

**Rum-Punch:**

Time series petroleum biomarker testing of the scenario that an actively leaking oil well is contributing to the MC20 sea surface sheen

Prepared for Unified Command

by

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**Introduction:**

This analysis is presented as follow-up to the December 2017 MC20 Unified Command (UC) meeting question raised by Lars Herbst, BSEE incident commander, regarding the utility of sheen hydrocarbon composition to identify if an active input (i.e. leaking well) is contributing to the sheen. Specifically, what would be the minimum threshold for this methodology to detect if a leaking well was actively contributing to the MC20 sheen source?

During the UC meeting, a qualitative discussion introduced how serial enrichment of contaminated sediments by a leaking well would cause the hydrocarbon composition of the sheen to become more homogeneous (exhibiting less statistical variance) and trend toward the endmember composition (i.e., the leaking well's composition). The analogy that was presented to UC was a “rum punch” scenario. In this example, if a bowl filled with fruit punch was repeatedly spiked with rum, and after each cup of rum was added to the punch bowl, the rum punch was stirred and an equal sized cup of rum punch was removed (thereby conserving the overall volume in the bowl), over time the composition of the rum punch would trend toward consistently increasing rum content.

The mechanism for serial enrichment of MC20 sheen hydrocarbons by a leaking well can be characterized and quantitatively bounded by coupling time series records of the site’s hydrocarbon chemical dynamics (2012 through 2017) with direct observations of the sheen source’s seafloor geometry and associated structures. This document provides a quantitative analysis of the MC20 sheen source using these methods and a summary of findings, including calculated minimum limits of detection and estimated time to detection for a range of hypothetical well leak rates, along with their associated 95% confidence bounds.

### Sheen source location:

Although surface sheens emanating from the MC20 site exhibit biomarker signature variability, the ensemble biomarker composition for sheen samples from July 2012, Feb 2013, and March-April 2017 more closely correlate with the February 2013 sediment samples collected around the containment Dome C than the July 2012 sediment samples collected near the former well bay and locally around the area (Fig 1). Detailed hydrocarbon forensics by the SSLWG corroborate this finding [1]. Furthermore, all 2017 acoustic data collected by the SSLWG indicate that the sheen source is from the Dome C&D site [2].

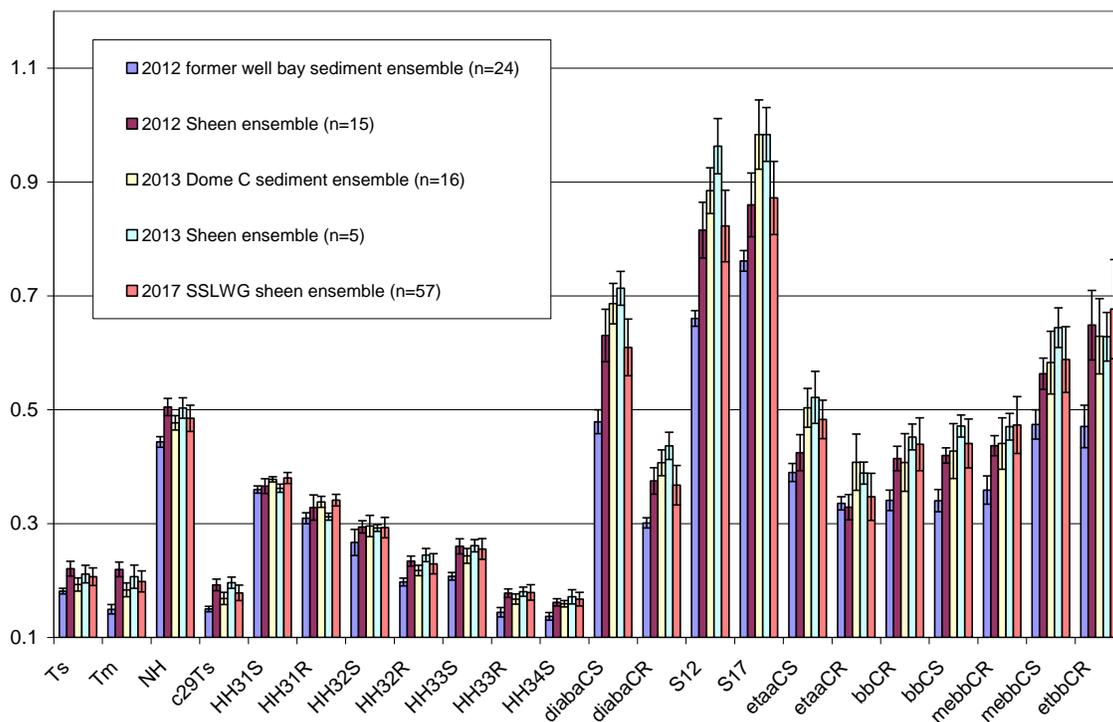


Figure 1: Statistical hydrocarbon composition comparison of the ensemble former well bay sediments, Dome C sediments, and sea surface sheen samples (2012, 2013, and 2017) using 22 biomarker ratios. These ratios were chosen for studying the sheen chemistry as they would be least likely to weather when released from the seafloor to the sea surface and thereafter. Error bars indicate  $\pm 1$  standard deviation. Ensemble is defined as the combined value of all samples from that time period, “n=” refers to the number of samples.

In addition to the utility of chemical forensics for characterizing the provenance of individual sheen samples, it can be used to identify if oil from a leaking well is a significant component of surface sheens. This is because an active well input will alter the chemical composition of the sediment source and sea surface sheens in two observable ways. First, over time the characteristic biomarker ratios will trend toward those of the leaking well. Second, as this shift toward the endmember composition occurs, the sheen source sediments as well as the resulting surface sheens will become progressively more homogeneous in their chemical composition. Thus, if hydrocarbons from one or more actively leaking wells are being sourced to the sediments and sheen, a

monotonic (i.e. continuous and non-reversing) trend toward the endmember biomarker ratios along with a characteristically decreasing variance in the biomarker ratios will occur. Multiple leaking oil wells or multiple oil reservoirs flowing into a single leaking well would still result in a singular endmember because these reservoir fluids would blend together resulting in a homogeneous composition at the point of discharge.

In 2017 the SSLWG conducted a detailed investigation of the historical samples previously analyzed at the site and selected 24 biomarkers to further evaluate prior findings by the United States Coast Guard's Marine Safety Laboratory that surface sheens had "matches" to sediments around Dome C and were not from a single source of oil. While all petroleum hydrocarbons are capable of weathering (breaking down or changing in their basic skeleton structure), diagnostic compounds were chosen that would be resistant to any weathering on the short time-scale of when small drops of oily residue travel through the water column from the seafloor to the sea surface. These ratios were also chosen because they are unlikely to breakdown in sunlight or evaporate on the sea surface prior to immediate sampling. Two of the diagnostic ratios were eventually not used by the SSLWG after a test (requested by NOAA representative Mr. Charlie Henry following the June 2017 meeting), showed these ratios to have greater than 5% uncertainty and were subsequently dropped from the SSLWG analysis. Thus, only 22 ratios were used. Additional analysis of replicate samples collected by Clean Gulf Associates in April 2015 indicates that analytical precision across all 22 biomarker ratios is on average  $\pm 1.6\%$  with a range of  $\pm 0.2\%$  to  $\pm 5\%$ . These diagnostic compounds are routinely recognized for their forensic value. All samples presented here were analyzed and reported by Alpha Analytical, one of the premiere laboratories for forensic hydrocarbon analysis.

Examination of the SSLWG sheen samples (collected 3/8-4/7, 2017; nine collection days) reveals multiple biomarker ratio trend reversals and discontinuities, which are inconsistent with inputs from a leaking well that would result in the biomarkers trending to a source endmember (Fig 2). This finding is corroborated in the SSLWG chemical analysis, which states that the collected sheen samples "were generally similar, yet none of the samples contained the exact same chemical compositions, indicating the oily residues were genetically different and not from a single homogeneous source" [1]. Furthermore, comparison of ensemble biomarker compositions from the 2012, 2013 and 2017 sheen samples with the Dome C sediment cores, show no trend in variance in any of the 22 biomarkers (Fig 3). Collectively, these biomarker dynamics indicate that the sheen source is not becoming more homogeneous with time and provide direct evidence that there has not been a significant hydrocarbon contribution to surface sheens from a leaking well in the 4 ½ year period from 2012 to 2017.

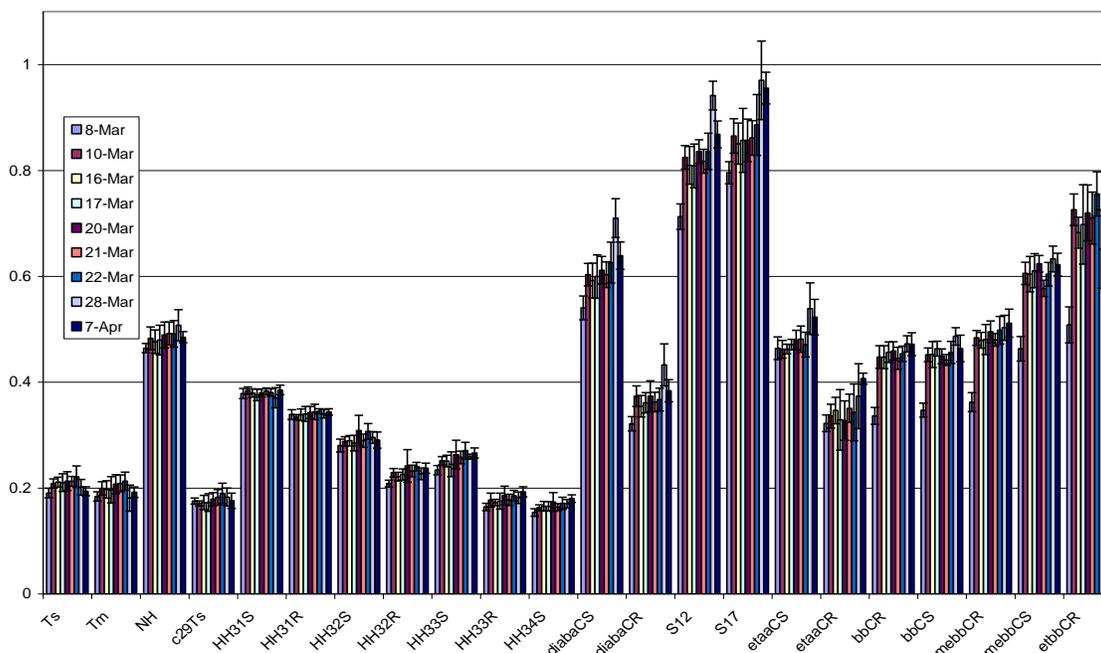


Figure 2: Time series plot of 22 biomarker ratios recorded from sheen samples collected from Mar8-Apr 7, 2017 (nine different days). Error bars represent  $\pm 1$  standard deviation.

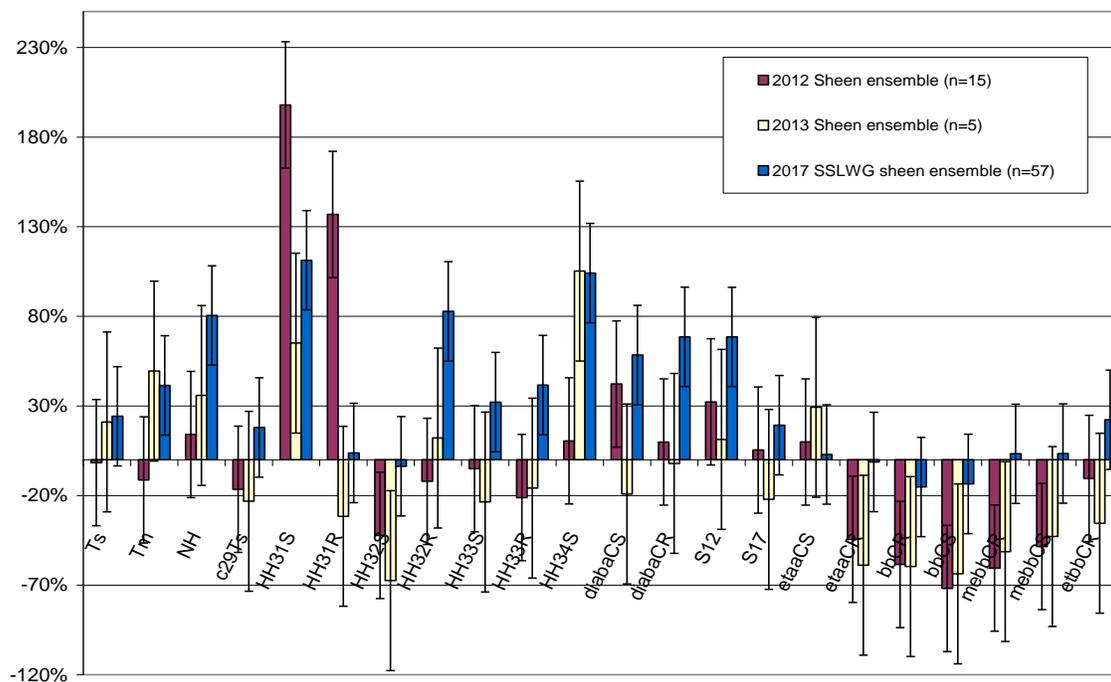


Figure 3: Variance trends in 2012, 2013, and 2017 surface sheen sample biomarker ratios relative to 2013 sediment cores collected at the Dome C. Positive Y-axis values indicate increased variance in sheen biomarker composition relative to the 2013 sediment cores, negative Y-axis values indicate decreased variance. Error bars denote sampling error at a 95% confidence interval.

**Oil mixing and detection limits:**

Detailed analysis of the Dome C&D pit structure based on the 2017 SSLWG sonar survey reveals that it is conically shaped and in a location that is relatively unchanged from its observed position in 2015 [2]. When considered in combination with the chemical forensics, these constraints allow for two possible scenarios, either

1. There is not an active oil well leaking into the Dome C&D pit sediments and the sheen is being generated by a continuing release of remnant oil from the contaminated sediments, or
2. There is a leaking oil well with an input rate to the sediments that is below the chemical limits of detection and is less than or equal to the mass lost from the Dome C&D pit (i.e., the volume of oil input by the leaking well is less than or equal to the volume of oil and sediment lost from the pit)<sup>\*</sup>

The maximum release rate for both scenarios can be calculated by coupling a physical model of the sheen source with the previously described chemical analysis. Using the estimated Dome C&D sheen source location diameter of approximately 160 ft [2], and the well conductor burial depth at the jacket of 69 ft below the mudline [3], a potentially active sediment volume can be modeled as a cone of approximately 510,000 ft<sup>3</sup> (14,000 m<sup>3</sup>) as of when the containment domes were placed in 2009 [4]. Using the SSLWG sonar estimated Dome C&D pit depth of approximately 20 ft and approximately 160 ft diameter at the mudline [2], the volume of sediments eroded from this conically shaped pit between 2009 and 2017 is estimated at 150,000 ft<sup>3</sup> (4,200 m<sup>3</sup>). This is equivalent to an average rate of roughly 19,000 ft<sup>3</sup>/yr (530 m<sup>3</sup>/yr) for that time period. Quantitative analysis of differences in pit volume observed during the 21 months between the 2017 SSLWG survey and previous 2015 survey [5] indicates that the pit has continued to erode, increasing in size by approximately 20,000 ft<sup>3</sup> (570 m<sup>3</sup>)<sup>†</sup>. The sediment erosion rate of this subsampled 21-month interval is approximately 11,000 ft<sup>3</sup>/yr (320 m<sup>3</sup>/yr), which is within a factor of two of the pit's estimated long-term erosion rate and indicates that release of remnant oil from the sediments is likely to be continuing at the site.

By subtracting the conical volume of the pit from the cone volume using the 2009 mudline depth, the present day active sediment volume is estimated at 360,000 ft<sup>3</sup> (10,000 m<sup>3</sup>). The oil concentration within this active sediment volume can then be calculated using the 2012 sediment core samples. Using the measured total petroleum hydrocarbons (TPH) of these 16 sediment samples (four cores, each consisting of four sediment depth horizons) along with their water content [1], an estimated oil specific gravity of 0.88, and a sediment specific gravity of 2.68 [6,7], the average oil contained in these sediments is 2.8% ±0.7% by volume (assuming a 95% confidence interval).

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<sup>\*</sup> If steady state mass balance is not maintained and the rate of well oil leakage into the sediments exceeds the combined sediment loss and oil flow into the water column, the sediments at the Dome C&D pit would inflate, creating an obvious feature that would be readily identifiable with sonar survey.

<sup>†</sup> This comparative bathymetric analysis accounts for any slumping of the pit's side walls which may have occurred during this time interval.

The maximum oil release rate of scenario #1 can be bounded by simply multiplying the pit volume of 150,000 ft<sup>3</sup> (4,200 m<sup>3</sup>) by the average oil content (2.8 ±0.7%) and dividing by the time interval of approximately 8 years (2900 days). Assuming that all oil contained within these sediments is liberated into the water column, the maximum average release rate cannot exceed 10.7 ±5.2 gallons/day (0.26 BOPD). For comparative purposes, if the 21 month period from the June 2015 to March 2017 is examined as a subsample and the same 2.8% oil content is applied, the maximum average release rate (assuming all oil from the eroded sediment volume is released to the water column), cannot exceed 6.6 ±3.2 gallons/day. This subsampled remnant oil release rate is statistically indistinguishable from the long-term release rate.

Results from prior sediment core analysis [1,8] indicates that oil concentrations drop to background levels at a radius of less than 90 ft (27 m) from the center of the pit, making it thermodynamically unfavorable for remnant oil at lower concentrations outside the pit's perimeter to migrate inward toward the higher remnant oil concentrations within the pit's active region. Moreover, samples collected and analyzed from prior soil borings [9] reveal that remnant oil and gas within the contaminated sediments are characteristically present as localized globules and blisters within the clay sediments, indicating that the remnant oil is not preferentially transported (i.e., flowing) through the sediments, but instead has remained confined in place. Finally, comparative time series analysis of the areas surrounding the erosional pit show no detectable bathymetric change, indicating that mass is not being transferred laterally through the sediments as a result of lateral oil transport into the pit from surrounding soils. Therefore, these calculated remnant oil release values are considered maximum rates.

The maximum release rate of scenario #2 can be calculated by adding the maximum release rate of scenario #1 to the maximum well input rate. The average maximum well input rate can be calculated using the “rum punch” model. First, we multiply the present day active sediment volume by the average oil contained in the sediments. This yields a total volume of oil contained in the remaining active sediments (i.e., oil-in-place) of 10,000 ±4,900 ft<sup>3</sup> (75,000 ±37,000 gal or 1,800 ±880 bbls). Next, using this oil-in-place estimate of sediment contamination along with a steady-state mass balance (i.e., rate of oil flowing from a leaking well into the sediments equals the rate of oil exiting the sediments into the water column), standard mixing models can be applied to estimate the time required for the sheen's chemical composition to change. This rate of change can be bounded by two conventionally accepted mixing conditions: plug flow, and fully mixed flow. Plug flow conditions represent the lower bound (shorter time) required for the oil entering the water column to be altered in its composition, whereas a fully mixed regime represents an upper bound (longer time) required for the sheen's chemical composition to shift from the sediment endmember composition to the leaking well endmember composition.

Using the previously described biomarker ratio analytical uncertainty of ±5%, a minimum limit of detection can be established for any point in time after the onset of an oil well leak at the Dome C&D site (e.g. the average release rate detection limit after 1 day of release, 1 year, 10 years). For the plug flow discharge regime, the minimum limit

of detection is roughly the amount of time required for the cumulative well release volume to exceed 5% of the oil in place ( $1800 \pm 880$  bbls  $\times$  5% =  $90 \pm 44$  bbls). Over a 4 ½ year period of time the minimum limit of detection is approximately  $2.3 \pm 1.1$  gallons/day ( $0.05 \pm 0.025$  BOPD). If a fully mixed regime is assumed for the well oil transport through the sediment, the detection threshold increases marginally, by less than 0.1 gallons/day (Fig 4).

As previously described, no statistically significant change in oil composition or decreasing variance trend was detected in the 4 ½ year time interval between the 2012 and 2017 sheen samples. Therefore, the theoretical maximum average well leakage rate for scenario B over this 4 ½ year time period cannot have exceeded an average of  $2.4 \pm 1.2$  gallons/day ( $< 0.06 \pm 0.03$  BOPD).

Using the fully mixed model for a leaking well, the time to detect a theoretical worst case 3.8 BOPD (160 gallons/day) release from a corrosion leak of the A3 well [10] would be approximately  $25 \pm 12$  days, assuming fully mixed flow ( $23 \pm 11$  days in the case of plug flow). Because this detection threshold is integrative over time, intermittent releases have the same cumulative detectability as a continuous release. For example, if a well leak triggered an intermittent release that periodically flowed at 3.8 BOPD (160 gallons/day) it would be detectable after a cumulative  $25 \pm 12$  days of flow (a time frame which is shorter than the 2017 SSLWG field operations). Hypothetical leaks of greater magnitude would have proportionally shorter times to detection.

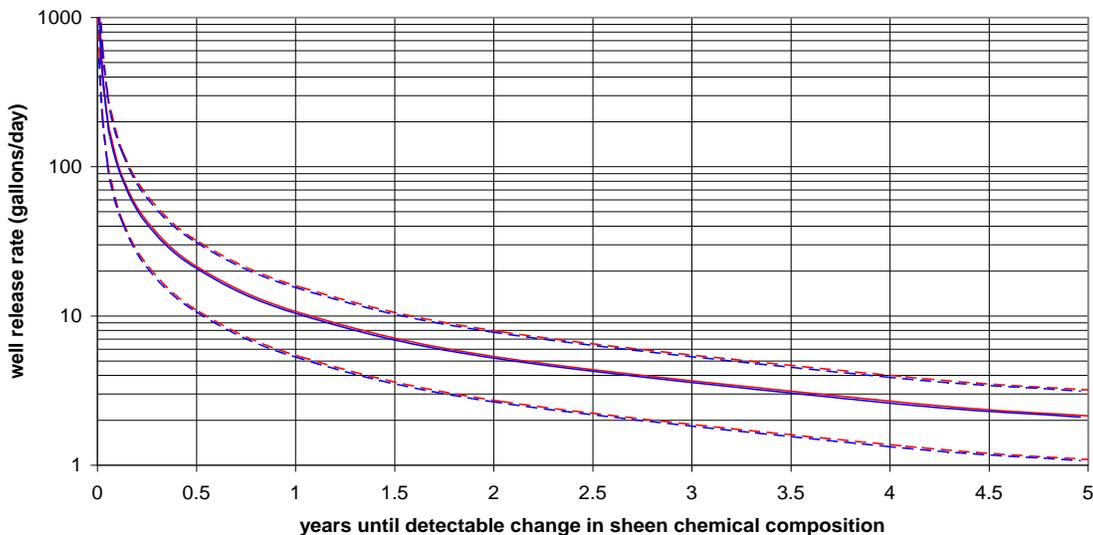


Figure 4: Plot showing the required time to detect a well leak based on the cumulative duration of oil well leakage at a given flow rate. The solid red line represents fully mixed flow, the solid blue line represents plug flow; dashed lines indicate  $\pm 95\%$  confidence bounds. Well release rate (Y-axis) is shown on a logarithmic scale.

**Summary:**

Analysis of the MC20 sheen and sediment hydrocarbon biomarker ratios in conjunction with physical observations of the MC20 site and standard mixing models indicates the following:

1. There is no detectable contribution to the sea surface sheen from an actively leaking well. All evidence suggests that the sheen is being generated by remnant oil sparged from the sediments within the Dome C&D erosional pit.
2. There is no evidence of a worst case (or greater) corrosion-induced well leak having occurred during the 2012-2017 time period.
3. If a well is actively leaking and contributing to the sheen, its flow rate is below detection limits and contributes, on average, less than 2.4 gallons/day ( $\pm 1.2$  gallons/day at 95% confidence) to the sheen.
4. If a well leaked intermittently during the 2012-2017 time period, its cumulative oil release was less than 4,200 gallons ( $\pm 2000$  gallons at 95% confidence), or 100 barrels ( $\pm 49$  barrels at 95% confidence).
5. The theoretical maximum average remnant oil contribution to the sheen from sediments at the Dome C&D site is less than 10.7 gallons/day ( $\pm 5.2$  gallons/day at 95% confidence).
6. The theoretical maximum average sheen source rate from the Dome C&D site (combining the maximum remnant oil release rate with the maximum average undetectable leak rate) from 2012-2017 is less than 13 gallons/day ( $\pm 6.3$  gallons/day at 95% confidence).
7. If a significant well leak (continuous or intermittent) were to occur in the future, it would alter the sheen chemistry permanently, enabling detection both while the input was occurring and after the input ceased.
8. Returning to the rum-punch analogy, the results of this analysis does not support the scenario that "rum" (oil from a leaking well) is being added to the sheen source "punch".

**References:**

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