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MEASUREMENT OF THE HUMIDITY OF SMALL SAMPLES OF AIR USING GAS LIQUID CHROMATOGRAPHY

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ABSTRACT

The humidity of 4.9 x 10^{-6} m^3 samples of air was measured by GLC. They were captured in a Teflon-lined syringe that is heated to 33°C. The standard deviation of sets of results at -15°C and 20°C dewpoint were 0.8°C and 0.15°C respectively. Samples stored for up to 7200 s tested within 6% of the correct humidity ratio. Correct technique was found to be important.

Nous avons traité dans un rapport précédent de l'emploi de la chromatographie gaz-liquide pour déterminer l'humidité de l'air. Des développpements subséquents du système font le sujet de ce rapport; nous tenons à démontrer comment un échantillon d'air de 4,9 x 10^{-6} m^3 pris au moyen d'une seringue spéciale permettra la détermination des propriétés de quantités menues d'air humide que l'on trouve dans les espaces internes d'un mur de bâtiment. Une seringue en acier inoxydable enduite de Téflon, chauffée par un fil électrique à l'extérieur a rendu possible de garder l'échantillon pendant trente minutes avec une perte d'humidité de moins de 6%. Nous avons trouvé que la technique est importante. Dans un tube rempli de Poropak Q, des échantillons d'air de 4,9 x 10^{-6} m^3 ayant un point de rosée de -15°C ont donné un coefficient de variation d'humidité de 7%, puis, et pour des échantillons ayant un point de rosée de +20°C, un coefficient de 1%.

Introduction

Gas liquid chromatography affords a method of measuring small quantities of moisture [1-6]. It is of interest in the present case because it constitutes a possible method of determining the properties of small samples of moist air, such as might be drawn from inaccessible spaces in building components of laboratory specimens and equipment.

A previous paper [7] reported the character of the air and water signals as affected by sample size, humidity level, sensor current, carrier gas flow rate and column temperature, and evaluated the attainable accuracy and sensitivity of the method.

During the initial stages of the previous investigation, samples of moist air were introduced into a chromatograph by means of a syringe with a volume of less than $5 \times 10^{-6} m^3$. Reproducibility was poor, and the method was abandoned in favor of a continuous flow system that was not subject to this difficulty.

The authors concluded:

> "Using gas chromatography to determine the humidity ratio of moist air in the range of 21°C to -18°C dewpoint, a nearly linear relation was found to exist between peak area ratio and humidity ratio when other operating variables are fixed.
>
> The investigation indicated that:
> 1. calibration curves showing the relation between area ratio and humidity must be obtained at a fixed sample size and filament current, because the two variables cause considerable variation;
> 2. a lower dewpoint temperature requires a larger sample to retain the same precision as the higher dewpoints;

3. the tailing problem is markedly reduced when column packing materials and operating conditions are carefully selected;
4. problems of reproducibility were solved by heating the Beckman valve and using an automatic integrator and constant filament current supply.

The GLC system of measuring humidity ratio (using a Beckman valve) can produce results accurate to 1/4°C at 20°C dewpoint and better than 1°C at -18°C dewpoint. The present system does not permit the measurement of humidity using small samples obtained with a syringe, but the development of a suitable sampling technique would permit this system of humidity measurement to be more versatile."

This paper reports the refinements in techniques that were necessary to overcome the difficulties of measuring the humidity of small samples ($4.9 \times 10^{-6} m^3$) of moist air taken with a syringe.

Equipment and Technique

Room air was pumped through a saturator [8] which produced a humidity level known within 0.1°C dewpoint. A $4.9 \times 10^{-6} m^3$ sample, taken from the saturator outlet with a $10^{-5} m^3$ Teflon-lined hypodermic syringe, was injected into a gas-liquid chromatograph. Details of construction and operation of the gas-liquid chromatograph are given in Table I.

TABLE I

Equipment

Column: stainless steel tube 2.44 m x 6.3×10^{-3} m O.D., temperature 126°C

Packing: Poropak Q 80-100 mesh

Helium flow rate: $10^{-6} m^3/s$

Detector: 0.20 a in 4 filament resistance type bridge

Output to digital integrator

Series of tests were made at dewpoint temperatures ranging from 4 to 21°C. The scatter of these and other results coupled with experience obtained in earlier work prompted the incorporation of several changes in equipment and techniques.

1. The barrel of the syringe was wrapped with electrical heating tape and warmed to about 33°C to reduce moisture sorption on the interior surfaces.

2. Leakage at the septum after a series of needle thrusts affected the results. Such a loss reduces sample size and affects the instrument output [7]. A silicone rubber plug was installed behind a 3×10^{-3} m thick brass washer with a 8×10^{-3} m hole in it. alsoa light film of vacuum grease was applied to the plunger of the syringe.

3. The needle was wiped with a cloth before injecting the sample to remove any stray droplets of moisture on it.

4. Series of tests in which the sample was stored in the plunger for up to two hours suggested that a significant exchange with the ambient air caused errors (Fig. 1). To control such exchange a valve was placed on the needle (Fig. 2). With the addition of the valve, however, another problem was created. If the sample was strongly compressed by pushing the plunger, inconsistent results were obtained possibly due to condensation in the system. The problem occurs at the time of injection when the operator tends to increase force to resist the pressure of the helium carrier gas that follows opening of the valve. A mechanical stop placed in the syringe prevented premature movement of the plunger and appeared to resolve the problem.

5. Experience supported the statement by Cotton et al[9] that the column packing deteriorates and should be replaced periodically.

Calibration

With this apparatus and technique, a calibration curve was developed*. At selected dewpoint temperatures between -18 and

*It should be noted that the relationship between area ratio and humidity ratio varies with conditions e.g. filament current and sample size, hence calibration is necessary.

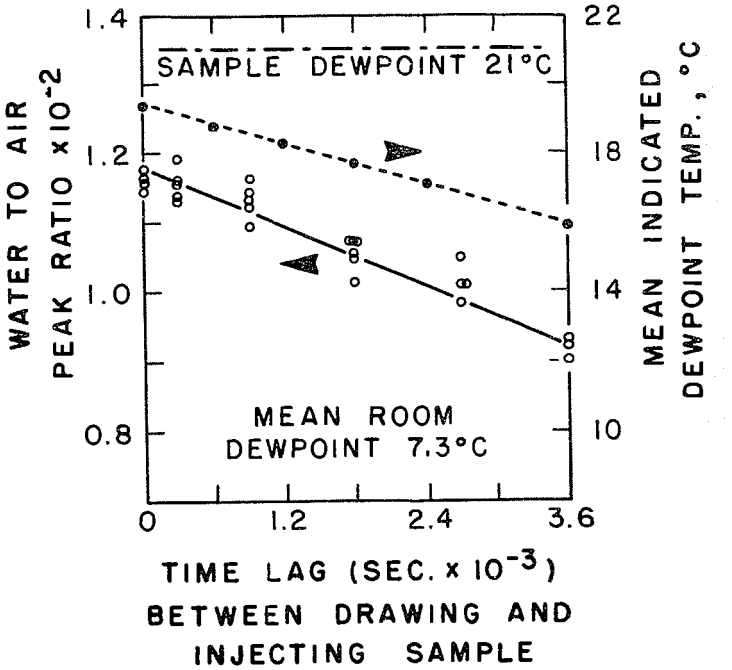

FIG. 1

Decay of sample in syringe without valve

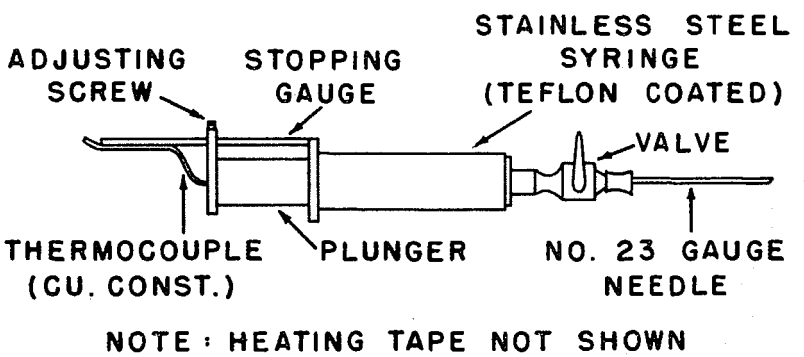

FIG. 2

Detail of syringe used in final measurements

22°C six to ten samples were tested in the chromatograph. The water-air peak area ratio and coefficient of variation were found at each point (Fig. 3). It was evident that the humidity-ratio/area-ratio plot was only approximately linear, not linear as assumed in the previous paper.

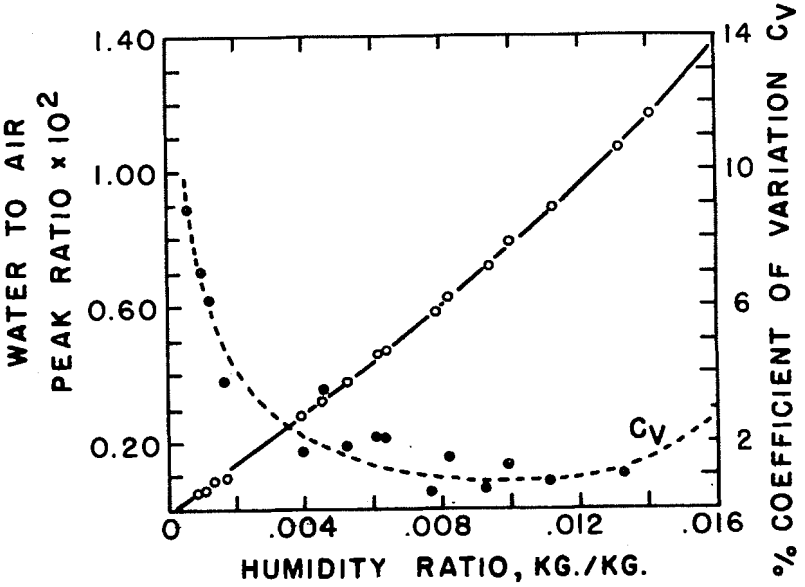

FIG. 3

Calibration curve and coefficient of variation.

The coefficient of variation of area ratio at -15°C dewpoint was 7.2% and at 16°C dewpoint it was 1.0% corresponding to standard deviations of 0.8 and 0.15°C dewpoint respectively. The same data are used to plot area ratio against dewpoint temperature (Fig. 4).

A series of tests was carried out to evaluate the effect of retention time in the syringe on the accuracy of the result. The room dewpoint temperature was 5°C and the air samples were at 12.8°C dewpoint. Thirty-one tests were made, 15 with no time

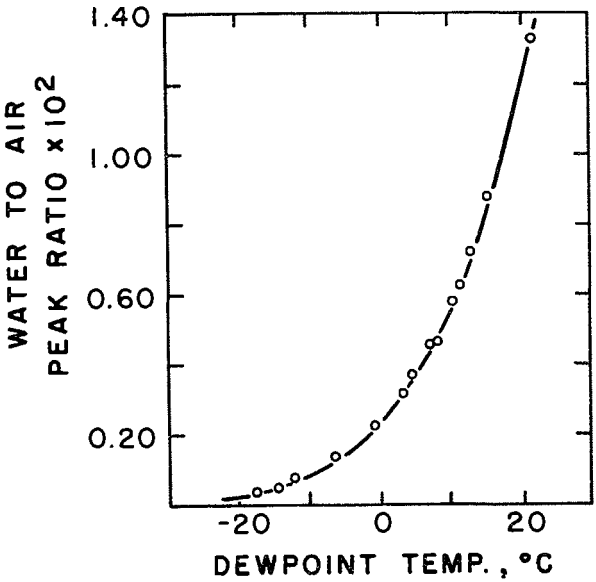

FIG. 4

Calibration curve - water to air peak area ratio vs. dewpoint temperature.

delay and 16 with retention times ranging up to 120 minutes (Fig. 5). Beyond 10 minutes the retention time did not appear to affect the result very much. The average dewpoint temperature indicated by the chromatograph, for retention times of 20 minutes or more was 12.2°C, 0.6°C below the correct value.

A series of seven tests comparing the dewpoint temperatures found with an aspirated wet and dry bulb psychrometer and those found with the gas liquid chromatograph using room air, had an average difference of 0.3°C and maximum difference of 0.8°C.

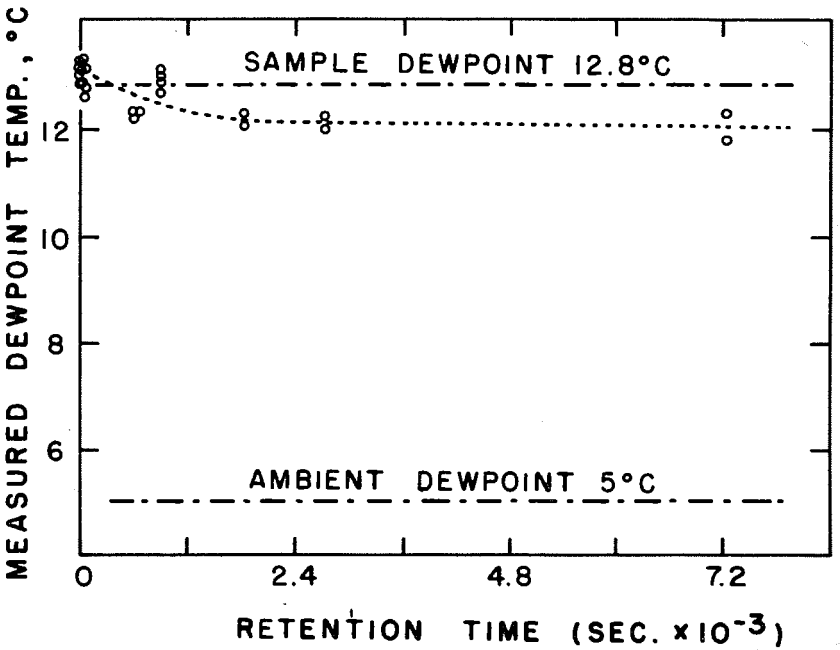

FIG. 5

Change in sample humidity with storage time in syringe with valve.

Conclusions

A calibration curve was established for the system using 4.9 x 10^{-6} m^3 air samples in the humidity range from -18 to 22°C. At -15°C dewpoint the standard deviation for a series of measurements was 0.8°C and at 16°C was 0.15°C.

Samples were retained in the syringe for up to two hours before using them. On average the measured humidity was about 0.7°C below the correct value.

In a series of measurements the dewpoint temperatures given by the GLC differed on average by 0.3°C from those obtained with an aspirated psychrometer.

These results were obtained using the following apparatus and technique.

A heated Teflon-lined syringe with a valve on the needle and a mechanical stop on the barrel was used to obtain and inject the air samples.

The technique included the following steps:

(1) Minimize leakage at syringe with a layer of vacuum grease.

(2) Prevent leaks at the septum.

(3) Use a mechanical stop on the syringe to prevent condensation caused by pressurization.

(4) Wipe the needle with a cloth at a constant condition to establish constant needle moisture conditions.

(5) Establish gas chromatograph operating states, suitable for water-air separation.

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