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HUMIDITY MEASUREMENT USING GAS-LIQUID  
CHROMATOGRAPHY

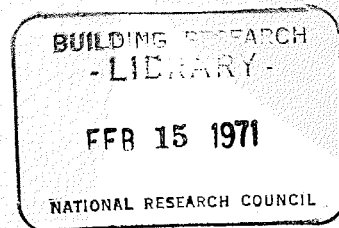
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## MESURE DE L'HUMIDITE UTILISANT LA CHROMATOGRAPHIE GAZ-LIQUIDE

### SOMMAIRE

Des expériences ont été faites pour étudier la possibilité d'utiliser la chromatographie gaz-liquide pour mesurer la teneur en humidité des petits échantillons. Le système a employé une cellule à conductivité thermique pour la détection et un intégrateur digital pour mesurer les endroits de pointe. Différents matériaux ont été essayés dans les colonnes, mais 2 pourcent de Carbowax sur Haloport F a été choisi parce qu'il causait relativement très peu de résidus.

On a déterminé que la pointe pour l'eau variait d'une façon presque linéaire avec le niveau de l'humidité. Les pointes pour l'air et l'eau variaient avec la grandeur de l'échantillon, les deux diminuaient d'une façon marquée avec le taux d'augmentation du débit de gaz, et les deux diminuaient avec une diminution du courant dans le filament.

L'exactitude a varié d'à peu près  $\pm \frac{1}{4}^{\circ}$  C à une température de  $21^{\circ}$  C jusqu' à  $+1^{\circ}$  C à  $-18^{\circ}$  C point de rosée pour les échantillons dont la grandeur variait de 4.9 à 15.9 cc. A cause de la petite quantité d'eau employée l'adsorption sur les murs des tubes peut constituer une source importante d'erreurs.

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# Humidity Measurement Using Gas-Liquid Chromatography

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## Abstract

Experiments were carried out to study the feasibility of using a gas-liquid chromatograph for measuring humidity of small samples. The system employed a thermal conductivity cell for detection and a digital integrator to measure the peak areas. A number of column packings were tried, and 2% Carbowax on Haloport F was selected because it caused relatively little tailing.

Water peak areas were found to vary almost linearly with humidity level. Air and water peak areas varied with sample size; both decreased markedly with increased carrier gas flow rate, and both decreased with a decrease in filament current.

Accuracy ranged from about  $\pm 1/4$  C deg dew-point at 21°C dew-point temperature to  $\pm 1$  C deg at -18°C dew-point temperature for sample sizes ranging from 4.9 to 15.9 cm<sup>3</sup>. Because of the small amounts of water involved, sorption on tubing walls can constitute an important source of error.

Gas liquid chromatography has been used to measure the moisture content of a variety of liquids (1-4) and of air (5,6). It affords a method of measuring small quantities of moisture and is of interest in the present case because it constitutes a possible method of determining the properties of small samples of moist air withdrawn from spaces in building components or laboratory specimens and equipment.

The literature contains little detailed information about the use of GLC for hygrometric work. Experiments were undertaken, therefore, to determine 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 to evaluate the attainable accuracy and sensitivity of the method.

## Method

During the initial stages of the investigation samples of moist air were introduced into a chromatograph by means of a syringe with a volume of less than 5 cm<sup>3</sup>. Reproducibility was poor, possibly owing to the effects of sorption on the walls of the syringe, and the method was abandoned in favor of a system that would avoid this difficulty.

Room air was pumped through a saturator, which produced a humidity level known to within 0.1 C deg dew-point (7), to a Beckman valve that allowed air samples of known volume to be metered into the carrier gas stream and analysed. Sample chambers of

15.9, 8.2 and 4.9 cm<sup>3</sup> were used. The volumes of the sample chambers were measured by determining the amount of water required to fill them. The additional volume contributed by the Beckman valve was estimated to be 0.2 cm<sup>3</sup>. The entire Beckman valve was heated to about 110°C because sorption on the metering chamber walls at room temperature was sufficient to produce a marked effect on the results.

A number of column packings were tried. These included calcium carbide to produce acetylene, which could then be detected, Poropak R®, (Waters Assoc., Framingham, Mass.), Ucon 550 on Haloport, Chromosorb W, and Carbowax on Haloport F. On the basis of the observed reproducibility and tailing, 2% Carbowax on Haloport F was selected as the most suitable for work in the range of interest. The packing material was chilled to -30°C to simplify loading, and the column (stainless steel tube, 1/4 in., i.d., and 9 ft 6 in. long) was vibrated to improve the uniformity of packing. The column was operated at approximately 90°C.

The sensing element was a thermal conductivity cell with a four-filament bridge in a system similar to that discussed by Lawson and Miller (8). Results appeared to be more reproducible when a constant current was supplied to the bridge, and this procedure was employed in the tests.

The electrical output from the thermal conductivity cell was transmitted to an Aerograph 470 digital integrator, which gave the areas of the air and water peaks separately in digital form, the units being millivolt-seconds (mV-sec). The water peak areas at low dew-point temperatures were so small that it was not

1. Casazza, W. T., and Steltenkamp, R. J., *J. Gas Chromatog.* 3, 253 (1965).
2. Hollis, O. L., and Hayes, W. V., *J. Gas Chromatog.* 4, 235 (1966).
3. Swensen, R. F., and Keyworth, D. A., *Mater. Res. Std.* 7, 524 (1967).
4. Kung, J. T., Whitney, J. E., and Cavagnol, J. C., *Anal. Chem.* 33, 1505 (1961).
5. Burke, D. E., Williams, G. C., and Plank, C. A., *Anal. Chem.* 39, 544 (1967).
6. Charlson, R. J., "Humidity and Moisture—Its Measurement and Control in Science and Industry," Wexler. Vol. I, Reinhold, 1965, p. 591.
7. Hedlin, C. P., *Mater. Res. Std.* 6, 25 (1966).
8. Lawson, A. E., and Miller, J. M., *J. Gas Chromatog.* 4, 273 (1966).

Table I. Test Series.

Investigation	Sample Size	Dew-Point °C	Column Temp °C	Filament Current mA	Helium Flow cm <sup>3</sup> /min	Remarks
Reproducibility	15.9	-18	71	240	50	$C_v = 4.37\%$
	8.2	21	90	190	50	$C_v = 1.70\%$
	4.9	21	90	190	50	$C_v = 1.75\%$
Sample Size	15.9	-18 to 21	90	240	180	<i>Area Ratio</i> decreased nonlinearly with decreasing sample size and filament current; linear with humidity ratio
Filament Current	8.2	-18 to 21	90	240	180	
and Humidity Ratio Changes	4.9	4.5 to 21	90	240	50	
Helium Flow Rate	8.2	15.5	90	197	50 43 32	<i>Area Ratio</i> independent of helium flow
	4.9	15.5	90	197	50 43 32	
Column Temperature	15.9	21	99	77	202	<i>Area Ratio</i> independent of column temperature
	8.2	21	99	77	202	

$C_v$  = COEFFICIENT OF VARIATION = Standard deviation/mean reading  
BECKMAN VALVE TEMPERATURE 110° ALL TESTS

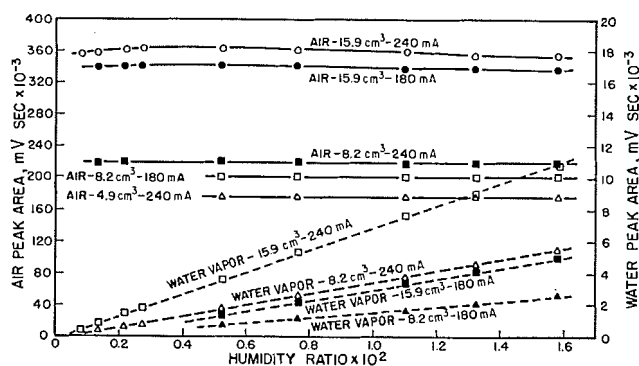


Figure 1a. Air and water peak areas versus humidity ratio for three sample sizes and two detector filament currents.

possible to measure them accurately by manual means, and the integrator was essential for these measurements. Despite the large difference in the areas of the air and water peaks, satisfactory measurements were obtained without attenuating the air peak.

### Results and Discussion

Table I gives the operating conditions selected for each test and a brief summary of the results. In the studies on reproducibility, twenty-four 15.9-cm<sup>3</sup> samples of air at -18°C dew-point temperature (0.000787 humidity ratio at STP) were tested. The peak area ratios showed a coefficient of variability of 4.4%. At a dew-point temperature of 21°C a similar series of tests with 8.9-cm<sup>3</sup> and 4.9-cm<sup>3</sup> samples gave a coefficient of variability of 1.7%. Nearly all of the varia-

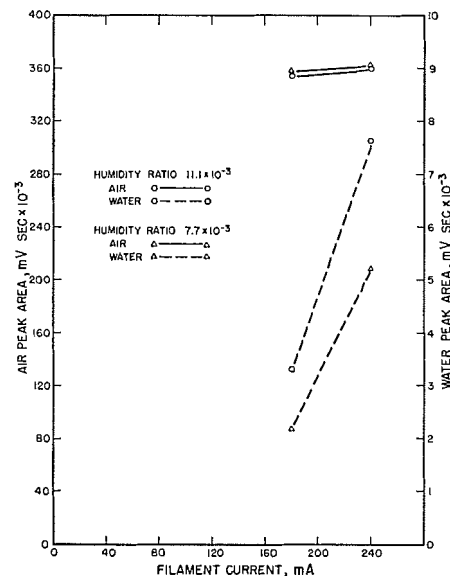


Figure 1b. Air and water peak areas versus filament current.

bility occurred in the measurement of the humidity component.

Figures 1a, 1b and 1c contain data taken from the same set of results plotted in three different ways. In Figure 1a the peak areas for air and water vapor are plotted separately against humidity ratio for two filament currents and several sample sizes. The air peak areas are substantially constant; the amount of air in the samples changes very little, but the water peak areas decline in an apparently linear manner as the humidity ratio is decreased.

Figure 1b illustrates the areas again plotted against filament current at two humidity ratios. Changing the

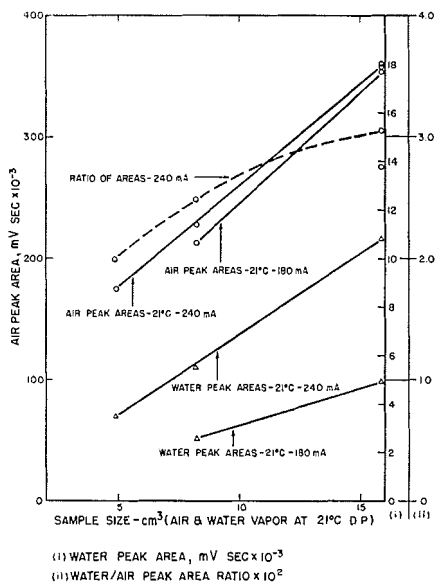


Figure 1c. Air and water peak areas and the water/air peak area ratio versus sample size for two filament currents.

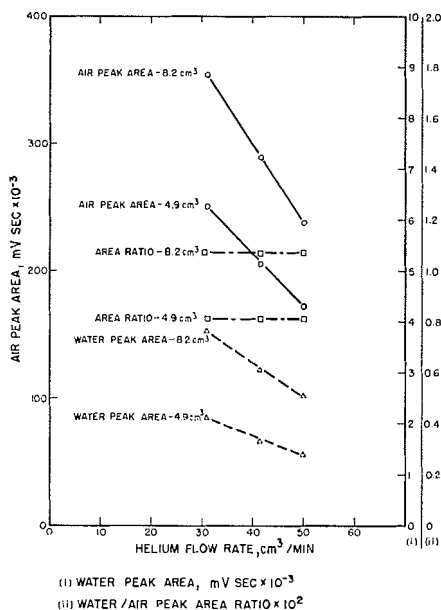


Figure 2. Air and water peak areas and the water/air peak area ratio versus helium flow rate for two sample sizes.

filament current from 180 to 240 mA increased sensitivity to air by about 5% and sensitivity to water vapor by about 100%; thus, under these conditions at least, higher filament currents will increase the size of the water peak in relation to that of the air peak. Schmauch and Dinerstein (9) also found that variation in filament current caused substantial variation in the response for n-hexane and methanol.

Individual areas and ratio of water vapor to air are plotted against sample size in Figure 1c. The area for air decreases with sample size, but linear extrapolations of the lines do not pass through the origin of the plot. Although the plot of water area is linear and extrapolates nearly through the origin, the ratio

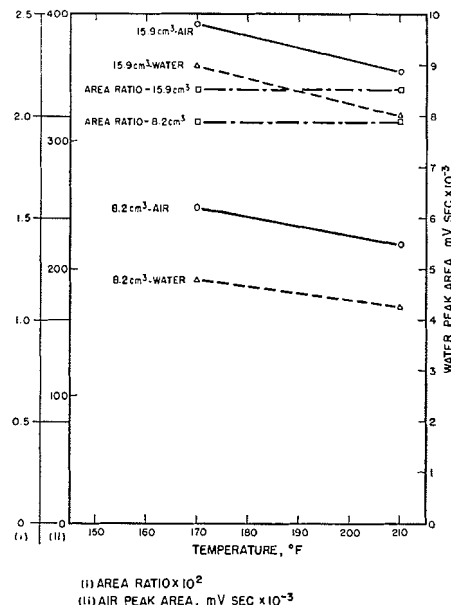


Figure 3. Air and water peak areas and the water/air peak area ratio versus column temperature for two sampling sizes.

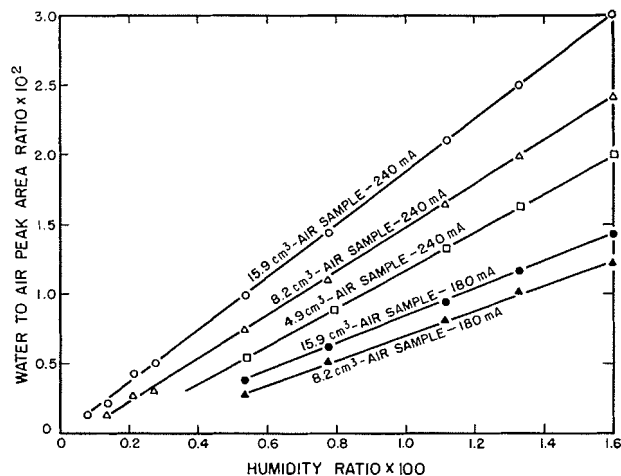


Figure 4. Water/air peak area ratio versus humidity ratio for several sample sizes and two detector filament currents

of water to air areas is non-linear. Some of the factors that could contribute to non-linearity are: varying thermal conductivity with concentration, varying concentrations with time, and time lag in the sensing elements.

The ratio of the areas of air and water peaks was unaffected by a change in helium flow despite the change in their absolute values (Figure 2). Too small a helium flow rate caused tailing. Reducing the column temperature increased the area of water vapor peak and air peak slightly while retaining the same ratio, but eventually the lower column temperature produced tailing of the water peak (Figure 3).

Peak area ratios are plotted against humidity ratio in Figure 4, demonstrating the type of calibration

9. Schmauch, L. J., and Dinerstein, R. A., *Anal. Chem.* **32**, 343 (1960).

curves needed when such an instrument is used to test an unknown sample.

### Conclusions

Using gas chromatography to determine the humidity ratio of moist air in the range of 21°C to -18°C dew-point, a nearly linear relation was found to exist between peak area ratio and humidity ratio when other operating variables are fixed.

The investigation indicates 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 dew-point temperature requires a larger sample to retain the same precision as the higher dew-points;
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 inte-

grator 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 21°C dew-point and better than 1°C at -18°C dew-point. 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.

### Acknowledgment

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