Indirect Gas Chromatographic Measurement of Water for Process Streams

Topical Report

F. A. Barbour

May 1993

Work Performed Under Contract No.: DE-FC21-86MC11076

For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia

By
University of Wyoming
Western Research Institute
Laramie, Wyoming

MASTER

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SUMMARY

This project was conducted to develop a moisture measurement method for process gas streams generated by thermal degradation of fossil fuels. The objective was to provide a measurement of the molar concentration of water in a gas stream without having to rely on flow measurements. The method developed has been incorporated into the hydrocarbon gas analysis method currently used at Western Research Institute.

A literature search of the types of direct measuring moisture sensors was conducted, and a list of sensors available is given in Appendix A. Most of the sensors were not capable of surviving in the environment of the process streams to be analyzed.

Several indirect methods of moisture measurement also surfaced during the literature search. Indirect methods of measuring water involve changing the water via reaction to a compound that can be more readily measured. Several types of reactions have been explored. These methods react water with various reagents to form hydrogen, acetylene, and acetone. The method chosen for this study uses a calcium carbide reaction column to convert the water present in the gas stream to acetylene for analysis.

The relative deviation for the daily determination of water varied from 0.5 to 3.4%. The chosen moisture measurement method was tested for linearity over a wide range of gas stream water content. The response over the 2 to 15 mole % water appears to be linear with a correlation coefficient of 0.991.

INTRODUCTION

The Western Research Institute (WRI) conducts research in engineering and science projects in fossil fuel extraction and conversion research. Most processes that are involved in the production of organic liquids or gases by thermal decomposition of fossil fuels produce water as a by-product. The measurement of this moisture usually involves condensing the liquid and recording the amount collected. To relate this measurement back to the product stream, one has to also have accurate flow measurements of the total gas stream. This method can produce errors in both measurements because of: (1) water that is not condensed and (2) the difficulty of conducting flow measurements on dirty gas streams. One possible way around these problems would be to measure the water directly in the product stream as an absolute value. This value would be independent of the flow measurements.

Over the past 40 years, thousands of publications have dealt with the measurement of water. This literature has been well described in a three volume series entitled "Aquametry" (Mitchell and Smith 1977). The earlier methods were generally based on the Karl Fischer titration method and were restricted to laboratory measurements on grab samples. Lately, electronic sensors have become available that can be placed in the process streams for direct measurement of the moisture. Most of these sensors are designed to work in rather simple process streams with only a few components. Process streams from thermal decomposition of fossil fuels often contain too many interfering components for most of these sensors.

Gas chromatographs (GC) have been used for real time analyses of product streams from thermal decomposition of fossil fuels. The chromatographic characteristics of water are such that good quantitative measurement of water by GC is not always possible. A way to overcome the poor chromatographic characteristics of water would be to react the water with some chemical and measure a by-product that has good chromatographic characteristics.

MOISTURE MEASUREMENT CONSIDERATIONS

Selection of On-Line Moisture Sensors

A relatively complete list of moisture sensor types is given in Appendix A. The method of detection as well as some of the strong points and weaknesses of each sensor are given. For the measurement of moisture only, there are two sensors recommended: (1) silicon and (2) aluminum oxide.

The first objection to the use of silicon and aluminum oxide sensors is that they show slow drifts (aluminum oxide more so than the silicon). Some gases, high temperatures, and high humidities tend to accelerate drift and, therefore, these instruments require more frequent maintenance and calibration. In addition, the silicon and aluminum oxide probes are attacked by corrosive gases (NH_3 and SO_3). Another objection to the silicon and aluminum oxide probes is that they are not absolute sensors, and they need frequent calibration.

Where water is required as just one of a number of compounds in a process stream, on-line gas chromatography (GC) may be used to determine moisture content; but because of the need for sampling system maintenance, GCs are rarely used for simple moisture determination. Since gas analysis by GC is a part of nearly all of the pyrolysis and combustion tests run at WRI, it would seem natural to incorporate a good moisture determination technique into one of the GC gas analysis methods.

Another point to be considered when choosing a moisture measurement method is ease of calibration. The equipment necessary for the generation of a good moisture calibration gas requires a great deal of care to assure good performance. Some of the needed precautions are listed in the following section on sampling systems.

Sampling Systems

It is preferable to mount the moisture sensor directly in the pipe, tank, or reactor where the determination is required, since this eliminates errors introduced by a sampling system and gives the most rapid response. However, many times the sensor cannot be mounted directly in the process stream because of high temperatures, entrained solids, or liquids. In these cases a sampling system must be used to carry a representative uncorrupted sample to the sensor. A discussion of sampling system designs is given by Cornish et al. (1981). In this book a wide variety of process streams and special requirements of a good sampling system are addressed.

While designing and building a sampling system is beyond the scope of this project, one must still take into account some of the major points of a good sampling system when developing a moisture measurement method. In designing a sampling system for moisture determination, several basic rules must be observed:

1. The sampling line should be kept as short and simple as possible (extra length delays sensor response and increases the possibility of adsorption or desorption of moisture).
2. The system should not be subject to wide fluctuations in temperature (this can cause variations in the amount of water adsorbed on the system's inner walls).
3. The whole system should be kept at a temperature 10 to 15°C (18 to 27°F) above the highest expected temperature at which water can condense. Electrical tracing is the preferred method.
4. The best material for sampling system construction is either stainless steel or nickel tubing. Teflon can also be used, but shows significant permeability to water vapor when low concentrations are being determined. Other plastics should be avoided because they take up and desorb water over long periods of time.
5. The sample stream may need to be conditioned prior to measurement. Filtration is best carried out with the use of sintered stainless

steel or nickel filters. Small cyclones may be used for particle or droplet removal if flow is sufficiently high.

6. It is good practice to use the pressure of the sampled line to maintain flow of gas through the sampling system. Pumping can cause problems because leaks can corrupt the sample by drawing ambient air into the sampling system.

Gas Chromatographic Methods

The first attempts at measuring water by gas chromatography were made in the early 1960s, not long after the development of gas chromatography itself. Generally, the separation of water resulted in broad and unsymmetrical peaks. Sensitivity, precision, and accuracy were poor compared to other compounds. Of the two gas analysis methods used at WRI, one exhibits the poor chromatographic characteristics mentioned above, and the other employs flame ionization detection (FID) which cannot detect water directly.

Gas chromatographic methods for water determination can be divided into two types; direct and indirect. The direct method, as the name implies, measures the water directly and very often results in the poor chromatographic peaks described previously. New porous-polymer column packings have been developed (Pollack et al. 1984) that do a very good job of direct analysis of water in specific cases. However, none can handle all of the compounds in a thermal decomposition product stream and water.

Some of the newer chromatographic systems have overcome this problem, but systems analyzing hydrocarbons and permanent gases at the same time require several columns and switching valves. This can require a great deal of maintenance with dirty process gases. These systems are generally run at some isothermal temperature slightly above ambient. This is convenient because no cryogenic cooling is required, but is quite inconvenient if a dirty sample containing a large amount of liquid is inadvertently injected on the column.

Indirect methods of measuring water involve changing the water via reaction to a compound that can be more readily measured. Several types of reactions have been explored. These methods react water with various reagents to form hydrogen, acetylene, and acetone.

Calcium carbide was first used for indirect measurement of water by Bayer (1957) by placing a small reaction chamber filled with calcium carbide between the injection port and the chromatographic column. The water reacted with the calcium carbide to form acetylene which was separated on a dinonylphthalate column and detected by thermal conductivity. The calcium carbide - gas chromatography technique has been applied to measuring trace water in hydrocarbon gas streams (Knight and Weiss 1962). A reactor tube packed with 20-30 mesh calcium carbide was placed in the process stream. The continuous flow system permitted equilibration of the water - calcium carbide reaction prior to being diverted to the chromatographic column.

The water and calcium carbide reaction has also been investigated as an analytical method for the quantitative determination of water using headspace gas chromatography (Loeper and Grob 1988). Samples containing water were introduced into a dry vial containing calcium carbide. The resulting acetylene was then measured by headspace analysis and the original concentration of water in the sample calculated. The method was used to measure water in organic solvents in the 60 to 400 ppm range.

The reaction of water with hydrides has also been examined as an indirect method of measuring water. Most of the methods used either calcium hydride or lithium aluminum hydride (Mitchell and Smith 1977). The reaction generates hydrogen and is not of any use with pyrolysis products containing hydrogen as one of the major components.

Martin and Knevel (1965) used the acid-catalyzed reaction between 2,2-dimethoxypropane (DMP) and water to form acetone and methanol. Their method calls for reacting the sample with the reagents in a separate reaction vessel and then analyzing the mixture by gas chromatography. The concentration of acetone is used to determine the water content of the sample. This technique has been used to analyze natural products (Mary 1969). The method generally requires about five minutes for the acetone concentration to reach equilibrium (Dix et al. 1989).

The reaction of water with an ortho ester (such as triethyl orthoformate) proved to be more complete than the DMP reaction (Chen and Fritz 1991). The reaction was found to be almost instantaneous but still required the addition of the sample to a reaction vessel containing the reagents. The resulting solution was then analyzed by capillary gas chromatography for ethanol.

Of the methods previously discussed, the best to adapt to existing WRI gas chromatographic process gas analysis methods appears to be one using a calcium carbide reaction. The solid calcium carbide does not need any other reagents for the completion of the reaction. The rapid reaction of water with calcium carbide is also important and necessary. In addition, the thermal decomposition processes examined by WRI do not appear to contain measurable amounts of acetylene. Analyses performed by Lawrence Livermore National Laboratory (LLNL) on Fischer assay products did not show any acetylene in the gaseous product slate (Singleton et al. 1982). Similarly, work by McLendon (1985) on retorting oil shale at low void volumes did not show any acetylene present in the gas stream. Other projects dealing with thermal conversion of tar sands (Johnson et al. 1980) and underground coal gasification (Barbour and Covell 1989) did not report any acetylene present in the gas stream. This author's experience with process gas streams similar to the ones mentioned above has not revealed any acetylene present. The development of the hydrocarbon GC with flame ionization detection was specifically set up to determine if additional hydrocarbon species did exist. The use of the FID provided additional sensitivity for quantifying trace amounts of hydrocarbons and the Chemipak C₁₈ column gave the needed separation to isolate acetylene from the other hydrocarbon gases.

A distinct advantage of using an indirect method is that the calibration of the method can be performed using the compound being analyzed and not water itself. In most cases it is much easier to obtain a good calibration gas whose concentration does not vary with respect to temperature. This is the biggest problem encountered using water vapor, itself, as a calibration gas. The use of a calibration gas that is always ready for use and does not require a great deal of care and attention to generate it would simplify the calibration of the method. In the case using calcium carbide as a reactant to convert the moisture in the gas stream, the calibration could be performed using acetylene. Ultimately, the calibration for water could be performed, using a hydrocarbon standard, at the same time as the calibration for the other gases to be analyzed.

EXPERIMENTAL

Calibration Gas

As mentioned previously, one of the overall objectives in establishing a moisture measurement method was that of an easy calibration method. The calibration of the indirect method would not be dependent on the generation of a water vapor standard, but use a hydrocarbon standard instead. However, in order to evaluate the use of calcium carbide as a reactant for the conversion of water, the completeness of the reaction does need to be examined using a water standard.

The generation of a water vapor standard is most easily done by using available published information on the saturated vapor pressure of pure water at controlled temperatures (Hodgman et al. 1966). The dry calibration gas is saturated with moisture by bubbling it through a column of water at controlled temperatures. Care has to be taken not only to dry the gas completely to a point that will not affect the concentration of the standard, but also to ensure that the construction materials for gas-contacting components of the system do not adsorb or desorb water in sufficient quantities to invalidate the standard.

The moist air used for this project was generated by passing air through a column of water as depicted in Figure 1. The air is dispersed by a fine-sintered glass sparger at the bottom of a water column. As the bubbles rise through the water, the air is saturated with water. The moist gas then passes through a plug of glass wool to remove any entrained water aerosol. A portion of the moist gas then passes onto the reaction column where the water in the gas reacts with calcium carbide to form acetylene. Most of the gas is passed by a relative humidity meter and thermocouple, and then exits to the atmosphere. The relative humidity and temperature measurements are used to ensure moisture saturation (100% relative humidity) of the air at the desired temperature.

A thermocouple at the bottom of the water column provided water temperature information to be used to calculate the amount of moisture in the air. This was based on vapor pressure of water at a given temperature, and these calculations are demonstrated in Appendix B.

Figure 1. Apparatus for Generating Moisture Calibration Gas

The amount of water contained in the calibration gas is changed by heating the water column. This is accomplished by a heating tape wrapped around the entire air saturating apparatus and gas venting area. The whole sparger system is then insulated with glass cloth. The heating tape is controlled by a Variac. As the temperature of the water is raised, the amount of water contained by the air also increases. The air is maintained at the set temperature until it passes the thermocouple and relative humidity probe. Moisture contents from approximately 3 to 15 mole % (19, 23, 38, and 50°C [66, 73, 100, and 122°F]) were generated using this device.

Gas Chromatographic Method

Currently, WRI gas analysis of process streams is being performed using two chromatographic systems. These systems both use column oven temperature programming as a method of eluting the higher molecular weight components and cryogenic cooling of the column oven to separate the permanent, low-molecular-weight gases. The biggest single advantage in using these systems is that operating at elevated temperatures at the end of the analysis aids in cleansing the column when a dirty sample is injected. Since many of the engineering projects are several days or weeks in duration, the gas analysis system runs unattended for several hours each day. If the system could not cleanse itself during operation, this would cause too many lost gas analyses.

The first gas analysis method uses a 20 ft by 1/8 inch stainless steel column packed with 60-80 mesh Chromosorb 102. The column is cryogenically cooled to -50°C (-58°F) to separate hydrogen, nitrogen, oxygen, argon, and carbon monoxide and is then temperature programmed to 180°C (356°F) to elute carbon dioxide and light hydrocarbons. Detection is by thermoconductivity (TCD) resulting in detection limits near 0.05 vol %.

The second method incorporates a 10 ft by 1/8 inch stainless steel column packed with 80-100 mesh Chemipak C₁₈. The column is temperature programmed from above ambient to 160°C (320°F). Detection is by flame ionization (FID) and the method analyzes for light hydrocarbons (methane-octane) in the the 25 ppm to low percentage levels.

Reaction Tube

The reaction column is made by packing an 18 inch by 1/8 inch Teflon column with -40, +100 mesh calcium carbide. The calcium carbide is crushed and sieved fresh for each column to prevent loss in reactivity. It is not necessary to crush the carbide in a dry atmosphere. The column is then attached to the sampling valve of the gas chromatograph and allowed to purge for several minutes before analysis is started.

Two reaction column configurations have been tested. In the first configuration, the reaction column is placed between the sampling valve and the chromatographic column. This results in only the moisture contained in the sample loop being injected onto the column. The second configuration has the reaction column in the process stream. The injected gas contains acetylene as a result of moisture reacting with the calcium carbide in the reaction column.

RESULTS AND DISCUSSION

Reaction Column Preparation

The reaction of water with calcium carbide was selected as the best reaction system for the following reasons:

1. Acetylene, the reaction product analyzed, is rarely found in any of the pyrolysis gas streams analyzed.
2. The reaction is relatively complete.
3. No other reactants are required.
4. The reaction takes places rapidly.

The reaction column can be easily and safely prepared in the relatively dry air in Laramie, Wyoming. No significant difference in the activity of the calcium carbide could be detected, whether the reaction columns were prepared in a dry box or on the bench top.

Comparison of Gas Chromatographic Methods

Both of the two GC gas analysis methods currently used at WRI were evaluated for use with the reaction column. The evaluation consisted of testing the two columns with respect to the chromatography of acetylene, the product of the water and calcium carbide reaction, and other gaseous components generally found in pyrolysis gases. A comparison of the chromatograms is shown in Figures 2 and 3.

The first chromatographic column tested was the Chromosorb 102 using a calibration gas mixture with acetylene added. The acetylene co-eluted with ethylene. This would compromise the usefulness of the technique for gas analysis as ethylene is one of the main hydrocarbon gases generated during thermal degradation processes. Another problem with the use of the Chromosorb 102 column is that acid gases such as carbon dioxide (CO_2) and hydrogen sulfide (H_2S) may be scrubbed out of the gas stream by the calcium hydroxide formed by the water - calcium carbide reaction. Both of these gases are analyzed by this method.

The second chromatographic method is used to analyze hydrocarbon gases in the parts per million to percentage range. This column (Chemipak C_{18}) was tested using the same calibration gas. Acetylene eluted after ethylene and before propane, not compromising the analysis by co-elution with one of the gases currently being analyzed. Because this column is not used for analysis of CO_2 or H_2S , the problem associated with these gases being scrubbed by the $\text{Ca}(\text{OH})_2$ is of no importance. For these reasons this method was selected for evaluation of a moisture measurement method.

Figure 2. Chromatogram of Acetylene and Calibration Gas on Chromosorb 102 Column

Figure 3. Chromatogram of Acetylene and Calibration Gas on Chemipak C₁₈ Column

Comparison of Reaction Tube Configuration

The reaction column was tested in two positions with respect to the sampling valve. The first involved placing the reaction column between the sampling valve and the chromatographic column. The second configuration had the reaction column in the process stream. The resulting chromatograms from these two configurations are shown in Figure 4.

The first configuration with the reaction column placed after the sample loop was preferred because the calcium carbide only comes in contact with water contained in the sample loop during injection. This greatly reduces the amount of calcium carbide consumed by the analysis and enhances the lifetime of the reaction column. However, the water requires time to traverse the reaction column and to contact the calcium carbide. The movement of the water through the reaction column is apparently slower than the movement of the acetylene formed by the reaction. This results in peak broadening. Two modifications were attempted to overcome the problem of peak broadening: (1) increasing the temperature of the reaction column and (2) cryofocusing (focusing the solute on the front portion of a GC column by cryogenically cooling the column low enough to retard movement of the solute) the acetylene on the front portion of the chromatographic column.

Increasing the reaction column temperature did appear to reduce the amount of peak broadening, but resulted in another problem. The increased temperature apparently dehydrated the calcium hydroxide formed by the reaction of the water with the calcium carbide. This had been reported in earlier work by Knight and Weiss (1962). Since water was only in contact with the reaction column immediately after injection, the calcium hydroxide slowly dried out between injections. When the next sample was injected, a portion of the water in the sample was adsorbed by the dry calcium hydroxide rather than being converted to acetylene for detection. The water retained as calcium hydroxide was slowly released and the resulting acetylene only increased the baseline near the end of the chromatogram.

Cryofocusing the acetylene on the front portion of the chromatographic column also produced some success. The chromatogram in Figure 4 (after the sample valve) results from attempting to focus the acetylene. While the peak broadening was reduced to some extent, tailing was still evident. This tailing could interfere with the propane peak which elutes immediately after acetylene. In addition, the time for the analysis increased because of component retention during the cryofocusing step.

The second configuration tested involved placing the reaction column in the process stream immediately before the sampling valve. This permitted the calcium carbide in the reaction column to be in continuous contact with the moist process stream. The gas sample injected on the chromatographic column contained acetylene from the reaction rather than the water itself as was the case in the previous configuration. The resulting chromatogram, shown in Figure 4 (before the sample valve), has a much sharper acetylene peak, which elutes faster than in the cryofocused case.

After Sample Valve

<u>Time</u>	<u>Area</u>
6.358	74115

Before Sample Valve

<u>Time</u>	<u>Area</u>
1.88	73499

Figure 4. Comparison of Chromatograms Obtained with Reaction Column After and Before the Sampling Valve

The major problem with the second configuration is that the calcium carbide is always reacting with the moisture in the gas stream. This results in much more calcium carbide being used during sampling. However, this does not present an insurmountable problem if the gas stream flow is adjusted properly. A flow of 1 mL/min, just fast enough to ensure that the reaction column is continuously swept, provides good equilibrium without excessive depletion of the calcium carbide. The reaction can be followed by visually observing the change in color of the reaction column. The calcium carbide, which is quite dark, changes to a white powder (calcium hydroxide) forming a very sharp reaction front. At the above mentioned flow rate, a gas stream containing from 2 to 15 mole % water can be sampled continuously for 4 days and only depletes about 2 inches of the 1/8 inch diameter reaction column. An additional benefit from this configuration is that the dehydration of the calcium hydroxide does not occur once equilibrium has been reached with the moisture in the gas stream.

Compatibility of Reaction Tube with Hydrocarbon Gases

The reaction tube must be compatible with hydrocarbon gases if this system is to be used in conjunction with the hydrocarbon GC. The data presented in Table 1 suggest that there are no adverse effects on the hydrocarbons in the calibration gas tested. The data were obtained without and with the reaction tube placed in a dry process stream. The data presented are an average of 10 determinations for each test case. The data from the two tests indicate that there is no difference between the two tests (without and with the reaction column) and the results agree extremely well with the calibration values for the gas.

Table 1. Dry Calibration Gas With and Without Reaction Column In-Line

Compound	Conc. ^a	Without Reaction Column		With Reaction Column	
		Average Response	mole %	Average Response	mole %
Methane	10.11	283122	10.11	282997	10.11
Ethane and Ethylene	8.97	488633	8.97	489193	8.98
Acetylene	0.00	0	0.00	0	0.00
Propane	5.03	408070	5.03	407035	5.02
Propylene	1.99	165380	1.99	166051	2.00
Butane	2.99	325357	2.99	324468	2.98
Butylene	1.00	117145	1.00	116877	1.00
Total	30.09		30.09		30.08

^a Concentration of each component in the calibration gas

In addition to testing the reaction tube for possible interferences when analyzing dry gas streams, the hydrocarbon calibration gas was tested after moisture had been added. The moisture was added to the calibration gas by bubbling the gas through the water sparger system, discussed earlier, prior to passing the gas through the reaction column.

The data presented in Table 2 indicate that there are no interferences by the reaction column with the hydrocarbon calibration gases in the presence of water. The amount of acetylene determined (1.85 mole %) would be equivalent to 3.7 mole % of water present in the gas stream.

Table 2. Moist Calibration Gas With Reaction Column In-Line

Compound	Calibration Concentration	Predicted Concentration ^a	Measured Concentration	Percent Deviation
Methane	10.11	9.92	9.98	0.60
Ethane and Ethylene	8.97	8.80	8.70	1.18
Acetylene	0.00	0.00	1.85	0.00
Propane	5.03	4.94	4.98	0.79
Propylene	1.99	1.95	1.98	1.21
Butane	2.99	2.93	2.93	0.00
Butylene	1.00	0.98	0.98	0.00
Total	30.09	29.53	29.55 ^b	

^a Predicted concentration is based on the calibration gas containing 1.85 mole % acetylene as a result of 3.7 mole % water added to the calibration gas.

^b The total for the measured concentrations excludes the amount of acetylene present.

Comparison of predicted values and determined values is also given in Table 2. Each of the hydrocarbon gases in the calibration gas was reduced by the appropriate amount as a result of the addition of the acetylene. The predicted concentration of each hydrocarbon gas present in the calibration gas was calculated by correcting for the amount of acetylene present in the gas after passing through the reaction tube. These values are in good agreement and the total amount of hydrocarbon differs by only 0.02 mole %. The final column in the table gives a percent deviation for each of the components. The largest deviation is only 1.2% and is within the generally accepted range for GC analysis.

The amount of acetylene formed by the moist calibration gas passing through the reaction tube also indicates that other gases in the calibration gas do not interfere with the water - calcium carbide reaction. In addition to hydrocarbons, the calibration gas also contained carbon dioxide, carbon monoxide, and hydrogen; major gases that would be present in most gas streams generated by thermal degradation processes.

Repeatability

The moisture measurement method was tested for 3 days to determine repeatability from day to day. A moisture calibration gas was generated by bubbling air through a column of water and saturating the air with water. The data presented in Table 3 indicate that reasonable repeatability was achieved for 3 consecutive days. Several determinations for each day are listed. The average values for each day agree quite well with one another and only vary about 1.5% from the average value.

The standard deviation from day to day varied from 0.01 to 0.14, which is in a range that is generally acceptable for gas chromatographic analysis. The larger spreads observed on Day 1 may be caused by the inability to maintain exactly the same amount of moisture in the calibration gas over the duration of the test. Because the amount of moisture was dependent on the room temperature, small variations in room temperature may be responsible for part of the variation in the data. Each degree Celsius would increase the amount of water in saturated air by 0.2 mole %

Table 3. Daily Variation of Moisture Method Measurement, mole %

Determination	Day 1	Day 2	Day 3
1	2.55	2.38	2.66
2	2.56	2.87	2.64
3	2.58	2.66	2.64
4	2.58	2.64	2.62
5	2.61	2.66	
6	2.57	2.67	
7	2.55		
8	2.69		
9	2.82		
Average	2.61	2.65	2.64
Average Deviation	0.07	0.09	0.01
Standard Deviation	0.09	0.14	0.01
Range	0.27	0.23	0.02

Calibration Range

The moisture measurement method was tested for linearity over a wide range of water content. The moisture calibration gas was generated by saturating air with water as discussed previously. The concentration of the water in the gas was changed by increasing the temperature of the water and maintaining saturation until the gas sample entered the reaction tube.

A calibration gas was generated by saturating air (100% relative humidity) at four different temperatures (19, 23, 38, and 50°C [66, 73, 100, and 122°F]) and allowed to come to equilibrium before analyses were made. The results of these analyses are depicted in Figure 5. The individual measurements are represented by the data points on the graph. The lower line on the graph was generated by least square regression of the data points. The response over the 2 to 15 mole % water is linear with a correlation coefficient of 0.991.

The upper line in Figure 5 was derived by calculating an expected detector response for each concentration of water. This was done by estimating a response factor for acetylene using those factors determined for the other hydrocarbons. Since a FID is for the most part a carbon counter, the response factors obtained from the calibration gas were compared on a per carbon basis. These data are given in Table 4.

Figure 5. Comparison of Detector Response Determined by Gas Chromatography and Calculation

Table 4. Response of Calibration Gases on a per Carbon Basis

Compound	No. Carbons	Response	Response/Carbon
Methane	1	0.36	0.36
Ethane and Ethylene	2	0.18	0.37
Propane	3	0.12	0.37
Propylene	3	0.12	0.36
Butane	4	0.09	0.37
Butylene	4	0.09	0.34

The molar response factors obtained for each of the hydrocarbon gases in the calibration gas were used to calculate a response factor based on the amount of carbon present in each compound. These were calculated by multiplying the number of carbons in the particular compound by the molar response factor. The response factors based on the amount of carbon are quite similar for all of the compounds tested. This implies that the molar response factor determined for ethane/ethylene would be about the same as the molar response factor for acetylene, since all of these compounds contain two carbons atoms.

A response factor for water was calculated using the estimated response factor for acetylene and the stoichiometry of the water - calcium carbide reaction. It takes two molecules of water to react with a single molecule of calcium carbide to form a single molecule of acetylene:

This indicates that the amount of acetylene generated would only represent one half of the water in the gas stream if all the water was reacted. Using this assumption, the response factor for the amount of water present in the gas stream should be twice that of the acetylene.

As mentioned previously, the upper line in Figure 5 was generated by calculating the detector response for each of the moisture concentrations tested. It is interesting to note that the two lines are reasonably close, indicating that the theoretical line (upper line) and the experimental line are in good agreement. This would also indicate that the reaction must be very nearly complete as was indicated by the uniform reaction front. The wide range in the data at the highest concentration in Figure 5 may be an indication of difficulty in producing an accurate moisture calibration sample at that temperature. Those samples were generated at 50°C (122°F) and heat loss to the surrounding air may have lowered the gas temperature enough to reduce the amount of moisture entering the reaction column. Support for this is indicated by the fact that the experimental line appears to be low at 8 mole % water. Dropping the 15 mole % data and calculating a least squares line for only the lower three water concentrations results in a line that more closely approximates the theoretical line. This indicates that not only is the reaction fairly complete, but there is nearly quantitative transfer and detection of the acetylene.

The similarity in the slopes of the experimental and theoretical data suggest that the reaction between the water and the carbide follow the stoichiometry closely. This is in agreement with the findings of Knight and Weiss (1962), who compared the water and carbide reaction analysis with that determined by Fischer titration. While the simple design for the calibration gas generation may not have produced the most stable saturated air sample for analysis, it did seem to work well enough to establish the stoichiometric relationship of the water and carbide reaction.

Glass wool was used to aid in removal of aerosol that may have been entrained in the calibration gas. If any aerosol had passed through the glass wool then the experimental data points would be expected to be significantly higher than the theoretical line in Figure 5, which is based on 100% relative humidity at the specified temperature. Because the highest experimental data for each concentration examined were very near the theoretical line, it is believed that very little, if any, aerosol was passing through the glass wool.

The concentration range examined for this method was one that was considered likely for many of the thermal processes examined at WRI. Material balance data for oil shale retorting (McLendon 1985) suggest that moisture content in the process gas stream would be in the 7 to 14 mole % range. This gas stream represents moisture concentrations expected in gas streams generated by thermal conversion and is in the same concentration range that was tested during method development. Process data from Rocky Mountain 1 underground coal gasification (UCG) tests (United Engineers and Constructors Inc. 1989) suggest that the moisture contents between 30 to 50 mole % were present in the production stream. Steam/oxygen injection ratios between 1:1 to 2:1 were used during these tests and were responsible for the high moisture contents. Gas streams with 50 mole % would probably be out of the range of the method as it was developed. However, the range can be changed easily by replacing the sample loop with one of a different size. In the case of examining the higher moisture contents of the UCG process stream, the loop may have to be decreased in size to get the proper FID response.

CONCLUSIONS

Determination of water concentration in a gas stream using the indirect method of converting water to acetylene appears to work. The reaction between water and calcium carbide is rapid and appears to go to completion. No interferences between the reaction column and other major pyrolysis gases could be detected and none of the hydrocarbons usually present altered the results of the moisture measurement method. In addition, other gases tested (hydrogen, carbon dioxide, and carbon monoxide) did not interfere with the analysis.

A comparison of the experimentally determined data with values based on the stoichiometric relationships of the reactants show good agreement. Because of this agreement between the experimental and theoretical data, the use of an elaborate moisture calibration gas generator is not necessary. The response factor for water can be calculated directly from a molar response factor for acetylene.

ACKNOWLEDGEMENT

The author expresses appreciation to the U.S. Department of Energy for funding this work under Cooperative Agreement Number DE-FC21-86MC11076.

DISCLAIMER

Mention of specific brand names or models is for information only and does not imply endorsement by Western Research Institute or the U.S. Department of Energy.

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APPENDIX A.

Moisture Sensor Types

MOISTURE SENSOR TYPES

There are a great number of moisture sensors readily available today. The major sensors used for water measurement in process streams have been described by Carr-Brion (1986). A short description of each is given in the following paragraphs. In addition to the method of detection, some of the uses and shortcomings are also listed.

Mechanical

These sensors depend on the change in length of a sensitive material such as human hair, silk, or a specially developed polymer. Generally used for humidity control in factory rooms.

Wet and Dry Bulb Sensors (psychrometer)

These sensors measure the temperature of the gas stream and of a porous substance saturated with pure water in equilibrium with the sample gas flowing over it. The depression in temperature of the porous material can be correlated with relative humidity.

Dew Point Sensors

These sensors measure the temperature at which dew is deposited on a surface at a closely controlled decreasing temperature. An optical mirror made with a gold, rhodium, platinum, or specially electroplated nickel surface is normally mounted on a thermoelectric cooler and covered by a cell in which a light source and detector are positioned. The gas to be monitored flows over the mirror at rates between 0.25-2.5 L/min through a fine ($<25\mu\text{m}$) sintered metal filter. Condensable or corrosive gases can interfere with these sensors. These include NH_3 , SO_2 , SO_3 , HCl , Cl_2 , and many hydrocarbons.

Electrolytic Sensors

These sensors have a layer of phosphorus pentoxide placed between two noble metal electrodes which have a DC voltage applied to them. When water is adsorbed, the hydrated pentoxide becomes conducting and electrolysis takes place due to the voltage difference. Oxygen and hydrogen are evolved at the electrodes and, in theory, the pentoxide is restored. The resulting current is dependent on the rate that water is adsorbed. Gases to be avoided are corrosive ones such as Cl_2 , and HCl ; and alkaline gases such as ammonia and amines which neutralize the acidic pentoxide. Unsaturated hydrocarbons polymerize on the oxide forming a solid or liquid coating which clogs the cell. These sensors require a constant gas flow.

Lithium Chloride Hygrometers

These sensors have a thin layer of lithium chloride with an additive (e.g., polyvinyl alcohol) to improve wetting between two noble metal electrodes which have an AC voltage applied to them. The lithium chloride takes up moisture, becomes conducting and allows an alternating current to flow. The current does not cause electrolysis but heats the

sensing element until the water is driven off and the conductivity drops off. This temperature is sensed and is used in conjunction with the ambient temperature to calculate the relative humidity of the gas. When in equilibrium with a gas, the sensing element water content will depend on the relative humidity of that gas. Gases to be avoided include SO_2 , SO_3 , NH_3 , high concentrations of CO_2 , H_2S , and condensable hydrocarbons.

Aluminum Oxide Hygrometers

These sensors consist of a strip of wire of high purity aluminum with a surface chemically oxidized to produce a pore-filled insulating layer of partially hydrated aluminum oxide. A water-permeable but conductive gold film is deposited on the oxide layer to form the second electrode of a capacitor with the aluminum oxide as the dielectric. The oxide layer is in the form of a mass of tubular pores running up from the metal base to the exposed surface. Water is adsorbed in these tubules in amounts directly related to the moisture content of the gas. The amount of water is sensed electrically by measuring the change in capacitance produced by the water. These sensors are free from interferences from gases such as hydrocarbons, CO_2 , and CO . Certain corrosive gases such as NH_3 and SO_3 attack the sensing element and should be avoided.

Silicon Hygrometers

These sensors are capacitive types similar to aluminum oxide sensors. They are relatively inert to chemicals and can withstand immersion. They can show drift when operating in certain gases such as CO_2 .

Polymer Humidity

These sensors use an organic polymeric element which adsorbs or desorbs water as the relative humidity of the gas surrounding it changes. They are more sensitive to chemical interference and attack than the aluminum oxide types. Alcohols and amines can give high readings while aromatic hydrocarbons, acid vapors, and acidic oxides such as SO_2 and NO_2 can be destructive.

Crystal Oscillator Sensor

These sensors determine moisture content on line by measuring the changes in resonance frequency of vibration of a quartz crystal with a hygroscopic coating. The crystal is alternately exposed to "as-received" and dried gas, and the resulting shift in frequency is due to the change in the mass of the crystal and coating due to water uptake. The gas sample needs to be filtered prior to measurement.

Infrared Moisture Sensor

Infrared gas analyzers can determine moisture content in a gas stream. The transmitted intensity of infrared radiation at a wave length selectively adsorbed by water vapor is measured. A number of gases can adsorb at the same frequency causing interference.

REFERENCE

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APPENDIX B.

Water Concentration Calculation

WATER CONCENTRATION CALCULATION

The calculation of the water concentration in a calibration gas is most easily done using available published information on the saturated vapor pressures in mm of Hg, at controlled temperatures (Hodgman et al. 1966). This data are represented in Figure B-1 as the natural logarithm of the pressure at a given temperature versus the reciprocal of the absolute temperature in degrees Kelvin.

A least squares fit of the data to a straight line results in the following equation.

$$\ln(P) = -5.15161 \times (1000/T) + 20.46375$$

$$R^2 = 0.99992$$

Extracting the natural logarithm of both sides of the previous formula will result in a form that can be used to calculate the vapor pressure at any given temperature, where temperature is given in degrees Celsius.

$$\text{Vapor Pressure} = e^{(-5151.61/(t+273) + 20.46375)}$$

The amount of water present in the gas stream can then be represented as a mole fraction from the following equation.

$$\text{Mole Fraction Water} = \text{Vapor Pressure Water} / \text{Atmospheric Pressure}$$

Figure B-1. Correlation between Temperature and Vapor Pressure of Water at that Temperature

REFERENCE

Hodgman, C.D., R.C. Weast, and S.M. Selby, ed., 1966, Handbook of Chemistry and Physics. The Chemical Rubber Publishing Co., Cleveland, OH, p 2326 - 2331.

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