# [PS]Statistical Comparison of Hydrocarbon Gas Composition and Isotopic Ratios from Multiple Sampling Methods*

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## Abstract

A standard aspect of formation evaluation is an inferential analysis of hydrocarbon gases encountered in the subsurface. The nature of these gases can indicate fluid saturation, phase, quality, provenance, and many other unknowns that are fundamental to understanding the petroleum system as well as commerciality of the respective well. Currently, there are four principal sampling and analysis techniques employed. These include well site mud gas analysis, offsite analysis of collected mud gas (IsoTubes®), headspace analysis from cuttings samples (IsoJars®), and analysis of flashed gas from down-hole fluid-sampling tools (e.g. MDT). The interpretation of these data is imperative to any petroleum systems analysis, but, as is often the case in applied exploration science, only one or two sampling methods may be prudent to collect during operations. Additionally, historic data may be incomplete or limited, and an understanding of relationships and inherent biases in the sampling and analytic methods can help to increase confidence when dealing with such limited datasets. This study offers a statistical comparison of these four methods, in the context of applied analysis of a deepwater dataset, to quantify sampling and analytical uncertainty. It has been observed in limited case studies that normalized gas composition measurements are variable between IsoTube® and MDT samples, but a statistical analysis on a large dataset across multiple hydrocarbon plays with both compositional and isotopic variables has not been published. This comparison, combined with well-site GC and headspace gas analysis, creates a robust analytic tool that can help to overcome the problems of data sufficiency and cost associated with running redundant analyses.

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# Statistical Comparison of Hydrocarbon Gas Composition and Isotopic Ratios from Multiple Sampling Methods

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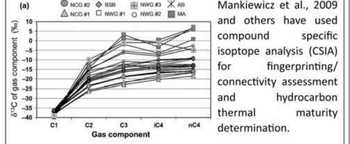
## Abstract

A standard aspect of formation evaluation is an inferential analysis of hydrocarbon gases encountered in the subsurface. The nature of the gases can indicate fluid saturation, phase, quality, provenance, and many other unknowns that are fundamental to understanding the petroleum system as well as commerciality of the respective well. Currently, there are four principal sampling and analysis techniques employed. These include well site mud gas analysis, offsite analysis of collected mud gas (IsoTubes), headspace analysis from cuttings samples (Isolars), and analysis of flashed gas from down-hole fluid sampling tools (e.g. MDT). The interpretation of these data is imperative to any systems analysis, but, as it often the case in applied exploration science, only one or two sampling methods may be prudent to collect during operations. Additionally, historic data may be incomplete or limited, and an understanding of relationships and inherent biases in the sampling and analytic methods can help to increase confidence when dealing with such limited datasets. This study offers a statistical comparison of these four methods, in the context of a deepwater dataset, to quantify sampling and analytical uncertainty. It has been observed in limited case studies that normalized gas composition measurements are variable between IsoTube and MDT samples, but a statistical analysis on a large dataset across multiple hydrocarbon plays with both compositional and isotopic variables has not been published. This comparison, combined with well-site has chromatography and headspace gas analysis, creates a robust analytic tool that can help to overcome the problems of data sufficiency and cost associated with running redundant analyses.

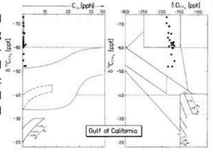
## Motivation and Objectives

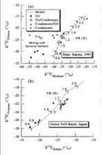
Analaysis of subsurface gases has routinely been performed during drilling since the earliest days of mud logging. It has evolved such that gas composition and isotopic ratios are powerful tools to evaluate what the drillbit is encountering in the subsurface and what the implications are for the petroleum system understanding.




Mankiewicz et al., 2009 and others have used compound specific isoptope analysis (CSIA) for fingerprinting/ connectivity assessment and hydrocarbon thermal maturity determination.

Schoell, 1983 developed methods for determing origin (bio- vs. thermo-genic), maturity, and degrees of genetic mixing using carbon and hydrogen isotopes and gas composition.



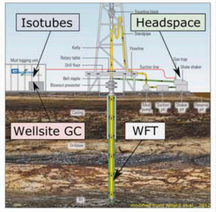



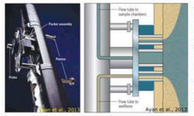
In 1996, Berner and Faber published a method for determing the Ro% of the source rock at the time of expulsion of associated gases by cross-plotting carbon isotopic ratios of methane, ethane, and propane. This methodology can prove especially useful for calibrating basin and petroleum system models, but the isotopic ratios of the kerogen is needed for the most effective analysis.

These are only a few of the published tools for hydrocarbon gas analysis (notable others include Bernard et al., 1978 and Chung et al., 1988). The missing piece of the analyses lie in the inferential uncertainty associated with different sampling methods. Those engaged in petroleum systems anlayses are often working in areas of extremely limited and poorly documented data, but the scarcity of the data necessitate inclusion of all types. This study seeks to overcome the individual limitations of such data by taking a statistical approach and documenting the uncertainty from a dataset of different plays, ages, depths, and fluid qualities.

## Data Sources

There are three locations in which subsurface gases are sampled throughout the drilling process: the wellbore, the shale shaker, and the mud logging unit. Downhole wireline formation testers are generally the highest confidence, but the samples are extremely expensive and often only taken after minimum commercial or geologic success criteria. It is uncommon to have more than a few WFT sample points in a well, so much less expensive samples are generally taken at the shale shaker and in the mudlogging unit with greater frequency. In fact, the wellsite gas chromatograph is nearly always run continously for drilling safety and monitoring reasons. Wellsite GC analysis is returned as a curve commonly displayed on the mud log, and the other samples are sent offsite and returned as a spreadsheet with composition and isotope data.




**Wireline Formation Testers (WFTs)**

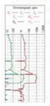
Downhole tools have the ability to sample pressurized formation fluid directly from the reservoir. Hydraulic pistons push the probe, sealed with a packer, through the mudcake and and into the formation. Fluid is then pumped through the tool until contamination from invaded filtrate is lowered to an acceptable level. Then, a vessel in the tool is filled with the formation fluid and then sent offsite for controlled PVT analysis. (Ayan et al., 2013)

**Headspace Gas (Isojars)**

Returning drilling fluid contains cuttings from the drilling process that are separated before it is recirculated back down the drillpipe. These cuttings contain formation gases that will desorb in time. By scooping a cuttings sample from the shale shakers into a small sealed container, such as an Isojar, a desorbed gas sample from formation rock fragments can be obtained from the empty space in the top and analyzed in an offsite lab. This method is relatively inexpensive but is subject to depth uncertainty and sampling (scooping) bias.


**Isotubes**

While returned drilling fluid and suspended cuttings are arriving to the shake shakers, a vacuum line pulls the liberated formation gas from the fluid through a vacuum line to the mudlogging unit. These gases, that are dissolved in fluid under high pressure during drilling, are then diverted at planned intervals into a small tube-shaped vessel. The depth (or depth interval) is calculated from the mud return lag time and written on the tube. The are placed in a box and, when full, shipped to an offsite lab for analysis.

**Wellsite Gas Chromatography (Mud log)**

The vacuum line (typically the same line that feeds the Isotube manifold) also runs to a gas chromatograph in the mud logging unit. This is the only gas sample collection and analysis that is done on-site. The typical wellsite GC will report methane through pentanes, but some advanced units now have in-line mass spectrometers to report through decanes as well as simple aromatics and alkenes. Analyses are reported continuously while drilling and are regularly calibrated. Interpretation of the real-time data is well established and is commonly reported on petrophysical logs. (Ablard et al., 2012; Haworth et al., 1985)

## Dataset and Statistical Methods

A proprietary dataset of deepwater wells was used for this study. A total of 20 individual sample points were included across 12 different organic compounds/isotopic ratios resulting in 240 individual samples. Nine individual wells were included in the dataset.

An assumption was made that downhole sampling tools (or wireline formation testers - "WFT") produce the most representative samples of true formation fluids (see Data Sources section for additional information). In order to protect the proprietary nature of the data and to calibrate the representativeness of the additional three sampling methods, the depth and associated values of the downhole samples were normalized to zero and the additional three sampling methods are represented as positive or negative distributions of values about this normalized downhole sample value.

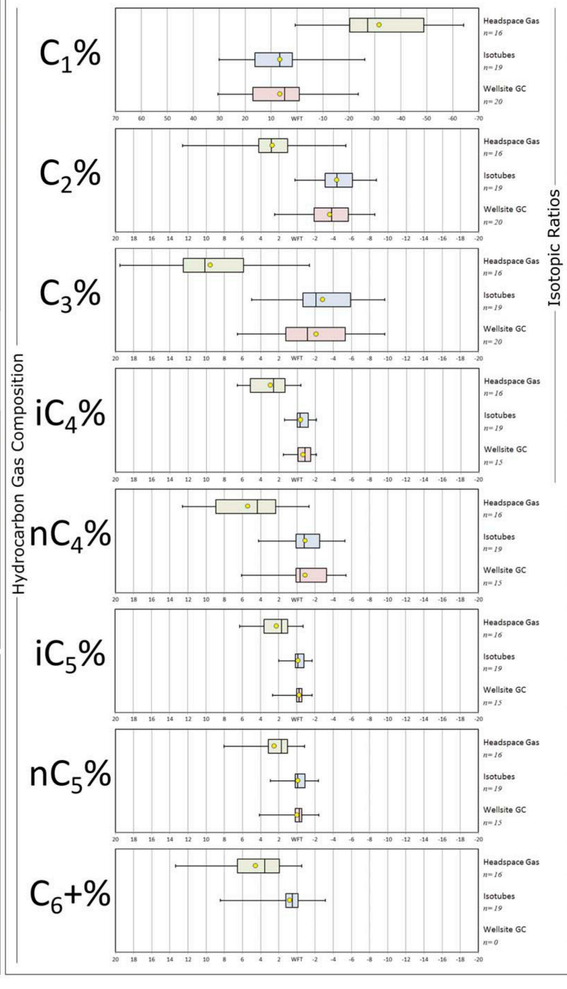
A generalized depth uncertainty has been ascribed to the various sampling methods that includes +/- 20 reported feet both shallower and deeper than the downhole sample. This is intended to address wireline stretching or misreporting of the downhole sample as well as uncertainty of the lag time associated with mud returns. There is no weighting of the individual samples within the 40 foot window. Due to the great variation in rate of penetration, mud weight balance, reservoir permeability, and other factors between wells and individual samples, the following data conditioning steps were taken:

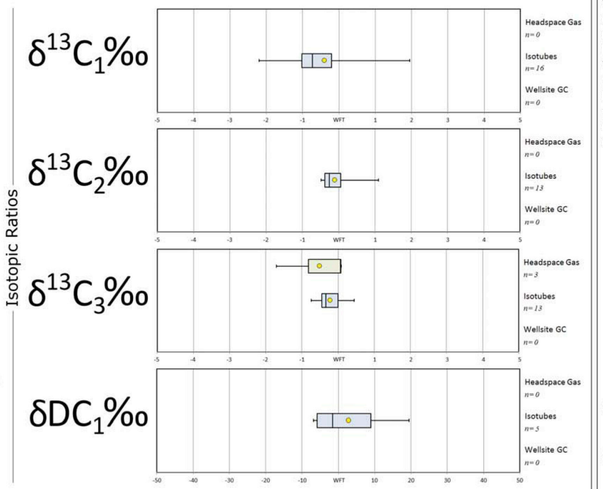
-Wellsite GC: A 40 foot moving average was taken from the .las file. The downhole sample depth was used.

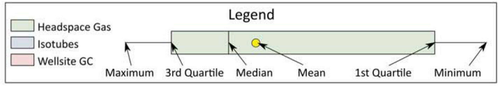
- Isotubes: Individual reported depths within +/- 20 feet of downhole samples were included. Interval depths were averaged and included as samples when the averaged depth was within +/- 20 feet.

-Headspace Gas: The same technique was used as Isotube samples. For slightly broader interval spacing (i.e. <50 feet), the values from the interval covering the downhole sample were used.

## Results




- In general, **wellsite GC and Isotube samples are compositionally more consistent** with WFTs than headspace gas samples.
- **Isotube and wellsite GC samples are consistent with each other**; Isotubes may have a slightly tighter distribution but the mean is not consistently closer to WFT samples.
- By far, **the greatest compositional sample bias is in methane concentration (note scale).**
  -Headspace gas under-represents methane concentration by a median value of 24%.
  -Isotubes and wellsite GC over-represent methane by median values of 5% and 4%, respectively.
- Because methane is over- or under-represented, representation of another compound will be skewed.
  -**Headspace gas over-represents propane** the most, by a median value of 10%.
  -**Isotubes and wellsite GC under-represent ethane** the most by median values of 4%.
- **All carbon isotopic ratios appear to be represented with great accuracy by Isotubes.**
- Isotopic ratios from headspace gas may also be consistent with WFTs, but more samples are needed.
- Hydrogen isotopic ratios may be generally accurate with slightly more uncertainty.
- Because outliers due to container failures may skew the mean, **median values appear to be more representative** as a central tendency.

## Conclusions

Though a relatively limited dataset has been used for this study, enough notable trends have emerged that a tool for general correction can be developed. At this point, it is certainly most applicable for conventional plays, and an area of future work can be to broaden the basin and play types in the sample distributions.

The following table is for correction of headspace gas, Isotube, and wellsite GC samples to WFT samples. It is only for compositional correction as no isotopic correction is necessary between Isotubes and WFTs. The recommended bulk correction is the median of the variance distribution for each compound. Because the entire distribution is reduced to one number, it is important to be familiar with the original plots if a specific analysis could depend on small variation.

*Hydrocarbon Gas Composition Correction Table*

*All values in mol% for comparison with wireline formation tester samples*

| | $C_1$ | $C_2$ | $C_3$ | $iC_4$ | $nC_4$ | $iC_5$ | $nC_5$ |
|---|---|---|---|---|---|---|---|
| Isotube | -7% | +4% | +2% | - | +1% | - | - |
| Wellsite GC | -5% | +4% | +1% | - | - | - | - |
| Headspace | +24% | -3% | -10% | -3% | -4% | -2% | -2% |

*No correction recommended for isotopic ratios!*

**Recommended workflow:**

1. **Check notes on individual samples and remove obvious outliers due to poor sample handling or shipping.**
2. **Observe isotopic values for sample range - methane carbon isotope ratios less than -60ppm may need less or no correction (these are likely to be microbial in origin).**
3. **Apply the recommended correction for the sample type and specific compound and check results (observe quartile ranges as well).**
4. **Compare data with WFTs or with each other.**

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