



清华大学 能源与动力工程系  
Department of Energy and Power Engineering, Tsinghua University

# LIBS research group

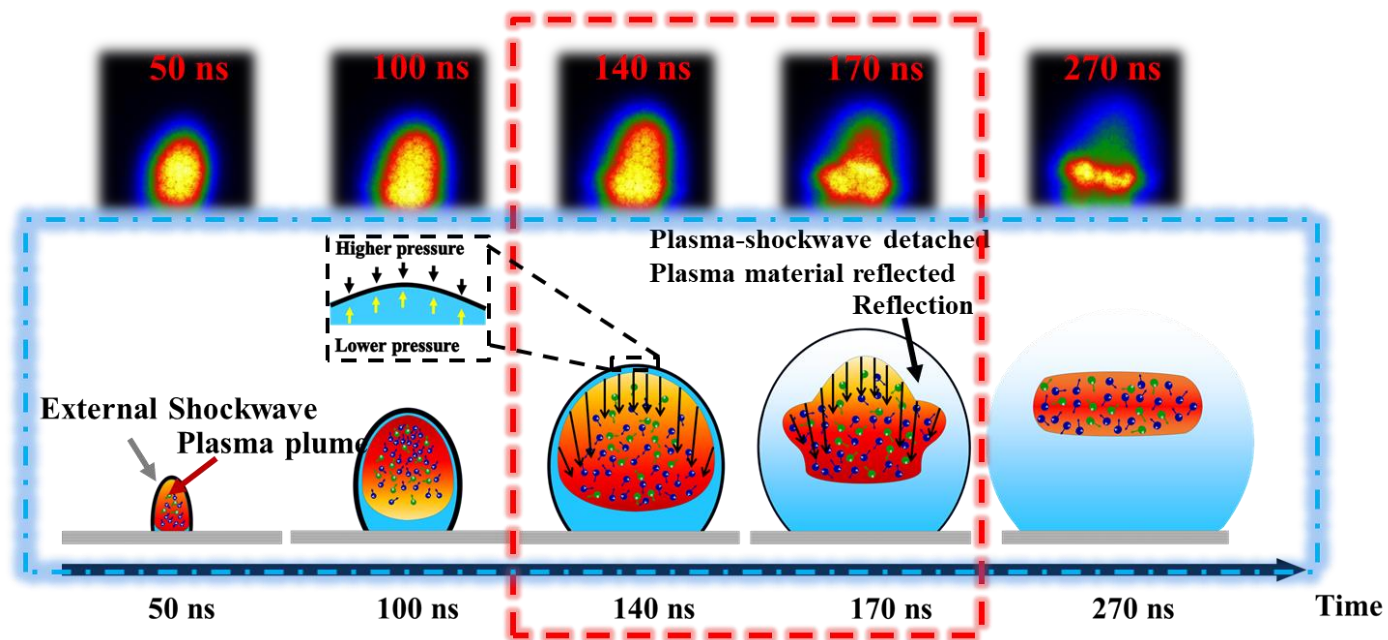
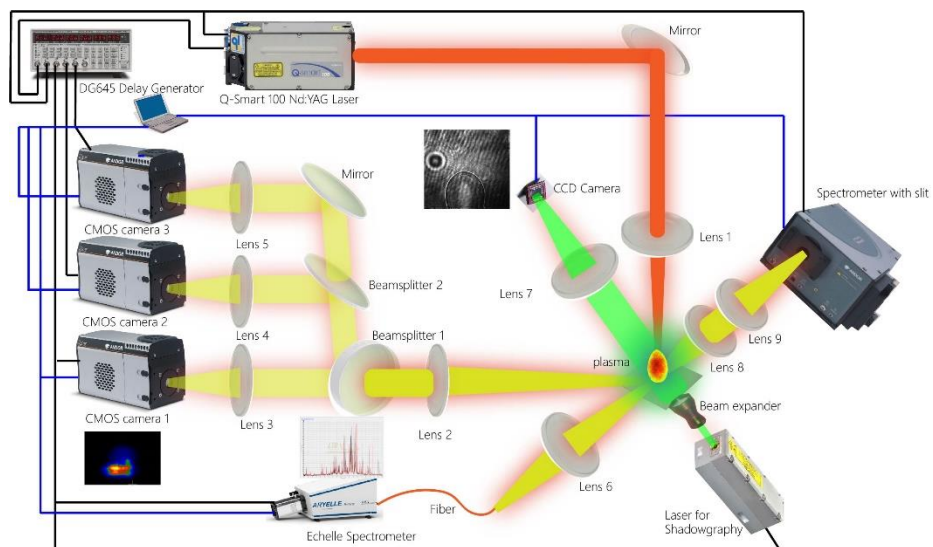
- Our group was initiated in 2008 with the research interest focused on fast and online coal analysis to underpin clean and efficient utilization of coal. With the deepening of research and development of economy and society, we devoted to improve the quantification performance of LIBS and promote the application of LIBS to various fields such as metal, cement, and mineral.





## Fundamental research: uncertainty origination

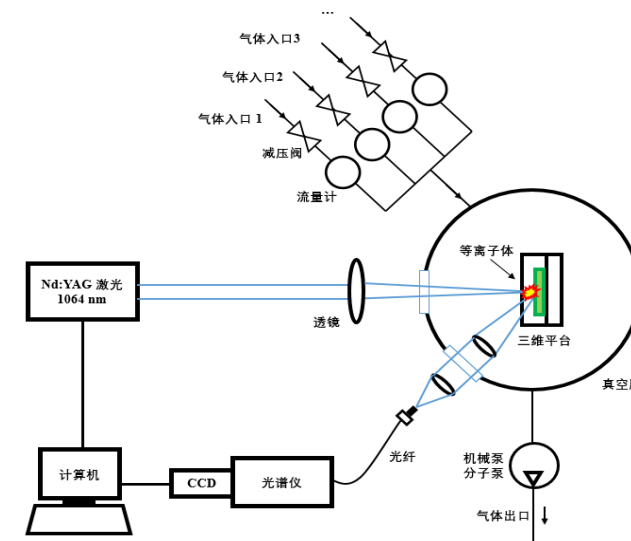
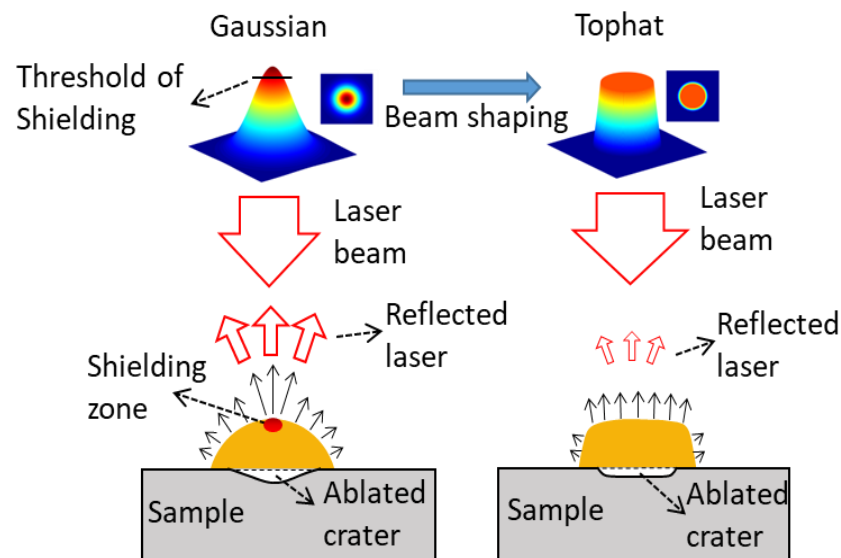
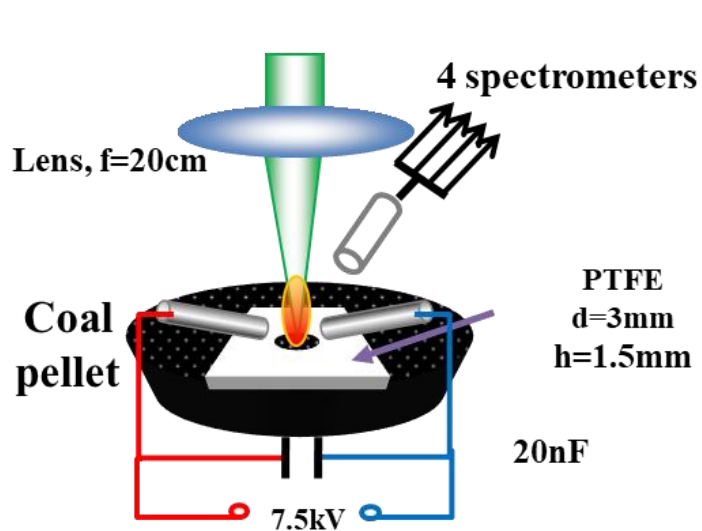
- We built a transient diagnosis platform of LIBS to investigate the plasma evolution and revealed the mechanism of LIBS uncertainty origination: Rayleigh-Taylor instability, surface roughness → initiate the instability → plasma evolution (mixing and expansion of plasma in ambient gas) → plasma frontier material dash-down and crash the lower part (critical period) → large instability of plasma morphology → signal uncertainty.





## Key technology: plasma modulation

- We developed a series of plasma modulation technologies to regularize the interaction of laser-sample-plasma-ambient gas, so as to reduce the fluctuation of plasma morphology and improve the repeatability of LIBS signal.
  - Spatial confinement, beam shaping, gas mixture, etc.





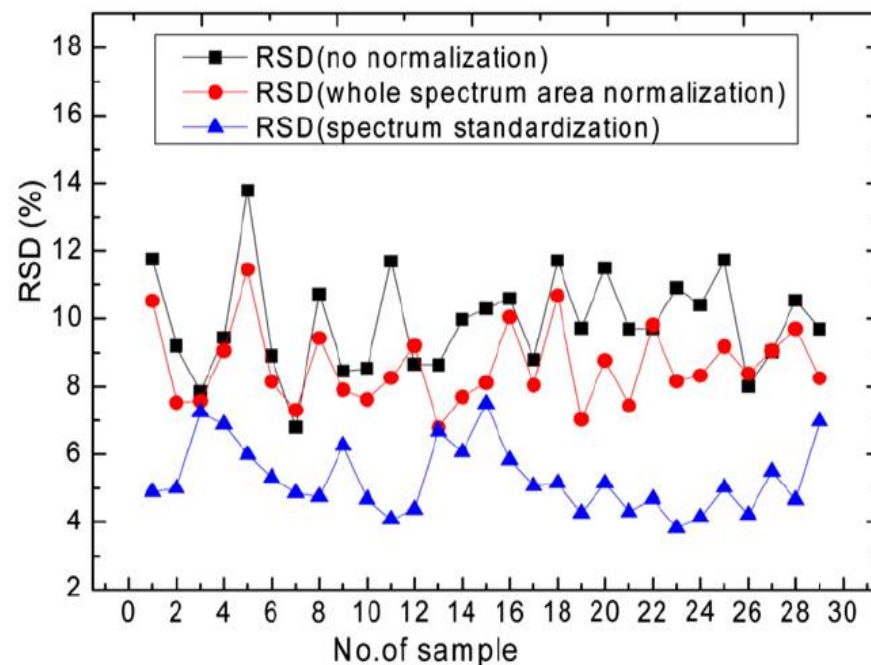
## Key technology: spectrum standardization

- It was assumed that the uncertainty of LIBS can be attributed to the deviation of plasma state from a standard plasma state (with standard temperature  $T$ , electron density  $n_e$  and total number density of species  $n_s$ ).
- Spectrum standardization method was proposed to compensate the deviation of plasma state from the standard plasma state:  $dT$ ,  $dn_e$  and  $dn_s$ , so as to reduce the uncertainty of LIBS.

$$I_{ij}(n_s, T, n_e) \approx I_{ij}(n_{s0}, T_0, n_{e0}) + \left( \frac{\partial I_{ij}}{\partial n_s} dn_s + \frac{\partial I_{ij}}{\partial T} dT + \frac{\partial I_{ij}}{\partial n_e} dn_e \right) \Bigg|_{(n_{s0}, T_0, n_{e0})}$$

$$I_{ij}(n_{s0}, T_0, n_{e0}) \approx I_{ij}(n_s, T, n_e) - (K_1 dn_s + K_2 CdT + K_3 Cdn_e)$$

$$I_{ij}(n_{s0}, T_0, n_{e0}) = K_0 C = K_0 \frac{b_1 I_{ij} + b_2 I_T + b_5}{1 - b_3 \left( \ln\left(\frac{I_2}{I_1}\right) - \left(\ln\left(\frac{I_2}{I_1}\right)\right)_0 \right) - b_4 (\Delta\lambda_{\text{stark}} - (\Delta\lambda_{\text{stark}})_0)}$$





## Key technology: dominant factor based model

- Dominant factor: based on physical laws, with a wide range of application, reliable
- Statistical method correction: compensate the residue of dominant factor with full spectrum
- Improve the accuracy and robustness of calibration model

**Dominant Factor**

Self-absorption  
Interference

$$C_i = C_0 \ln\left(\frac{bC_0}{a + bC_0 - I_i}\right)$$

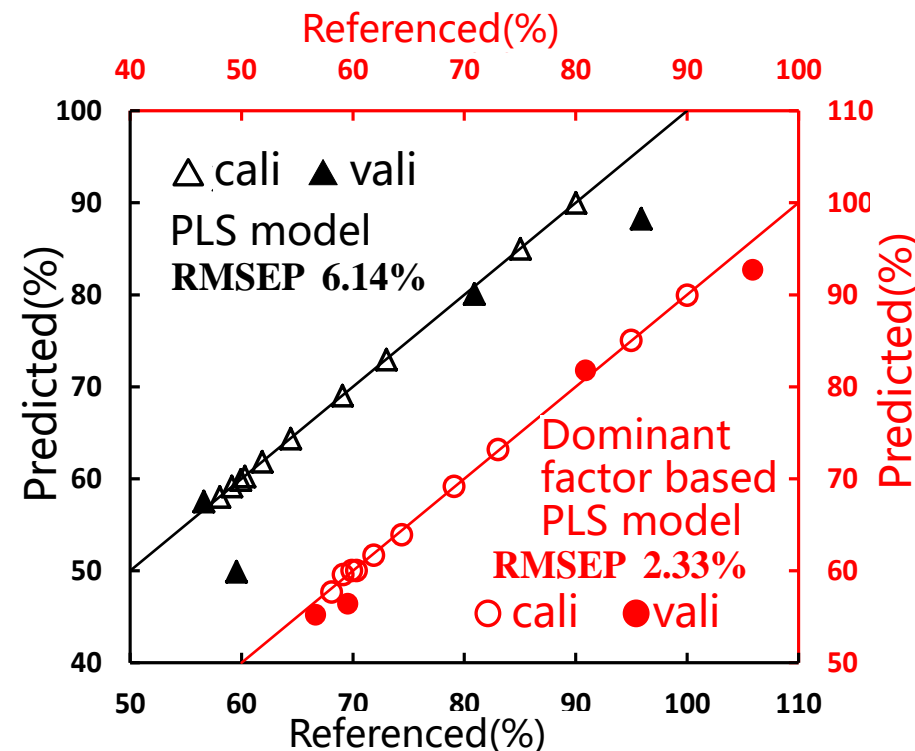


$$C_i = C_0 \ln\left(\frac{bC_0}{a + bC_0 - I_i}\right) + g(I_k)$$



$$C_i = C_0 \ln\left(\frac{bC_0}{a + bC_0 - I_i}\right) + g(I_k) + \sum_{j=1}^n b_j I_j + b_0$$

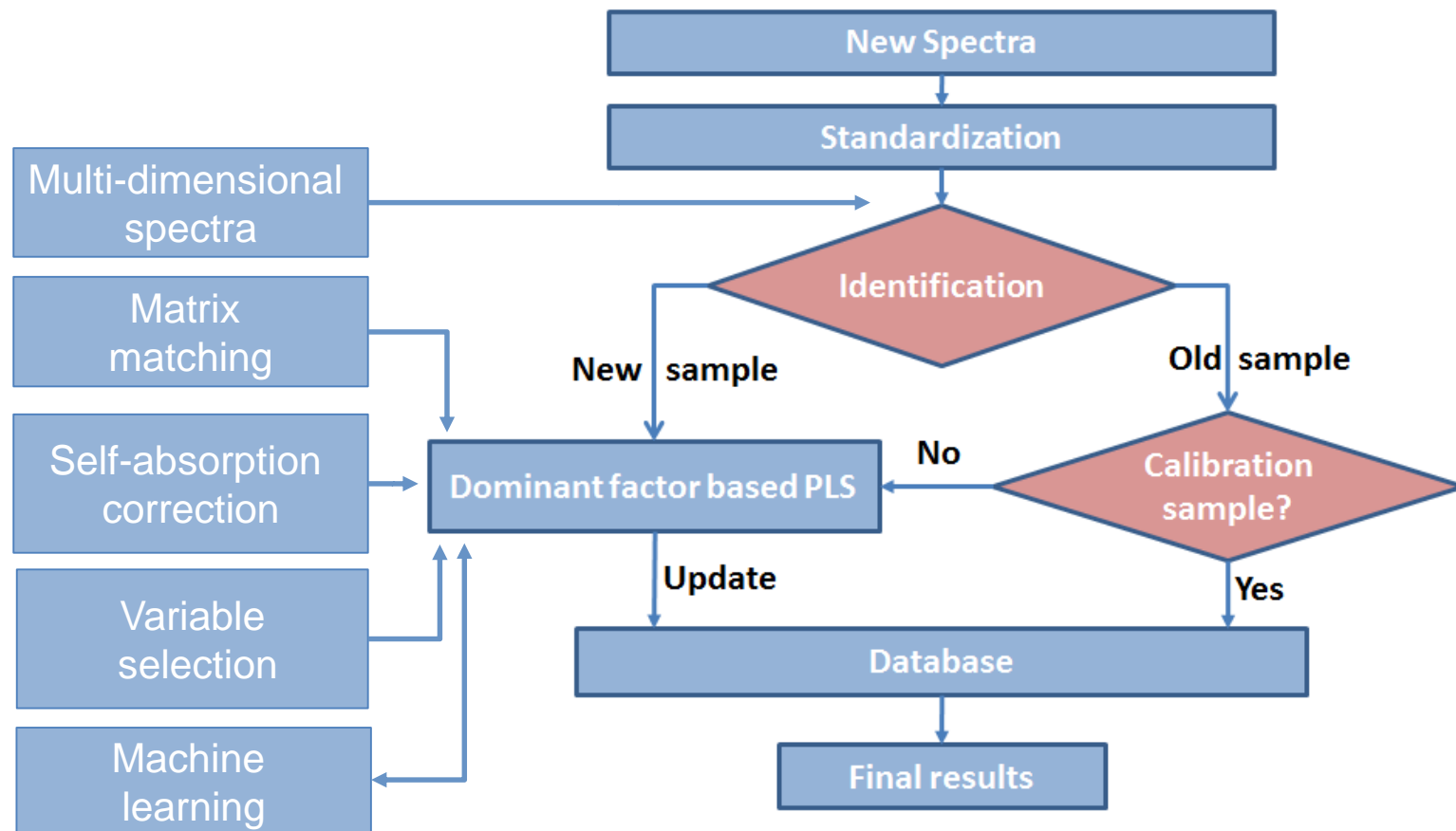
**PLS Correction using full spectral information**





## Key technology: hybrid quantification model

- We firmly believe that quantification model has to be based on the principle of LIBS and combined with modern machine learning methods
- We developed a set of methods to improve the measurement repeatability, reproducibility, sensitivity, accuracy, and matrix adaptability





## Application

- Our patented technology has been licensed and transferred to companies at home and abroad.
- A set of LIBS products and systems have been developed and applied in different fields including coal, metal, and cement etc.



Handheld steel analyzer



Desktop coal analyzer



Online coal analysis system



Online cement analysis system



## Contribution to LIBS society

- 2014, held the 8<sup>th</sup> International Conference on LIBS
- 2015, initiated the Asian Symposium on LIBS
- 2016, initiated the LIBS Committee of China
- 2019, initiated the International Summit on LIBS and held the 1<sup>st</sup> International Summit on LIBS
- Attended LIBS related conferences more than 30 times







## Selected publications

- Z Wang, MS Afgan, W Gu, Y Song, Y Wang, Z Hou, W Song, Z Li, Recent Advances in Laser-induced Breakdown Spectroscopy Quantification: from Fundamental Understanding to Data Processing, *TrAC Trends in Analytical Chemistry*, 143(2021),116385
- W. Song, Z. Hou, W. Gu, H. Wang, J. Cui, Z. Zhou, G. Yan, Q. Ye, Z. Li, Z. Wang, Industrial at-line analysis of coal properties using laser-induced breakdown spectroscopy combined with machine learning, *Fuel*, 306 (2021) 121667.
- W. Gu, W. Song, G. Yan, Q. Ye, Z. Li, M.S. Afgan, J. Liu, Y. Song, Z. Hou, Z. Wang, Z. Li, A data preprocessing method based on matrix matching for coal analysis by laser-induced breakdown spectroscopy, *Spectrochimica Acta Part B: Atomic Spectroscopy*, 180 (2021) 106212.
- Y. Fu, W. Gu, Z. Hou, , M.S. Afgan, T. Li, Y. Wang, Z. Wang, Mechanism of signal uncertainty generation for laser-induced breakdown spectroscopy, *Frontiers of Physics*, 16 (2020) 22502.
- W. Song, Z. Hou, M.S. Afgan, W. Gu, H. Wang, J. Cui, Z. Wang, Y. Wang, Validated ensemble variable selection of laser-induced breakdown spectroscopy data for coal property analysis, *J Anal Atom Spectrom*, 36 (2021) 111-119.
- J. Yu, Z. Hou, Y. Ma, T. Li, Y. Fu, Y. Wang, Z. Li, Z. Wang, Improvement of laser induced breakdown spectroscopy signal using gas mixture, *Spectrochimica Acta Part B: Atomic Spectroscopy*, 174 (2020) 105992.
- Z. Hou, M.S. Afgan, S. Sheta, J. Liu, Z. Wang, Plasma modulation using beam shaping to improve signal quality for laser induced breakdown spectroscopy, *J Anal Atom Spectrom*, 35 (2020) 1671-1677.
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- S. Sheta, M.S. Afgan, Z. Hou, S.-C. Yao, L. Zhang, Z. Li, Z. Wang, Coal analysis by laser-induced breakdown spectroscopy: a tutorial review, *J Anal Atom Spectrom*, 34 (2019) 1047-1082.
- Y. Fu, Z. Hou, T. Li, Z. Li, Z. Wang, Investigation of intrinsic origins of the signal uncertainty for laser-induced breakdown spectroscopy, *Spectrochimica Acta Part B: Atomic Spectroscopy*, 155 (2019) 67-78.
- Y. Fu, Z. Hou, Z. Wang, Physical insights of cavity confinement enhancing effect in laser-induced breakdown spectroscopy, *Optics Express*, 24 (2016) 3055-3066.
- Z. Hou, Z. Wang, T. Yuan, J. Liu, Z. Li, W. Ni, A hybrid quantification model and its application for coal analysis using laser induced breakdown spectroscopy, *J Anal Atom Spectrom*, 31 (2016) 722-736.



- We'll keep on working to improve the quantification performance of LIBS and promote LIBS to other fields
- Make the "future superstar" to real "superstar" !

