USING PERMEATION TUBES TO CREATE TRACE CONCENTRATION MOISTURE STANDARDS

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ABSTRACT

Moisture standards have traditionally been prepared by techniques which saturate the gas at known conditions. Preparing standards at trace concentrations (low ppm, ppb) requires saturation at cryogenic temperatures. Standard techniques require large cumbersome apparatus, and are generally not well suited for field use. Additionally, the method cannot be used with condensable gases frequently of industrial interest.

Permeation tubes can be used to dispense precisely known quantities of moisture. Using permeation tubes to make standard additions of moisture to a flowing gas stream offers a technique which can be used in the field and in a wide range of matrix gases.

This paper discusses the permeation tube method and special techniques needed to use permeation tubes to created trace concentration moisture standards.

INTRODUCTION

In the global marketplace where product quality and competitiveness are brought into sharp focus, the need to monitor for trace concentrations of moisture in a wide variety of gases is rapidly growing. Even trace concentrations of water vapor in process gases can affect the product quality and/or yield in many processes. Examples include such diverse areas as the production of micro electronic devices, the manufacture of high grade polymers and other chemical products, and welding and heat treating of high alloy components subject to extreme stresses such as those found in jet aircraft engines.

Unfortunately, there are no true absolute analytical systems for moisture which can be applied to this variety of applications. In most cases the response is affected by the background gas, and all are subject to poisoning by certain contaminants. This is especially true as the concentrations to be measured go to sub ppm levels. In some cases the analyzer will cease to respond when exposed to a dry sample for an extended time. Thus, there is a critical need for a generally applicable method of preparing trace concentration moisture standards, and particularly one which can be used in industrial "field" conditions.

There is a second, and equally difficult, collateral problem. That is, assuming one has a perfect moisture standard, how does one insure that the standard is not changed in delivering it to the instrument to be calibrated? The pervasiveness of water in our atmosphere combined with the highly polar nature of the water molecule make the delivery problem at least as difficult as the preparation problem.

Several methods have been used for generating trace moisture standards. In the most absolute method a gas stream is saturated under known conditions. This method establishes an absolute reference point. However, for trace concentrations, cryogenic saturation temperatures are required. As a result, this method is relatively cumbersome to use and is not well suited for field applications. It is also limited to gases which will not condense at the temperatures required to obtain very low concentrations.

Conventional static mixtures do not work for trace concentrations of moisture. Because of the pervasiveness of environmental moisture there is no effective way to predetermine the concentration of the final mixture. Partly, the problem is the storage container itself. While it might be possible to add a known quantity of moisture to a known volume of matrix gas in the container, the contribution of the container itself to the final concentration is not known. It may add or remove moisture to the mixture. Furthermore, the concentration may vary over the life of the mixture due to variations in temperature and pressure of the contents.

Additional uncertainty is introduced with the matrix gas. The matrix itself will contain some residual moisture, and additional unknown amounts may be introduced by the process of transferring the matrix to the container.

The problems outlined above can be largely circumvented by using a "standard addition" technique rather than attempting to prepare and deliver an absolute standard. The standard addition method adds a known amount of moisture to an unknown background. While this does not establish an absolute reference point, it offers the advantage that it can be used under field conditions, and can be applied to a wide variety of background gases.

The key to success for this method is finding a way to add a known amount of moisture to the matrix stream. That is where permeation tubes enter the picture.

THE PERMEATION TUBE METHOD .

Permeation tubes are devices using the permeation of vapors through a membrane, in this case Teflon, to produce a very stable, very low gas flow source. Figure 1 shows a diagram of a basic permeation tube device. Essentially it is a length of Teflon tubing with water sealed inside. Water vapor passes slowly through the tube wall and into the surrounding atmosphere. If we then maintain a flow of clean dry gas over the tube, we add a known amount of moisture to that flow. The rate of flow of moisture emitted from the tube is measured by holding the tube at constant temperature in a stream of dry gas for an extended period of time and periodically weighing the tube to measure the rate of weight loss. Figure 2 shows the basic concept of generating a calibration mixture using permeation tubes. The permeation tube is immersed in the flow of clean dry gas. The permeate and dilution flows combine to form a mixture to which a known amount of moisture has been added. The concentration of this added moisture is given by

$$C = \frac{f}{f+F} 10^6 \qquad \text{Equation 1}$$

where

C is the concentration in ppm.
f is the permeation flow of moisture
F is the flow of dilution gas.

Recall that the flow of moisture from the permeation tube is extremely small, (nanoliters per minute) and the dilution flow is substantially larger, (typically liters per minute). Hence, Eq. 1 reduces to:

$$C = \frac{f}{F} 10^6 \qquad \text{Equation 2}$$

The flow of moisture from the tube is described by the equation

$$f = \frac{k \cdot A \cdot \Delta p}{t} \qquad \text{Equation 3}$$

where

f is the permeation flow
k is the permeability of the membrane to water
A is the surface area of permeation
Δp is the partial pressure difference of water across the membrane
t is the thickness of the membrane

Operating at a fixed temperature, the rate of addition of moisture to the stream can be set by choosing permeation tubes with different areas or thicknesses.

Additionally, the emission rate of any tube can be varied by changing the operating temperature of the tube. Two factors affect the temperature dependence of permeation. First, the vapor pressure of water varies as the temperature is varied, so the partial pressure difference of moisture across the membrane, Δp, will vary exponentially with inverse temperature. The permeability of the membrane also varies exponentially with inverse temperature.

$$k = k_0 \, \mathrm{Exp}\,(-B/T) \qquad \text{Equation 4}$$

where

k_0, B are equal constants
T is the absolute temperature

The flow of moisture from a permeation tube is strongly dependent on the temperature of the tube, so temperature must be carefully controlled to make accurately known standards.

Permeation tubes can be built in a variety of configurations to give a wide range of concentrations. The photo in Figure 3 shows several designs. These range from a very short length of membrane tubing attached to a non-permeable reservoir to large refillable canisters containing many meters of permeation membrane. The very small tubes are used to make low ppb additions. The large canisters can be used to add hundreds or even thousands of ppm to a stream.

Figure 4 shows a typical flow diagram for an instrument used to generate trace concentrations of moisture. The dry dilution gas enters at the lower left of the schematic. This dilution gas is pressure regulated to form a stable reference point for flow control. The dilution flow passes through, a mass flow meter, and then divides into two streams. One stream, controlled at a constant flow rate, passes continuously over the permeation tube and mixes with the moisture emitted by the tube. This stream is kept flowing constantly to keep the emitted moisture purged from the permeation chamber. The second flow will normally be the larger portion of the total dilution flow and can be switched off to save use of extremely dry dilution gas.

In use, the main dilution flow is first switched on and the system allowed to reach equilibrium with the moisture in the dilution gas to obtain a "zero" response. Then, the span solenoid is switched to introduce moisture from the permeation tube to the dilution gas. Flowing this mixture to the analyzer introduces a known level of concentration change. By varying the dilution flow a variety of concentrations changes can be generated.

CALIBRATION BY STANDARD ADDITION

One of the key problems in the calibration of moisture analyzers is the absence of a true zero. The moisture concentration in the dilution stream may be very significant compared to the calibration level desired. Additionally, the calibration system itself may contribute to the background moisture either through out gassing, or from leaks in the system. To compensate for this unknown background we use the method of standard additions.

To use this method, first obtain a response from the analyzer due to the dilution gas alone, i.e., the "zero addition response". Then add the permeated moisture flow to this stream and obtain a response due to the known concentration change. Since the dilution gas concentration is constant, several known addition responses can be obtained by changing the dilution gas flow rate. Using the difference between two known addition responses, calculate the sensitivity S of the system to the known addition.

$$S = \frac{\Delta R}{\Delta C} \qquad \text{Equation 5}$$

where

ΔR is the change in response of the analyzer
ΔC is the change in concentration introduced

Apply this response factor S to the observed response to zero to estimate the original background concentration.

$$C_O = \frac{R_O}{S} \qquad \text{Equation 6}$$

Using this estimate for the background concentration, C_O, the calibration curve can be adjusted to more accurately reflect true concentration. Figure 5 shows this graphical estimation of concentration from standard additions.

If only one standard addition is used to estimate the background concentration, the method would obviously assume the linearity of the response curve through zero. Generally, the error introduced by this assumption is small. Multiple additions can be used to estimate response linearity or define nonlinear response curves. For best accuracy, standard addition concentrations should be large compared to the background concentration

SPECIAL PROBLEMS IN CALIBRATING MOISTURE ANALYZERS

There are several special problems associated with calibrating trace moisture monitors. Of particular significance are (a) assuring low background concentration, (b) excluding all external moisture, (c) obtaining adequate dry-down of the system, (d) transmitting concentration changes to the analyzer, (e) preventing transient shifts, and (f) interfacing to the analyzer.

If the matrix gas to be tested is nitrogen or some other relatively inert gas, a variety of methods maybe used for reducing the background concentration to a very low value. Table 1 shows several options for obtaining very dry streams. Experience has shown that values in Table 1 are conservative, and concentrations lower than those shown are often obtained. When the background (diluent) gas is reactive, however, the choices are much more limited. Usually, molecular sieves are the only effective option for drying these gases.

The exclusion of atmospheric contamination from the mixture is also a very significant problem. If one considers a dry background stream as having one ppb moisture, the contamination potential from air saturated at 20°C is approximately $2.5 \times 10^7 : 1$. The leakage specification for high quality tube fittings is typically 4×10^{-9} cc / sec per fitting. This translates to a contamination potential in 1 l/min. of 0.24 ppb from each tube fitting. We have found, however, that for carefully made tube connections the actual contamination tends to be much lower than that value. Also, we have found no significant leakage difference between Swagelok compression ferrule fittings and VCR face seal fittings. The VCR fittings, however, do offer advantages in that there are no spaces where moisture can be trapped and released slowly over a long period. Additional improvement can be made by immersing the entire system in dry gas.

To obtain good dry-down characteristics the choice of components and materials is of extreme importance. We have found that the materials used in all components must be of high quality, surface area should be minimized, and all components must be thoroughly cleaned of any possible impurities. Tubing used in the system should be internally electropolished. Tubing can be somewhat passivated to moisture adsorption by heating in the presence of high purity nitrogen.

In our work we have found that a key element in obtaining adequate dry-down is knowing what to expect. Figure 6 is a simulation of a typical dry-down curve. In the initial dry-down phase, the reduction of moisture in the system is exponential as would be expected. However, this initial dry-down will often asymptotically approach some unexpectedly high value. Applying heat to the various components in the system will evolve moisture, but when the heat is removed and the temperature of the component returns to ambient, the resulting moisture level will often be unchanged. After an extended period at this level the moisture content in the system may drop rather suddenly, almost step-wise, to a new lower value. This new level will persist for a time and then drop again. Each succeeding step is generally smaller in size than the previous step. The cleaner the system is initially the fewer steps observed. Also, the higher the temperature of the system during dry-down, the shorter time between steps. In drying down moisture generating systems we have found two things that always help: (1) use heat, and (2) be patient. Once a system has gone through an initial dry-down, we find that it is usually much easier to dry the system down thereafter.

Once a system has reached dry-down it is also important to test the system to be sure that it will transmit changes in moisture concentration. Moisture should be sequentially added to and removed from the system to insure that the overall system will respond rapidly to changes in moisture concentration. High quality stainless steel components, if they are clean, will transmit adequately. If a sluggish response is observed, it should be assumed that there is some area in the system that has not been adequately cleaned, or that some undesirable material has been inadvertently included in the system.

Proper use of a permeation system to calibrate trace moisture monitors requires careful consideration of the interface between standards generator and analyzer. Figure 7 shows an interface system which can be used with most moisture monitors. With this arrangement the flow of dilution gas through the calibration unit can be adjusted over a wide range to vary the mixture concentration. A back pressure regulating device holds a constant pressure on the sample line and allows the flow to the analyzer to remain constant regardless of the flow coming from the calibration unit.

Maintaining a constant back pressure on the sample line has a second desirable effect. When pressure in the sample line rises, more moisture is adsorbed by the tubing. This causes a temporary reduction in concentration delivered to the analyzer. Conversely, when the pressure is lowered the sample line releases moisture and causes a temporary elevation in the moisture delivered to the analyzer. Thus, simply changing back pressure on the sample lines can give the appearance of changing moisture concentrations even when the moisture level is constant. Back pressure control eliminates this error source. Similar effects can be caused by changes in the temperature of the sample line. Thus, it is desirable to heat, or at least insulate the sample line so as to minimize changes in temperature.

Some basic guidelines for proper interfacing of the calibration instrument to the moisture analyzer include (a) match the calibration conditions to the sample input conditions, (b) make the calibration gas flow and the analyzer input flow independent, (c) arrange the system so that calibration gas flow is never blocked, (d) use clean, inert tubing and other components in the interface, (e) set up the system so that zero integrity can be assured, (f) run the system under constant back pressure, and (g) keep interconnecting lines at constant temperature.

Some consideration should also be given to the quantity of calibration gas to be delivered. We have found that for most applications delivering a quantity in the range of .5 to 5 l/min. is optimal. At low concentrations there are advantages to using higher flow rates. For example, the contamination concentration caused by any stray leakage is reduced at higher flow rates. Permeation tubes in general can be certified more quickly and more accurately for higher emission rates. High flow rates also tend to speed response of the overall system and shorten the dry-down time. The down side of using high flow rates is that the demand for zero gas is increased.

BACKGROUND GAS CONSIDERATIONS

The emission rate of water from permeation tubes has been found to be essentially independent of the background gas for most gases. With some gases, however, there are interactions between the moisture molecule and the background gas molecules which make it difficult to deliver the standard to the analyzer. In some gases the moisture reacts rapidly with the background gas to form some other compound. An example of this situation occurs with moisture in WF_6. In other cases the moisture and background gas do not actually react but rather associate to form an aerosol, or some other particle-like entity. These pseudo particles tend to stick to the walls of the sample transmission tubing much more aggressively than moisture would in its free form. For these interactive mixtures it is sometimes desirable to set up the system so that the moisture is actually added to a small flow of inert carrier gas and transported in that gas to a junction point right at the analyzer. The reactive dilution gas can then be mixed with the moisture-containing carrier just before the mixture enters the analyzer. Thus, the effects of reaction or association of the water and the background gas are minimized.

SUMMARY

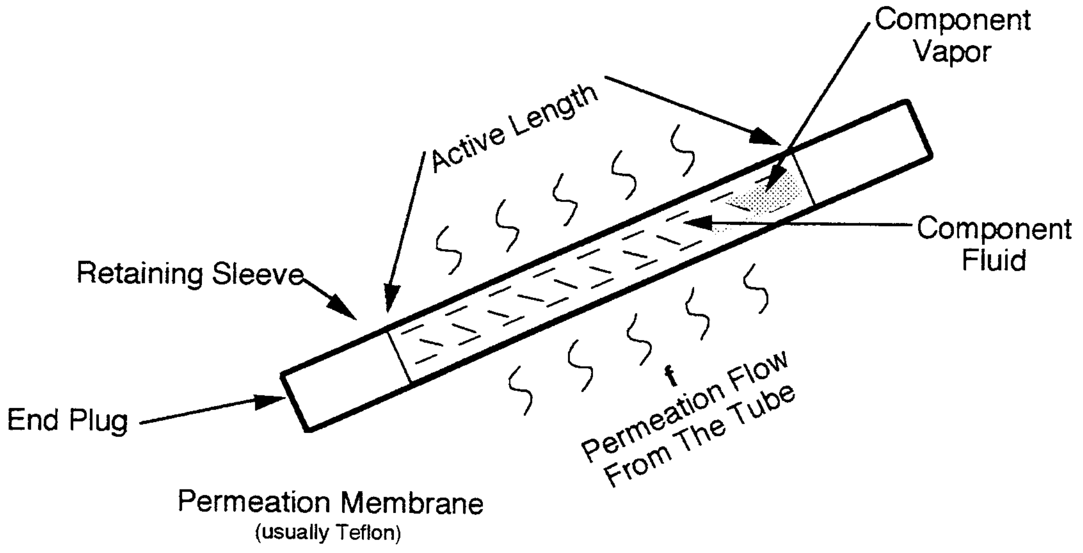
Trace moisture systems need frequent calibration checks to insure their proper operation. Many of these systems tend to drift to zero under very low moisture conditions, i.e., they die of starvation. Because there is no available absolute zero reference for most gases, the method of standard additions is the most practical one to use for moisture calibration. Permeation tubes are a good, convenient source for making known additions to a flowing gas stream. The method can be used over a wide concentration range and with a variety of background gases. Standard addition methods, while they do not establish an absolute reference point, offer the advantage that they are simple to use under field conditions, and can be applied to a wide variety of background gases. The key to this method is that it must provide a means of adding an accurately known change in concentration to a relatively dry background stream.

REFERENCES

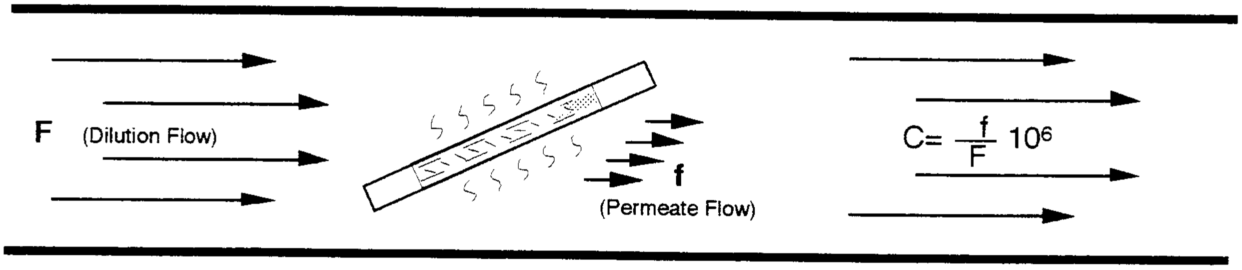
[1] Zatco, Dr. David, and Daniel J. Ragsdale, 1988. Determination of H_2O.In The Part Per Billion Region In High Purity Gases. Paper No. 10249. Presented at the 39th Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy.

METHOD	MINIMUM CONCENTRATION [1]	
NEW MOLECULAR SIEVES	5 - 7	(ppb)
USED MOLECULAR SIEVES	20 - 40	
METAL GETTERS	3	
ORGANO - LITHIUM GETTERS	6	
CRYOGENIC DRYERS	Very Low	

TABLE 1
GENERATING ZERO GAS

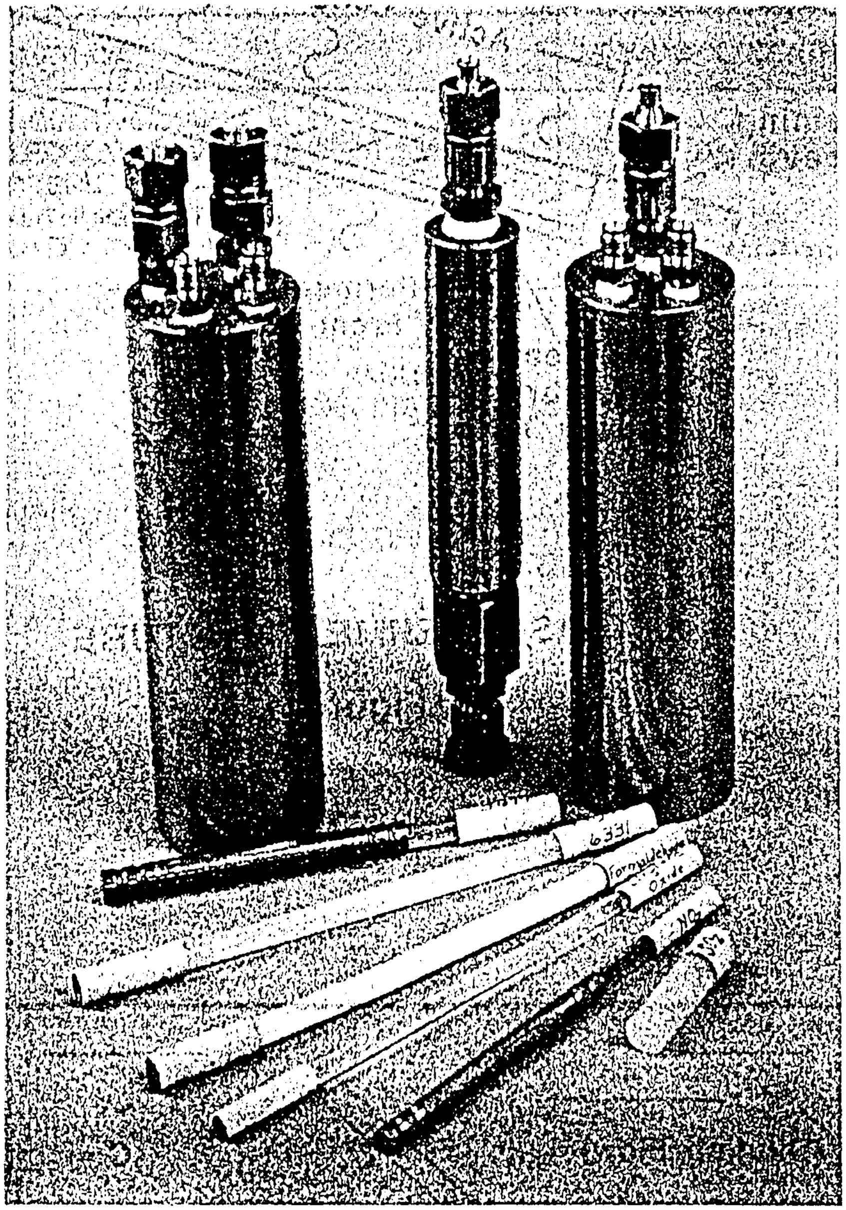


BASIC PERMEATION TUBE
FIGURE 1



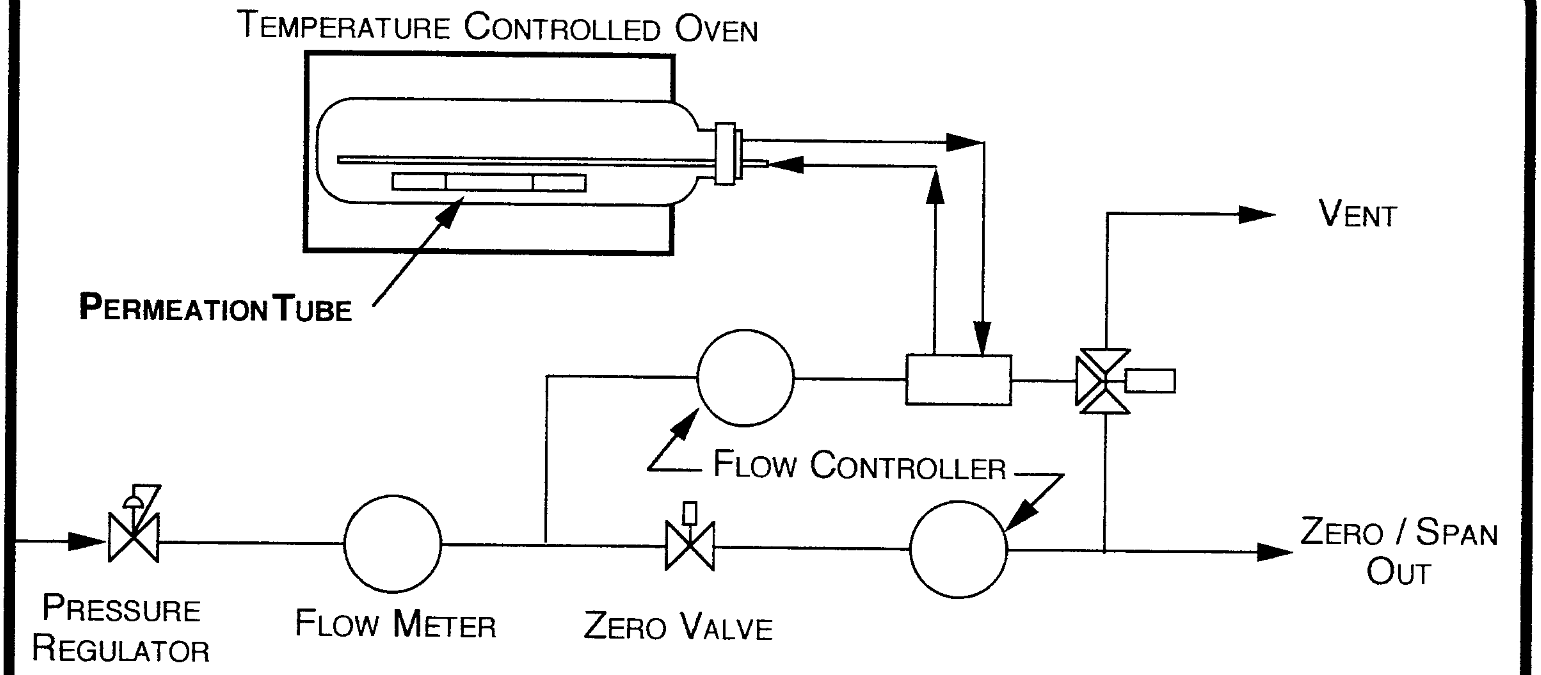
$$C= \frac{f}{F} 10^6$$

USING PERMEATION TUBES TO GENERATE TRACE CONCENTRATION MIXTURES
FIGURE 2

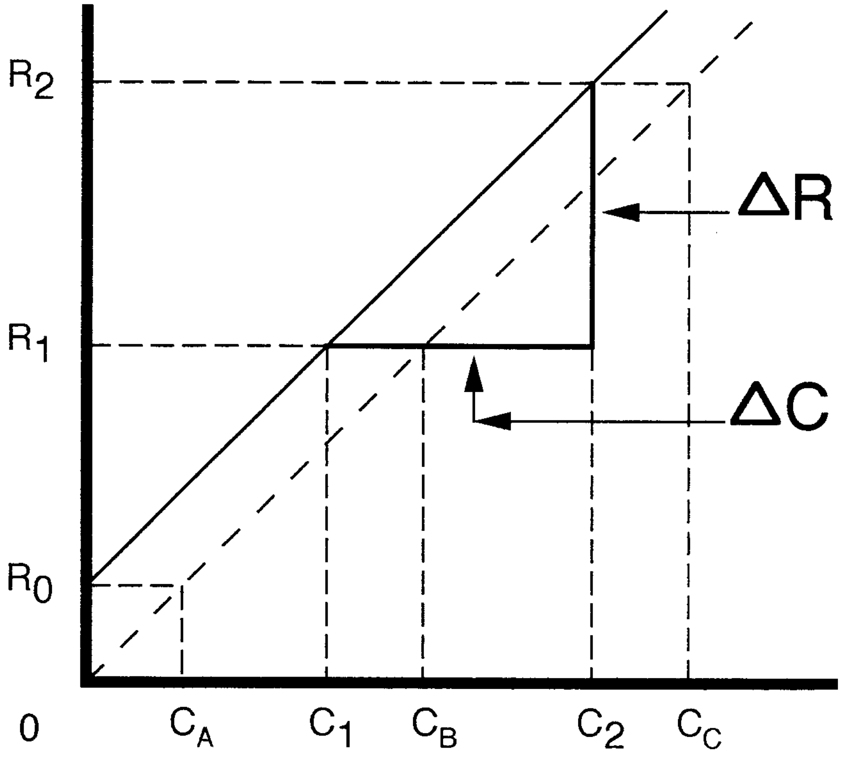


PERMEATION TUBES

Figure 3



FLOW DIAGRAM
MOISTURE STANDARDS GENERATOR
FIGURE 4

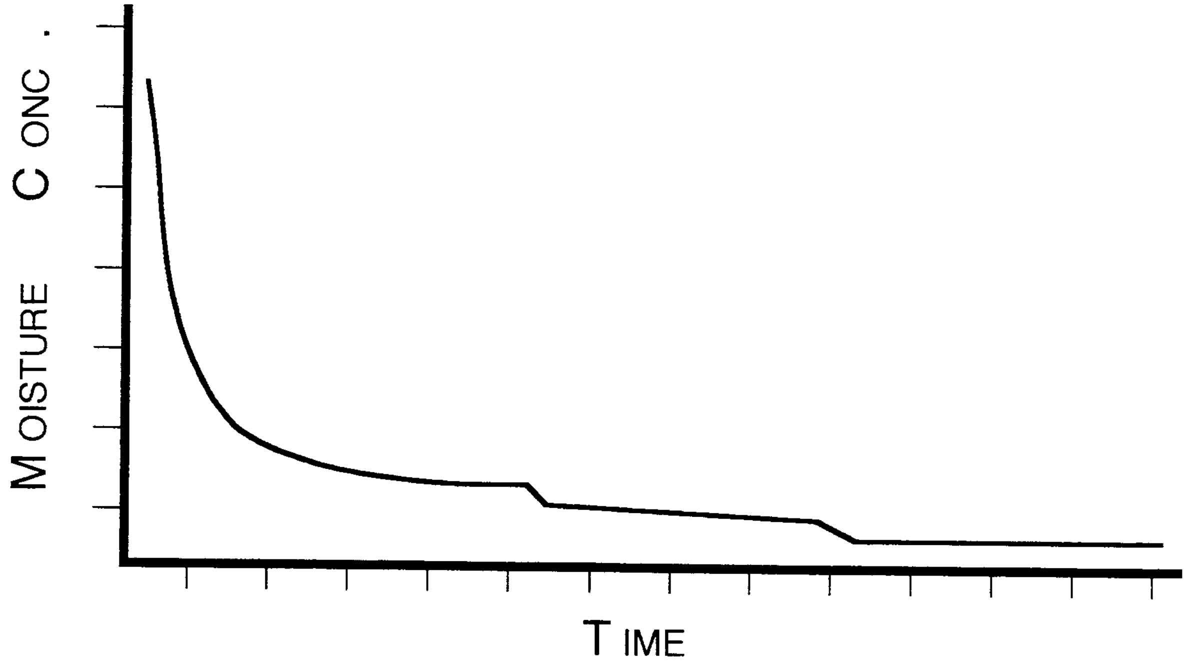


C_1, C_2 ARE STANDARD ADDITIONS

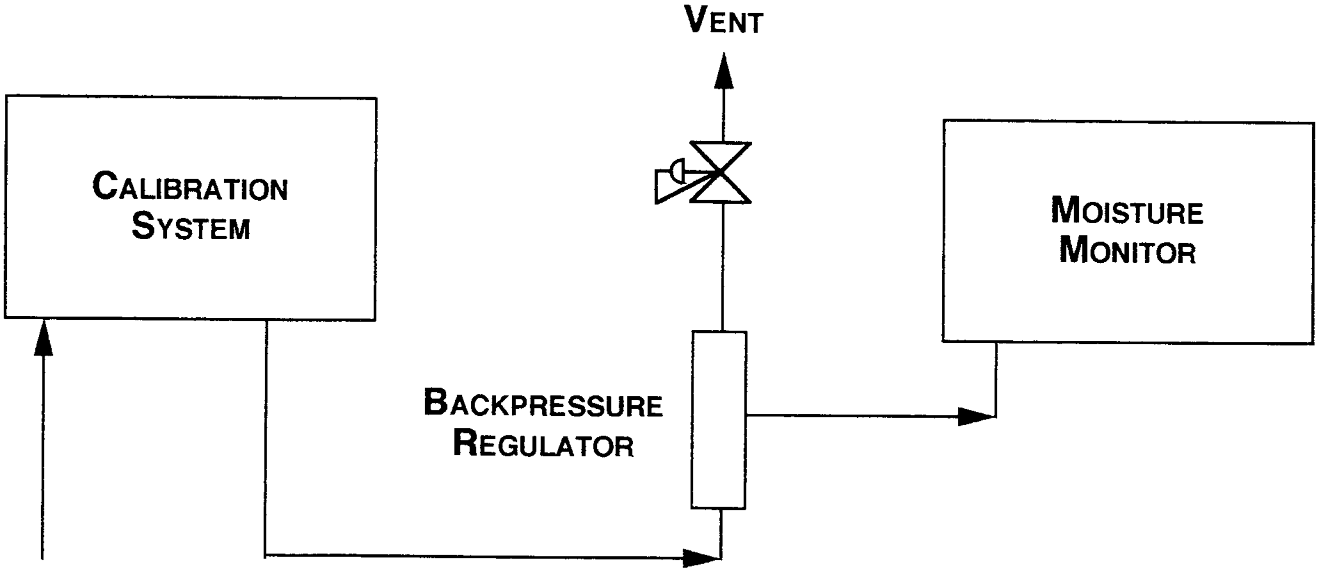
C_A =ESTIMATED BACKGROUND GAS CONC.

$C_B = C_A + C_1$ $C_C = C_A + C_2$

CALIBRATION BY STANDARD ADDITIONS
FIGURE 5



SIMULATED DRY DOWN CURVE
FIGURE 5



INTERFACE SYSTEM
FIGURE 7