AEC RESEARCH AND DEVELOPMENT REPORT

MASTER

A PRACTICAL LOW-RANGE MOISTURE GENERATOR

R. F. Wolny

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE   Y-12 PLANT

operated for the **ATOMIC ENERGY COMMISSION** *under* **U. S. GOVERNMENT** Contract W-7405 eng 26

DISCLAIMER

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Document___Y-1791

TID-4500

UNION CARBIDE CORPORATION
Nuclear Division

OAK RIDGE Y-12 PLANT

Operated under Contract W-7405-eng-26
With the US Atomic Energy Commission

A PRACTICAL LOW-RANGE MOISTURE GENERATOR

R. F. Wolny

Date Issued - May 5, 1971

Oak Ridge, Tennessee

Document Y-1791

TID-4500

DISTRIBUTION

Atomic Energy Commission

Keller, C. A.
Zachry, D. S., Jr

Oak Ridge Gaseous Diffusion Plant

Jordan, R. G.
Wilcox, W. J., Jr

Oak Ridge Y-12 Plant

Bell, B. B.
Bernander, N. K.
Briscoe, O. W.
Burditt, R. B.
Burkhart, L. E.
Denny, A. (2)
Ellingson, R. D.
Evans, G. W.
Foulk, D. L.
Haeusler, K. R.
Hemphill, L. F.
Jackson, V. C.
Kahl, K. G.
Keith, Alvin
Kite, H. T.
McLendon, J. D.
Mitchel, G. W.
Oliphant, G. W.
Smith, R. D.
Stoner, H. H.

Trotter, T. C.
Weathersby, W. E.
Wesley, R. L.
Wolny, R. F. (10)
Yaggi, W. J.
Y-12 Central Files (5)
Y-12 Central Files (master copy)
Y-12 Central Files (route)
Y-12 Central Files (Y-12RC)

Paducah Gaseous Diffusion Plant

Winkel, R. A.

In addition, this report is distributed in accordance with the category UC-37, Instruments, as given in the "USAEC Standard Distribution Lists for Unclassified Scientific and Technical Reports", TID-4500.

ABSTRACT

Magnesium perchlorate tetrahydrate has been used for several years for laboratory and field calibration of low-range moisture monitors at the Oak Ridge Y-12 Plant.

For the past two years, this material has been investigated in the Y-12 Plant Physical and Electrical Standards Laboratory to determine its potential range and accuracy for moisture calibration. Results indicate that by controlling the pressure and temperature of the material, a stable and convenient source of moisture can be obtained for the 0.2-to-2,000 ppm range. The lowest range of moisture generated by this source permits accuracies which cannot readily be achieved with gas cooling equipment or two-pressure humidity generators.

All work in the ppm moisture range requires careful attention to setup and technique, and some procedures have been developed to achieve the desired performance.

This device should prove valuable to calibration laboratories, manufacturers of low-range moisture instruments, and for use as a transfer standard.

4

CONTENTS

SUMMARY

Requirements for a practical moisture generator include: (1) a constant moisture output, (2) a sufficient moist gas flow rate, (3) theoretically acceptable operation, (4) relatively inexpensive and simple construction, and (5) relatively simple controls. Moisture generators using magnesium perchlorate tetrahydrate plus hexahydrate (paired hydrate) are being used at the Oak Ridge Y-12 Plant[a] for one-point calibration. The generator described in this report is basically the same device, with the addition of temperature and pressure controls to provide moisture values < 2 to 1,000 ppm-v.

Moisture output, in terms of the logarithm of the equilibrium partial pressure, is related to temperature of the paired hydrate by the Clausius-Clapeyron equation; moisture output, in terms of ppm-v, is related to absolute pressure by Dalton's Law of Partial Pressures.

To prepare the hydrate system, a measured amount of anhydrous magnesium perchlorate is exposed to 40 - 50 percent relative humidity for three or four days, then the product is bottled and stored after the desired weight increase has been obtained.

A linear relation between the logarithm of the water vapor pressure and the inverse temperature was verified experimentally. Intercept and slope values were found for moisture data, with and without corrections from a National Bureau of Standards calibration.

The effect of increases in the pressure and sample flow rate was observed at three temperatures. Reasonable agreement with the expected results was noted. Also, the empirical value of the molar latent heat appears to be reasonable, based on published values of heats of hydration and vaporization.

(a) Operated by the Union Carbide Corporation's Nuclear Division for the US Atomic Energy Commission.

INTRODUCTION

Measurements of moisture in the 2 to 1,000-ppm-v range are being made routinely by many industries, including the Oak Ridge Y-12 Plant. As accuracy requirements increase, the choice of a calibration method can be difficult, since time and cost can become considerable. Prime requirements for any calibration method are: (1) a constant moisture output, (2) a sufficient moist gas flow rate to assure equilibrium conditions, and (3) a theoretically acceptable operation.

Requirement 3 is necessary if the variables in the calibration technique are to be understood and controlled. Other criteria for a calibration system include: (1) it must be reasonably compact, (2) relatively inexpensive to construct, (3) relatively inexpensive to operate, and (4) have relatively easy-to-operate controls or adjustments.

The moisture generator described in this report satisfies these requirements reasonably well. It employs a system of magnesium perchlorate hydrates and is similar to the more limited generators in use at this Plant for several years.[1] Typical of the generators described by Montgomery, et al, is the portable unit shown in Figure 1. These units have proved themselves to be useful for one-point calibrations in the field, usually between 20 and 45 ppm-v. Corrections for pressure and ambient temperature are obtained from a graph attached to each generator. Calibration at one point, as well as a time-constant measurement, are performed in the Y-12 Physical and Electrical Standards Laboratory using a system of magnesium perchlorate hydrates.

After the theory of operation for salt-hydrate systems is presented, construction of a moisture generator and preparation of the magnesium perchlorate tetrahydrate-magnesium perchlorate hexahydrate mixture [$Mg(ClO_4)_2 \cdot 4H_2O$ + $Mg(ClO_4)_2 \cdot 6H_2O$] will be described. A summary of the experimental results and a discussion follow.
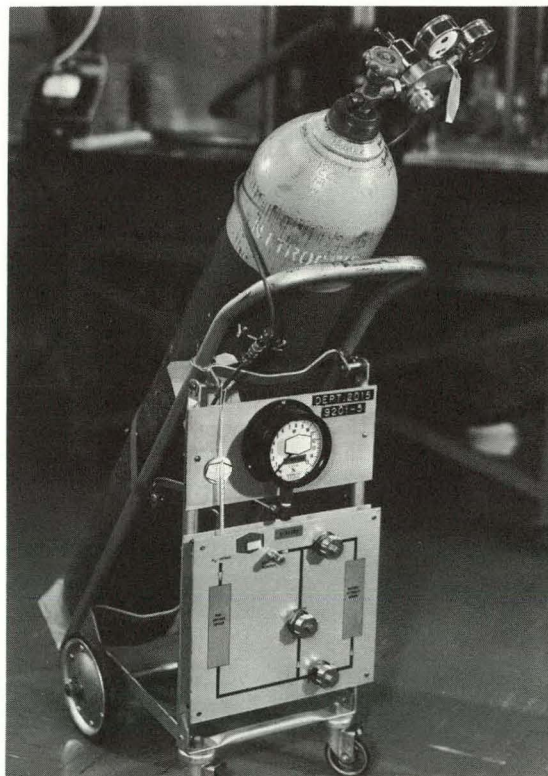
138923

Figure 1. PORTABLE MOISTURE GENERATOR.

A LOW-RANGE MOISTURE GENERATOR

THEORY

A system of paired salt hydrates [such as $Mg(ClO_4)_2 \cdot 4H_2O + Mg(ClO_4)_2 \cdot 6H_2O$] has a definite water vapor pressure which is a function of its temperature. Vapor pressures for the di- and tetrahydrate as well as for the tetra- and hexahydrate systems have been reported.[2] Much of the early work was an attempt to prove or refute the existence of a trihydrate compound.[3] Since then, the nonexistence of this hydrate has been substantiated.[4]

Figure 2 presents a graphical representation of the vapor pressures for the various hydrates of magnesium perchlorate. The lowest plateau is bounded by 100 percent anhydrous magnesium perchlorate on the left and 100 percent magnesium perchlorate dihydrate on the right. (Between these extremes in composition, the vapor pressure is constant for a given temperature.) At the first discontinuity, a higher vapor pressure equilibrium results, causing the second plateau—bounded by 100 percent di-hydrate on the left and 100 percent tetrahydrate on the right. The third plateau, resulting from a mixture of the tetra- and hexahydrate, or paired hydrate, is the subject of this study.
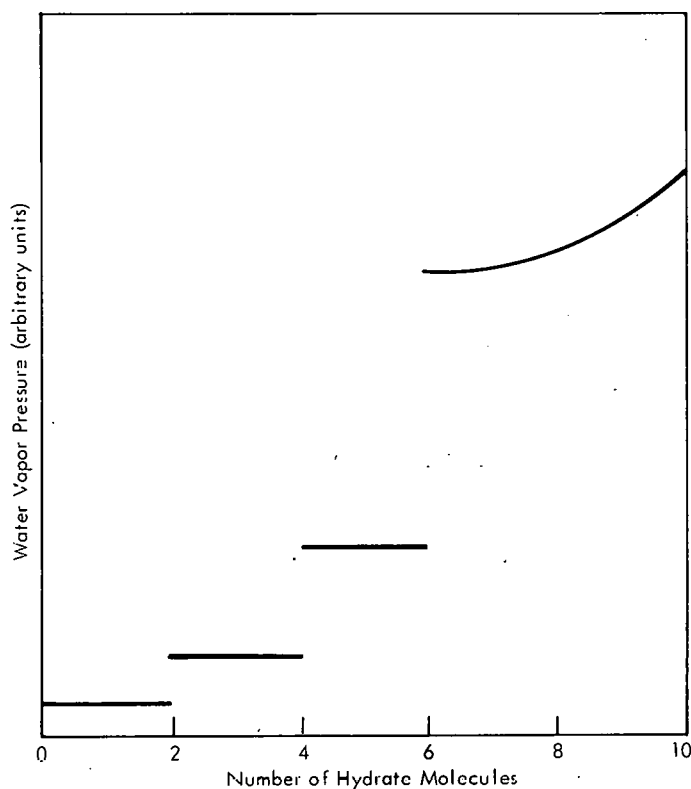

Figure 2. VAPOR PRESSURES FOR THE VARIOUS HYDRATES OF MAGNESIUM PERCHLORATE.

As a first-order approximation, the vapor pressure equilibrium versus temperature function for the paired hydrate can be described by the Clausius-Clapeyron equation:

$$\frac{dp}{dT} = \frac{L}{T\Delta V_t} ,$$ (1)

where:

p represents the partial pressure at equilibrium,

T the absolute temperature,

L the molar latent heat, and

V_t the molar volume of the water and water vapor.

This relationship is a consequence of Maxwell's relation and the Second Law of Thermodynamics.[5] Since the molar volume of the condensed phase is negligible compared to the volume of the vapor:

$$\Delta V_t = V_{vapor} .$$ (2)

Then:

$$V_{vapor} \simeq \frac{RT}{P} ,$$ (3)

where:

R represents the universal gas constant, and

P the absolute pressure.

Substituting for V_{vapor} and integrating Equation 1 gives:

$$\ln p = -\frac{L}{R}\left(\frac{1}{T}\right) + C .$$ (4)

This relation is in a form convenient for experimental evaluation.

It is possible to develop a more comprehensive theory by considering the specific heats of the vaporous and condensed states separately. Using Kirchhoff's equation, which distinguishes between specific heats of the two phases (ΔC_p), results in a second-order term:

$$\left(\frac{\Delta C_p}{R}\right) \ln T .$$

If a linear relation between ΔC_p and temperature is postulated, another term involving the critical temperature, T_c, is introduced:

$$\frac{\Delta C_p}{R} \left(\ln T - \frac{T}{2T_c} \right) .$$

The difference in specific heats must then be evaluated at the critical temperature.

Applying Dalton's Law of Partial Pressures to the nitrogen-water vapor atmosphere in equilibrium with the paired hydrate, the moisture output becomes:

$$ppm-v = \frac{10^6 p}{P} . \tag{5}$$

DESCRIPTION OF THE GENERATOR

The generator was constructed using accepted techniques and materials for moisture work. Clean, stainless steel tubing and metal valves were employed that were designed for $< 10^{-7}$ torr vacuum service. Since a separate, controlled temperature bath was not available, the paired-hydrate container was located in a water bath used with a two-pressure humidity generator. Three stainless steel tubes connected the 2-inch-OD by 7.9-inch-long (5 cms OD x 20 cms L) container or tower with the generator controls and allowed gas to flow to and from the tower, as well as measure the pressure at the tower. The distance between the tower and controls was 36 feet (11 meters). The pressure line and return gas line were 1/8 inch OD while the dry gas line was 1/4 inch OD. Eighteen feet of 1/4-inch-OD tubing was wound around the tower to ensure that the inlet gas approached the bath temperature before mixing with the paired hydrate.

A piping schematic for the generator is given in Figure 3. Because of the valving arrangement at the tower, the paired hydrate could be bypassed for system dry down. Tower pressures above 115 psia (7.2 bars) were controlled using a two-stage regulator, after valving out the low-pressure regulator and indicating gage.

A moisture analyzer, calibrated at the National Bureau of Standards in December 1970, was included with the generator. The generator and analyzer unit can be seen in Figure 4.
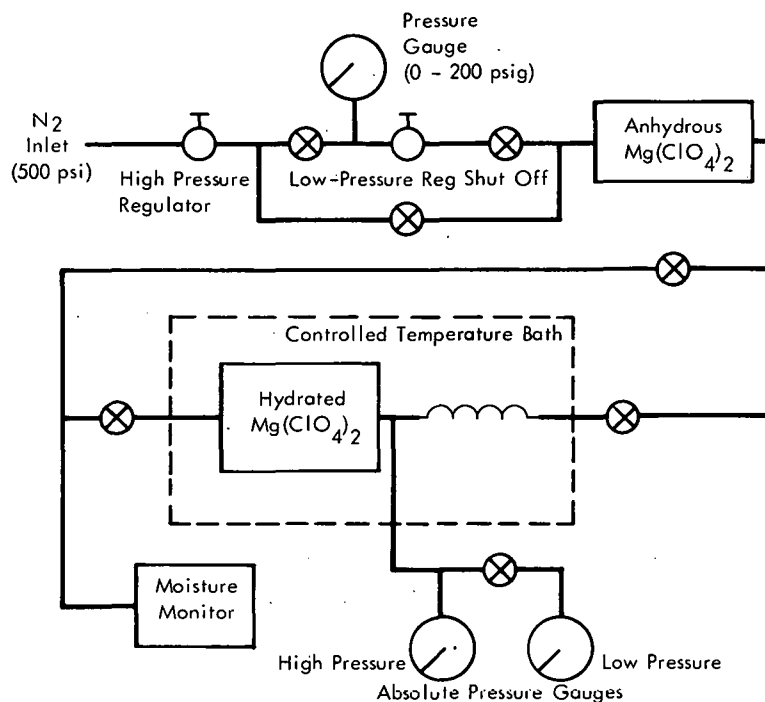
Figure 3. PIPING ARRANGEMENT FOR THE MOISTURE GENERATOR.

PREPARATION OF THE PAIRED HYDRATE

Anhydrous magnesium perchlorate is first weighed and then spread in a pan or on plastic to a depth of 0.8 inch (2 cms). The material, which is stirred daily, is exposed to room air having a relative humidity between 40 and 50 percent. The desired weight increase is generally obtained within three or four days. The final product is then bottled and stored until needed. Attempts to add water by other methods resulted in an unsatisfactory final product.

The formula for calculating the required weight of absorbed water is:

$$y = \left(\frac{322.21}{223.21}\right) x ,$$ (6)

where:

 y represents the net weight of $Mg(ClO_4)_2 \cdot 5\ 1/2 H_2O$ (really a mixture of the tetra- and hexahydrates), and

 x the net weight of anhydrous magnesium perchlorate.

The molecular weights of the "y" and "x" materials are 322.21 and 223.21, respectively.
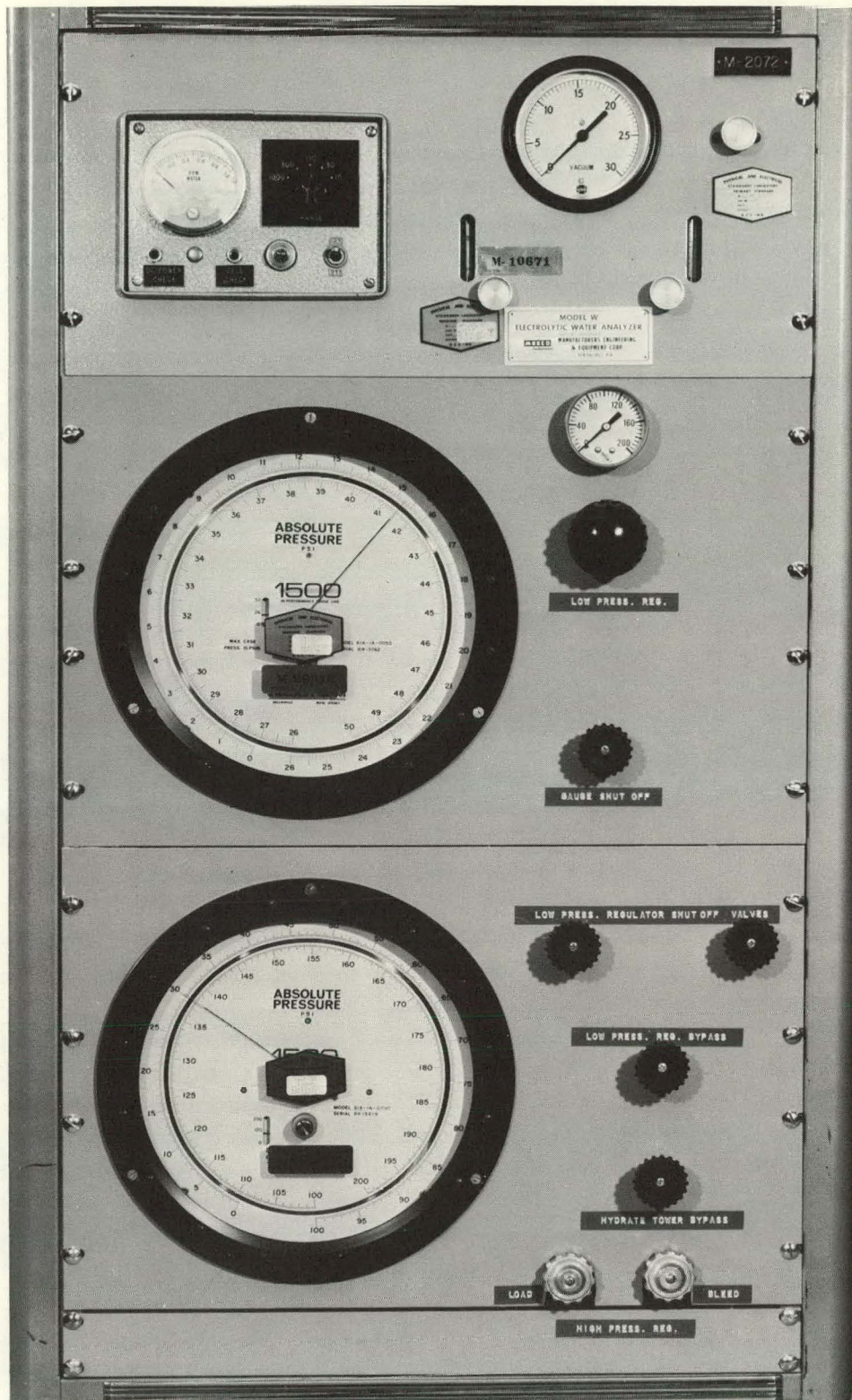
138924

Figure 4. THE LOW-RANGE MOISTURE GENERATOR AND ANALYZER.

EXPERIMENTAL RESULTS

The purpose of the experimental work was to determine the relation between pressure and temperature of the paired hydrate and the moisture output from this system. The following data were recorded: date, time, tower pressure, bath temperature, moisture analyzer reading and scale, time for the collection of 100 cubic centimeters of gas, room temperature, and barometric pressure. Furthermore, information relating to the test, such as "increased pressure to 90 psia at 10:20 am", was also logged on the datasheet.

Measurement accuracies are listed in Table 1. The first value presented is in the units recorded; the value in parentheses is the SI (international system) equivalent.

Table 1

MEASUREMENT ACCURACIES

Measurement	Accuracy	Measurement Range
Tower Pressure	0.04 psi (2.3 mb)	0 to 50 psia (0 to 3.45 bars)
	0.13 psi (9.1 mb)	50 to 200 psia (3.45 to 13.8 bars)
Bath Temperature	0.1° C	-2 to 50° C
Gas Collection Time	0.15 second	30 to 65 seconds
Room Temperature	0.1° C	23 to 24.5° C
Barometric Pressure	0.02 inch (Hg)(0.68 mb)	28.8 to 29.3 inches (Hg) (976 to 993 mb)

Calibration of the moisture analyzer was performed in December 1970 at the National Bureau of Standards (Report of Calibration 213.03/2130603) with moist gas known to 10 percent of the value for the range from 2 to 12 ppm-v, 3 percent of the value for the range from 12 to 250 ppm-v, and 0.5 percent of the value for the range from 250 to 1,000 ppm-v. Because of uncertainties which must be considered when using any coulometric hygrometer, the actual readings were probably accurate to no better than twice the values reported for the NBS two-pressure humidity generator. Nevertheless, this method of moisture measurement was considered the best compromise between precision, accuracy, convenience, and response time. The correction curve for the moisture analyzer is presented in Figure 5.

For comparison purposes, a second coulometric hygrometer of different manufacture was also read. Differences between readings were always < 2.0 ppm-v for the range from 6 to 100 ppm-v and < 5 ppm-v for the range from 100 to 150 ppm-v after correcting for the flow rate. A single anomaly occurred at 39.4° C during a repeat run when the second monitor read 15 ppm-v high. Both instruments agreed within 0.5 ppm-v when the temperature of the tower was reduced to 21.0° C.
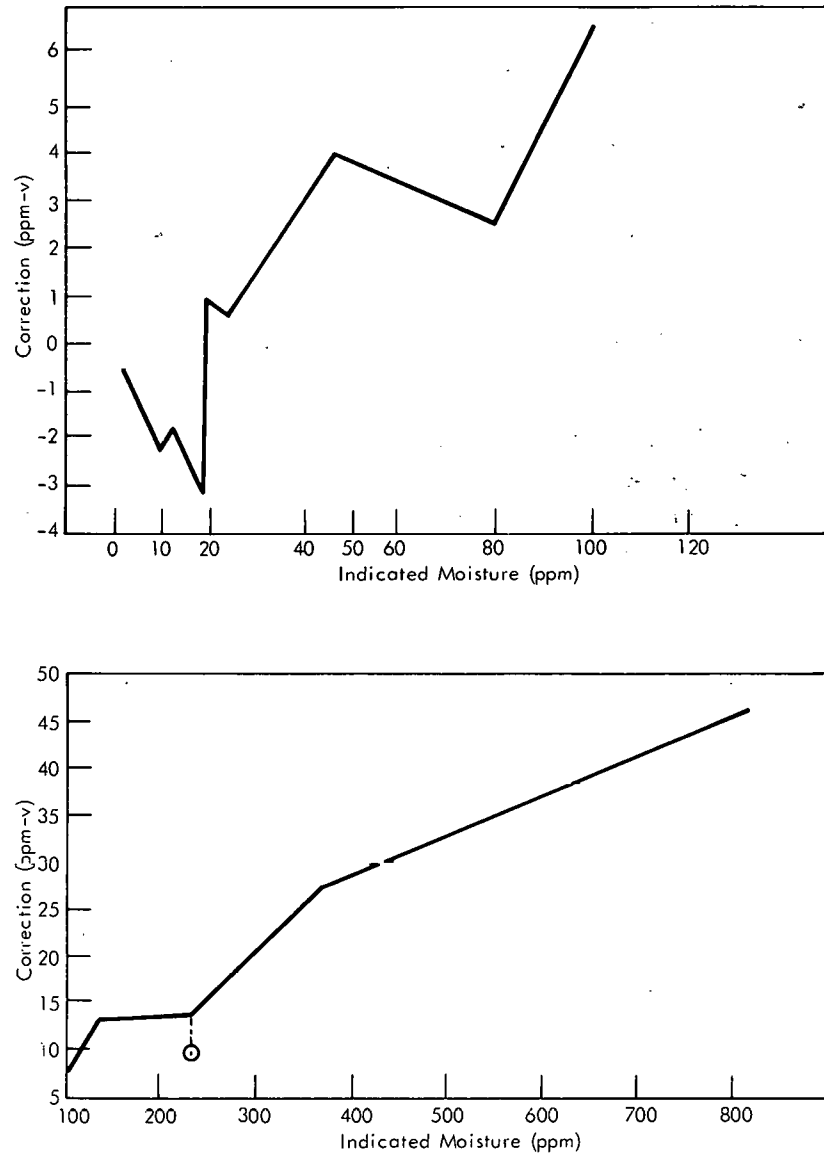
Figure 5. CORRECTION CURVES FOR THE MOISTURE ANALYZER.

Because of the relatively long (11-meter) distance between the tower and moisture monitor, by-pass flow rates (about 300 cc/min) were maintained while moisture readings were equilibrating. The by-pass valve was closed, however, before the final series of readings were taken at a given bath temperature. Thus, the flow rate through the tower was decreased from about 500 cc/min to 200 cc/min for the data considered to be steady state. It should be noted, however, that except for one or two-minute transients, the moisture-monitor readings did not change when the by-pass flow rate was increased from zero to 600 cc/min after a steady-state reading has been recorded.

Nine moisture measurements, used to establish the relation between ln p and T^{-1}, were made over a bath temperature range from 7.8 to 39.6° C. Equations 7 and 8

and their estimates are based on data obtained from the moisture analyzer calibrated at the NBS. Results were calculated from Figure 5 for flow-corrected moisture readings with and without NBS corrections. Equations 7 and 8 were obtained using a least-squares analysis for an FI relation:[6]

$$\ln p = -8213.1 \left(\frac{1}{T}\right) + 17.601 \text{ (without NBS correction to ppm-v data), and} \quad (7)$$

$$\ln p = -9091.8 \left(\frac{1}{T}\right) + 20.568 \text{ (with NBS correction to ppm-v data).} \quad (8)$$

The computed regression lines for the data used to obtain Equations 7 and 8, along with the 95 percent confidence interval estimates, are indicated by the graphs of Figures 6 and 7. Estimated variance in the slope of Equation 7 is 123, and the estimated variance in the intercept is 0.418. Estimated variance in the slope of Equation 8 is 187, and the estimated variance in the intercept is 0.633.
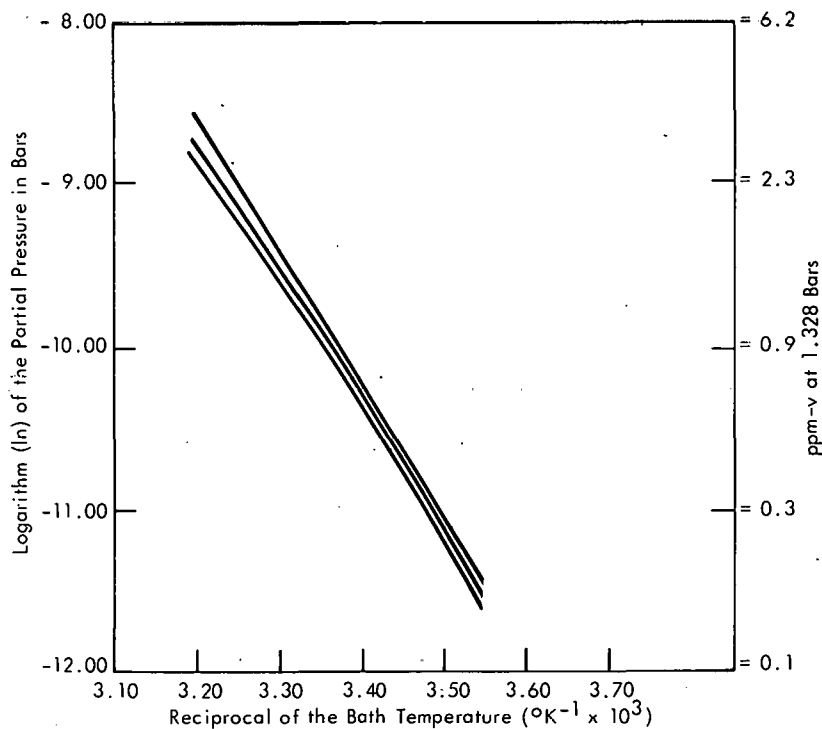

Figure 6. REGRESSION LINE AND CONFIDENCE INTERVAL. (Uncorrected Moisture Data)

DISCUSSION

Equilibration of moisture readings required three to twelve hours. Unquestionably, the time required for steady-state readings will be less when the paired-hydrate
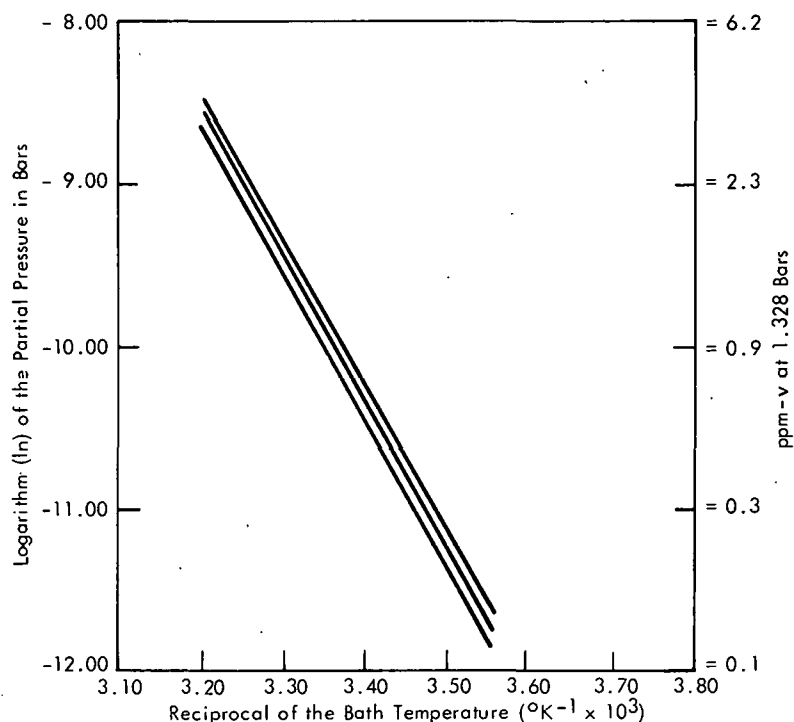
Figure 7. REGRESSION LINE AND CONFIDENCE INTERVAL. (Corrected
Moisture Data)

tower can be located next to the control panel. Steady state is achieved in less
than one hour with the portable moisture generators which do not have controlled
temperature baths.

Moisture readings were recorded at temperatures as low as -16.1° C. Data included
in this report have been limited to values above 6 ppm-v, since this is the lowest
reading included in the NBS calibration. Although techniques for reducing very
low ppm-v data have been developed,[7] it was obvious that the theoretical rela-
tion could be better investigated at moisture values above 6 ppm-v.

The effect of increases in tower pressure and in flow rate through the moisture mon-
itor cell was observed. According to Equation 5, moisture readings should be in-
versely proportional to the absolute pressure in the tower. On the other hand,
moisture readings are proportional to the mass flow rate through the cell, over a
limited range. The results of four measurements at a bath temperature of 21.0/
21.15° C, are reported in Tables 2 and 3. Moisture values are reduced to a tower
pressure of 19.25 psi (1.328 bars). The data in Table 3 include corrections based
on the NBS calibration.

Correcting the moisture data for the NBS calibration resulted in better agreement
for an increased sample flow rate and tower pressure. Data in these tables are
typical; similar agreement was observed at two higher temperatures. Although

Table 2

EFFECT OF INCREASING THE TOWER PRESSURE AND SAMPLE
FLOW RATE THROUGH THE MOISTURE MONITOR
(Without NBS Corrections from Figure 5)

Bath Temperature (° C)	Tower Pressure (bars)	Sample Flow Rate (cc/min)	Flow-Corrected Moisture Reading, Reduced to 1.328 Bars (ppm-v)
21.0	1.330	102.6	25.5
21.05	6.917	100.8	30.7
21.1	6.896	150.0	32.2
21.15	1.328	150.0	22.9

Table 3

EFFECT OF INCREASING THE TOWER PRESSURE AND SAMPLE
FLOW RATE THROUGH THE MOISTURE MONITOR
(With NBS Corrections from Figure 5)

Bath Temperature (° C)	Tower Pressure (bars)	Sample Flow Rate (cc/min)	Flow-Corrected Moisture Reading, Reduced to 1.328 Bars (ppm-v)
21.0	1.330	102.6	27.6
21.1	6.917	100.8	23.5
21.1	6.896	150.0	29.1
21.15	1.328	150.0	26.2

estimated variances in slope and intercept were somewhat larger for moisture data corrected for the NBS calibration, additional points on Figure 5 would have smoothed the curve and probably resulted in less variance.

The graph of Figure 8 relates moisture to temperature of the paired-hydrate system for nitrogen pressures of 19.25 psia (1.328 bars) and 101.5 psia (7.0 bars). The lower pressure (about 5 psig) is sufficient to allow the needed flow rate through the tubing, valves, and a moisture monitor discharging into the atmosphere. The higher pressure is near the upper limit of many compressed gas distribution systems. Extrapolated data should be verified and the equations adjusted before the moisture generator is used outside the temperature range from 7 to 40° C.

There are precautions which must be observed with magnesium perchlorate. An explosion is reported to have occurred upon heating this substance to 220° C in the presence of hydrocarbons.[8] The same reference also cautions against allowing the material to come into contact with acids. Neither precaution should detract from the usefulness of the generator, however. If a flammable gas instead of nitrogen is required for calibration, or the paired hydrate must be heated much above 60° C, another hydrate system or type of moisture generator should be considered.

Equation 8 indicates that the molar latent heat is 18.06 kilocal/mole. Taking -68.32 kilocal/mole for the heat of formation of water[9] and -438.6 kilocal/mole
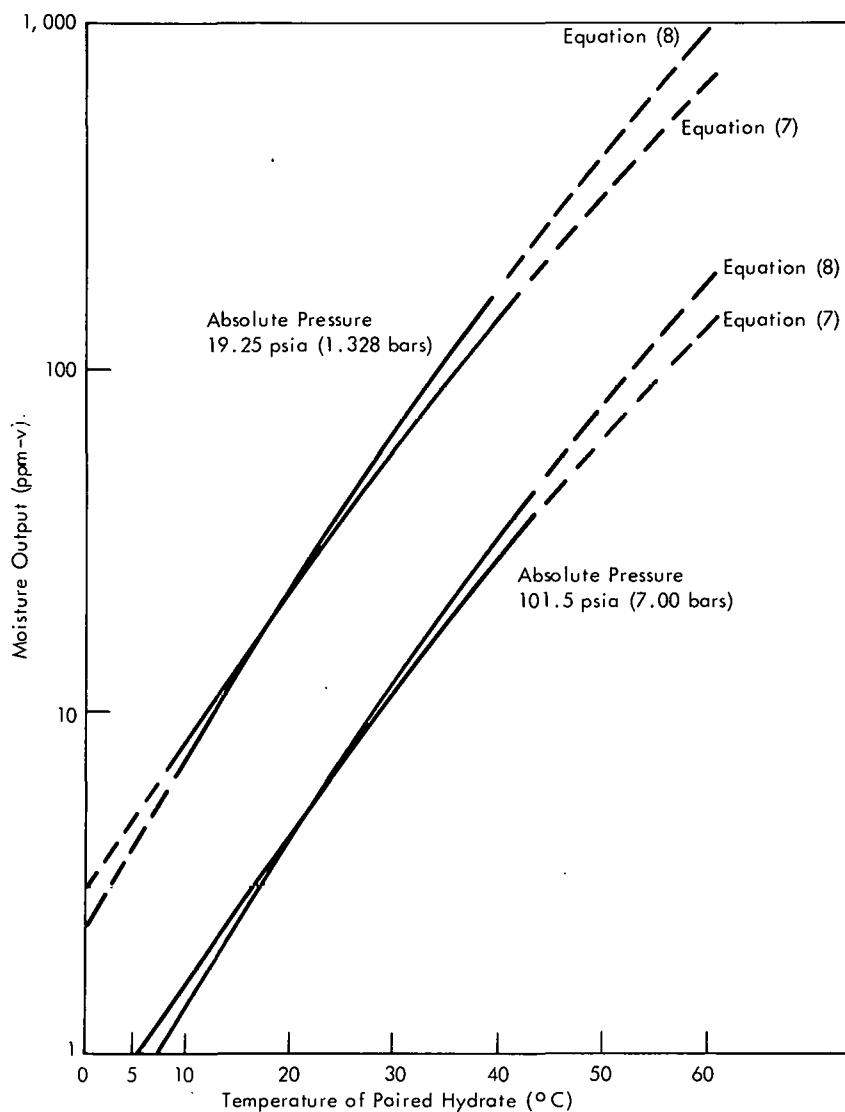
Figure 8. MOISTURE FROM THE GENERATOR AS A FUNCTION OF THE PAIRED-HYDRATE TEMPERATURE.

for the heat of formation of the tetrahydrate[10] gives a total of -575.2 kilocal/mole. Since the heat of formation for the hexahydrate is -583.2 kilocal/mole,[10] the -8.0 kilocal/mole deficit must represent the molar latent energy. Approximating the heat of vaporization of water as 10.5 kilocal/mole,[11] and subtracting this value from the empirical value of 18.06 kilocal/mole, gives a latent energy of 7.56 kilocal/mole, in fair agreement with the derived value.

CONCLUSIONS AND RECOMMENDATIONS

The linear relationship between the inverse temperature of the paired hydrate and the logarithm of the equilibrium partial pressure, expressed in Equation 4, has been

verified within the limits stated (Page 14). Until more accurate measurements can be made, or the operating temperature range of the generator extended beyond 0 to 40° C, obtaining second- or third-order terms is unnecessary.

Although more data will be required, Equation 5 relating moisture output to absolute pressure appears to be valid. This expression increases the usefulness of the generator, since fractional ppm-v values could be produced at relatively high tower pressures and moderately low temperatures. Experimental work below 2 ppm-v is difficult since almost no commercially available equipment has the needed accuracy and resolution.

The value of the NBS calibration is obvious. Any moisture measurements, made with equipment calibrated inhouse and without direct traceability to the NBS, become suspect. This problem is aggravated by the accuracy and repeatability specifications which can be quite optimistic.

The moisture generator described in this report should be useful as a working or secondary standard. As better values for the heats of hydration become available, the method may become more nearly a primary standard.

REFERENCES

(1) Montgomery, C., Googin, J., and Phillips, L.; "Moisture Monitor Testing and Calibration", Humidity and Moisture Measurement and Control in Science and Industry, 3 (1965).

(2) Copeland, L. and Bragg, R.; "The Hydrates of Magnesium Perchlorate", J Phys Chem, 58, p 1075f.

(3) Smith, G., Rees, O., and Hardy, V.; "New Hydrates of Magnesium Perchlorate. Their Structural Relation to Known Forms of the Hydrated Perchloric Acids and Properties as Intensive Dehydrating Reagents", J Am Chem Soc, 54, p 3513f (1932).

(4) Zinov'ev, A. and Chudinova, L.; "Thermal Decomposition of the Perchlorates of Magnesium, Calcium, Barium, and Aluminum", J Inorg Chem, USSR, 1, p 1722f (1956).

(5) Moelwyn-Hughes, E.; Physical Chemistry, Second Edition; Pergamon Press, p 275 (1961).

(6) Natrella, M.; "Experimental Statistics", National Bureau of Standards Handbook 91, Chapter 5; US Government Printing Office (1966).

(7) Belkin, H., Jhaveri, D., and Kapani, M.; "Getting the Most Out of Electrolytic Hygrometers", Instrumentation Technology, 17, p 57f; July 1970.

(8) Heertjes, P. and Houtman, J.; "An Explosion of Magnesium Perchlorate", Chem Weekblad, 38, p 85 (1941).

(9) Handbook of Chemistry and Physics, 41st edition, p 1883; Chemical Rubber Publishing Company.

(10) Ibid, p 1886.

(11) Ibid, p 2318.

ACKNOWLEDGEMENTS