

Analysis of High Pressure Samples by Gas Chromatography

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ABSTRACT

High molecular weight compounds dissolved in gases at elevated pressures and temperatures in reservoirs often present production problems. These can range from precipitation of solids which foul chillers and tubing to plasticizing membranes used for gas component separations. Quantitative analysis of such samples is problematic because they are frequently present in sample vessels as two phases (gas and solid or liquid). This paper describes a technique for rendering samples collected at high temperature and pressure single phase and analysis by gas chromatography. Results of this technique to the analysis of gases containing diamondoids and other high molecular weight hydrocarbons are presented.

INTRODUCTION

The analysis of hydrocarbon gases is usually done by gas chromatography. Common analyses performed include a natural gas analysis which provides the hydrocarbon composition through n-pentane, a hexanes plus value, nitrogen, oxygen, and carbon dioxide. The analysis of these hydrocarbon gases by gas chromatography using a flame ionization detector is also often used to provide details about the hydrocarbons present in the C1 to C8 range. If it is necessary to extend the analysis range to C12, or in the extreme to C28, this can be done by careful heating of the sample and sampling lines to the appropriate temperatures to make sure that the higher boiling hydrocarbons are not lost due to adsorption or cold spots. It is possible to get around these sampling problems which lead to discrimination by sampling under supercritical conditions.

EXPERIMENTAL

SFC grade carbon dioxide was obtained from Air Liquid. An Isco syringe pump was used to pressurize samples with the carbon dioxide. A 6 port valve allowing sample pressures up to 6000 psi with a 30 μ L sample loop was used. The sample inlet line and valve was heated to about 60°C. The restrictor used between the valve and the injection port was between 5 and 10 cm of 50 μ m id fused silica tubing. This is similar to the approaches taken in SFE/GC techniques (1). The gas chromatograph was a Hewlett-Packard 5890 equipped with both FID and FPD detectors. A high pressure gauge reading from 0 to 10,000 psi was positioned between the valve and the waste outlet. Flow at the outlet was controlled with a needle valve (see Figure 1). Samples were in stainless steel cylinders ranging from 150 cc to 500 cc.

To do the extended hydrocarbon analysis first a conventional natural gas analysis was obtained. This was done in order to get the concentrations of nitrogen, oxygen, carbon dioxide, and the C1 to C4 hydrocarbons. At this time the sample pressure was also measured along with the cylinder weight. Based on the amount of methane and carbon dioxide present the quantity of carbon dioxide necessary to bring the sample to a reduced density of 1 or greater was calculated. Using the syringe pump this quantity of carbon dioxide was added to the sample and the sample was reweighed. The weighing helped verify that the right amount of carbon dioxide really was added to the cylinder. The sample was then allowed to equilibrate (usually overnight) at 60°C until sampling.

Sampling was done at cylinder pressure and temperature. The sampling line was heat traced along with the valve. Another high pressure line to the valve from the ISCO pump supplied carbon dioxide at or slightly above the cylinder pressure as measured by the pressure gauge. Prior to sampling the sample was allowed to flow through the sampling system for at least 2 to 3 minutes at about 100 mL/min. In order to keep methane through butane on scale a range change from lower to higher sensitivity was done automatically after the elution of n-butane. The magnitude of this change was generally a factor of 512, but for some samples with high concentrations of hydrocarbons it was lower.

RESULTS AND DISCUSSION

The data indicate that reduced densities of at least one are sufficient to give quantitative results for most samples. This is shown by the results in figures 2-4. Most importantly this data indicates that by sampling under the proper conditions it is possible to significantly reduce or eliminate any discrimination between low boiling and high boiling hydrocarbons. Quantitative results for the hydrocarbons are calculated by using the natural gas results for the amount of methane through butanes in the sample. Using this value as an internal standard amount the quantities of other hydrocarbons in the sample can be calculated based on a carbon equivalent response for the FID (2). It is possible to determine adamantanes and other hydrocarbons quantitatively at concentrations of 1 ppm with detection limits around 0.05 ppm. The actual quantitative limits depend on the initial state of the sample. Samples which require the addition of large amounts of carbon dioxide will have higher detection limits, and those requiring little carbon dioxide will have lower detection limits. Obviously this analysis excludes water. If water is present is not expected to significantly impact the results obtained except for its exclusion.

REFERENCES

- (1) Lee, M. L.; Markides, K. E. *Analytical Supercritical Fluid Chromatography and Extraction*; Chromatography Conferences, Inc.: Provo, Utah, 1990; PP 335-344.
- (2) Scanlon, J. T. Willis, D. E. *J. Chromatogr. Sci.* 1985, 23, 333.

FIGURES

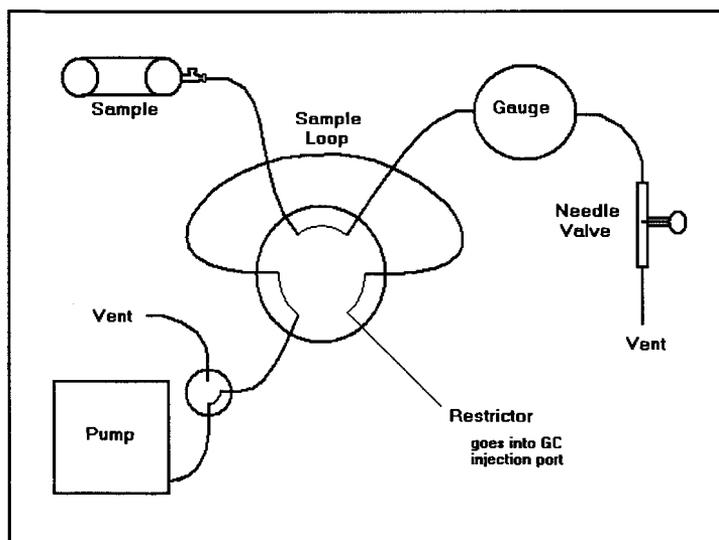


Figure 1. Diagram of the sampling system.

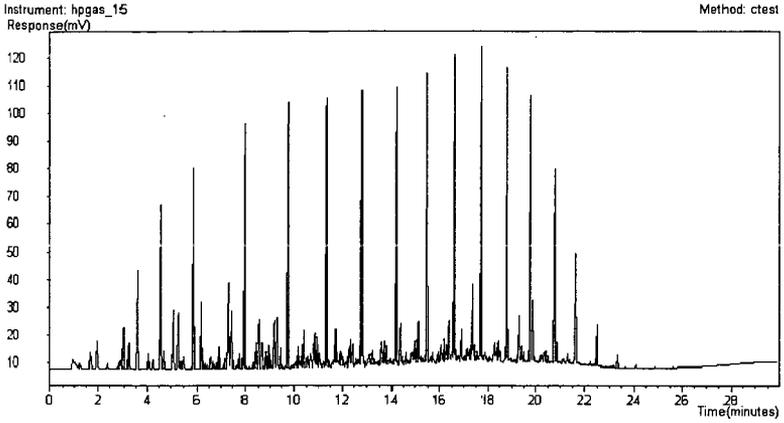


Figure 2. Results at a reduced density of 0.5.

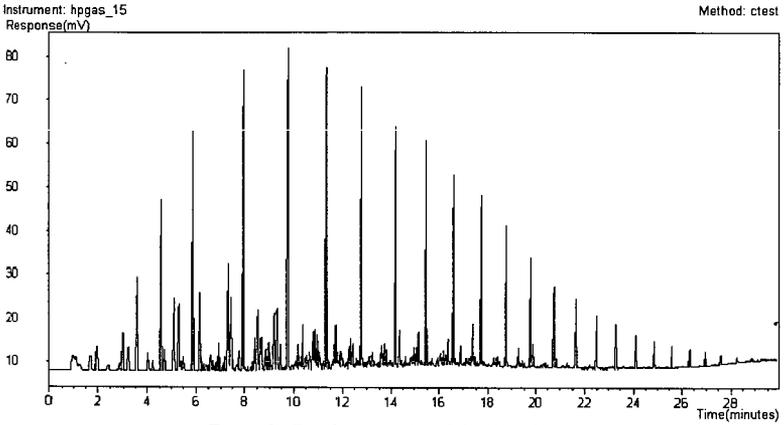


Figure 3. Results at a reduced density of 1.0.

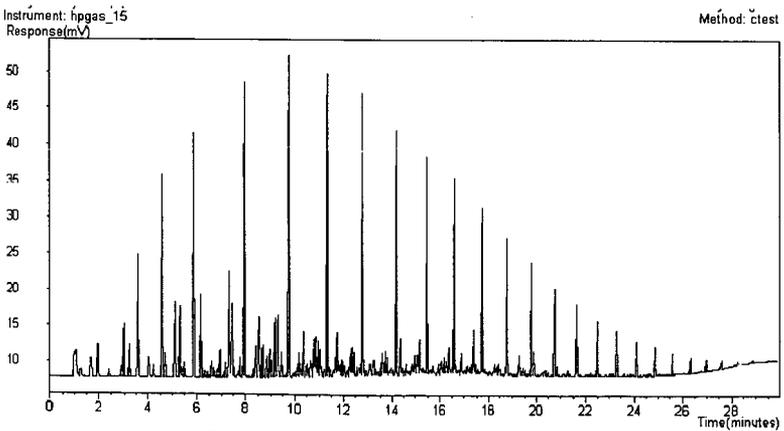


Figure 4. Results at a reduced density of 1.2.