The Implementation of a newly devised Analytical Performance Value (APV) Methodology to Assess the Performance Capabilities of Laboratory Instruments, specifically for the Petroleum Industry

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ABSTRACT

A need for the simplified review of method performance capability based on precision statement is required for commercial analytical instruments. A simplified applied statistical approach would benefit and assist laboratory managers, process engineers, commercial traders, lab chemists, lab technicians and operators. The numerical expression rating system based on performance relative to two or more points within the operating value of each parameter is defined in any standard method containing full precision, and is defined as repeatability and reproducibility. A process and computational expression is described and defined as analytical performance value (APV).

This newly devised performance value would be contained in any standard method for use as a quantitative evaluation of test method performance. The proposed technique is to define a systematic method which provides for establishing an analytical performance value based on precision criteria relative to parameter measurements. The APV can be expressed as a scaled value percentage, which can then be used to assess acceptability and capability of the instrument or test method. This poster discusses the derivation of the APV methodology and analyzes two examples from the oil and gas industry of a repeatability and reproducibility assessment by applying the APV technique to these two ASTM methods.

INTRODUCTION

A need for the simplified review of method performance capability based on precision statement is required for commercial analytical instruments. A simplified applied statistical approach would benefit and assist laboratory managers, process engineers, commercial traders, lab chemist, lab technicians and operators. A process and computational expression is described and defined as analytical performance value.

The energy and chemical industry would benefit from a reliable and straightforward statistically based system since it allows for determining the value added performance of any test method. The proposed technique uses a systematic method that establishes an analytical performance value (APV) based on precision criteria relative to parameter measurements. Standard method precision criteria are used to establish an estimated APV value based on repeatability and reproducibility at the lowest and highest operating concentration range.

The application advantages include:

- Application of test performance based on established parameters in units of measurement
- Parameters and measurements are evaluated based on the repeatability or reproducibility
- Comparison of either individual laboratory or intra-laboratory data is often performed daily
- Time efficiency to perform each calculation extensively

APV DERIVATION

Equation 1 – Analytical Performance Value

APV = estimated repeatability value / minimum detection limit * 100

Equation 2 - Scalable APV Assigned for Each Method Parameter

APV_1 = assigned when APV = X or < 5%

APV_2 = assigned when APV = X or > 5% or < 10%

APV_3 = assigned when APV = X or > 10 % or 15%

APV_4 = assigned when APV = X or > 15%

Where X = a value established by industry experts or commercial production and trade requirements.

The simplified scheme proposal is to applied to Equations 1 and 2 (or one obtained by consensus) to both method repeatability and reproducibility at the defined minimum and maximum operating limit values defined within the scope of the standard test method. These equations provide a simplified pre-calculated degree of variation relative to the specific points of the method operating window. It also provides a strategy for assessing a test methods acceptability based on its specifications and corresponding parameters with sufficient confidence. This evaluation can justify the precision for between-laboratory testing in order to standardize the methods performed in an efficient way.

Equation 1 has been applied to test method ASTM D7423-16$^{\varepsilon1}$, resulting in the equations shown in Table 1 for repeatability and reproducibility. In the example provided, a rating tolerance value is provided in Table 2, and Table 3 based on industry typical values. The rating tolerance applied to methods would be defined by:

- Industry production operating specification requirements
- Governing bodies
- Initial technology prime tolerances.

APV APPLIED TO ASTM D7423

Table 1. APV Applied to Repeatability and Reproducibility of ASTM D7423

Analyte	Repeatability	Reproducibility
Acetone	0.1821*X*0.5985	0.4424*X*0.5985
Acetaldehyde	0.2595*(X+0.0001)*0.595	1.0439*(X+0.0001)*0.595
Diethyl Ether	0.1869*(X+0.0001)*0.5981	0.5966*(X+0.0001)*0.5981
Dimethyl Ether	0.05321*(X+0.0001)*0.9273	0.2784*(X+0.0001)*0.9273
DIPE	0.1188*(X-0.6566)*0.5889	0.5219*(X-0.6566)*0.5889
ETBE	0.06778*X*0.8512	0.3613*X*0.8512
Ethanol	0.1626*(X+0.0001)*0.7649	0.6808*(X+0.0001)*0.7649
Iso-Proponal	0.2458*X*0.5108	1.1222*X*0.5108
MEK	0.2009*X*0.5094	0.7171*X*0.5094
Methanol	0.2870*X*0.4887	1.9695*X*0.4887
MTBE	0.1261*X*0.6368	0.2861*X*0.6368
N-Butanol	0.1179*X*0.9278	0.3890*X*0.9278
Sec-Butanol	0.1063*X*0.8057	0.5578*X*0.8057
TAME	0.2812*(X+0.0001)*0.4011	0.9946*(X+0.0001)*0.4011

Table 2. APV at Minimum Concentration of ASTM D7423

Analytical Performance Value at 0.5 mg/kg								
Analyte	Repeatability				Reproducibility			
	APVr1 (≤5%)	APVr2 (≤15%)	APVr3 (≤50%)	APVr4 (>50%)	APVR1 (≤10%)	APVR2 (≤30%)	APVR3 (≤100%)	APVR4 (>100%)
Acetone		X				X		
Acetaldehyde		X					X	
Diethyl Ether		X					X	
Dimethyl Ether	X					X		
DIPE	X					X		
ETBE		X				X		
Ethanol		X					X	
Iso-Proponal		X					X	
MEK		X					X	
Methanol		X					X	
MTBE		X				X		
N-Butanol		X					X	
Sec-Butanol		X					X	
TAME		X				X		

Table 3. APV at Maximum Concentration of ASTM D7423

Analytical Performance Value at 100 mg/kg								
Analyte	Repeatability				Reproducibility			
	APVr1 (≤5%)	APVr2 (≤15%)	APVr3 (≤50%)	APVr4 (>50%)	APVR1 (≤10%)	APVR2 (≤30%)	APVR3 (≤100%)	APVR4 (>100%)
Acetone		X				X		
Acetaldehyde			X				X	
Diethyl Ether		X					X	
Dimethyl Ether	X					X		
DIPE	X						X	
ETBE		X					X	
Ethanol		X					X	
Iso-Proponal		X					X	
MEK		X					X	
Methanol		X					X	
MTBE		X				X		
N-Butanol		X					X	
Sec-Butanol		X					X	
TAME		X					X	

APV COMPARISON OF INTER-STANDARD PRECISION

The APV technique can be used to compare any standard developed for testing the same parameter. An example of the ease of use is outlined in Table 4 and Table 5. APV values are tabulated for the same parameters obtained by ASTM D3606-10 and ASTM D5769-15 at the minimum operating concentration specified in the scope of each standard, accordingly.

Comparison of Table 6 and Table 7 provides a quantitative comparison of the same parameters for ASTM D3606-10 versus ASTM D5769-15 at the maximum operating concentration defined in the scope of each standard. The maximum APV (H-APVR1) data show that the use of ASTM D5769-15 for testing benzene at 4.0 volume percent would provide better performance

Table 4. ASTM D3606-10 APV at Minimum Operating Conditions

Compound	Concentration	Repeatability	Reproducibility
		L-APVr1	L-APVR1
Benzene	0.1 vol%	13.0	63
Toluene	1.7 vol%	4.1	15.1

Table 5. ASTM D5769-15 APV at Minimum Operating Conditions

Compound	Concentration	Repeatability	Reproducibility
		L-APVr1	L-APVR1
Benzene	0.09 vol%	4.6	28.9
Toluene	1.0 vol%	4.7	27.8

Table 6. ASTM D3606-10 APV at Maximum Operating Conditions

Compound	Concentration	Repeatability	Reproducibility
		H-APVr1	H-APVR1
Benzene	1.5 vol%	2.0	28.0
Toluene	9.0 vol%	6.9	12.8

Table 7. ASTM D5769-15 APV at Maximum Operating Conditions

Compound	Concentration	Repeatability	Reproducibility
		H-APVr1	H-APVR1
Benzene	4.0 vol%	3.1	14.1
Toluene	13.0 vol%	4.7	27.8

CONCLUSIONS

This poster has shown that the Applied Performance Value (APV) is useful in commercial standards applications, specifically in the petroleum industry. The relative precision can be established based on published standard precision statements to establish an APV for each test parameter. With proper evaluation of the APV values, the acceptability or capability can be determined. For example, an APV of <10% is defined as acceptable and a capable test method. From 10% - 30%, the test method is considered marginally acceptable. If the APV is >30%, the test method may have an issue or challenge, making the method unreliable and in need of further review.

APV values provide the user with the means to evaluate the performance of any standard without estimating each value for each parameter when they are incorporated into each standard. APV values can be used to quickly estimate the precision of individual laboratory or intra-laboratory performance. Also, APV values can be used to quickly compare the expected precision of a parameter determined by two individual standards to determine applicability. APV is incorporated into a new standard practice by ASTM D02.94 – ASTM D8146 "Evaluating Test Method Capability and Fitness for Use."

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