A123 – PETROLEUM TESTING GUIDANCE

Revision #1.2

September 14, 2018

CALA

Trust, measured accurately

INTRODUCTION

This guidance/interpretation document is for use in conjunction with A03-Rating Guide Appendix, when assessing methods specifically designed for testing in the petroleum industry. Where there are differences between A03, this guidance/interpretation document, the reference method, and ISO/IEC 17025, the requirements in the reference method and ISO/IEC 17025 shall prevail.

The clauses noted below correspond to the clause numbers in ISO/IEC 17025:2017.

GUIDANCE/INTERPRETATION

Selection, Verification and Validation of Methods
Clause 7.2.1.3

Some common petroleum-testing references include, but are not limited to, ASTM, GPA, API and UOP.

Clause 7.2.1.5

ASTM methods normally state expected method precision on two bases: "Reproducibility" and "repeatability". Reproducibility is the expected inter-laboratory variance.

ASTM methods include precision statements to provide a guideline on the variability expected between results obtained under prescribed conditions and assess, in general terms, its validity for specific applications. The repeatability (within lab variability) should normally be the basis for the lab repeatability in method validation/verification. However, these performance levels may not always be achievable unless using the same materials (e.g., performance levels determined from refined products may not be achievable for crude oils). It is not necessary that the lab achieves the repeatability performance specified in the reference, but it should use this as a guideline for expected variability.

Reproducibility (between lab variability) is probably useful in test method selection and service validation.

Clauses 7.2.1.5; 7.2.2 (and 7.6)

P19 (CALA Measurement Uncertainty Policy) covers estimation of MU for most petroleum-testing methods. For methods used in petroleum-testing that are more or less empirical, PT variability provide a reliable, comprehensive, quick and easy estimate.

Testing for compliance to a specification is common for many petroleum-testing methods. Gases and liquids transported in pipelines must meet certain specifications (this may be done to protect the pipeline or other vessels from corrosion etc.) There may be any number of specifications around custody transfer points. These are usually contractual and can vary from simple heating value / moisture content to more exotic concerns such as specific contaminants such as PCBs, metals, benzene. Per the standard, this has implications related to requirements for measurement uncertainty (client knowledge related to uncertainty is, as with most industries, limited). The lab can, as service, have policy and procedure related to notifying clients of nonconformance to product specification and using specifications for data verification / validation.

If a reference method is modified for screening purposes (such as pass/fail or other criteria), it must be stated explicitly as such, along with the rationale and scope of modification. As well, the difference in measurement uncertainty from the reference method must be stated.

Clause 7.2.1.1

Sample pre-treatment is important for many petroleum methods (e.g., cleaning oil, single phasing High Pressure (HP) liquids). Most tests on crude oil are performed on oil cleaned by centrifugation and are reported on an "after cleaning" basis.

Pressurized hydrocarbon samples may be anything from light gas mixtures consisting mainly of methane to gasified crude oils with everything from C1 to C30+ hydrocarbons. The latter are problematic to analyze since the components represent a very wide range of boiling points. Labs may have various approaches including separating the sample into gas and liquid phases stable at ambient conditions, measuring each phase for composition and volume or mass, then recombining these mathematically back into the original mixture.

Identification and measurement of individual hydrocarbon components is usually impractical in chromatographic analysis of hydrocarbon mixtures. Analysis usually involves grouping of peaks by retention time that approximates boiling point, which approximates carbon number.

Measurement is usually made on a mass basis but reported on mass, volume and mole bases. Conversion requires molecular weight and density that, in principle, can be estimated from the chromatographic analysis. However, because of the approximations indicated in the previous paragraph, and the error in assigning properties to a group based on carbon / boiling point, these estimates can seriously misrepresent the "true" result. These parameters can be measured, but normally only on the stabilized phase. It is important that the lab use a valid approach to calculation and that the calculations be compatible with the bases of all measurements made.

Data reduction is critical in some cases. The most important results for valuation of natural gas (density and heating value) are not measured directly, but are calculated from composition. If the scope is to include these, then the data reduction must be detailed.

Quite a bit of data validation normally goes on with pressurized samples for hydrocarbon composition (e.g. comparison to pipeline specs, equilibrium k-plots, calculated vs. measured properties such as density of gas, comparison to historical data, methane vs. pressure on liquids).

Normally for production testing:

Equilibrium k-plots (or equivalent) should be used i) to verify phase separation (if this is done) and ii) to verify sample integrity from associated gases and liquids (e.g. from an inlet separator). K-plots are thermodynamic diagrams based on the Clausius-Clapeyron equation indicate whether the gas and liquid are at equilibrium and can verify if results are mutually consistent.

It is recommended that historical data should be used where available and where applicable.

The lab should have protocols for comparing related parameters for compatibility / validity / expected behaviour. These can be such things as:

- A reasonably smooth variation of concentration vs. carbon number in natural materials.
- Historical consistency (where applicable)
- Geological and geographical consistency (fluids from the same geological pool in the same area can be expected to be broadly consistent).
- Measured properties vs. the same property calculated from composition (e.g., gas density).

Sampling
Clause 7.3

The sampling process is critical for pressurized samples. There are reference methods for gas and liquid sampling (GPA, ISO and ASTM have this). They are generally applicable but may not be applicable in all situations depending on the source composition, source conditions, ambient conditions etc. Sampling procedures that might work for lean gases may bias rich gases.

If accreditation is going to cover sample collection, the lab should be following good practices and have validated their sampling protocols for the types of samples collected. Samplers would have to be appropriately trained, be able to recognize potential problems, etc.

Hydrocarbons are generally sampled based on availability at agreed upon points using techniques based on sound physical principles and good practice. Usually samples will be collected from a single specific point along a flowing stream, variation is normally with time. "Statistical" sampling plans would therefore require a model of variation in the source over time and flow. "Spot" samples are collected at a single point in time and may be taken to represent the source over an assumed interval (this is quite reasonable if the stream is consistent). "Proportional" samples use special sampling equipment to collect sample in proportion with time or with flow rate. This technique is more costly, labour intensive and complex, but is more representative than spot samples or statistical techniques. Either way, this is normally based on agreement between lab and client; clients normally manage their own proportional sampling.

Generating representative samples is not a problem if dealing with a stable fluid. With high-pressure liquids, phase changes can occur which can result in bias if not controlled.

The validity of sampling and sub-sampling methods can be critical if dealing with multiphase samples. Sample integrity must especially be evaluated when the samples are gas and high-pressure liquids. Opening pressures, air contents, bubble points etc. **can be used to** establish whether the sample is representative of the source.

Procedures for handling, mixing and conditioning of samples must be based on ASTM D5854 Practice for Mixing and Handling of Liquid Samples to ensure that a representative sample is delivered from the primary sample container or receiver into the analytical test apparatus or into the intermediate containers.

The lab should be checking opening pressures / temperature of gas and liquid samples and should have nonconformance criteria and actions to taken for nonconformance based on source temperature and pressure.

The lab should measure O2 content of gas samples. O2 does not occur in natural gas and is normally assumed an artifact of sampling (due to air contamination). The lab should have a protocol for dealing with O2. Normally, small quantities of air can be corrected out, O2 and an amount of N2 in proportion to that found in air, is taken from the result and the remainder

renormalized - air free basis. Larger amounts of air indicate a seriously compromised sample and should normally rejected or – at minimum – a note added on the report.

Care must be taken when measuring and correcting for O2 as Ar may co-elute. There are ways of dealing with this (Ar carrier, cryo temperatures, suitable accounting in calculation...) the lab should have the means clearly defined.

Bubble points (essentially measuring the conditions required to return a sample to single – liquid – phase) are useful as well in determining sample integrity.

Many sample containers used in the oil and gas sector are NOT disposable and get cleaned and reused. Therefore, the lab must have a procedure for this step.

Auto samplers in use must meet requirements of ASTM D4177, or the frequency and volume of manual samples is varied to meet ASTM 4057 requirements to avoid product representation issues.

Samples should be stored in closed containers to prevent loss of light components and to be protected from weathering or degradation due to heat and/or light.

Equipment
Clause 6.4

In some situations, calibration is related directly to a piece of measurement equipment rather than to the method, i.e., some measurements are outputs directly from primary calibrated equipment. This may be a basic physical measurement such as temperature or pressure, or equipment such as viscometers, which may require external/manufacturer calibration.

Calibration for hydrocarbon composition by GC may involve determining relative response factors (RRF). A multilevel calibration may be redundant in situations where RRF's are used. RRF's may even be stipulated in reference methods.

Of relevance beyond device calibration is the device itself. Some of these methods are empirical. Most (e.g. ASTM) are quite detailed in measurement equipment requirements and configuration. If there are any modifications to equipment, this need to be both documented (clearly stated in the lab SOP) and verified that the changes are within the allowance specified in the referenced method.

The sample containers themselves should be stainless steel and capable of withstanding the sample pressure. They should also be suitable to the sampling technique (certain liquid displacement sampling methods require special equipment configuration). Carbon steel should not be used, it absorbs CO_2 and it corrodes so the integrity of the vessel can fail. Even stainless steel is inappropriate for sampling gases for trace sulfur species as these may be absorbed. Tedlar sample bags are typically used for reduced sulfur species. One the other hand, samples in Tedlar are generally not suitable for hydrocarbon composition analysis due to permeability to some constituents, and other effects that may result in bias.

For pressurized liquid samples test methods will dictate the use of a piston cylinder rather than a liquid displacement cylinder. The use of the incorrect cylinder could bias test results.

Technical Records
Clause 7.5

When measuring gases, it is important that conditions (temperature & pressure) be appropriately measured and compensated.

Volume correction to reference conditions can be critical, especially for gases. If necessary, the lab should have an appropriate means of measuring temperature and pressure.

With gases, it is critical to report the reference conditions and the basis of the measurement. There are at least a dozen different sets of "standard conditions". They should be stated directly and unambiguously (The Electricity and Gas Inspection Act of Canada specify 101.325 kPa and 15 °C which is slightly different from the conditions used by some US bodies). Use of "STP" or "NTP" is not acceptable.

Although gases are normally measured "as received", properties can be reported on different bases such as "moisture free" or "moisture and acid gas free". Both are valid, but these bases must be clearly indicated.

There are a few tests that may only be valid if done directly at the source (e.g. dew points by the chilled mirror method ASTM D1142).

Ensuring the validity of results
Clause 7.7

Duplicates may not always be applicable, due to issues with matrices, the volatility of the sample, or sample pre-treatment. For example, vapour pressure by ASTM D5191 cannot have duplicate analysis since it must be the first test done on the samples.