STABILITY STUDY OF STABLE ISOTOPIC COMPOSITION OF HYDROCARBON GASES

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Introduction

What's the isotopic shelf life of petroleum gas?

Valid shelf life of petroleum gases for isotopic analysis is relatively unknown from formal, designed experiments which require long-term planning of methodology and availability of appropriate resources (instrumentation, analysts, analytes, and storage).

Consider stability while in use and in storage.

Long-term study of the impact on isotopic composition from both repeated sampling from a single cylinder (***Operational stability***) and in cylinders stored for longer periods (***Storage stability***) requires dedicated samples, facilities and methods to ensure consistency and interpretation potential of results.

A comprehensive evaluation is now in progress.

We designed and created custom gas mixtures, a fit-for-purpose subsampling strategy, and a dedicated analytical campaign to study the operational stability, storage stability, and individual component stability of the C_1–C_3 carbon and C_1 hydrogen isotopes of standard gases.

Subsampling Method Evaluation

Methods Tested

Specifications	Advantages	Disadvantages
 **Scott* Septum Valve with regulator**		
Inlet P: 1000 psig max	Easy to change septum	Requires thorough evacuation
Flow: 0.3 LPM	Easy to connect/disconnect from cylinder	Cylinder pressure is too high (500 psig) so difficult to control injection volume
Cylinder: Scotty* 34 (500 psig)	Pressure reading useful to monitor gas in cylinder	Difficult to check for leaks
 **Septum Flow-Through Regulator**		
Inlet P: 1000 psig max	Easy to change septum and connect/disconnect from cylinder	Adapter on a glassware piece easily breakable and cannot be replaced on its own (need to replace the entire regulator)
Flow: 1 LPM	No evacuation needed with flow through feature	Difficult to check for leaks
Cylinder: Scotty* 34 (500 psig)	Pressure reading useful to monitor gas in cylinder	Higher gas usage
 **Gas Bag with Septum Regulator**		
Ref: Tedlar™ gas sampling bags (SKC)		
P: <3 psig	Septum regulator useful to monitor gas in cylinder	Need to carefully connect the gas bag to septum regulator
Capacity: 0.5 L		Takes a bit of time to connect to cylinder
Flow: N/A (single injections)		Leaks are observed from time to time
Cylinder: Scotty* 34 (500 psig)		Evacuation of the septum regulator needed; bag must be carefully evacuated before filling
 **Direct Subsampling**		
Ref: Simple Swagelok™ connection		
Inlet P: 240 psig max	Easy to change septum	No pressure reading to check remaining gas in cylinder
Flow: N/A (single injections)	No added connection needed/ Easy to connect to AS	High cylinder pressure (240 psig) so difficult to control injection volume
Cylinder: Scotty *14 (240 psig)	Easy to make leak free	
	Small dead volume to evacuate	
 **2-Stage Regulator**		
Ref: Scott® regulator 2S-MINI-X		
Inlet P: 3000 psig max	Easy to change septum	Requires thorough evacuation
Outlet P: 30 psig max	Pressure reading useful to monitor gas in cylinder	Heavy 2-stage regulator makes it more difficult to manipulate
Cylinder: Scotty* 110	Leak check possible	

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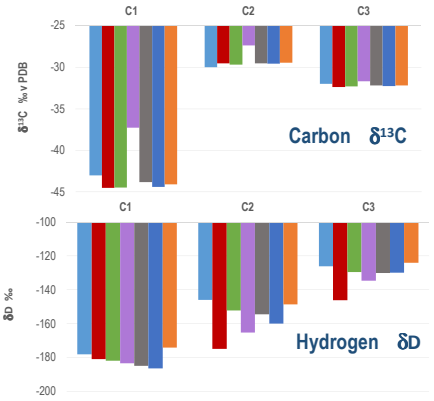
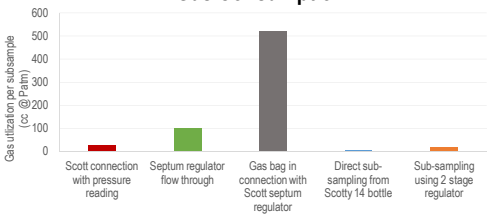
Isotopic Measurements

Standard Value · Scott septum valve · Septum reg. flow through · Gas Bag 1 · Gas Bag 2 · Direct Subsampling · 2 stage regulator

The **SEPTUM FLOW-THROUGH REGULATOR** yielded the lowest standard deviation for carbon isotope composition of C1 (0.2‰), C2 (0.1‰), and C3 (0.1‰) as well as hydrogen isotope composition of C1 (3‰). This subsampling method was chosen for its simplicity and repeatability.



Gas Consumption



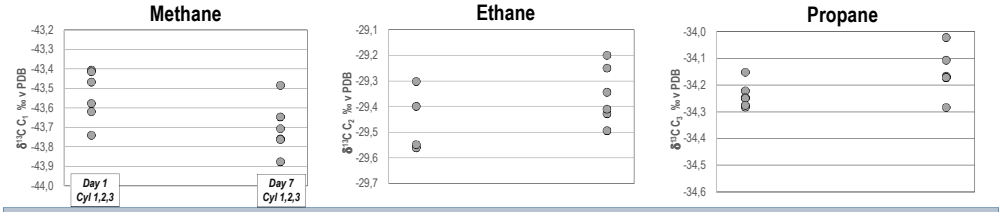
Operational and Storage Stability Study

Air Liquide performed the blending and filling of Scotty* 34 cylinders, once the subsampling method was established.
Composition: 87% C1, 7% C2, 3% C3 and minor (1.5% each) CO_2 and N_2.

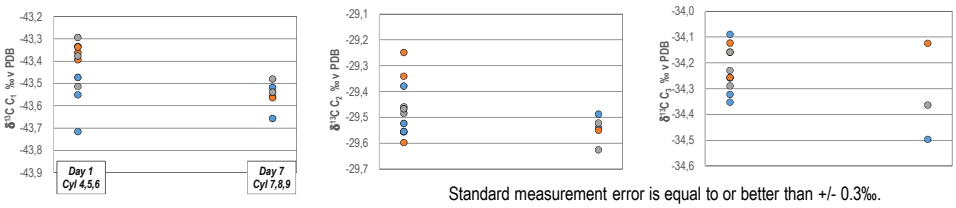
Schlumberger analyzed cylinders in sets of three.
Operational stability tests: Same cylinders analyzed repeatedly over years.
Storage stability tests: Remaining cylinders analyzed only once, sequentially over time.

Initial results show consistent values in the early re-sampling of cylinders 1,2, and 3, after 1 week of receipt, and the sampling from individual storage cylinders 4 – 9.

Operational Study



Storage Study



Standard measurement error is equal to or better than +/- 0.3‰.

Conclusions

Long Term Planning Requirements

- ✓ Testing subsampling methods
- ✓ Developing protocols for repetitive subsampling
- ✓ Filling and shipping cylinders with consistent isotopic compositions
- ✓ Preparing an extensive analytical program

Subsampling Method Evaluation

- ✓ The **two-stage regulator** with Scotty* 110 cylinder uses the least amount of sample with good repeatability, but is at high pressure and requires additional safety-handling procedures.
- ✓ The **septum flow-through regulator** yielded the lowest standard deviation for carbon isotope composition of C1-C3 as well as hydrogen isotope composition of C1.

Stability Study Results

- ✓ Study methodology is now well established.
- ✓ Initial measurements are consistent for both operational and storage stability studies.
- ✓ Study will progress over months to measure and understand variations in hydrocarbon gas compositions over the long term.