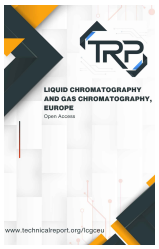

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RESEARCH ARTICLE

Hydration-Gated Detection-Margin Analysis for Wet and Dried LIBS Quantification of Bitumen in Oil-Sand Tailings

James Carter[1*] **and Daniel Thompson**[2]

[1]*Center for Chromatographic Research Midland Scientific University Canada*
[2]*Department of Environmental Analytical Chemistry Great Lakes University United States*
[*]*Corresponding author*

Corresponding author:
james_carter29@gmail.com

Abstract

Laser-induced breakdown spectroscopy (LIBS) offers rapid bitumen assessment for oil-sand tailings, but wet and dried measurements interrogate materially different targets. The central question is whether a wet target or a dried target provides the stronger analytical margin when low-end detectability, proportional validation error, and loss of the water-bearing matrix are considered in one calculation. Ten tailings samples were evaluated from S1 to S10, with bitumen contents of 0.5, 1.0, 2.0, 2.5, 3.0, 4.0, 4.5, 5.0, 5.5, and 6.0% and water contents of 72.55, 64.86, 62.95, 59.72, 59.24, 54.11, 60.63, 60.01, 61.77, and 61.52%, respectively. These values define a severe hydrated matrix, especially at S1 and S2, where the water/bitumen ratios are 145.10 and 64.86. A Hydration-Gated Detection Margin (HGDM) score was calculated from three explicit quantities: conservative detection reserve based on the upper limit of detection, validation retention based on the mean internal/external relative error, and state integrity based on whether the hydrated sample is preserved. Wet LIBS and dried LIBS have identical internal and external RMSE values of 0.3%, but wet LIBS has a lower mean relative error (6.0% versus 8.4%) and a lower conservative detection boundary (0.5% versus 0.9%). The mean HGDM score is 0.756 for wet LIBS and 0.543 for dried LIBS. Wet LIBS gives the higher score in all ten samples, enters the controlled band at 1.0% bitumen, and enters the strong band at 3.0% bitumen. Dried LIBS remains fragile through 1.0% bitumen, enters the controlled band only at 4.0%, and does not enter the strong band within the 0.5–6.0% range. The direct answer is that wet LIBS is the more defensible process-facing route for hydrated tailings because it preserves the matrix being measured while retaining the stronger low-concentration detection reserve.

Keywords: laser-induced breakdown spectroscopy, bitumen , oil-sand tailings , hydrated samples , limit of detection , multivariate calibration , analytical validation

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1. Introduction

Residual bitumen in oil-sand tailings must be measured in a matrix that is not a dry solid. The material contains mineral fines, process water, suspended solids, and residual hydrocarbon, and its water fraction can exceed one half of the total mass. A laboratory procedure that dries this material may simplify surface presentation for laser interrogation, but it also changes the analytical target. For process monitoring, the relevant question is not only how accurately a calibration predicts bitumen after preparation, but whether the preparation route leaves the sample close to the state that must be controlled.

LIBS is attractive for this task because it uses a focused laser pulse to form a microplasma and then relates the emitted optical spectrum to the composition of the ablated material. The method has become a mature analytical approach for solids, minerals, environmental materials, industrial materials, and process-oriented measurements [1–6]. Its strength is direct interrogation with minimal chemical preparation. Its difficulty is that plasma emission depends on ablated mass, surface condition, particle packing, plasma temperature, electron density, background emission, and matrix composition [7–10].

Hydrated samples intensify those difficulties. Water can reduce ablation efficiency, destabilize plasma formation, influence crater geometry, alter continuum background, and lower the repeatability of emission intensity. Direct LIBS measurement of liquids, oils, slurries, and wet

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particulate systems is therefore feasible but more demanding than measurement of dry, compact, homogeneous solids [11–15]. This difficulty does not automatically justify drying, because drying may remove the very matrix feature that defines the process material. A wet measurement route can be less convenient and still be analytically preferable if it keeps sufficient detection reserve and validation stability.

Bitumen quantification in oil-sand matrices is a useful case because LIBS has already demonstrated sensitivity to bitumen-bearing material. Harhira et al. showed rapid LIBS determination of bitumen in Athabasca oil sands [16]. Mohajan et al. later evaluated wet and dry preparation for LIBS bitumen measurement in oil-sand tailings [17]. The numerical record used here contains a strong tension: wet and dried LIBS have the same internal and external RMSE values of 0.3%, yet the routes differ in relative error, limit of detection (LOD), and sample-state preservation. A judgement based only on RMSE would therefore hide the most important distinction between the routes.

Quantitative LIBS research increasingly treats validation as a combined physical and statistical problem. Calibration design, spectral preprocessing, matrix-effect control, partial least squares modelling, feature selection, and uncertainty interpretation all influence whether a calibration remains useful outside the most favorable samples [18–22]. Multivariate calibration is valuable because LIBS spectra contain correlated emission variables and matrix-dependent backgrounds [23–25]. Detection-limit interpretation is equally important when the analyte lies near the lower range of interest [26–28]. In hydrated tailings, these concerns must be joined to sample-state preservation, because the dried route removes 54.11–72.55% water before laser measurement.

The research question addressed here is precise: for the ten-sample hydrated tailings series, which LIBS preparation route gives the larger conservative analytical margin when upper LOD, internal/external relative error, and water-state preservation are evaluated together? The answer is obtained through the Hydration-Gated Detection Margin (HGDM) score. HGDM is not a replacement for spectral calibration. It is a sample-level calculation that places detectability, route validation, and matrix preservation on the same numerical scale so that wet and dried preparation can be compared under the same low-end stringency.

The calculation uses three principles. First, each LOD interval is represented by its upper endpoint; the wet-route endpoint is 0.5% bitumen and the dried-route endpoint is 0.9%. This prevents the low-bitumen samples from being judged with overly favorable detection boundaries. Second, the mean of the internal and external relative errors is used to represent route validation retention; this gives 6.0% for wet LIBS and 8.4% for dried LIBS. Third, water removal is treated as a state penalty for dried LIBS because the samples contain more water than dry solids. These choices turn the comparison into a direct question of usable measurement margin rather than a general wet-versus-dry preference.

2. Materials and analytical construction

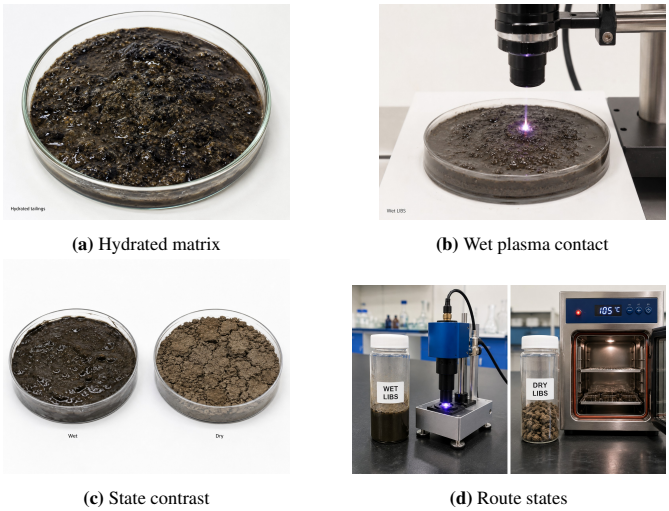
2.1. Tailings composition and hydration severity

The tailings record contains ten samples, labelled S1–S10, with bitumen increasing from 0.5 to 6.0%. The exact bitumen, water, solids, and water/bitumen values used in the calculation are listed in Table 1. Solids fraction was calculated as $100 - W_i$, where W_i is water content in percent. The water/bitumen ratio was calculated as W_i/C_i, where C_i is bitumen content in percent. The sample values follow the wet/dry LIBS tailings record of Mohajan et al. [17], and all quantities used for the HGDM calculation are displayed within the manuscript.

The values in Table 1 show that the concentration series is also a hydration-severity series. S1 contains only 0.5% bitumen but 72.55% water, giving a water/bitumen ratio of 145.10. S2 doubles the bitumen content to 1.0%, yet the water/bitumen ratio remains 64.86. Even the higher-bitumen samples retain 54.11–61.77% water. A dried measurement route therefore changes every sample substantially, not only the two lowest-concentration cases.

Table 1: Tailings composition.

Sample	Bitumen (%)	Water (%)	Solids (%)	Water/bitumen
S1	0.5	72.55	27.45	145.10
S2	1.0	64.86	35.14	64.86
S3	2.0	62.95	37.05	31.48
S4	2.5	59.72	40.28	23.89
S5	3.0	59.24	40.76	19.75
S6	4.0	54.11	45.89	13.53
S7	4.5	60.63	39.37	13.47
S8	5.0	60.01	39.99	12.00
S9	5.5	61.77	38.23	11.23
S10	6.0	61.52	38.48	10.25



(a) Hydrated matrix **(b)** Wet plasma contact

(c) State contrast **(d)** Route states

Figure 1: Hydrated sample states.

The visual sequence in Fig. 1 shows the physical reason for assigning a state term in HGDM. Wet LIBS and dried LIBS do not expose the laser to the same target. A wet target retains the water-rich slurry character, whereas a dried target is a transformed residue. This distinction is essential because the analytical objective is bitumen measurement in hydrated tailings, not bitumen measurement after the dominant sample fraction has been removed.

2.2. Route descriptors and conservative boundary values

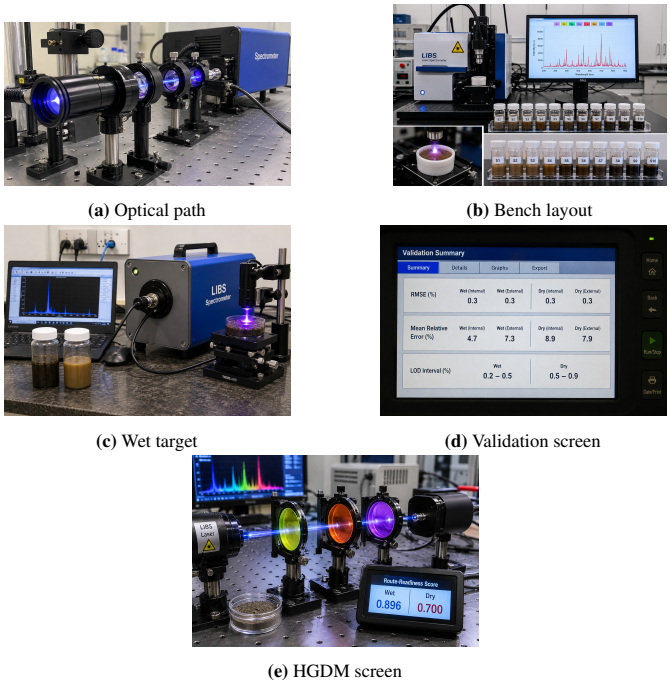
The route descriptors used for scoring are RMSE, relative error, and LOD. The wet and dried routes both have internal RMSE = 0.3% and external RMSE = 0.3%. Their proportional error values differ: wet LIBS has 4.7% internal relative error and 7.3% external relative error, while dried LIBS has 8.9% internal relative error and 7.9% external relative error. The mean relative error is therefore 6.0% for wet LIBS and 8.4% for dried LIBS. The LOD intervals are 0.2–0.5% for wet LIBS and 0.5–0.9% for dried LIBS; HGDM uses 0.5% and 0.9%, respectively, as conservative detection boundaries.

The descriptor set in Table 2 rules out a simple RMSE-based tie. Equal RMSE values show that both preparation routes can support calibration over the evaluated range, but the relative-error and LOD values identify the wet route as the safer option near the lower bitumen boundary. The wet route has the lower upper LOD and the lower mean relative error. Since dried LIBS does not obtain an RMSE advantage, it cannot offset the water-removal penalty through better validation performance.

The measurement record in Fig. 2 connects the scoring calculation to

Table 2: Route validation values.

Descriptor	Wet LIBS	Dried LIBS
Internal RMSE (%)	0.3	0.3
External RMSE (%)	0.3	0.3
Internal relative error (%)	4.7	8.9
External relative error (%)	7.3	7.9
LOD interval (%)	0.2–0.5	0.5–0.9
Upper LOD used for scoring (%)	0.5	0.9
Mean relative error (%)	6.0	8.4
Validation-retention value	0.625	0.543



(a) Optical path **(b)** Bench layout

(c) Wet target **(d)** Validation screen

(e) HGDM screen

Figure 2: LIBS measurement record.

the LIBS acquisition environment. Optical alignment, bench measurement, wet-target contact, and validation output are part of the same analytical chain. HGDM uses the numerical descriptors from that chain and adds a hydration penalty only where preparation removes water before the laser measurement.

2.3. Hydration-Gated Detection Margin calculation

HGDM has three components. The first component is conservative detection reserve, $D_{r,i}$, for route r and sample i. It compares bitumen content C_i with the upper endpoint of the route LOD interval, $L_r^{\max}$. Negative reserve is set to zero because a concentration at or below the conservative LOD has no usable low-end buffer.

$$D_{r,i} = \max\left(0,\ 1 - \frac{L_r^{\max}}{C_i}\right). \tag{1}$$

The second component is validation retention, V_r, calculated from the mean internal/external relative error, $\bar{E}_r$. Division by 10 places the percent error on a scale that changes the score meaningfully without allowing route-level error to dominate concentration-specific detection reserve.

$$V_r = \frac{1}{1+\bar{E}_r/10}. \tag{2}$$

The third component is state integrity, $P_{r,i}$. Wet measurement receives $P_{r,i} = 1$, because the hydrated target is preserved. Dried measurement receives the non-water fraction, $1 - W_i/100$, because water is removed before analysis.

$$P_{r,i} = \begin{cases} 1, & \text{wet route}, \\ 1 - W_i/100, & \text{dried route}. \end{cases} \tag{3}$$

The final score is:

$$\mathrm{HGDM}_{r,i} = 0.50D_{r,i} + 0.30V_r + 0.20P_{r,i}. \tag{4}$$

Detection reserve receives 50% of the score because low-end bitumen detectability is the limiting requirement. Validation retention receives 30%, because proportional prediction error determines whether a calibration result can be trusted. State integrity receives 20%, because the analysis is directed at hydrated tailings rather than dry residue. Scores below 0.35 are labelled fragile, 0.35–0.60 conditional, 0.60–0.80 controlled, and 0.80 or higher strong. These labels are internal analytical bands used to compare the two preparation routes under the same rules.

The sample series in Fig. 3 shows why hydration cannot be treated as a minor background condition. Wet heterogeneity is visible across the complete S1–S10 range. Higher bitumen content does not remove the water-rich character of the material. This supports the use of a state-integrity term and prevents the comparison from collapsing into concentration and RMSE alone.

The aliquot images in Fig. 4 illustrate that the route comparison concerns an organized measurement sequence rather than an isolated specimen. Replicate layout is important for calibration, but it does not remove the sample-state decision. A wet aliquot and a dried aliquot may both be measured by LIBS; only the wet aliquot retains the hydrated tailings condition.

3. Results and discussion

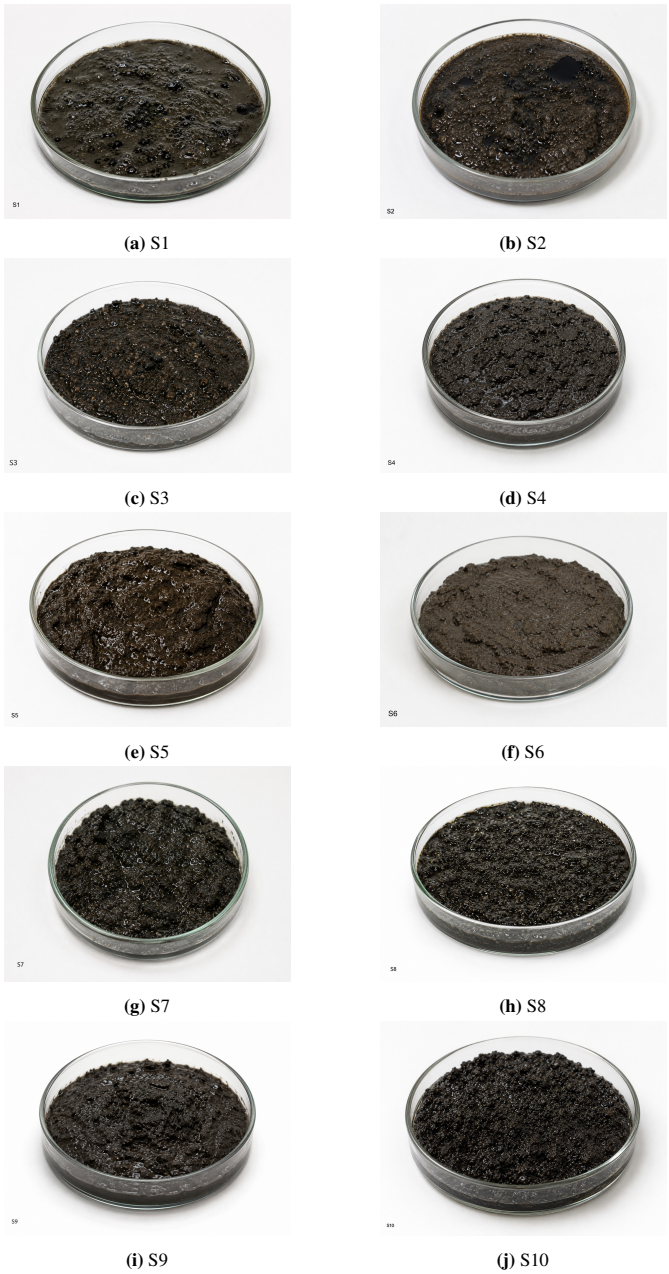
3.1. Low bitumen and high water create the most stringent samples

The strongest analytical stress occurs at the low-bitumen end of the sample series. S1 contains 0.5% bitumen and 72.55% water; S2 contains 1.0% bitumen and 64.86% water. These two samples combine weak analyte abundance with a matrix dominated by water. Higher-bitumen samples are easier for detection reserve, but they are still hydrated samples because water remains above 54% in every case.

This composition pattern is important for process use. A route that works well at 5–6% bitumen may still be unsuitable for monitoring low residual bitumen if its LOD is too close to the lower end of the concentration range. Conversely, a wet route that faces stronger plasma-water interference may still be better if its validation values show enough low-end reserve. The central comparison is therefore not convenience of drying versus difficulty of wet measurement; it is usable analytical margin in the matrix that process monitoring actually encounters.

3.2. Upper-LOD reserve exposes the route difference

The conservative detection reserve is zero when the bitumen content is equal to or below the upper LOD boundary. Under this rule, wet LIBS has no reserve for S1 because S1 is exactly 0.5% bitumen, the wet-route upper LOD. Dried LIBS has no reserve for S1 and only 0.100 reserve for S2 because its upper LOD is 0.9%. After S2, both routes improve as bitumen concentration increases, but the wet route keeps a larger reserve in every sample.



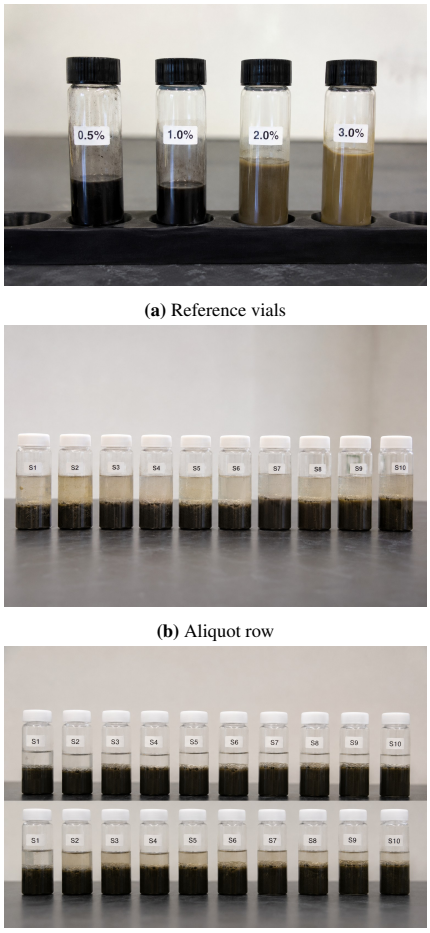
(a) S1 **(b)** S2 **(c)** S3 **(d)** S4 **(e)** S5 **(f)** S6 **(g)** S7 **(h)** S8 **(i)** S9 **(j)** S10

Figure 3: Wet sample series.

Table 3: Upper-LOD reserve.

Sample	Bitumen (%)	Water/bitumen	Wet reserve	Dried reserve
S1	0.5	145.10	0.000	0.000
S2	1.0	64.86	0.500	0.100
S3	2.0	31.48	0.750	0.550
S4	2.5	23.89	0.800	0.640
S5	3.0	19.75	0.833	0.700
S6	4.0	13.53	0.875	0.775
S7	4.5	13.47	0.889	0.800
S8	5.0	12.00	0.900	0.820
S9	5.5	11.23	0.909	0.836
S10	6.0	10.25	0.917	0.850

The values in Table 3 identify S2 as the decisive low-end separation point. Wet LIBS moves from zero reserve at S1 to 0.500 reserve at S2, while dried LIBS remains near the boundary with a reserve of only 0.100. This explains why equal RMSE values are insufficient for route selection. A route can have acceptable average prediction error while



(a) Reference vials

(b) Aliquot row

(c) Replicate rows

Figure 4: Prepared aliquots.

still being poorly buffered against the LOD at the low-concentration end.

3.3. HGDM favors wet measurement in every sample

Combining detection reserve, validation retention, and state integrity produces a consistent wet-route advantage. The mean score is 0.756 for wet LIBS and 0.543 for dried LIBS. The mean advantage is 0.213. The largest separation occurs at S2, where wet LIBS scores 0.638 and dried LIBS scores 0.283. S1 remains a cautionary sample: wet LIBS is conditional rather than strong, and dried LIBS is fragile.

Table 4: HGDM scores.

Sample	Water (%)	Wet HGDM	Wet band	Dried HGDM	Dried band	Wet advantage
S1	72.55	0.388	conditional	0.218	fragile	0.170
S2	64.86	0.638	controlled	0.283	fragile	0.354
S3	62.95	0.763	controlled	0.512	conditional	0.250
S4	59.72	0.788	controlled	0.564	conditional	0.224
S5	59.24	0.804	strong	0.595	conditional	0.210
S6	54.11	0.825	strong	0.642	controlled	0.183
S7	60.63	0.832	strong	0.642	controlled	0.190
S8	60.01	0.838	strong	0.653	controlled	0.184
S9	61.77	0.842	strong	0.658	controlled	0.184
S10	61.52	0.846	strong	0.665	controlled	0.181

The scores in Table 4 show that the wet-route advantage is not an artifact of the highest or lowest sample alone. Wet LIBS is favored at S1 because it preserves the hydrated state and has the better validation-retention value. It is favored most strongly at S2 because the detection reserve changes sharply in favor of wet measurement. It remains favored from S6 to S10 because drying continues to remove a large

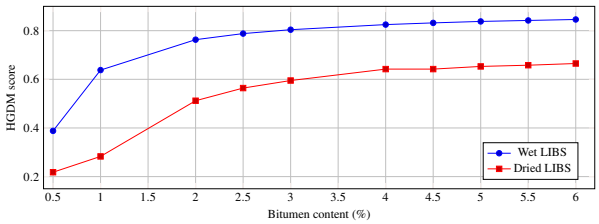


Figure 5: HGDM concentration profile.

water fraction while providing no improvement in RMSE, relative error, or LOD.

The concentration profile in Fig. 5 shows two distinct regions. Between 0.5 and 1.0% bitumen, wet LIBS rises rapidly because it moves beyond its 0.5% conservative detection boundary. Dried LIBS remains close to its 0.9% boundary and therefore stays fragile at S2. Above 3.0% bitumen, both curves flatten as the detection-reserve term approaches its maximum, but the vertical separation persists because wet LIBS retains the higher validation-retention value and full state-integrity value.

3.4. Analytical meaning for tailings monitoring

The result supports wet LIBS as the primary route when the analytical objective is rapid measurement of hydrated oil-sand tailings. This conclusion does not deny the difficulty of wet LIBS. Water can suppress emission and disturb plasma formation. The key point is that the wet route still carries the stronger numerical margin after LOD and relative error are included. Preserving the hydrated state becomes beneficial because the wet route does not pay for that preservation with poorer RMSE or poorer detection boundary.

Dried LIBS remains useful for laboratory confirmation, archive measurements, or settings where dry residue is the target material. It is weaker for process-facing tailings measurement because it removes 54.11–72.55% of each sample as water before the laser pulse. The dry route would need a compensating improvement in validation performance to justify that transformation, but the available descriptors show the opposite: identical RMSE, higher mean relative error, and a higher upper LOD.

The low-end behavior provides the most practical decision rule. At 0.5% bitumen, neither route should be treated as strong; wet LIBS is conditional and dried LIBS is fragile. At 1.0% bitumen, wet LIBS becomes controlled while dried LIBS remains fragile. At 3.0% bitumen, wet LIBS becomes strong while dried LIBS remains conditional. These thresholds give the study its direct operational answer: wet LIBS becomes the preferred route as soon as bitumen rises above the wet upper LOD, and its advantage remains through the rest of the evaluated range.

3.5. Connection with LIBS calibration practice

The HGDM result agrees with the broader direction of quantitative LIBS practice. Good LIBS calibration is not just a regression coefficient; it requires attention to matrix effects, spectral stability, validation error, LOD, and the physical meaning of sample preparation [18–22]. In hydrated tailings, sample preparation is not an external convenience. It determines whether the spectrum represents a wet process material or a dry residue.

Multivariate calibration remains essential for handling correlated LIBS spectral variables [23–25]. HGDM does not replace that step. It uses route-level validation values after calibration and asks which route has the larger usable margin for the samples at hand. The distinction is important: a calibration can be statistically acceptable within a prepared state, while the prepared state itself can still be less suitable for process monitoring.

3.6. Analytical boundaries of the calculation

The calculation is limited to sample composition, route RMSE, internal/external relative error, and LOD intervals. It does not use raw spectral intensities, individual emission-line stability, crater morphology, plasma temperature, electron density, or shot-level replicate variance. These additional quantities would allow a more mechanistic explanation of why the wet route obtains the lower LOD and lower mean relative error.

The chosen weights emphasize low-end detection reserve (50%), validation retention (30%), and hydrated-state preservation (20%). Other applications could choose different weights, but the route conclusion is not fragile under the stated values. Wet LIBS is not favored because a single term was tuned in its direction; it is favored because the dry route has a higher conservative LOD, higher mean relative error, and a large state penalty in every sample. Those three features point in the same direction across the complete S1–S10 series.

4. Conclusion

This study asked which LIBS preparation route provides the larger conservative analytical margin for bitumen quantification in hydrated oil-sand tailings when upper LOD, proportional validation error, and water-state preservation are evaluated together. The answer is wet LIBS. In the ten-sample series, wet LIBS gives a mean HGDM score of 0.756, compared with 0.543 for dried LIBS. Wet LIBS is favored for every sample, becomes controlled at 1.0% bitumen, and becomes strong at 3.0% bitumen. Dried LIBS remains fragile through 1.0% bitumen, becomes controlled only at 4.0% bitumen, and does not become strong within the 0.5–6.0% bitumen interval.

The conclusion is route-specific rather than general. Drying is not analytically invalid, and it may be useful when the target material is a dry residue or when laboratory confirmation is required. For process-facing tailings measurement, however, drying removes the dominant water fraction without improving RMSE, relative error, or LOD. Wet LIBS retains the water-bearing matrix and also has the lower conservative detection boundary and lower mean relative error. The defensible measurement route for hydrated tailings is therefore wet LIBS, especially above 1.0% bitumen, where its score enters the controlled band while dried LIBS remains fragile.

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