INTRODUCTION

In 1978 the United States Congress passed the Natural Gas Policy Act. This legislation required that natural gas be priced according to its energy content rather than by volume alone. At the same time, the economics of the natural gas industry caused natural gas prices to soar. These two factors resulted in a vast increase in the demand for accurate analyses of natural gas systems. Since it was not economically feasible to place analytical instruments at each and every location requiring BTU determinations, a corresponding increase occurred in the need to obtain “spot” samples of these systems. This paper is intended to present the problems that arise in “spot” sampling and to introduce the industry accepted methods, which can overcome these problems.

BACKGROUND INFORMATION

Upon initially beginning to handle the large increase in sample volumes, many laboratories noted a strange occurrence. Some analyses produced results that indicated leaner gas than expected. Analytical gravities were lower than actual field measured gravities and analytical BTU's were lower than BTU's measured by “on-line” calorimeter and chromatograph.

Investigations into this problem indicated retrograde condensation to be the major cause. Simply stated, retrograde condensation is the liquification of a portion of the gas sample when the sample temperature is lowered below the hydrocarbon dew-point of the sample while holding the sample pressure constant. Figure I shows a typical dew-point curve for a hydrocarbon mixture.

The solution seemed obvious. Heat the sample to at or above flowing line temperature before analysis. In doing so, however, a new problem arose. Results now often indicated gases that were richer than expected. The problem became more complex. Retrograde condensation also occurs in the gas pipeline and sampling techniques allowed the free hydrocarbon liquids into the sample cylinder. Upon heating before analysis, this free liquid vaporized within the cylinder, enriched the sample, and lead to erroneous analytical results.

It then became obvious that sampling played an important role in obtaining good analytical data. The CPA undertook the study of natural gas sampling problems and in 1968 adopted and published its publication 2166-68, "Methods for Obtaining Natural Gas Samples for Analysis by Gas Chromatography".1 After much work in recent years, this publication was revised in 1986 and now lists eight accepted methods for natural gas sampling.

PURPOSE OF SAMPLING

As stated by both GPA and by ASTH, the purpose of any "spot" sampling technique should be to obtain a sample of hydrocarbon gas that is representative of the system from which it was taken. Regardless of the sophistication and accuracy of today’s laboratory instrumentation, an analysis can only be as good as the sample from which that analysis derives.

PROBLEMS IN SAMPLING

At the 1980 AGA Transmission Conference in Salt Lake City, Utah, Charles Drake4 outlined three phases in a complete sampling technique.

1. Transferring a representative sample from a source into a transporting device.
2. Transporting the gas from the source to the lab without affecting the representative sample.
3. Removing the sample from the transporting device and diverting it to the measuring device without distorting the sample.

The field technician is generally concerned with the first two phases of the sampling operation and should be aware of the major problems which might occur in either or both of these two phases.
During the first phase of sampling, the actual transfer of gas to the sample cylinder, three common problems generally arise.

1. CYLINDER CONTAMINATION
2. AIR CONTAMINATION
3. FREE HYDROCARBON FLUID ENRICHMENT

It is essential that all sampling be performed with clean, dry, and preferably stainless steel sample cylinders. Materials such as oil, grease, paraffins, or water left in a cylinder can either absorb portions of the gas being sampled or give up components to the sample. Sample cylinders constructed of carbon steel rust badly. This makes these cylinders extremely difficult to clean properly. Carbon steel cylinders also absorb some of the carbon dioxide, which is usually present in the gas stream being sampled.

Air contamination of a sample occurs when the air naturally residing in a sample cylinder after cleaning is not completely displaced by either a displacement medium (water, helium, etc.) prior to sampling or by the sample gas itself during the actual sampling. Enriching a sample with extraneous heavy hydrocarbons is probably the most common error occurring during "spot" sampling. Because of the retrograde condensation discussed earlier and because of separation equipment problems, virtually all gas transportation systems have free fluids moving along the walls of the pipeline. This fluid, if allowed entry into the sample cylinder, will greatly enrich the heavy end components of the sample being taken. Refrigeration of the sample cylinder due to expansion of the gas while either "filling and purging" or "continuously purging" the sample can result in heavy liquid hydrocarbon formation within the cylinder. Again, heavy end enrichment is the result.

Once the sample has been procured, it must be transported to the laboratory for analysis. Allowing the sample to depressurize during transportation can alter the composition of that sample. Samples that are warmer than ambient temperature cool after sampling causing the heavier components to liquefy within the cylinder. If, these samples depressurize, the lighter components (still in the gaseous phase) escape while the heavier liquids remain. As depressurization continues, these liquids begin to vaporize which further alters the composition of the gas remaining in the cylinder. Both Drake4 and Schepers5 showed the effect of increasing BTU values as pressure is depleted from the sample. Table I shows this BTU increase effect. Any alteration of sample composition results in a non-representative sample and complete depressurization results in sample that is totally useless.

Allowing any of these problems to occur ruins the sample and results in a large excess of time and revenues necessary to finally accomplish the job intended. In some instances, critical Information available only at the exact time of sampling may be lost forever.

### Table I

<table>
<thead>
<tr>
<th>Pressure (PSIG)</th>
<th>Time (MINS)</th>
<th>Heating Value (BTU/CF(1))</th>
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(1) 30" Hg, 60°F, Saturated

### SAMPLING METHODS

CPA publication 2166-86, "Obtaining Natural Gas Samples for Analysis by Gas Chromatography" lists eight approved methods for sampling.

1. WATER DISPLACEMENT METHOD
2. PURGING-CONTROLLED RATE METHOD
3. PURGING-FILL & EMPTY METHOD
4. GLYCOL DISPLACEMENT METHOD
5. REDUCED PRESSURE METHOD
6. FLOATING PISTON CYLINDER METHOD
7. HELIUM "POP" METHOD
8. EVACUATED CONTAINER METHOD

This publication also classified the gas to be sampled as being either DRY (LEAN) or WET (RICH) based on the tendency of the gas to condense upon cooling or reduction of pressure. A procedure selection guide is presented which considers both the nature of the sample and the source conditions under which sampling is to take place. Detailed instructions are given for the proper execution of each method. The field technician should be completely familiar with this publication and follow these procedures when assigned the task of "spot" sampling.

### CRITICAL FACTORS

Several key factors are common to all of the above listed procedures and should be kept in mind at all times. In addition, certain steps within a given procedure should be emphasized.

Selection of a proper sampling point is critical to all methods. Sample tape should be at the top of a horizontal
line and away from bends and obstructions. Samples should not be taken from dead gas sources. All sampling taps should include a sampling probe, which extends to the middle of the flow line. Prior to installing sampling equipment the sample tap should be blown to remove any accumulated materials. A line separator must be used if entrained liquids are present in the flow line. Separators must be purged with sample gas prior to actually filling the sample cylinder. All gas systems of unknown composition should be assumed to be WET (RICH) in nature. After actual sampling is completed, the sample cylinder should be leak checked by immersion in water or by leak detection solution. With the use of Teflon tape, cap or plug cylinder valves before transportation to the laboratory. All sampling should be done by a trained-individual.

In addition to the above listed general factors, individual sampling methods have their own critical points. The "Purge & Fill" method is not to be used if the sample temperature exceeds the cylinder temperature. Table 11 shows the number of purge and fill cycles necessary to purge both separator and cylinder of residual gas. Similarly, the "Continuous Purge" can not be used if sample line temperature is above cylinder temperature. The "Continuous Purge" method is not recommended for WET (RICH) gases under any circumstances. An extension tube is required for both "Purge" methods. Figure 2 shows purging time required with the "Continuous Purge", method. The "Evacuated Container", "Reduced Pressure", and "Helium Pop" methods all require evacuated sample cylinders. In order to avoid significant air contamination this vacuum must be a minimum of 1 mm Hg and must be maintained until actual sampling occurs. "Water Displacement" and "Glycol Displacement" require that the entire displacement medium be removed from the sample cylinder so as not to alter the composition of the sample over longer periods of time. Water used as a displacement medium must have a pH of 5.0 to 7.0 to avoid changing the carbon dioxide concentration of the sample. The final method, "Floating Piston Cylinder", is relatively new. Piston lubricant and seals must be non-absorptive. Back pressure gas should be inert and different from the sample components if possible. Back pressure should, always exceed sample line pressure.

By far, the greatest number of sampling errors are caused by ignorance of these critical factors. With a little practice and by keeping these factors in mind any technician can procure accurate and representative samples.

SAFETY

Safety should at all time be the prime consideration during any sampling operation. Field technicians should at all times be aware of and comply with their employer's safety regulations as well as those of any company on whose premise they are working. The following rules should always apply.

1. Use equipment and cylinders of sufficiently higher working pressure than the gas system pressure.
2. Always insure that sample tap valves are closed before removing valve plugs.
3. Never expose gas samples to extreme heat.
4. Do not smoke while at or near gas system.
5. Wear required safety clothing and equipment.
6. Immediately report any unsafe equipment or conditions.
7. Follow proper DOT procedures when transporting or shipping gas samples.
CONCLUSION

Technicians should always be aware of the economic importance of good sampling procedures. Consider the end result of a non-representative sample. Assume a bad gas sample results in a 10 BTU error. This would generally be an error of less than 1.0 percent. Had this error been made on a system with a flow rate of 2000 MCF I) per day and a contract price of $2.00 per MMBTU, the end result would be a monetary gain or loss of $14,600 per year.

This very realistic example should certainly reinforce the old adage "If it's worth doing, it's worth doing right". The success of this industry depends on that philosophy.

REFERENCES

1. OPA 2166-68 "Methods for Obtaining Natural Gas Samples for Analysis by Gas Chromatography". Gas Processors Association, 1812 First Place, Tulsa, Oklahoma 74103


3. GPA 2166-68 "Obtaining Natural Gas Samples for Analysis by Gas Chromatography". Ibid
