

Improved ASTM G72 Test Method for Ensuring Adequate Fuel-to-Oxidizer Ratios

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History

- 1987 Montreal Protocol
 - CFC-113 phased out by 2010
 - Consumption and production of HCFCs to freeze by 2013
- 2001 CFC-113 Solvent Replacement Study
 - Ideally Solvents found “non-flammable”
 - AIT (G72) Low and High Pressure
 - Mechanical Impact (D2512/ G86)- 72ft/lbs
 - Asahi AK225 (HCFC) selected as replacement
- 2012 AK225G Solvent Replacement Study
 - Non-ignitability not always possible
 - All Candidate Solvents found to be ignitable
 - Even previously thought non-ignitable AK-225G ignites
 - Criteria existed allowing further consideration but unclear how to make best material selection.

Scope and Approach

- Reproduction/confirmation of historical results
- Re-familiarization with handling procedures
- Identification/Evaluation of variables for potential method improvement
- Retesting of materials using proposed method improvements

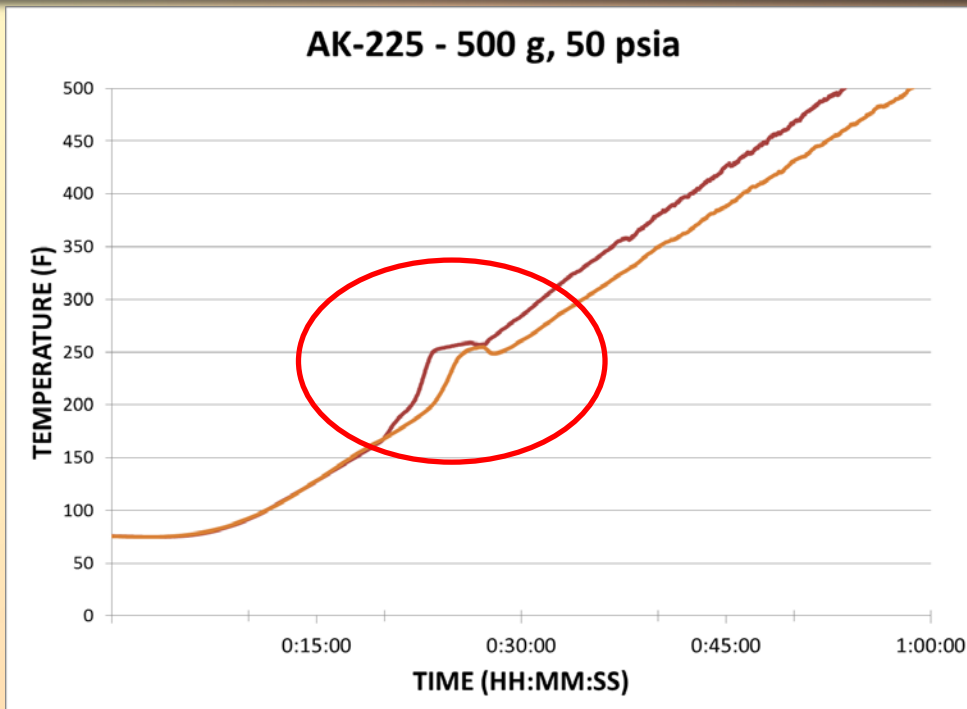
Historical & Reproduction Results

	345 kPa (50 psia)	13.8 Mpa (2000 psia)
AK-225	TL	TL
HFE-7100	TL	TL

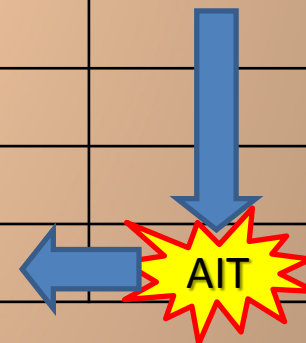
- Historical Data confirmed
- Interpreted as non-flammable under these conditions
- Questions to ask:
 - Are AITs really $> 430^{\circ}\text{C}$ (800°F)?
 - Was there an adequate oxidizer/fuel ratio?
 - Are solvents evaporating prior to installation into test chamber?

Sample Size

- Problems
 - Current ASTM G72 sample size 200 ± 30 mg.
 - Exotherms w/out ignition → Insufficient oxidizer:fuel
 - Evaporative loss of low boiling point material → insufficient sample size.
- Solution – Implement an incremental sample size increase until reproducible results are obtained.
- Approach
 - ~0.25 g step size until repeatable AIT data were obtained.
 - Evaluation of system safety limits
- Further Evaluation - effect of even larger test samples

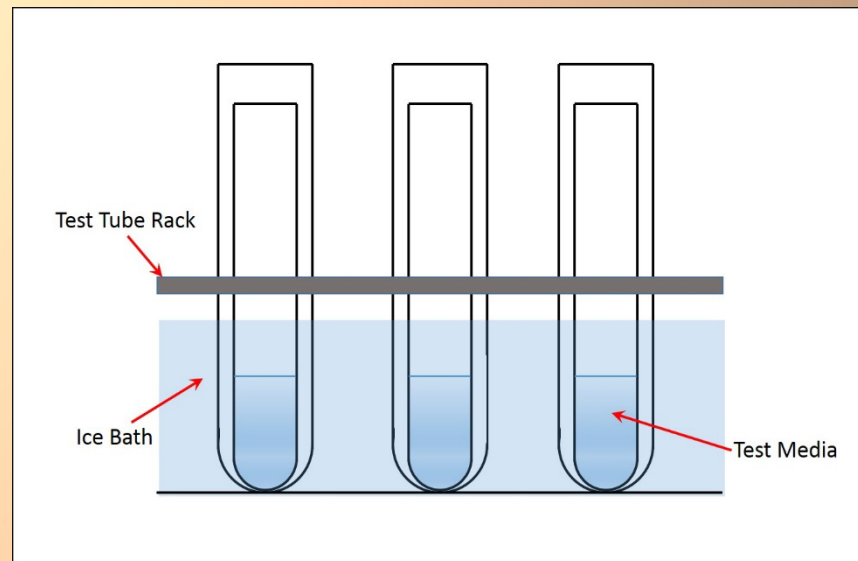


	345 kPa (50 psia)	13.8 Mpa (2000 psia)
200		
500		
750		
1000		



Sample Chilling

- Problem
 - Evaporative loss of low boiling point material → insufficient sample size.
- Solution – Test Sample Chilling
- Approach
 - Ice bath of test tubes containing known quantities of test material
 - Re-weighing sample just prior to loading into reaction vessel.
- Evaluation Approach
 - Performing Tests at different conditions on chilled and non chilled samples
- Further Evaluation - None



Reaction Vessel: To Purge or Not to Purge

- Suspected Problem
 - Tradeoff
 - Evacuation of trapped atmospheric gas
 - Encourages the evaporation/venting of volatized test material
 - Suspected insufficient Oxider:Fuel
- Evaluation Approach
 1. Measuring pretest sample weight
 2. Load sample into reaction vessel
 3. Performing three 1-min purges at test pressure
 4. Remove and re-weigh test sample.
- Further Evaluation - None

Test Pressure

- Suspected Problem
 - Lack of oxidizer at lower pressure
- Solution – Increase test pressure
- Approach
 - Evaluate for the existence of exotherms
 - Incrementally increase test pressure until reproducible AIT results are obtained
- Further Evaluation - None

Purge Mass Loss Evaluation

Purge Pressure Mpa (psia)	Target Pretest Mass (mg)	Avg. Mass Loss (mg)	Avg. Mass Loss (%)	Standard Deviation (mg)
AK-225G				
0.3 (50)	200	18.3	10.8	2.1
	500	15	2.9	8.9
6.9 (1000)	200	31.3	15.2	4.6
	500	34	6.8	4.4
13.8 (2000)	200	58.7	26.4	22.5
	500	40.7	8.3	4.0
HFE-7100				
0.3 (50)	200	13.3	6.2	3.8
	500	13	2.6	2.6
6.9 (1000)	200	27	12.5	4.6
	500	25	4.9	10.4
13.8 (2000)	200	28.3	12.8	11.6
	500	58.3	11.5	18.5

483 kPa (70 psia)					
		0 Purges		3 Purges	
		Avg (°F)	SD (°F)	Avg (°F)	SD (°F)
AK-225G	200	--	--	--	--
	500	--	--	--	--
	750	TL	--	TL	--
	100	TL	--	528	5

Final AIT Data using Modified Test Method

		50 psia			70 psia			200 psia			2000 psia			
		Chilled		NC	Chilled		NC	Chilled		NC	Chilled			NC
		Avg °F	SD °F	Test °F	Avg °F	SD °F	Test °F	Avg °F	SD °F	Test °F	Test °F	Avg °F	SD °F	Test °F
Solvokane	200	--	--	--	--	--	--	--	--	--	TL	--	--	--
	500	--	--	--	--	--	--	--	--	--	296	--	--	--
	750	--	--	--	--	--	--	--	--	--	290	--	--	--
	1000	496	22	476	489	29	493	--	--	--	308	305	3	301
Solstice PF	200	--	--	--	--	--	--	--	--	--	TL	--	--	--
	500	--	--	--	--	--	--	--	--	--	378	--	--	--
	750	--	--	--	--	--	--	--	--	--	369	--	--	--
	1000	464	16	--	477	7	--	--	--	--	359	360	5	--
L-14780	200	--	--	--	--	--	--	--	--	--	TL	--	--	--
	500	--	--	--	--	--	--	--	--	--	333	--	--	--
	750	--	--	--	--	--	--	--	--	--	334	--	--	--
	1000	TL	--	--	TL	--	--	454	--	--	332	322	15	--
AK225G	200	--	--	--	--	--	--	--	--	--	TL	--	--	--
	500	--	--	--	--	--	--	--	--	--	438	--	--	--
	750	--	--	--	--	--	--	--	--	--	456	--	--	--
	1000	TL	--	--	528	5	--	--	--	--	446	446	--	--
HFE-7100	200	--	--	--	--	--	--	--	--	--	TL	--	--	--
	500	--	--	--	--	--	--	--	--	--	639	--	--	--
	750	--	--	--	--	--	--	--	--	--	620	--	--	--
	1000	TL	--	--	732	12	--	--	--	--	629	629	--	--

TL = Temperature Limit, no AIT detected, heater went to full limit (>800°F,>425°C); SD = Standard Deviation; Avg = average; NC = Not Chilled * Only one test performed

Conclusions

- Low boiling point materials require extra measures to ensure adequate oxidizer:fuel
- Larger sample sizes are key
- Successful results by implementing the following:
 1. Use test samples of 1000 mg or greater until repeatable ignitions are obtained (while ensuring system safety limits are not exceeded).
 2. Pre-chill test material as good practice, but not required.
 3. Perform three pretest purges at test pressure to ensure sufficient oxidizer availability.
 4. Incrementally increase test pressure at low pressures until repeatable ignitions are obtained.
- High Pressure results should suffice due to conservative/severe conditions

G72 Changes as a Result of this Study

Changes: Increased Sample Size, Sample chilling , Increased pressure if TL observed at low P ranges (<1000psi),

8.2 Weigh out a 0.20 +/- 0.03-g sample, either in liquid or solid form, into the sample holder.

TO:

8.2 Weigh out a sample into the sample holder.

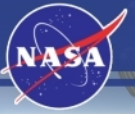
8.2.1 Solid or non-volatile liquid sample weight should be 0.20 +/- 0.03-g

8.2.2 For volatile liquids such as cleaning solvents, a larger sample weight up to 1.00 +/- 0.10-g may be required to obtain a valid AIT result. It is good practice to pre-chill volatile liquids with boiling points near or below room temperature using an ice bath to prevent excessive loss of solvent prior to test. It is recommended a final weight be taken immediately before test to verify quantity present.

Note: A lab may choose to incrementally approach the sample size of 1g evaluating pressure spikes and system safety limits as sample size increments are increased.

Note: A non ignition at maximum temperature when testing at lower pressures (<1000psi) may indicate an insufficient oxidizer to fuel ratio. When testing at lower pressures, if obtaining a non-ignition at maximum temperature it is recommended that testing be performed at higher pressures until an AIT is obtained. If suspected, testing at the standard 1500psia or higher and increased sample mass (suggested 1.0g) is recommended to confirm an unreactive material.

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WHITE SANDS TEST FACILITY



Back-up Slides

WHITE SANDS TEST FACILITY

Purge Pressure MPa (psia)	Pretest Temperature ° C (° F)	Pretest Mass (mg)	Posttest Mass (mg)	Mass Loss (mg)	Mass Loss (%)	Avg. Mass Loss (mg)	Avg. Mass Loss (%)	Standard Deviation (mg)
AK-225G								
0.3 (50)	2.2 (36)	169	149	20	11.8	18.3	10.8	2.1
	2.2 (36)	167	151	16	9.6			
	2.2 (36)	171	152	19	11.1			
	2.2 (36)	515	497	18	3.5	15	2.9	8.9
	1.7 (35)	506	484	22	4.3			
	1.7 (35)	505	500	5	1.0			
6.9 (1000)	2.2 (36)	185	151	34	18.4	31.3	15.2	4.6
	3.3 (38)	230	196	34	14.8			
	-1.1 (30)	210	184	26	12.4			
	3.9 (39)	519	488	31	6.0	34	6.8	4.4
	-1.1 (37)	496	457	39	7.9			
	3.9 (39)	485	453	32	6.6			
13.8 (2000)	0.6 (33)	227	146	103	35.7	58.7	26.4	22.5
	2.2 (36)	219	183	81	16.4			
	3.3 (38)	217	158	36	27.2			
	-1.1 (30)	482	446	59	7.5	40.7	8.3	4.0
	-0.6 (31)	488	445	36	8.8			
	0.6 (33)	502	459	43	8.6			

WHITE SANDS TEST FACILITY

Purge Pressure MPa (psia)	Pretest Temperature ° C (° F)	Pretest Mass (mg)	Posttest Mass (mg)	Mass Loss (mg)	Mass Loss (%)	Avg. Mass Loss (mg)	Avg. Mass Loss (%)	Standard Deviation (mg)
HFE-7100								
0.3 (50)	0.6 (33)	204	189	15	7.4	13.3	6.2	3.8
	-1.1 (30)	214	198	16	7.5			
	-1.1 (30)	235	226	9	3.8			
	-1.1 (30)	489	477	12	2.5	13	2.6	2.6
	-1.1 (30)	516	505	11	2.1			
	-1.1 (30)	516	500	16	3.1			
6.9 (1000)	-1.1 (30)	230	198	32	13.9	27	12.5	4.6
	-1.1 (30)	190	167	23	12.1			
	-1.1 (30)	226	200	26	11.5			
	-1.1 (30)	520	507	13	2.5	25	4.9	10.4
	-1.1 (30)	514	483	31	6.0			
	-1.7 (29)	514	483	31	6.0			
13.8 (2000)	-0.6 (31)	219	203	16	7.3	28.3	12.8	11.6
	0.0 (32)	223	184	39	17.5			
	0.6 (33)	223	193	30	13.5			
	2.8 (37)	507	438	69	13.6	58.3	11.5	18.5
	1.7 (35)	513	476	37	7.2			
	1.1 (34)	509	440	69	13.6			

		Method Parameter Evaluation Test Matrix, 345 kPa (50 psia)												
		AK-225G	200	TL	TL	TL	TL	--	TL	TL	TL			TL
			500	TL	TL	TL	TL	--	TL	TL	TL			TL
			750	TL	TL	TL	TL	--	TL	TL	TL			TL
			1000	TL	TL	TL	TL	--	TL	TL	TL			TL
Historical AK-225	200	--	--	--	--	--	TL	--	--	TL				
HFE-7100	200	TL	TL	TL	TL	--	TL	TL	TL	TL				
	500	388 (731)	389 (732)	391 (735)	389 (733)	1.1 (2)	TL	374 (705)	380 (716)	377 (711)				
	750	--	--	--	--	--	--	--	--	--				
	1000	--	--	--	--	--	381 (718)	392 (738)	393 (740)	389 (732)				
Historical HFE-7100	200	--	--	--	--	--	TL	--	--	TL				
Method Parameter Evaluation Test Matrix, 13.8 MPa (2000 psia)														
AK-225G	200	237 (458)	228 (443)	233 (452)	233 (451)	4.4 (8)	TL	TL	TL	TL				
	500	230 (446)	229 (444)	237 (459)	232 (450)	4.4 (8)	226 (438)	230 (446)	234 (454)	230 (446)				
	750	--	--	--	--	--	236 (456)	--	--	236 (456)				
	1000	--	--	--	--	--	230 (446)	--	--	230 (446)*				
Historical AK-225	200	--	--	--	--	--	TL	--	--	TL				
HFE-7100	200	TL	TL	TL	TL	--	TL	TL	TL	TL				
	500	341 (645)	336 (636)	334 (634)	337 (638)	3.3 (6)	337 (639)	341 (646)	336 (636)	338 (640)				
	750	--	--	--	--	--	327 (620)	--	--	327 (620)				
	1000	--	--	--	--	--	332 (629)	--	--	332 (629)*				
Historical HFE-7100	200	--	--	--	--	--	TL	--	--	TL				
AIT Method Improvement Test Matrix, 483 kPa (70 psia)														
AK-225G	200	--	--	--	--	--	--	--	--	--				
	500	--	--	--	--	--	--	--	--	--				
	750	TL	TL	TL	TL	--	TL	TL	TL	TL				
	1000	TL	TL	TL	TL	--	273	278	276	276				

WHITE SANDS TEST FACILITY

TABLE 3—Final AIT Data using Modified Test Method.

Material	Mass (mg)	345 kPa (50 psia)						483 kPa (70 psia)						1.38 MPa (200 psia)						13.8 MPa (2000 psia)					
		Chilled			NC			Chilled			NC			Chilled			NC			Chilled			NC		
		Test °C (°F)	Test °C (°F)	Test °C (°F)	Avg °C (°F)	SD °C (°F)	Test °C (°F)	Test °C (°F)	Test °C (°F)	Avg °F	SD °F	Test °C (°F)	Test °C (°F)	Test °C (°F)	Avg °C (°F)	SD °C (°F)	Test °C (°F)	Test °C (°F)	Test °C (°F)	Avg °C (°F)	SD °C (°F)	Test °C (°F)	Test °C (°F)	Test °C (°F)	Test °C (°F)
Polyvokane	200	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	TL	--	--	--	--	--
	500	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	147 (296)	--	--	--	--	--
	750	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	143 (290)	--	--	--	--	--
	1000	268 (515)	260 (500)	244 (472)	258 (496)	12.2 (22)	247 (476)	254 (490)	238 (459)	269 (517)	254 (489)	16.1 (29)	256 (493)	--	--	--	--	--	--	153 (308)	151 (303)	152 (305)	152 (305)	1.7 (3)	149 (301)
Elastice PF	200	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	TL	--	--	--	--	--
	500	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	192 (378)	--	--	--	--	--
	750	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	187 (369)	--	--	--	--	--
	1000	245 (473)	246 (474)	230 (446)	240 (464)	8.9 (16)	--	247 (476)	244 (471)	251 (484)	247 (477)	3.9 (7)	--	--	--	--	--	--	--	192 (359)	180 (356)	185 (365)	182 (360)	2.8 (5)	--
14780	200	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	TL	--	--	--	--	--
	500	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	167 (333)	--	--	--	--	--
	750	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	168 (334)	--	--	--	--	--
	1000	TL	TL	TL	TL	--	--	TL	TL	TL	TL	--	--	234 (454)	--	--	234 (454)*	--	--	167 (332)	152 (305)	166 (330)	161 (322)	8.3 (15)	--
K225G	200	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	TL	TL	TL	TL	--	--
	500	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	226 (438)	230 (446)	235 (454)	230 (446)	4.4 (8)	--
	750	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	236 (456)	--	--	236 (456)	--	--
	1000	TL	TL	TL	TL	--	--	273 (523)	278 (532)	276 (528)	276 (528)	2.8 (5)	--	--	--	--	--	--	--	230 (446)	--	--	230 (446)*	--	--
FE-7100	200	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	TL	TL	TL	TL	--	--
	500	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	337 (639)	341 (646)	336 (636)	338 (640)	2.8 (5)	--
	750	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	327 (620)	--	--	327 (620)	--	--
	1000	TL	TL	TL	TL	--	--	381 (718)	392 (738)	393 (740)	389 (732)	6.7 (12)	--	--	--	--	--	--	--	332 (629)	--	--	332 (629)*	--	--

TL = Temperature Limit, no AIT detected, heater went to full limit (>800°F,>425°C); SD = Standard Deviation; Avg = average; NC = Not Chilled * Only one test performed