVERSION**

by

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I. INTRODUCTION

The radioiodines are the most environmentally significant airborne emission from nuclear facilities. Accordingly, charcoal and silver zeolite adsorption media are commonly used to filter the off-gases. A continuous, real-time radioiodine monitor has a direct application to verify the efficiency of the charcoal or silver zeolite off-gas filters and to provide documentation of radioiodine emissions under both normal and abnormal operation. Direct detection by photon spectroscopy can be hindered by the simultaneous release radioisotopes of krypton and xenon. Therefore, the separation of the radioiodines from noble gases is needed before detection by photon spectroscopy.

An integrated ^{14}C , ^{129}I , and ^{85}Kr monitor was proposed by Fernandez, et al.¹ (Figure 1) that separates ^{129}I from ^{85}Kr by selective permeation across thin silicone rubber membranes. Subsequent studies of the permeation of CH_3I and I_2 through silicone rubber membranes demonstrated that I_2 transport across the membranes is too slow to be useful in a realtime monitor. Transport of methyl iodide, however, is rapid and gives a separation factor of greater than 100 from ^{85}Kr .

As a significant fraction (approximately 1/4 to 1/3) of the total iodine emissions from nuclear facilities was found to be elemental,² a method of on-line conversion of elemental iodide to methyl iodide is needed for selective permeation to be successful. The following discussions present the results of efforts for on-line conversion of I_2 to CH_3I .

II. REACTION SCHEME

The method of on-line conversion investigated is the reaction of the methyl radical with I_2 in the following reaction sequence:



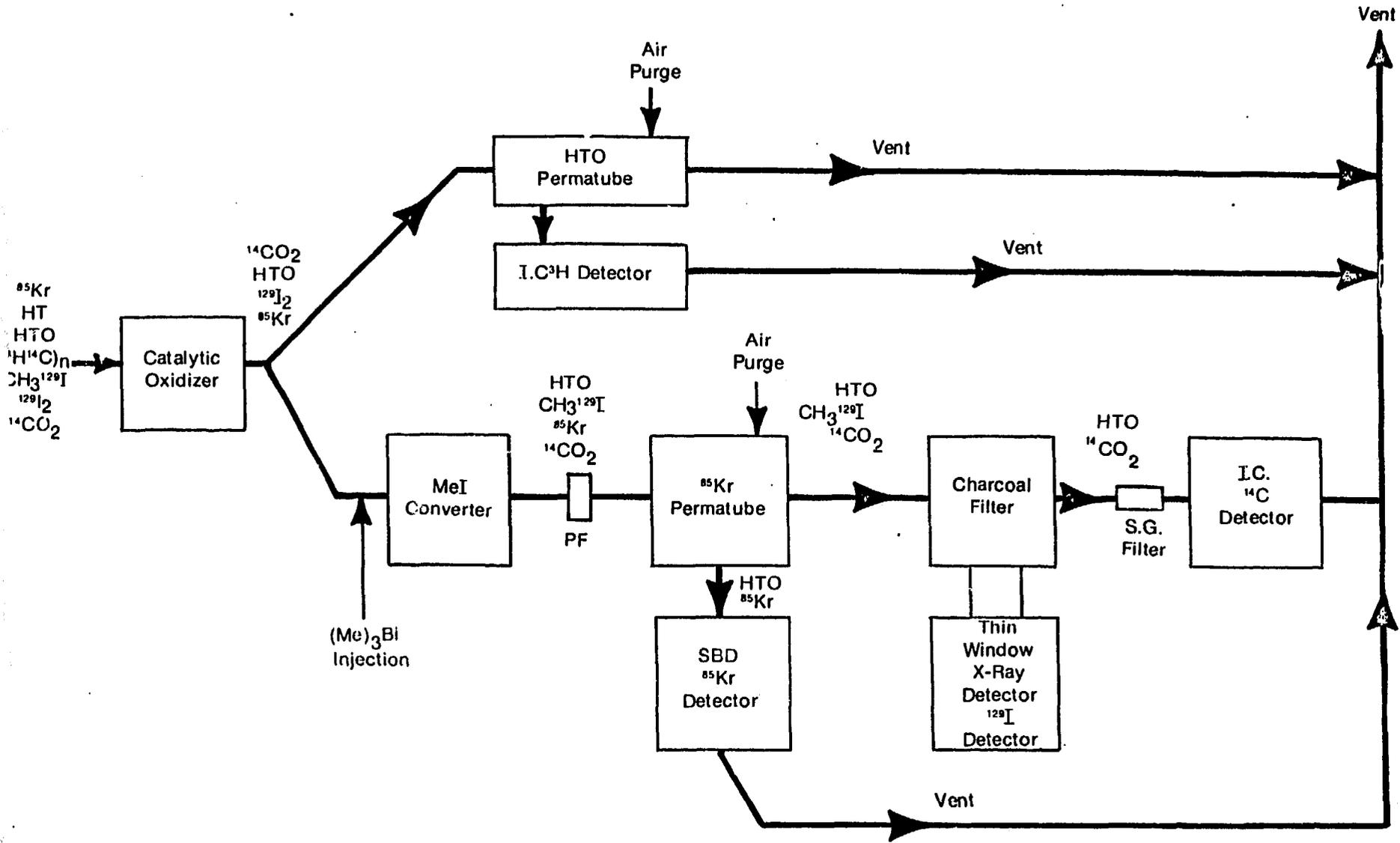


Figure 1. Integrated Monitor Flow Chart.

An external source of methyl radical is required to initiate reaction 1 through 3. To be useful, the source of methyl radical must:

- a) generate a large number density of high purity methyl radical in a sample stream with residence times on the order of 1.0 to 0.1 seconds;
- b) generate methyl radicals with high purity at absolute pressures greater than 600 torr to avoid unknown side reactions;
- c) be portable and adaptable to a gas flow apparatus.

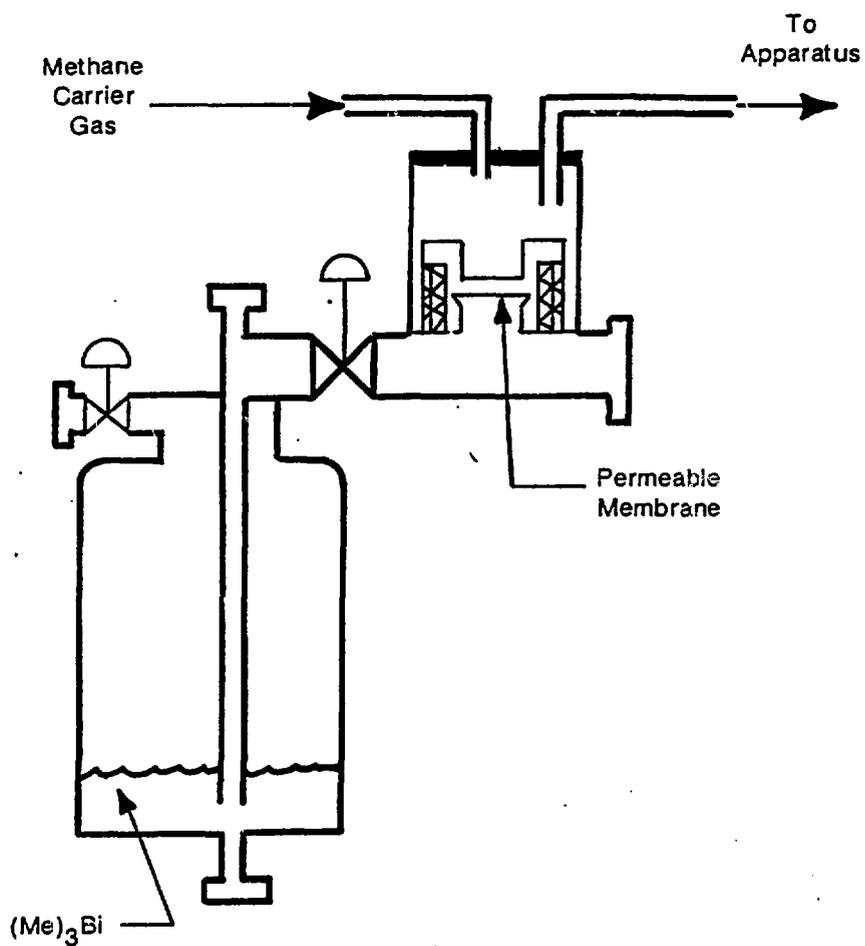
The generation of methyl radicals by the thermal decomposition of organic³ and organometallic compounds⁴ has been reported for more than fifty years. More recently,⁵ thermal decomposition of dimethylzinc, dimethylmercury, and trimethylbismuth has been used for high purity sources of methyl radicals. For this study, trimethylbismuth was selected because of its higher vapor pressure, i.e., high number density (molecules/cm³) at saturation and its lower pyrolysis temperature.

The apparatus designed to introduce the trimethylbismuth upstream of a pyrolysis chamber is shown in Figure 2. The trimethylbismuth in the headspace above the liquid permeates at a constant rate across the membrane and is transported to the sample stream by the methane carrier gas. The methane produces a dry, reducing atmosphere to prevent premature decomposition of the pyrophoric trimethylbismuth.

III. LABORATORY EXPERIMENTS

The objectives of the laboratory experiments were to optimize the conversion of I₂ to CH₃I by determining the effect of the following factors on conversion:

- a) I₂ concentration;
- b) pyrolysis temperature;
- c) residence time within pyrolysis zone;
- d) the free radical scavengers O₂, H₂O, NO.



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Figure 2. Trimethylbismuth Injection Device.

The experimental apparatus used to determine these effects is shown in Figure 3. The I_2 concentration was varied by changing the carrier gas flow over the I_2 crystals in the diffusion bulb. A later improvement was effected by replacing the I_2 crystals with an I_2 permeation tube using a silicone rubber tube in the manner of O'Keefe.⁶ Permeation rates on the order of 30-60 $\mu\text{g}/\text{min}$ were achieved with 0.25"X0.50"X4" tubes. The temperature of the pyrolysis zone was controlled using a conventional tube furnace. The pyrolysis zone was filled with a Pt-Pd on alumina catalyst. This catalyst aided in the reaction of O_2 with methane to lower the concentration of this free radical scavenger. Once the O_2 has been consumed, the Pt-Pd on alumina will catalyze the reduction of NO by methane.

The conversion was measured using a modified iodine species sampler developed by Keller, *et. al.*⁷ This modified species sampler contained an IPH (4-iodophenol) bed to collect inorganic forms of iodine such as I_2 , HI, and HOI; and an impregnated charcoal bed to collect organic iodides. Carrier-free ^{125}I was generated as I_2 or CH_3I using the methods published by Emel, *et al.*⁸ The conversion of I_2 to CH_3I was determined by analyzing the two beds for the characteristic ^{125}I characteristic x-rays with a Low Energy Photon Spectrometer (LEPS).

IV. RESULTS

The results of the experiments to determine the effect of I_2 concentration on conversion efficiency are shown in Table 1. The doubling

TABLE 1

EFFECT OF I_2 CONCENTRATION ON CONVERSION EFFICIENCY		
I_2 Concentration	Number of Runs	Conversion Efficiency in Percent
Carrier-free	7	43±2
15 mg/M ³	5	82±2

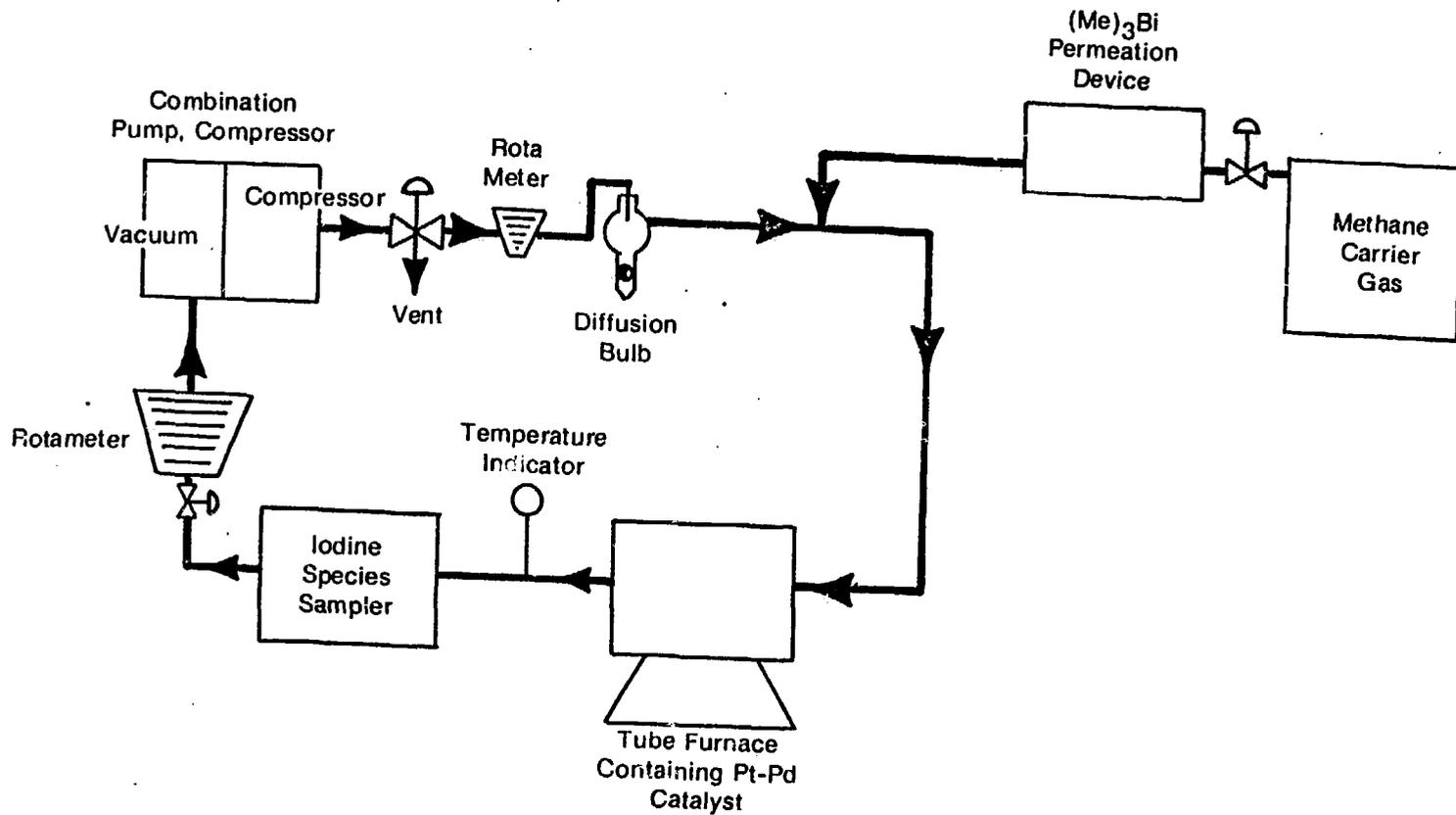


Figure 3. Conversion Efficiency Test Apparatus.

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of the conversion efficiency upon adding I_2 carrier to the sample stream is hypothesized to occur by the following mechanism. Instead of the recombination reaction of equation 2, an activated I' atom is more likely to encounter a methane carrier gas molecule, abstract a hydrogen atom, and initiate the following series of reactions:



The stoichiometry of the above reaction sequence would predict a conversion efficiency of one half that at carrier levels where recombination dominates, as was actually observed.

For this reason, an I_2 permeation tube was incorporated into the monitor to maintain the I_2 concentration in the reaction zone at carrier levels.

The effect of pyrolysis temperature on carrier-free conversion efficiency is shown in Table 2. The conversion efficiency appears to be relatively insensitive to temperature in the range of 300°C to 500°C,

TABLE 2

EFFECT OF PYROLYSIS TEMPERATURE ON CARRIER-FREE CONVERSION EFFICIENCY

<u>Temperature</u>	<u>Number of Runs</u>	<u>Conversion Efficiency in Percent</u>
300°C	3	40+4
500°C	4	43+4
700°C	1	15+5

but drops off sharply at 700°C. The reason for this is unknown, but may be due to either pyrolysis of the formed methyl iodide or the formation of H_2O (a known radical scavenger) from oxidation of the methane carrier gas. A design temperature of 500°C was selected for the monitor.

The effect of residence time on the conversion efficiency was examined by varying the flowrate through a 7cc fixed pyrolysis zone at 500°C. The results are shown in Table 3. There appears to be no significant dependence on residence time in the range studied. A design

TABLE 3
EFFECT OF RESIDENCE TIME ON CARRIER-FREE CONVERSION EFFICIENCY

<u>Residence Time in sec.</u>	<u>Number of Runs</u>	<u>Conversion Efficiency in Percent</u>
0.21	7	43+2
4.67	3	46±3

residence time of 0.21 seconds was used to minimize the monitoring system response time.

The effect of NO on the conversion efficiency was observed by directing known amounts of NO into the sample stream and measuring the resultant conversion. The results are shown in Table 4.

TABLE 4
EFFECT OF NITRIC OXIDE ON CARRIER CONVERSION EFFICIENCY

<u>NO Concentration in ppm</u>	<u>Conversion Efficiency in Percent</u>
0	83+2
12	16±3
186	10±2
36000	2±2

Obviously, the reduction of NO to N₂O or N₂ was inefficient. Therefore, the Pt-Pd catalyst was replaced with a rhodium on alumina catalyst. This catalyst was prepared by evaporating a 10% rhodium nitrate solution on 8-16 mesh alumina and baking at 500°C overnight. With this new catalyst, a conversion efficiency of 98±1% was obtained under the previously determined design conditions in NO concentrations up to 25%. The long-term stability of this catalyst has yet to be determined.

V. CONCLUSIONS

The major conclusions drawn from this work are the following:

- 1) Conversions of I_2 to CH_3I as high as 98% are possible only at carrier levels (15 mg/m^3).
- 2) The conversion efficiency is independent of temperature in the range of 300°C to 500°C .
- 3) The conversion is independent of residence time in the range of 0.21-4.67 seconds.
- 4) NO interference can be eliminated by using a rhodium on alumina catalyst.
- 5) Based on the developmental data, the integrated monitor shown in Figure 4 is ready for in-plant demonstration.

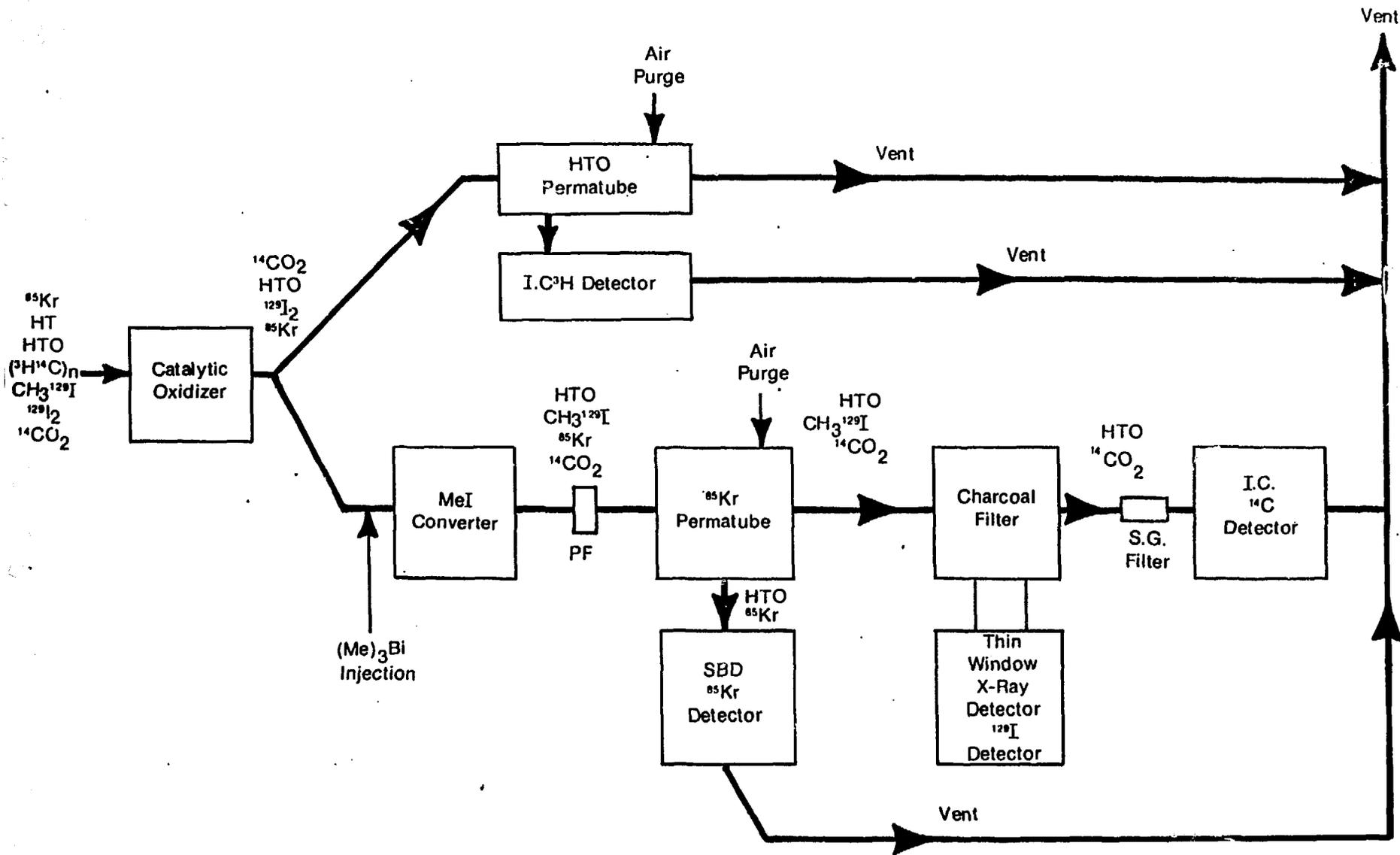


Figure 4. Integrated Monitor Flow Chart.

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