Analytical Performance Value of Laboratory Instruments

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PEFTEC 2017

Introduction

Establishing the Analytical Performance Value of Laboratory Instrument Methodology

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. The numerical expression rating system based on performance relative to two or more points within the operating value of each parameter defined in any standard method containing full precision is defined as repeatability and reproducibility. A process and computational expression is described and defined as analytical performance value (APV). An example of a standard precision statement is provided in Fig. 1.

TABLE 3 Repeatability and Reproducibility for Oxygenates (mg/kg)

NOTE 1—Where: X = the average individual oxygenate concentration of two results in mg/kg.

Analyte	Repeatability Limit (r)	Reproducibility Limit (R)
	$(0.1821)(X^{0.5985})$	$(0.4424)(X^{0.5985})$
Acetyaldehyde	$0.2595(X + 0.0001)^{0.595}$	$1.0439(X + 0.0001)^{0.595}$
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-Propanol	$(0.2458)(X^{0.5108})$	$(1.1222)(X^{0.5108})$
MEK	$(0.2009)(X^{0.5094})$	$(0.7171)(X^{0.5094})$
Methanol	$(0.2870)(X^{0.4887})$	$(1.9695)(X^{0.4887})$
MTBE	$(0.1261)(X^{0.6368})$	$(0.2861)(X^{0.9442})$
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	$0.2812(X + 0.0001)^{0.4011}$	$0.9946(X + 0.0001)^{0.4011}$

Figure 1. Precision statement ASTM D7423-16, Table 3 Repeatability and Reproducibility for Oxygenates

Discussion

Introduction

The energy and chemicals industry would benefit from a reliable and straightforward statistically based system which allows for determining the value-added performance of any test method. This performance value would be implemented into standard methods for use as a quantitative evaluation of test method performance.

Industry precedent has been established and incorporated into corporate finance defined as economic value added (EVA[1])[2] or return on assets (ROA). ROA is defined as the ratio of earnings to total assets. In a similar way to EVA, the analytical performance value (APV) is expressed in equation 1, 2, below where repeatability and reproducibility are represented relative to a known value.

Eq. 1 – Analytical Performance Value

APV = estimated repeatability value / minimum detection limit * 100

Eq. 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%

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

Figure 2: APV Equation and Scaled Values

The benefits of applied APV include:

- means to quickly apply test method performance based on established parameter value in units of measure;
- individual parameters and units of measure are evaluated based on the repeatability or reproducibility;
- means for comparison of either individual laboratory or interlaboratory data is often performed daily;
- time required to perform each calculation can be extensive when all of events are taken into consideration.

Discussion

Applied Precision

The simplified scheme proposal is to apply 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. A simplified scheme to provide a quantitative APV expressed as a scaled value percentage which defines the degree of variation based on a point within the operating range of any instrument is useful within the commercial trade industry. A standard method should contain an APV section which would contain the tabulated values for each parameter estimated by calculating repeatability at (for example) the minimum operating value (i.e. limit of detection) defined in the scope of any analytical method.

An example of this concept, equation (Eq. 1) has been applied to test method ASTM D7423-16[e1], as shown in Fig.3, Fig. 4, and Fig. 5. The rating tolerance applied to methods would be defined either by industry production operating specification requirements, governing bodies, and initial technology prime tolerances.

Applied Precision Statement ASTM D7423-16

ASTM D7423-16: Precision Statement			Applied Precision			
Analyte	Repeatability	Reproducibility	r	R	r	R
			0.5 mg/kg	0.5 mg/kg	100 mg/kg	100 mg/kg
	r	R				
Acetone	0.1821 * X 0.5985	0.4424 * X 0.5985	0.054	**0.132**	10.899	**26.478**
Acetyaldehyde	0.2595(X + 0.0001)0.595	1.0439(X + 0.0001)0.595	0.077	**0.311**	15.440	**62.112**
Diethyl Ether	0.1869(X + 0.0001)0.5981	0.5966(X + 0.0001)0.5981	0.056	**0.178**	11.179	**35.683**
Dimethyl Ether	0.05321(X + 0.0001)0.9273	0.2784(X + 0.0001)0.9273	0.025	**0.129**	4.934	**25.816**
DIPE	0.1188(X-0.6566)0.5889	0.5219(X-0.6566)0.5889	0.024	**0.106**	6.950	**30.533**
ETBE	0.06778 * X 0.8512	0.3613 * X 0.8512	0.029	**0.154**	5.769	**30.754**
Ethanol	0.1626(X + 0.0001)0.7649	0.6808(X + 0.0001)0.7649	0.062	**0.260**	12.437	**52.074**
Iso-Propanol	0.2458 * X 0.5108	1.1222 * X 0.5108	0.063	**0.287**	12.555	**57.322**
MEK	0.2009 * X 0.5094	0.7171 * X 0.5094	0.051	**0.183**	10.234	**36.529**
Methanol	0.2870 * X 0.4887	1.9695 * X 0.4887	0.070	**0.481**	14.026	**96.249**
MTBE	0.1261 * X 0.6368	0.2861 * X 0.9442	0.040	**0.135**	8.030	**27.014**
n-Butanol	0.1179 * X 0.9278	0.3890 * X 0.9278	0.055	**0.180**	10.939	**36.091**
Sec-Butanol	0.1063 * X 0.8057	0.5578 * X 0.8057	0.043	**0.225**	8.565	**44.942**
TAME	0.2812(X + 0.0001)0.4011	0.9946(X + 0.0001)0.4011	0.056	**0.200**	11.279	**39.893**

Figure 3: Applied Precision – ASTM D7423-16[e1]

Applied Examples

APV Applied to ASTM D7423-17

Analyte	Analytical Performance Value at 0.5 mg/kg				Analytical Performance Value 0.5 mg/kg			
	Applied to Repeatability				Applied to Reproducibility			
Rating	APV_{r1}	APV_{r2}	APV_{r3}	APV_{r4}	APV_{R1}	APV_{R2}	APV_{R3}	APV_{R4}
(Tolerance)	(</=) 5%	(</=) 15%	(</=) 50%	> 50%	(</=) 10%	(</=) 30%	(</=) 100%	> 1000%
Acetone		X				X		
Acetyaldehyde		X					X	
Diethyl Ether		X					X	
Dimethyl Ether	X					X		
DIPE	X					X		
ETBE		X				X		
Ethanol		X					X	
Iso-Propanol		X					X	
MEK		X					X	
Methanol		X					X	
MTBE		X				X		
n-Butanol		X					X	
Sec-Butanol		X					X	
TAME		X				X		

Figure 4. Analytical Performance Value at Minimum Operating Limit of Standard

Analyte	Analytical Performance Value at 100 mg/kg				Analytical Performance Value at 100 mg/kg			
	Applied to Repeatability (100 mg/kg)				Applied to Reproducibility (100 mg/kg)			
Rating	APV_{r1}	APV_{r2}	APV_{r3}	APV_{r4}	APV_{R1}	APV_{R2}	APV_{R3}	APV_{R4}
(Tolerance)	(</=) 5%	(</=) 15%	(</=) 50%	> 50%	(</=) 10%	(</=) 30%	(</=) 100%	> 1000%
Acetone		X				X		
Acetyaldehyde			X				X	
Diethyl Ether		X					X	
Dimethyl Ether	X					X		
DIPE	X						X	
ETBE		X					X	
Ethanol		X					X	
Iso-Propanol		X					X	
MEK		X					X	
Methanol		X					X	
MTBE		X				X		
n-Butanol		X					X	
Sec-Butanol		X					X	
TAME		X					X	

Figure 5. Analytical Performance Value at Maximum Limits of Standard D7423-16

APV Comparison of Inter-standard Precision

The APV technique can be used to compare any standard developed for testing the same parameter, Fig. 6 where APV values are tabulated for the same parameters obtained by ASTM D3606-10 and ASTM D5769-15.

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

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

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

Figure 6: APV Based Comparison of Precision

Analyte	Analytical Performance Value Applied to Repeatability (3.0 mg/kg)				Analytical Performance Value Applied to Reproducibility (3.0 mg/kg)			
	A.P.V.(r)	A.P.V.(r)	A.P.V.(r)	A.P.V.(r)	A.P.V.(R)	A.P.V.(R)	A.P.V.(R)	A.P.V.(R)
Rating	1	2	3	4	1	2	3	4
	5%	15%	50%	>50%	10%	30%	100%	>100%
Sulfur		13.3					33.3	

Analyte	Analytical Performance Value Applied to Repeatability (10000 mg/kg)				Analytical Performance Value Applied to Reproducibility (10000 mg/kg)			
	A.P.V.(r)	A.P.V.(r)	A.P.V.(r)	A.P.V.(r)	A.P.V.(R)	A.P.V.(R)	A.P.V.(R)	A.P.V.(R)
Rating	1	2	3	4	1	2	3	4
	5%	15%	50%	>50%	10%	30%	100%	>100%
Sulfur	2.4				6.9			

Analyte	Analytical Performance Value Applied to Repeatability Low Level of Operating Range				Analytical Performance Value Applied to Reproducibility Low Level of Operating Range			
	A.P.V.(r)	A.P.V.(r)	A.P.V.(r)	A.P.V.(r)	A.P.V.(R)	A.P.V.(R)	A.P.V.(R)	A.P.V.(R)
Rating	1	2	3	4	1	2	3	4
	5%	15%	50%	>50%	10%	30%	100%	>100%
Gasoline (RFG)	0.06					12.7		
Distillates	0.02				4.0			

Analyte	Analytical Performance Value Applied to Repeatability High Level of Operating Range				Analytical Performance Value Applied to Reproducibility High Level of Operating Range			
	A.P.V.(r)	A.P.V.(r)	A.P.V.(r)	A.P.V.(r)	A.P.V.(R)	A.P.V.(R)	A.P.V.(R)	A.P.V.(R)
Rating	1	2	3	4	1	2	3	4
	5%	15%	50%	>50%	10%	30%	100%	>100%
Gasoline (RFG)	0.06					11.5		
Distillates	0.02				3.64			

Analyte	Analytical Performance Value Applied to Repeatability Low Level of Operating Rang				Analytical Performance Value Applied to Reproducibility Low Level of Operating Rang			
	A.P.V.(r)	A.P.V.(r)	A.P.V.(r)	A.P.V.(r)	A.P.V.(R)	A.P.V.(R)	A.P.V.(R)	A.P.V.(R)
Rating	1	2	3	4	1	2	3	4
	5%	15%	50%	>50%	10%	30%	100%	>100%
20 (kPa)	5.4				9.1			

Analyte	Analytical Performance Value Applied to Repeatability High Level of Operating Range				Analytical Performance Value Applied to Reproducibility High Level of Operating Range			
	A.P.V.(r)	A.P.V.(r)	A.P.V.(r)	A.P.V.(r)	A.P.V.(R)	A.P.V.(R)	A.P.V.(R)	A.P.V.(R)
Rating	1	2	3	4	1	2	3	4
	5%	15%	50%	>50%	10%	30%	100%	>100%
100 (kPa)	1.56				2.6			

APV Comparison - Multiple Standard Precision

Examples of APV technique applied to compare multiple standards which measure the same parameter.

Analyte	Analytical Performance Value Applied to Repeatability (0.2 mass %)				Analytical Performance Value Applied to Reproducibility (0.2 mass %)			
	A.P.V.(r)	A.P.V.(r)	A.P.V.(r)	A.P.V.(r)	A.P.V.(R)	A.P.V.(R)	A.P.V.(R)	A.P.V.(R)
Rating	1	2	3	4	1	2	3	4
	5%	15%	50%	>50%	10%	30%	100%	>100%
Methanol	5.3					22.6		
Ethanol	3.7					13.1		
Iso-Propanol	2.2					28.1		
tert-butanol	2.2					12.7		
n-Propanol	1.7				6.3			
MTBE	2.8				8			
Sec-Butanol	0.2					29.5		
DIPE	4.5					28.1		
iso-Butanol	4.5					28.1		
ETBE	4.1					27.4		
tert-Pentanol	2.4				8.6			
n-Butanol	3.7					12.5		
TAME	3.5					15.8		

Analyte	Analytical Performance Value Applied to Repeatability (12 - 20 mass %)				Analytical Performance Value Applied to Reproducibility (12 - 20 mass %)			
	A.P.V.(r)	A.P.V.(r)	A.P.V.(r)	A.P.V.(r)	A.P.V.(R)	A.P.V.(R)	A.P.V.(R)	A.P.V.(R)
Rating	1	2	3	4	1	2	3	4
	5%	15%	50%	>50%	10%	30%	100%	>100%
Methanol	5.3					22.6		
Ethanol	3.7					13.1		
Iso-Propanol	2.2					28.1		
tert-butanol	2.2					12.7		
n-Propanol	1.7				6.3			
MTBE	2.8				8			
Sec-Butanol	0.2					29.5		
DIPE	4.5					28.1		
iso-Butanol	4.5					28.1		
ETBE	4.1					27.4		
tert-Pentanol	2.4				8.6			
n-Butanol	3.7					12.5		
TAME	3.5					15.8		

Analyte	Analytical Performance Value Applied to Repeatability (0.1 mass %)				Analytical Performance Value Applied to Reproducibility (0.1 mass %)			
	A.P.V.(r)	A.P.V.(r)	A.P.V.(r)	A.P.V.(r)	A.P.V.(R)	A.P.V.(R)	A.P.V.(R)	A.P.V.(R)
Rating	1	2	3	4	1	2	3	4
	5%	15%	50%	>50%	10%	30%	100%	>100%
Methanol	3.4					21.5		
Ethanol	2.8					21.6		
Iso-Propanol	2.2					14.9		
tert-butanol	3.3					16		
n-Propanol	1.4					15		
MTBE	2.9					9.5		
Sec-Butanol	1.6					12.4		
DIPE	3.3					11.3		
iso-Butanol	2.4					15.8		
ETBE	3.4					19.8		
tert-Pentanol	2.1				9.9			
n-Butanol	2.8				6.6			
TAME	2.3					16.6		

Analyte	Analytical Performance Value Applied to Repeatability (20 mass %)				Analytical Performance Value Applied to Reproducibility (20 mass %)			
	A.P.V.(r)	A.P.V.(r)	A.P.V.(r)	A.P.V.(r)	A.P.V.(R)	A.P.V.(R)	A.P.V.(R)	A.P.V.(R)
Rating	1	2	3	4	1	2	3	4
	5%	15%	50%	>50%	10%	30%	100%	>100%
Methanol	3.4					21.5		
Ethanol	2.8					21.6		
Iso-Propanol	2.2					14.9		
tert-butanol	3.3					16		
n-Propanol	1.4					15		
MTBE	2.9					9.5		
Sec-Butanol	1.6					12.4		
DIPE	3.3					11.3		
iso-Butanol	2.4					15.8		
ETBE	3.4					19.8		
tert-Pentanol	2.1				9.9			
n-Butanol	2.8				6.6			
TAME	2.3					16.6		

Conclusions

Applied Performance Value is Useful in Commercial Standards Application

- The relative precision can be established based on published standard precision statements to establish an APV for each parameter.
- 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 intralaboratory performance.
- APV values can also be used to quickly compare the expected precision of a parameter determined by two individual standards to determine applicability.
- Analytical Performance Value (APV) is being incorporated into a new standard practice by ASTM Committee D02.94 – WK52522" Evaluating Test Method Capability and Fitness for Use"