



## Article: Sulfur Testing - VPS Quality Approach

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For over a decade, both regional ECA and global sulphur limits within marine fuels have reduced significantly. As a consequence, it has become increasingly important for Laboratories to continue to produce precise and accurate test results. The question is what measures are taken by testing Laboratories to produce accurate, robust results with 95% confidence level?

In order to produce precise and accurate test results with 95% confidence level, laboratories should have stringent quality procedures within a globally recognised accredited quality management system, i.e. ISO/IEC17025, which control the day to day process but at the same time monitor and trend the results and data produced. Each process involves an uncertainty of measurement and how Laboratories consider these uncertainties for their evaluation.

An effective Quality Control and Management system does not mean simply running a quality control sample but involves numerous processes and evaluations to achieve precise and accurate test results with 95% certainty. The statistical approach of evaluating the results of an unknown sample, quality control sample, certified reference standard, or a standard reference material may be different. A very clear understanding is required when we consider all these aspects and any testing Laboratory accredited to ISO/IEC 17025 is forced to follow a high quality system to achieve the target of producing results with 95% confidence level.

The basic criteria in a quality control process is to obtain an accurate calibration curve and from there the whole process starts. If the uncertainty involved in the calibration is wide then it affects the accuracy of the quality control process. ***VPS has carried out extensive research to establish the basic criteria to be considered by Laboratories to obtain a calibration curve with a satisfactory correlation coefficient (Figure 1 & 2) which satisfies the requirement to produce results with 95% confidence.***



## VPS Stringent Process to Produce Precise and Accurate Test Results

VPS Laboratories follow stringent quality measures to produce 95% confident test results:

1. The highest quality, certified, traceable standards available are used for the calibration within the same matrix as the sample (NIST and NIST traceable standards). Examples of two calibration curves, low level sulfur (diesel fuel matrix) and high level sulfur (fuel oil matrix) are given below, with excellent correlation obtained.

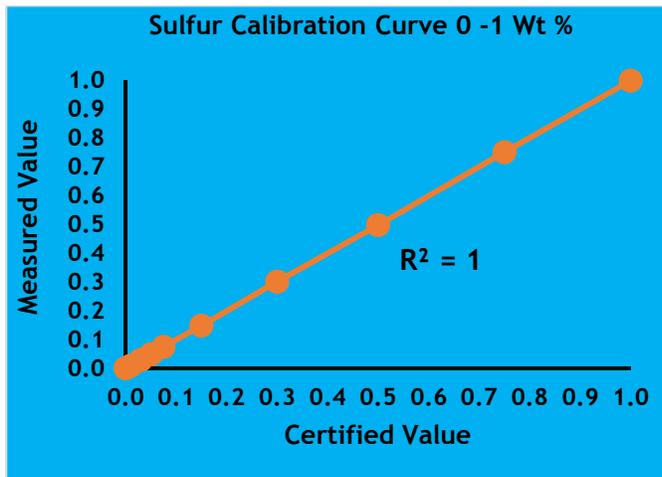


Fig1 VPS Sulfur Calibration Curve (Diesel Oil Matrix)

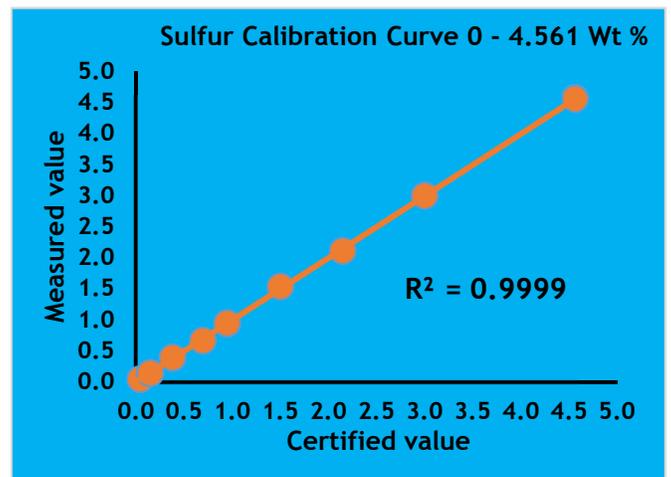


Fig 2 VPS Sulfur Calibration Curve (Fuel Oil Matrix)

2. Evaluation of the calibration curve is done periodically with traceable certified standards to monitor if any potential drifting of the calibration curve has taken place over this period of time. This ensures that the 95% confidence has always been maintained.
3. Quality Control (SQC) samples of varying concentration ranges are tested on a daily basis and evaluated statistically to ensure that the results produced are within the 95% confidence level.
4. Method validation is performed to ensure the repeatability, reproducibility, measurement of uncertainty, accuracy, detection limit, reporting limit and linearity achieved by the Laboratory are equal or better than the International standard methods in use.
5. Results produced by VPS Laboratories are evaluated by external bodies, globally by participating in major International correlation programs. Examples of VPS global correlation results are given (Figure 3 & 4) for both fuel oil and diesel oil. The results are within the 95% confidence level with no systematic error observed.

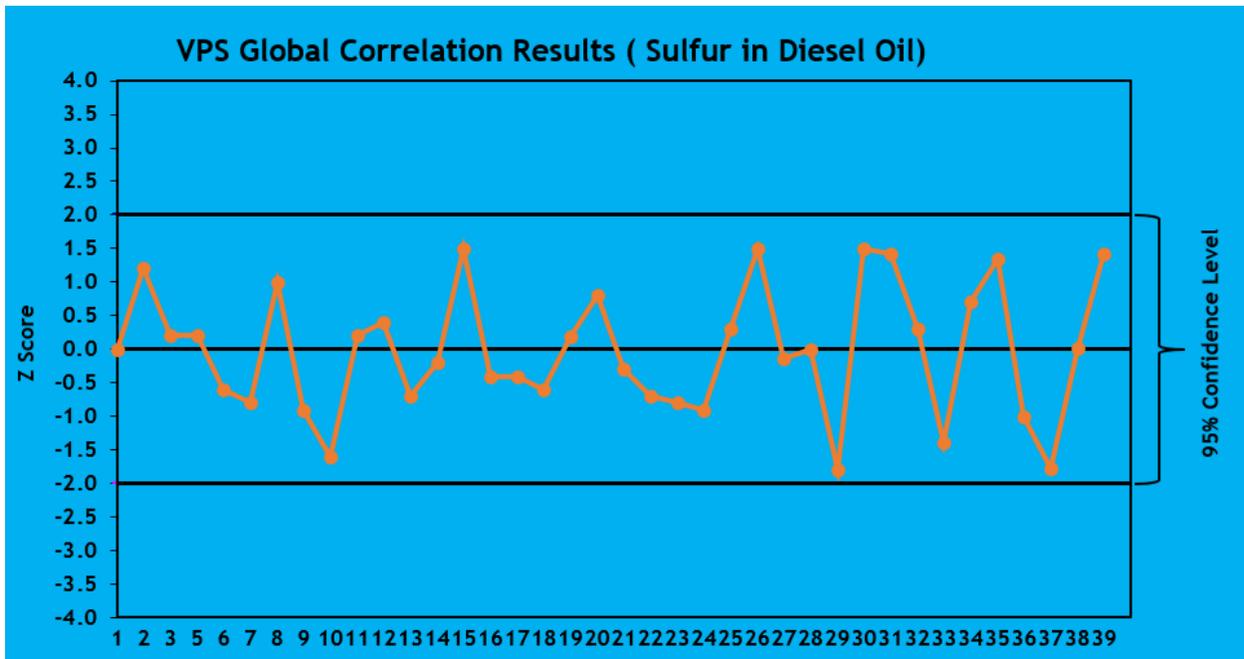


Figure 3 Example of a VPS Global Correlation Results (Sulfur in Gas Oil)

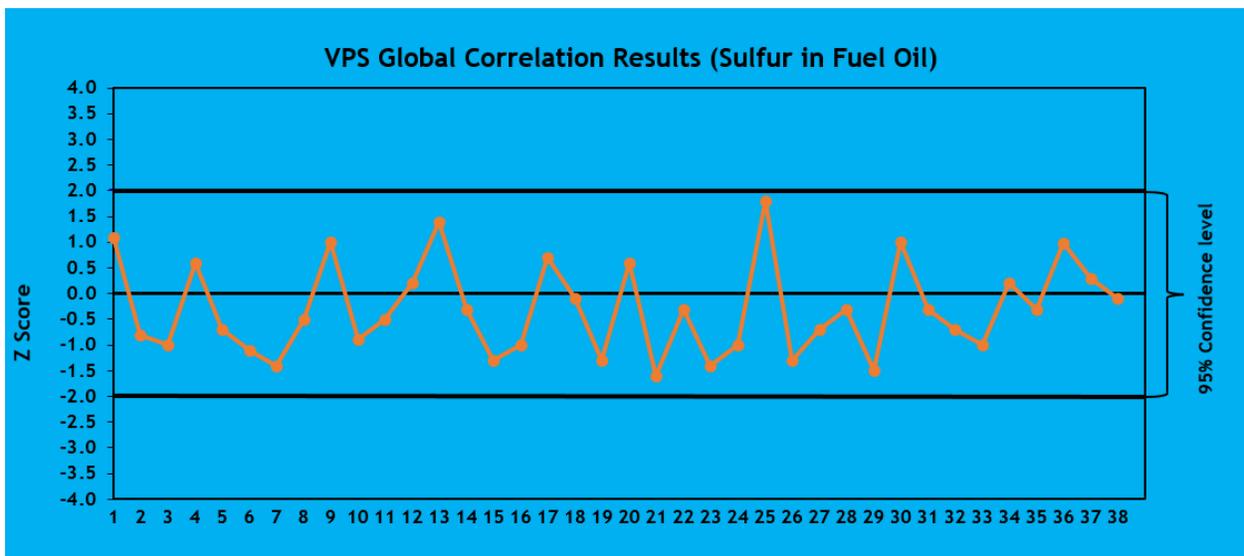


Figure 4 Example of a VPS Global Correlation Results (Sulfur in Fuel Oil)

6. VPS implemented a retest criteria in order to ensure the reported results are within 95% confidence level.

The basic question is what are the various criteria a Laboratory should follow to ensure production of precise and accurate test results?



- Use traceable certified reference materials for calibration in the same matrix as the samples for analysis.
- Achieve a calibration curve with minimum standard deviation which is equal or better than suggested by the international test method and in addition the analytical equipment manufacturer.
- Evaluate the confidence level of the calibration curve periodically using certified reference materials.
- Establish internal quality control chart to make sure the results reported are with 95% confidence level.
- Participate in International correlation programs and statistically evaluate the results.
- Validate the test method to make sure that the internal precision and accuracy is equal of better than specified by the International standard.
- Develop measurement uncertainty.
- Establish retest criteria
- Achieve and obtain test accredited to ISO/IEC 17025 which ensures the confidence in producing precise and accurate results

## **Why the test shall be accredited to ISO/IEC 17025**

ISO/IEC 17025 accreditation requirements ensure the Laboratory produces precise and accurate results by implementing the following procedures

- Validate the test method (Determine repeatability, reproducibility, measurement uncertainty, accuracy, detection limit, reporting limit, linearity)
- Internal quality control measures
- Equipment calibration with traceable reference standards
- Periodical evaluation using check standards to maintain the calibration confidence
- Participation in International correlation programs



Globally all VPS Laboratories are accredited to ISO/IEC 17025 quality system which ensures that the reported results are within 95% confidence level.

### VPS internal precision versus ISO 8754 and ASTM 4294 precisions

It is necessary to have an internal precision which is equal or better than the precisions given by the international ISO 8754 and ASTM D4294 standards. VPS has carried out extensive work to determine the whole concentration range precision in terms of repeatability, reproducibility, accuracy and measurement uncertainty. Results given in Table1 shows the comparison between the VPS internal precision against the ISO 8754 and ASTM D4294 precisions. Fig 5 shows the accuracy determination for the entire concentration range. The measurement uncertainty for low to high concentration ranges which is based on the combined correlation and QC results, correlation results and the internal precision results is given in Table 2.

Table 1 VPS internal precision versus ISO 8754 and ASTM 4294 precisions

Concentration Range (%m/m)	ISO 8754 Repeatability	ASTM Repeatability	VPS Repeatability	ISO 8754 Reproducibility	ASTM Reproducibility	VPS Reproducibility
0.045(D)	0.004	0.002	0.001	0.017	0.010	0.002
0.091(D)	0.005	0.004	0.001	0.020	0.015	0.004
0.576(D)	0.016	0.012	0.005	0.059	0.051	0.010
0.867(D)	0.022	0.015	0.015	0.083	0.066	0.017
0.434(F)	0.013	0.010	0.004	0.047	0.042	0.010
1.176(F)	0.028	0.018	0.006	0.108	0.081	0.020
2.105(F)	0.048	0.027	0.009	0.183	0.117	0.071
3.000(F)	0.068	0.033	0.020	0.255	0.148	0.087
3.389(F)	0.076	0.036	0.016	0.287	0.160	0.083

(D) Diesel oil and (F) Fuel oil

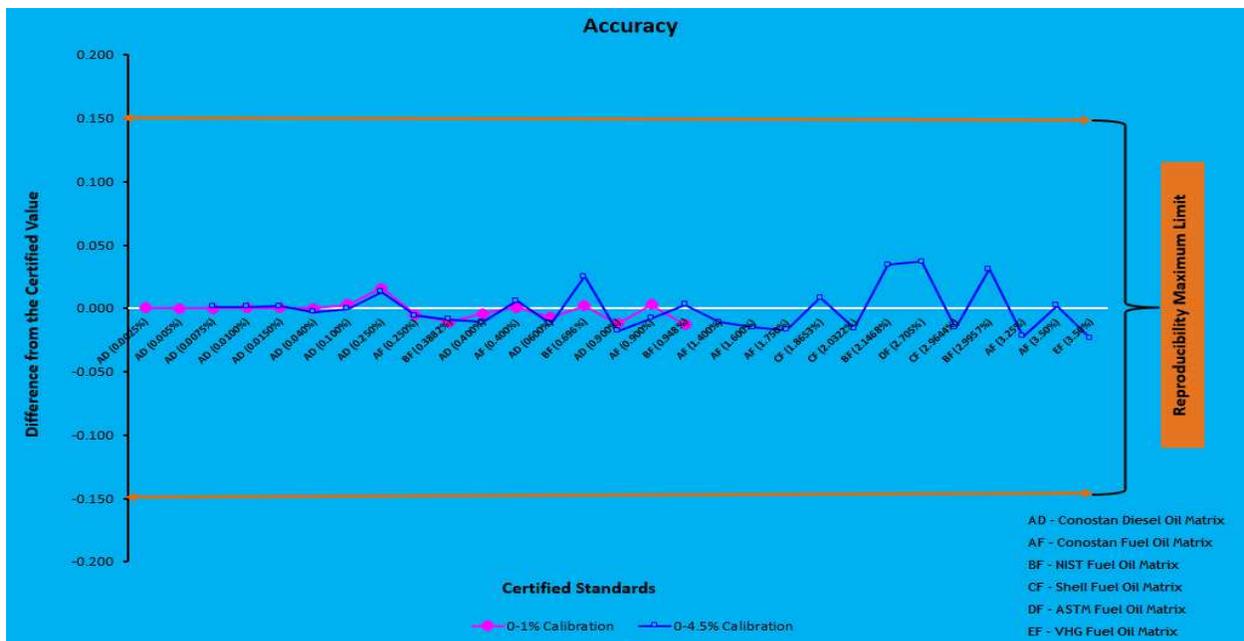


Figure 5 Accuracy Results from low to high sulfur concentration



Table 2 VPS Measurement Uncertainty

Product	Concentration Range (%m/m)	Based on correlation and QC results	Based on correlation results	Based on internal precision results
D	0.01 - 0.20	-	0.008	0.001
F	0.30 - 0.90	0.059	0.054	0.009
F	1.0 - 2.0	0.093	0.065	0.029
F	2.5 - 3.5	0.153	0.117	0.054

D - Diesel Oil and F- Fuel Oil

VPS precision, accuracy and measurement uncertainty results attained a high level confidence compared to the International ISO 8754 and ASTM D 4294 standards.

### Global Sulfur limit and VPS 95% confidence level

The 95% confidence level for a sulfur content of 3.50 wt% is calculated and represented in figure 5 based on the method ISO 8754, and ASTM D4294 and VPS internal precision. VPS achieve higher precision than the ISO 8754 and ASTM D4294 standards which in turn provides a high level of confidence in our test results reporting to the customers on a day to day basis. This can be achieved only through the rigorous quality process in practice.

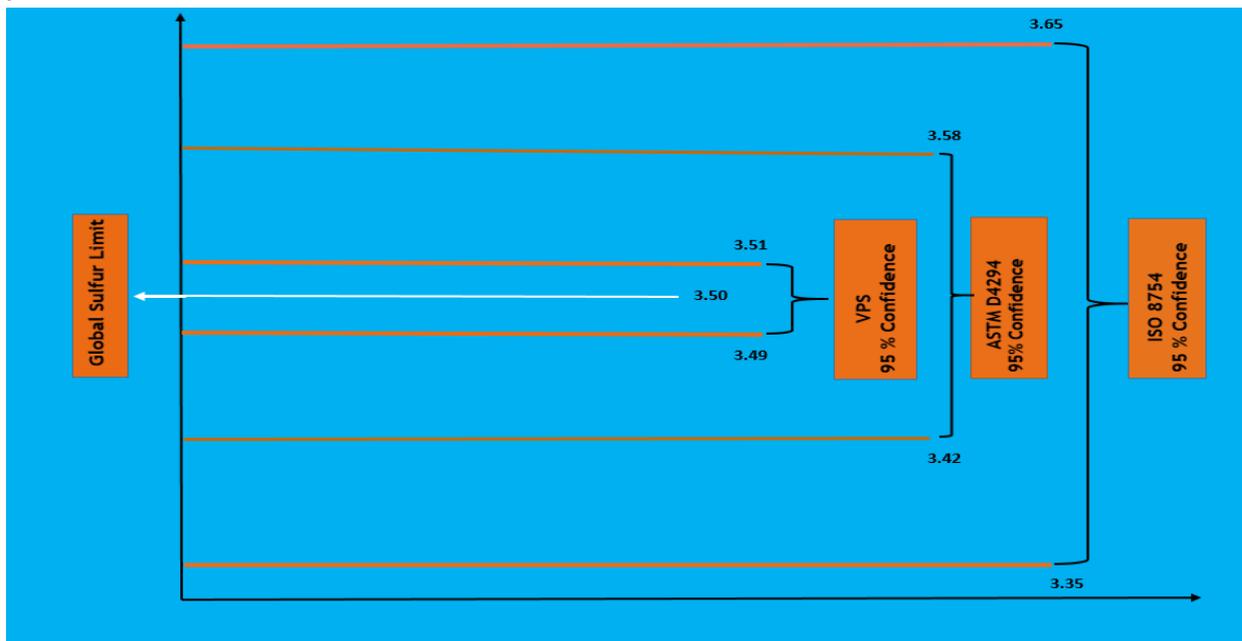


Figure 6 Global Sulphur Limit 3.50% and 95% Confidence Level Comparison of ISO 8754, ASTM D4294 and VPS

***Stringent quality processes carried out by VPS Laboratories ensure precise and accurate test results are produced and reported.*** For comments and further discussion, Dr. Sunil Kumar can be contacted as follows:

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