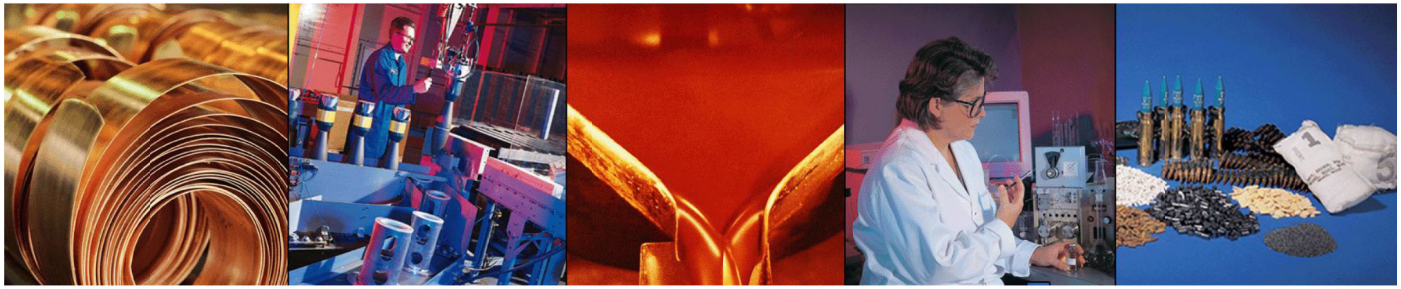
GENERAL DYNAMICS

Ordnance and Tactical Systems–Canada Valleyfield



Preparation, certification and reaction dynamics of Methyl Violet Paper for the 134.5°C stability test

6th International Nitrocellulose Symposium
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The 134.5°C stability test using Methyl Violet Paper

The main method of evaluation of stability of NC in North America is the Methyl Violet Paper test (MVP)

The Bergmann-Junk test (BJ) is now accepted method but is not widespread in North America.

Both tests detect the amount of NO_2 produced during heating under isothermal condition. Above a definite quantity of NO_2, the test will fail and the material will be deemed not sufficiently stable to be used.

The main negative comments about the test are:

- -lack of procedure for the preparation of the paper (not provided in the Mil-DTL)
- -lack of traceability to national standards

GD-Valleyfield has been preparing MV papers since the 1990's and has proposed a method of preparation and certification for addition in the next revision of the Mil-DTL-286

The 134.5°C stability test using Methyl Violet Paper

The method is fast, easy to be performed and is not as 'risky' as the BJ test since it will last only 26 minutes at 135°C instead of 2hrs at 132°C.

For the MVP test, the test is interrupted at 30% of the TSAD while the BJ test is interrupted 25% after the end of the TSAD.

Note: The removal of the NO_2 while running the BJ test somewhat delay the TSAD.

Test	Isothermal Temperature	Weight (g)	Time to end-point (minutes)	Estimated TSAD at test temperature
MVP	134.5°C	2.5	Typically 35	82.5 minutes
BJ	132°C	2.0	Fix 120	94.7 minutes

The preparation of paper is based on a method that has been around since the beginning of the 20th century.

Aspect of 4.0g of NC kept at 134.5°C for
30 minutes 55 minutes 61 minutes

Recommended modifications to the method

Nitrocellulose stability test: 134.5°C Heat test
(Methyl Violet Paper Test).

Recommended modifications

Reagents.

Standardized methyl violet test papers approximately 70 ± 1.0 mm long and 20 ± 0.6mm wide as manufactured and supplied by Naval Surface Warfare Center Indian Head EOD Technology Division, Indian Head, MD 20640 or methyl violet test papers prepared and tested using the following method:

i. Preparation of the indicator solution.

ii. Preparation of the methyl violet paper.

iii. Certification of the methyl violet paper.

No modification Apparatus.

No modification Procedure.

No modification Calculation.

Recommended modifications to the method
Preparation MV paper

Preparation of the indicator solution.

To prepare 100 ml of indicator solution (note: if different amount of solution is required, it can be prepared while respecting these proportions):

-0.250 g of **basic rosaniline (equivalent to CAS number 632-99-5)** is weighed into a porcelain dish, and about 10ml of reagent grade acetic acid is added.

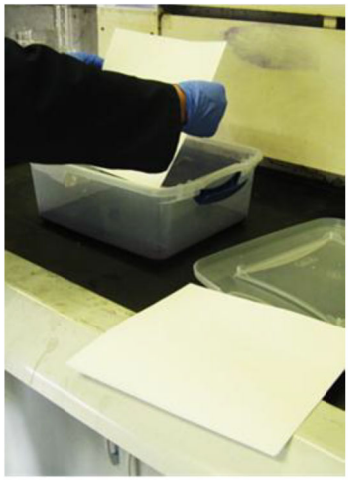
-The dish is heated on a water bath until all excess acid is removed.

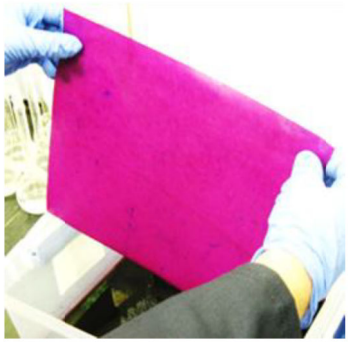
-In a 100 ml graduate cylinder, 0.168 g of **crystal violet (equivalent to CAS number 548-62-9)** is dissolved in 30 ml of high purity water and 5.0 g (4 ml) of reagent grade glycerine is added.

-The content of the porcelain dish is added to the cylinder using ethanol (minimum 95%v/v) and adjusted to produce 100 ml of solution.

-The solution is mixed thoroughly.

Recommended modifications to the method
Preparation MV paper





Preparation of the methyl violet paper.

-Sheets of paper are prepared by cutting filter papers (equivalent to **Whatman 597**, typically 580mm x 580mm with a grammage of about 8.5 mg/cm2) into square parts that will fit into a low edge dish large enough to fit the cut sheet (typically cut in 4 square parts about 290mm by 290mm).

-In a fume-hood, the methyl violet solution is poured into the low edge dish.

-Separately, each cut sheet of paper is dipped completely into the solution for **about 30 seconds.**

-The strip is removed from the solution and the wet sheet of paper rotated vertically until the solution stops dripping (excess alcohol will evaporate in about 1 minutes).

-The strip is hung up overnight to dry in a room free from deleterious fumes. When dry, the strips are cut in the size of **70 ± 1.0 mm long and 20 ± 0.6mm wide**.

Once certified, they are kept in tightly closed amber glass bottles or opaque plastic bottles with a maximum of 200 papers per bottle. The bottle shall be kept closed, stored at room temperature, and out of direct light at all times except to briefly extract indicator papers.

Recommended modifications to the method
Certification of MV paper

Certification of the methyl violet paper.

Confirmation of moisture content of MV paper:

-About one paper from each 200 is tested for the content in water by oven drying and shall be between 7.5% and 15%. If required, the paper may be rehydrated by keeping the paper in a controlled humidity chamber set between 60 to 80%RH until the right water content is obtained.

Confirmation of reactivity of MV paper:

-To confirm that the reactivity of the methyl violet paper is acceptable, about 1 paper from each 200 shall be tested using nitrogen dioxide gas of known concentration in air between 1500 and 2500 ppm (v/v). The gas may be obtained already diluted and certified or obtained by dilution using pure nitrogen dioxide.

-The gas concentration shall be known with an accuracy of ±2.5%. Based on the concentration of the nitrogen dioxide gas, the required flowrate for an end-point centered at 55 minutes is given by: Flowrate (ml/min) = 83636 / Gaz concentration in ppm (v/v) of nitrogen dioxide gas. The flowrate shall be maintained within ±1.5 ml/min of the calculated value during the certification of the paper. The paper is tested using the standard gas and a cylindrical flow cell of about 30 ml containing one paper (the flow cell diameter is similar to the MV paper width). The end-point is obtained when the paper is completely salmon pink after 55 ± 7 minutes.

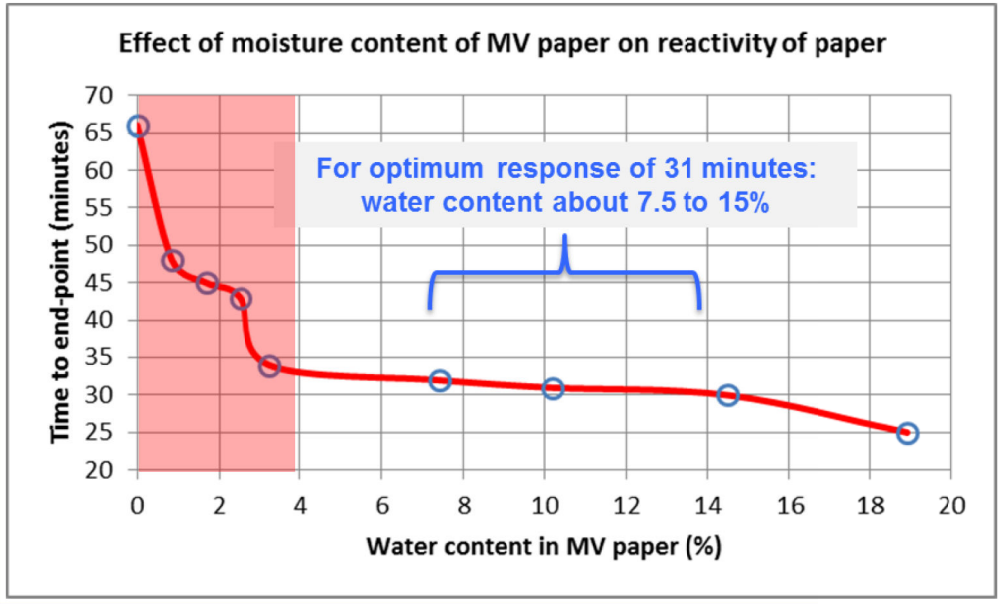
Only the batches that meet those 2 criteria (water content and reaction time) will be considered certified methyl violet paper.

Recommended modifications to the method *Certification of MV paper*

Confirmation of moisture content of MV paper:

-About one paper from each 200 is tested for the content in water by oven drying and shall be between 7.5% and 15%. If required, the paper may be rehydrated by keeping the paper in a controlled humidity chamber set between 60 to 80%RH until the right water content is obtained.

The MV indicator requires water for the reaction to proceed.



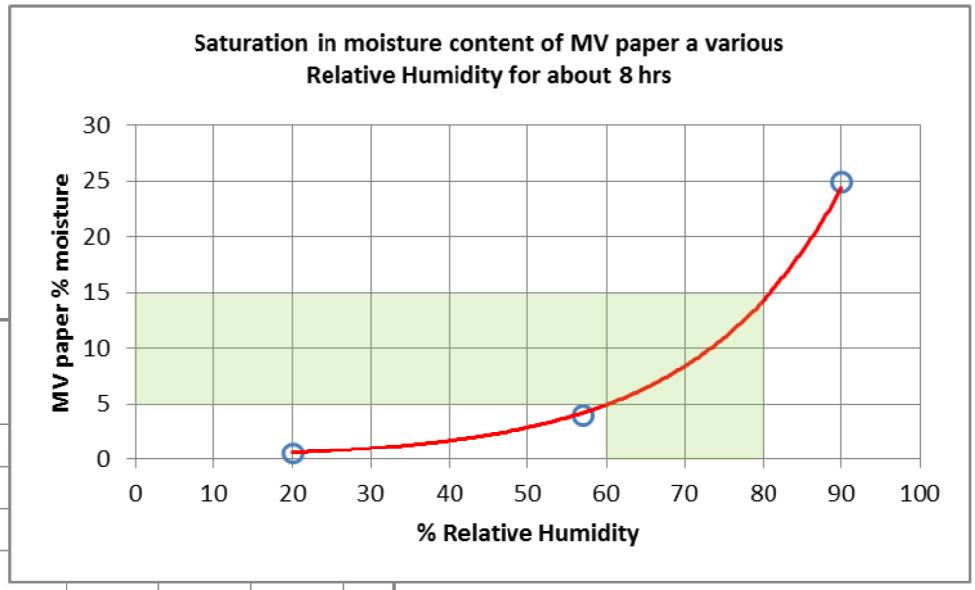
If moisture is not provided by the MV paper, it must be acquired from the decomposing NC which takes time and delays the response of the MV paper.

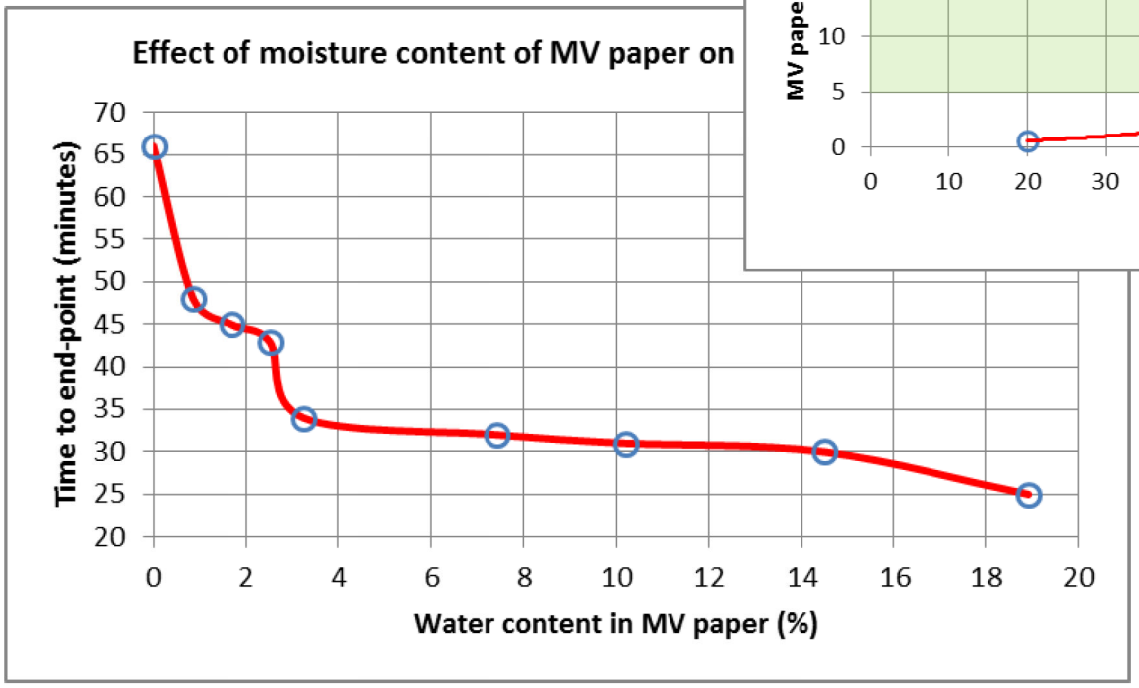
Since the papers are prepared under various %RH in labs, the time to end-point may be affected.

It is therefore recommended to test the moisture content of the MV paper in addition to the certification by standard gas.

Recommended modifications to the method *Certification of MV paper*

If required, the paper may be rehydrated by keeping in a control humidity chamber set between 65 to 80%RH until the right moisture content is obtained.





Beware: MV paper used or stored in an environment with low RH (<50%RH) will rapidly begin to over estimate the stability of NC

Recommended modifications to the method
Certification of MV paper

To confirm the reactivity of the methyl violet paper is acceptable:

Standard gas

-tested using nitrogen dioxide gas of known concentration in air between 1500 and 2500 ppm (v/v) with an accuracy of ±2.5%

-gas may be obtained already diluted and certified or obtained by dilution using pure nitrogen dioxide

Flow rate

-the required flowrate for an end-point centered at 55 minutes is given by

Flowrate (ml/min) = 83636 / [Gaz] in ppm (v/v) of NO2

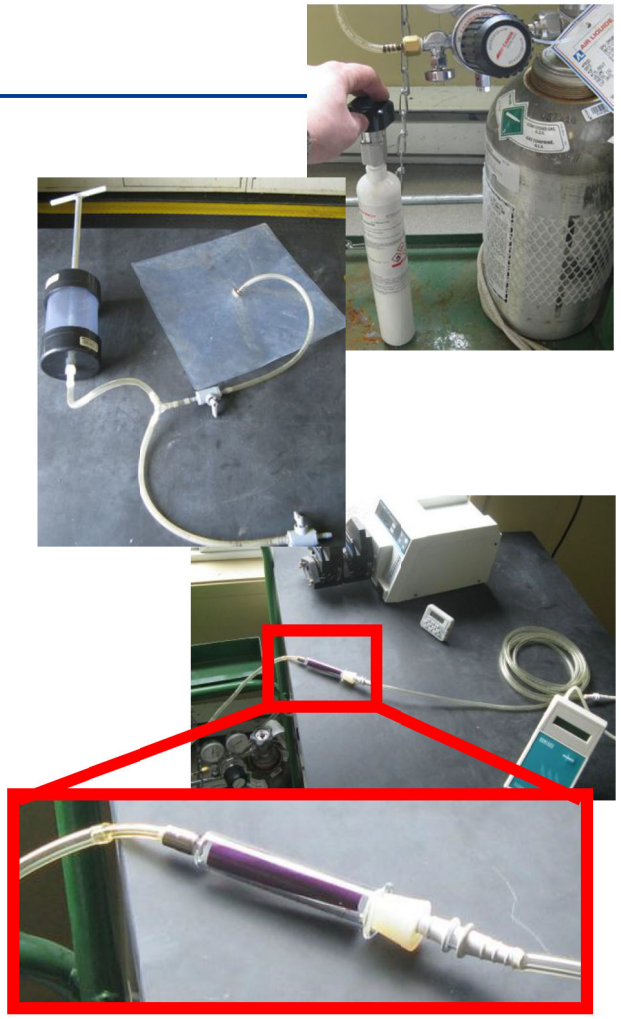
-maintained within ±1.5 ml/min of the calculated value during the certification of the paper.

Flow cell

-The paper is tested using the standard gas and a cylindrical flow cell of about 30 ml containing one paper (the flow cell diameter is similar to the MV paper width).

End-point

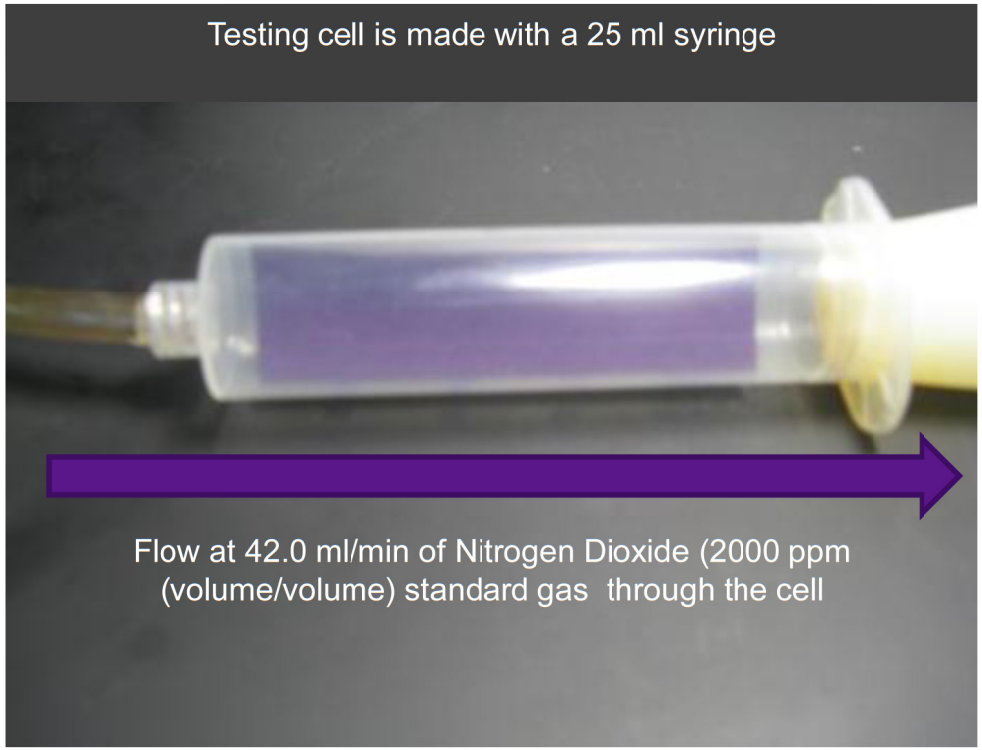
The end-point is obtained when the paper is completely salmon pink after 55 ± 7 minutes.



Only the batches that meet those 2 criteria (moisture and reaction time) will be considered certified methyl violet paper.

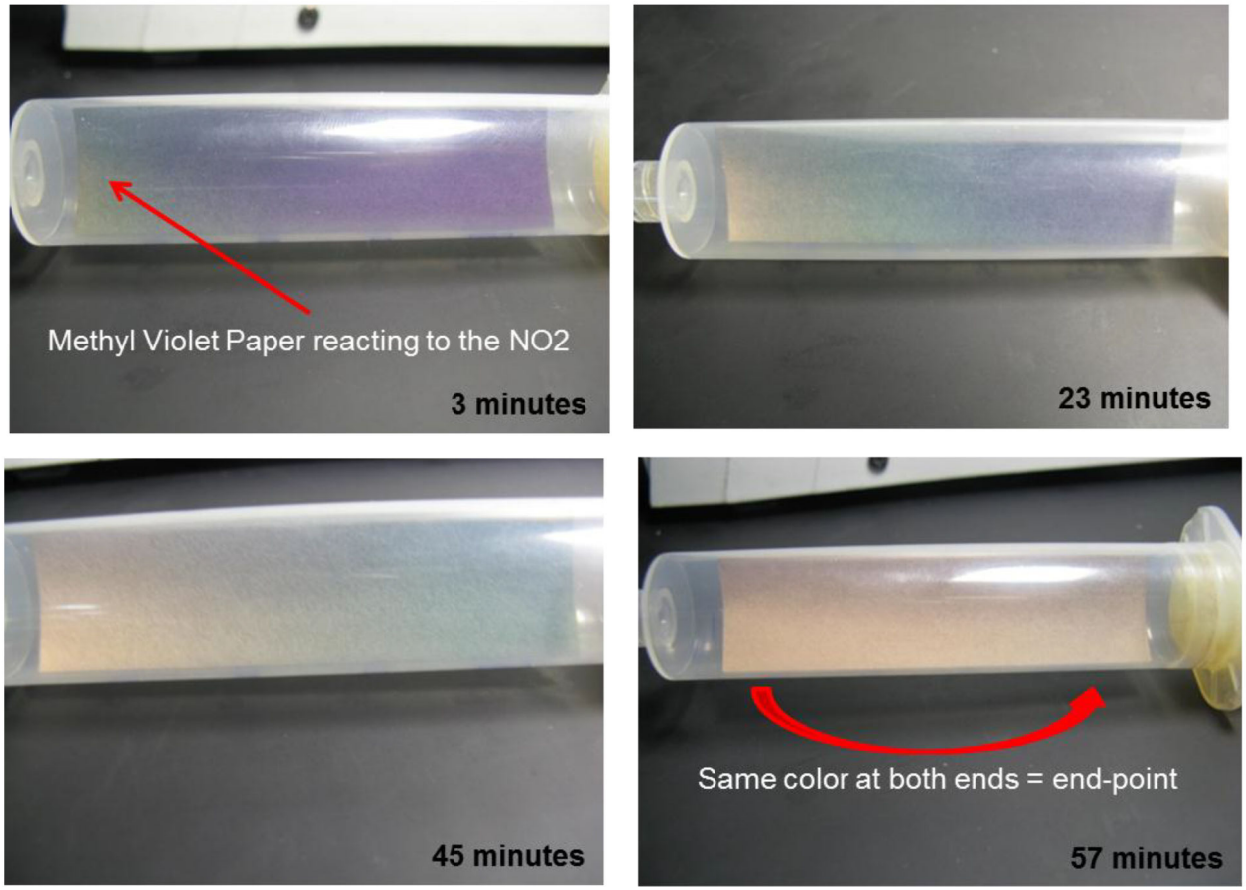
Recommended modifications to the method
Certification of MV paper

Test cell for certification of MV paper using standard NO_2 gas

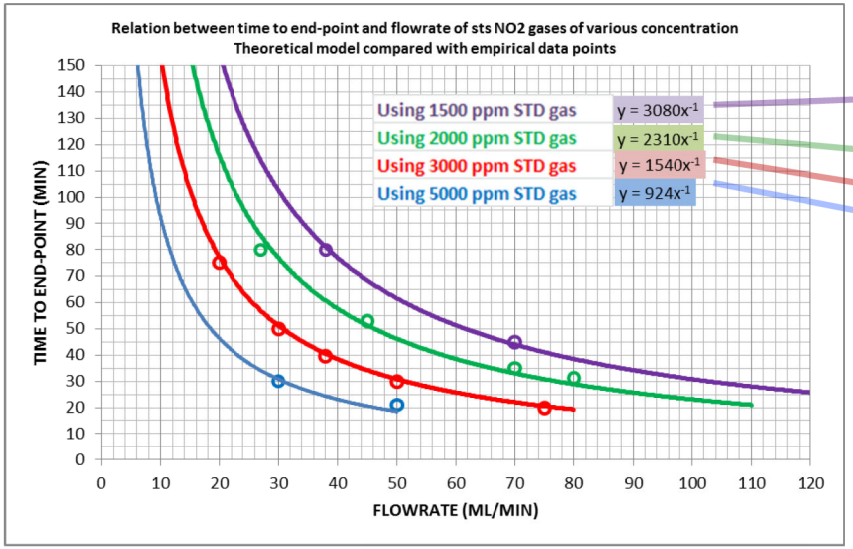


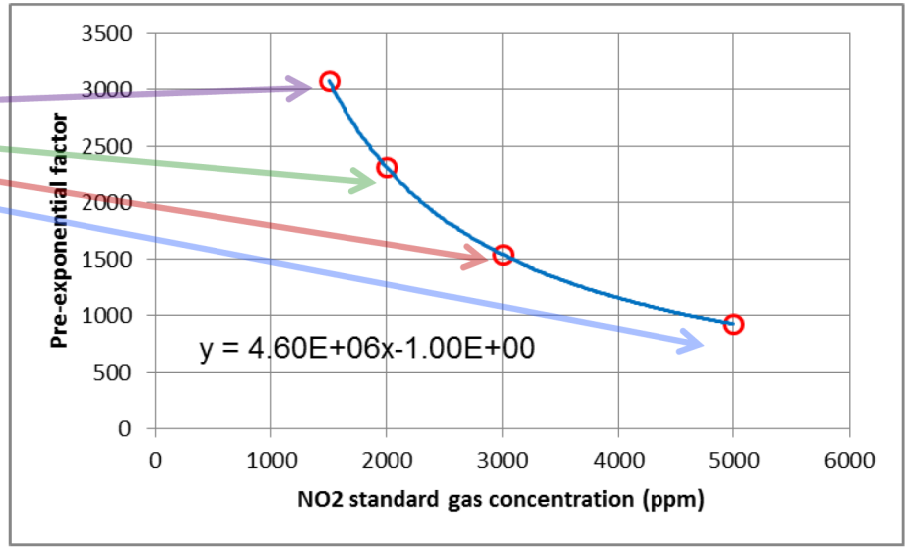
Recommended modifications to the method
Certification of MV paper

Changes in color of MV paper during certification using standard NO_2 gas



Recommended modifications to the method
Certification of MV paper



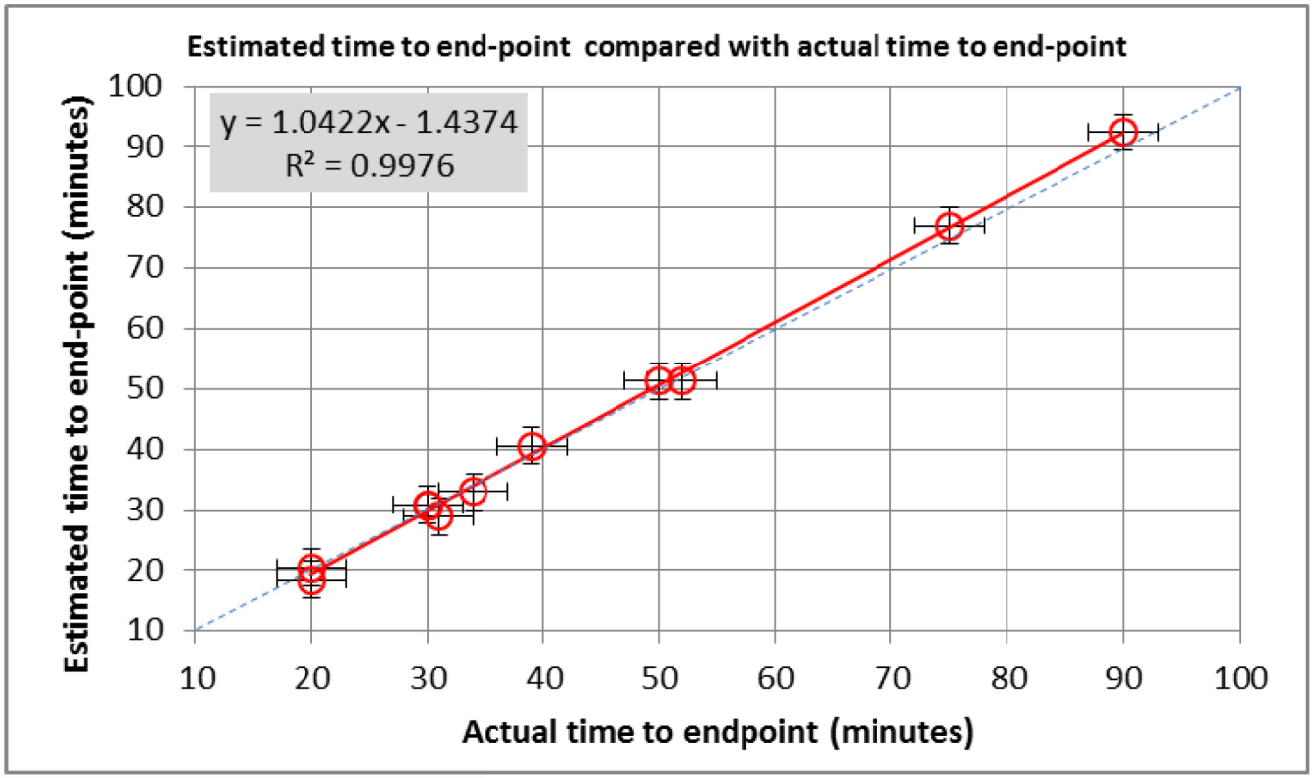


Fitting a power law on empirical results

A paper will react with about 4.6 ml of NO_2 near room temperature and standard pressure

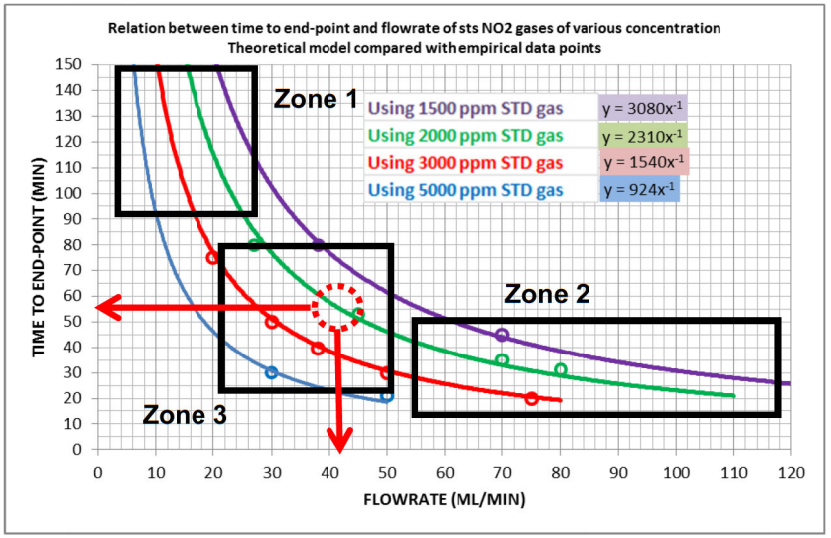
Time to end-point =	**4.60 x 1x10^6 / ([Gas] x flowrate)**
	4.60 x 10^6 / ([Gas] x flowrate)
Where:	
Time	**to end-point in minutes**
[Gas]	**concentration of NO2 in ppm (volume/volume) or ml NO_2 per m^3**
Flowrate	**in ml of std gas per minutes**
1 000 000	**ml per m^3**
4.60	**ml of NO2 per paper**

Recommended modifications to the method
Certification of MV paper



Recommended modifications to the method
Certification of MV paper

Based on this information, conditions for certification can be selected. Numerous combinations of conditions are possible:



In zone 1:

-Small variations in flowrate and/or concentration of gas → large variations in response times.

In zone 2:

-Small variation in concentration of gas → large variations in response times

-Paper response time becomes an important variable, short exposure to the gas , NO_2 will not have time to react with the indicator

In zone 3:

-Finding the middle ground

Therefore, standard conditions in zone 3 are preferred

1500-2500 ppm	56-33 ml/min	55 minutes
At 2000 ppm	42 ml/min	55 minutes

Recommended modifications to the method *Certification of MV paper*

Effect of deviations in certification using standard NO_2 gas

Variable affected	Concentration of gas	Flowrate of gas	Estimated time to end-point	Effect on time relative to optimum	
	ml NO^2/m^3	ml/min	(minutes)	(minutes)	
Higher cencentration	2050	42	53.7	-1.3	± 1.5min
Optimum	2000	42	55.0	0.0	
Lower concentration	1950	42	56.4	1.4	
Higher flowrate	2000	43.5	53.1	-1.9	± 2.0min
Optimum	2000	42	55.0	0.0	
Lower flowrate	2000	40.5	57.0	2.0	
Higher concentration and flowrate	2050	43.5	51.8	-3.2	± 3.5min
Optimum	2000	42	55.0	0.0	
Lower concentration and flowrate	1950	40.5	58.5	3.5	

About ±6.4% maximum variation from testing conditions

Recommended modifications to the method
Certification of MV paper

In order to get an idea of the typical variations in dimensions and weight of standard MV paper, a sample of 100 std papers from a lot were measured:

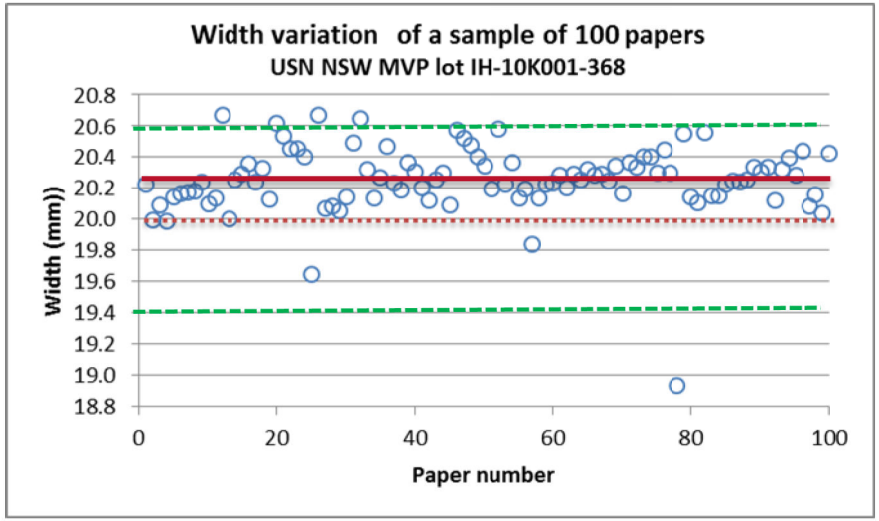
Reference : USN NSW MVP lot IH-10K001-368

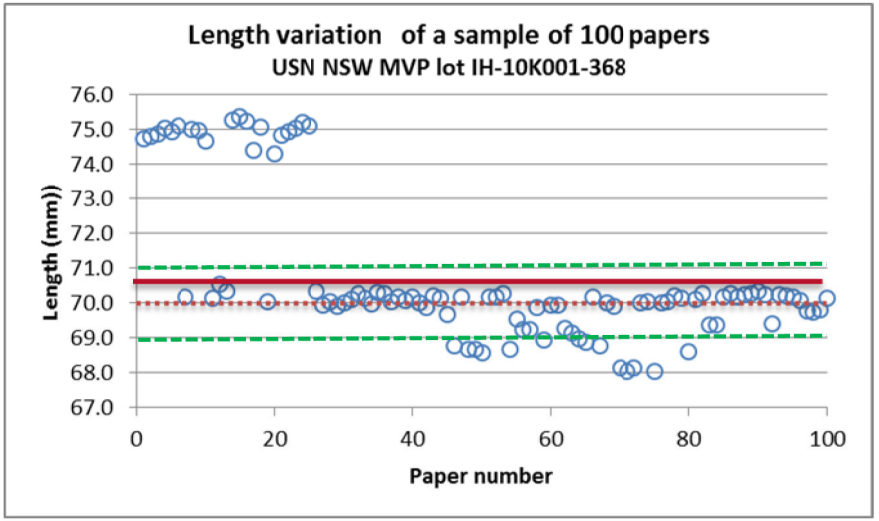
	Weight (g)	Width (mm)	Length (mm)	Density (g/cm2)		Weight (g)	Width (mm)	Length (mm)	Density (g/cm2)		Weight (g)	Width (mm)	Length (mm)	Density (g/cm2)
1	0.13455	20.225	74.742	0.0089	35	0.12771	20.271	70.293	0.0090	68	0.13564	20.249	70.007	0.0096
2	0.13609	19.997	74.810	0.0091	36	0.13270	20.471	70.279	0.0092	69	0.12934	20.342	69.907	0.0091
3	0.13821	20.094	74.887	0.0092	37	0.13481	20.230	70.040	0.0095	70	0.13044	20.165	68.135	0.0095
4	0.13127	19.984	75.045	0.0088	38	0.13020	20.188	70.173	0.0092	71	0.12655	20.364	68.037	0.0091
5	0.12757	20.145	74.941	0.0085	39	0.12891	20.366	70.056	0.0090	72	0.13056	20.337	68.141	0.0094
6	0.13907	20.168	75.107	0.0092	40	0.13452	20.308	70.179	0.0094	73	0.12914	20.405	70.015	0.0090
7	0.12898	20.172	70.165	0.0091	41	0.13011	20.203	70.001	0.0092	74	0.13268	20.399	70.047	0.0093
8	0.13855	20.181	75.004	0.0092	42	0.13090	20.118	69.862	0.0093	75	0.12916	20.301	68.047	0.0093
9	0.14346	20.236	74.967	0.0095	43	0.12949	20.257	70.202	0.0091	76	0.13253	20.447	70.008	0.0093
10	0.13783	20.095	74.677	0.0092	44	0.13544	20.300	70.149	0.0095	77	0.13059	20.296	70.048	0.0092
11	0.12263	20.138	70.134	0.0087	45	0.12917	20.093	69.665	0.0092	78	0.13316	18.930	70.203	0.0100
12	0.13091	20.672	70.531	0.0090	46	0.13225	20.570	68.759	0.0094	79	0.13154	20.550	70.152	0.0091
13	0.12939	20.000	70.328	0.0092	47	0.12923	20.518	70.162	0.0090	80	0.13019	20.139	68.608	0.0094
14	0.14205	20.253	75.272	0.0093	48	0.13628	20.478	68.672	0.0097	81	0.12489	20.106	70.111	0.0089
15	0.13659	20.294	75.394	0.0089	49	0.12788	20.404	68.654	0.0091	82	0.12988	20.558	70.267	0.0090
16	0.13774	20.358	75.242	0.0090	50	0.12860	20.341	68.554	0.0092	83	0.12967	20.150	69.379	0.0093
17	0.13803	20.236	74.405	0.0092	51	0.13050	20.195	70.167	0.0092	84	0.13007	20.153	69.360	0.0093
18	0.13771	20.325	75.075	0.0090	52	0.12999	20.579	70.158	0.0090	85	0.12928	20.223	70.176	0.0091
19	0.13017	20.128	70.024	0.0092	53	0.13026	20.221	70.278	0.0092	86	0.12973	20.246	70.259	0.0091
20	0.13479	20.621	74.314	0.0088	54	0.12969	20.365	68.653	0.0093	87	0.12945	20.242	70.176	0.0091
21	0.13657	20.539	74.845	0.0089	55	0.12822	20.133	69.540	0.0092	88	0.12966	20.252	70.225	0.0091
22	0.13642	20.456	74.957	0.0089	56	0.12610	20.193	69.218	0.0090	89	0.13110	20.333	70.260	0.0092
23	0.14041	20.454	75.054	0.0091	57	0.12896	19.837	69.239	0.0094	90	0.13017	20.304	70.339	0.0091
24	0.13905	20.406	75.201	0.0091	58	0.12853	20.134	69.877	0.0091	91	0.13011	20.334	70.222	0.0091
25	0.13384	19.644	75.128	0.0091	59	0.13056	20.225	68.924	0.0094	92	0.13339	20.121	69.399	0.0096
26	0.13158	20.673	70.330	0.0090	60	0.12740	20.234	69.930	0.0090	93	0.12813	20.323	70.223	0.0090
27	0.12791	20.071	69.943	0.0091	61	0.13019	20.281	69.944	0.0092	94	0.13529	20.392	70.200	0.0095
28	0.12550	20.086	70.041	0.0089	62	0.12984	20.205	69.272	0.0093	95	0.13533	20.283	70.186	0.0095
29	0.12562	20.057	69.900	0.0090	63	0.13346	20.293	69.123	0.0095	96	0.13132	20.438	70.060	0.0092
30	0.13009	20.146	69.994	0.0092	64	0.12879	20.254	68.959	0.0092	97	0.12719	20.085	69.754	0.0091
31	0.12904	20.494	70.113	0.0090	65	0.12706	20.318	68.852	0.0091	98	0.13978	20.161	69.719	0.0099
32	0.12771	20.644	70.280	0.0088	66	0.12709	20.285	70.179	0.0089	99	0.12831	20.039	69.791	0.0092
33	0.13242	20.323	70.139	0.0093	67	0.12776	20.289	68.759	0.0092	100	0.13337	20.421	70.136	0.0093
34	0.12705	20.137	69.955	0.0090										

Recommended modifications to the method
Certification of MV paper

Typical variations in dimensions of standard MV paper, a sample of 100 std paper from a lot were measured:

Reference : USN NSW MVP lot IH-10K001-368





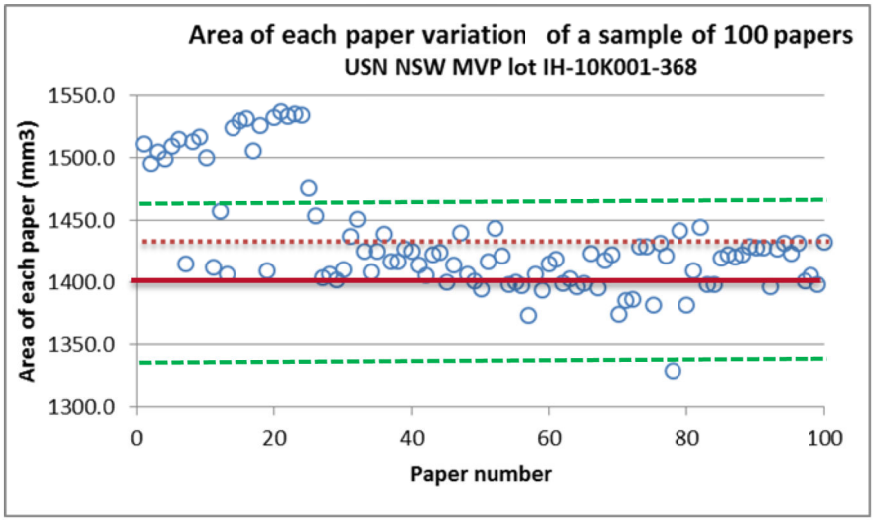
Average width	20.26	
StDev	0.22	
2xStDev	0.44	19 time out of 20

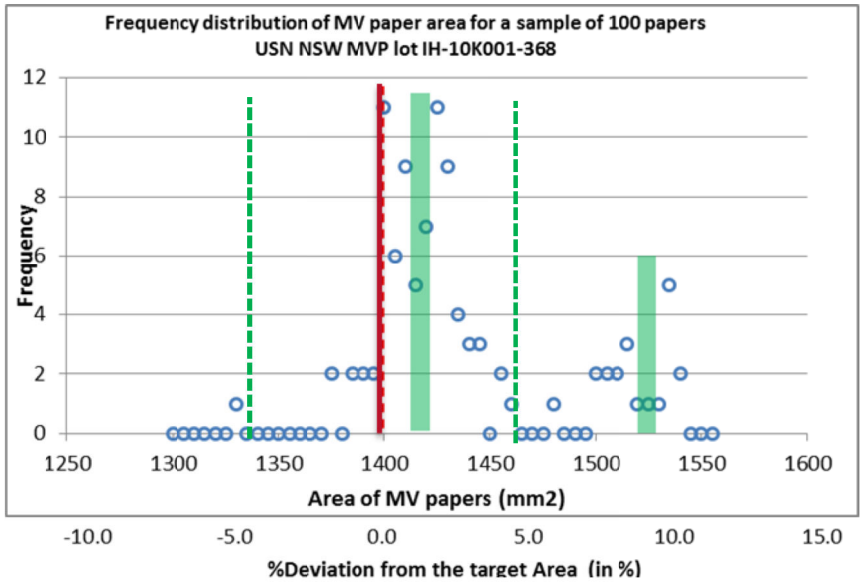
Average length	70.793	
StDev	2.2	
2 x StDev	4.3	19 time out of 20

Recommended modifications to the method *Certification of MV paper*

The dimensions expressed as surface area of MV paper: :

Reference : USN NSW MVP lot IH-10K001-368

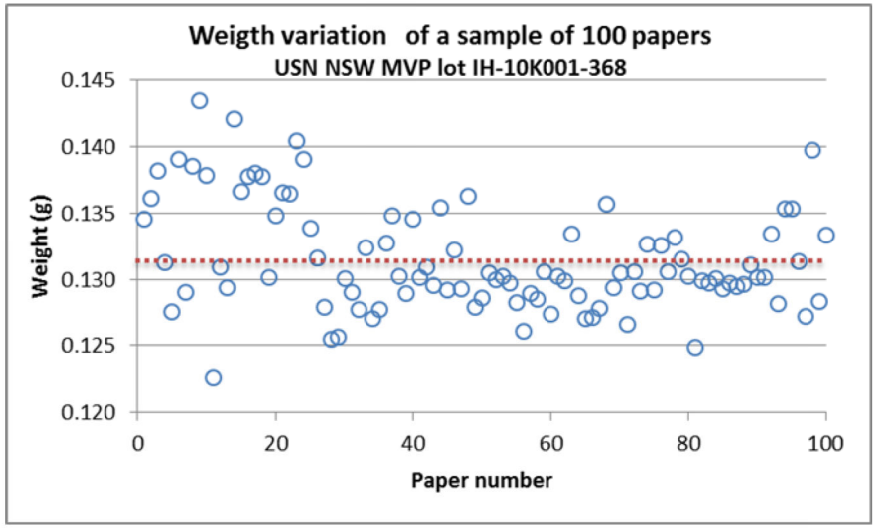




Average Area	1434	
StDev	45.9	
2 x StDev	91.7	
% (2xStDev)	6.4	19 time out of 20

Recommended modifications to the method
Certification of MV paper

Reference : USN NSW MVP lot IH-10K001-368



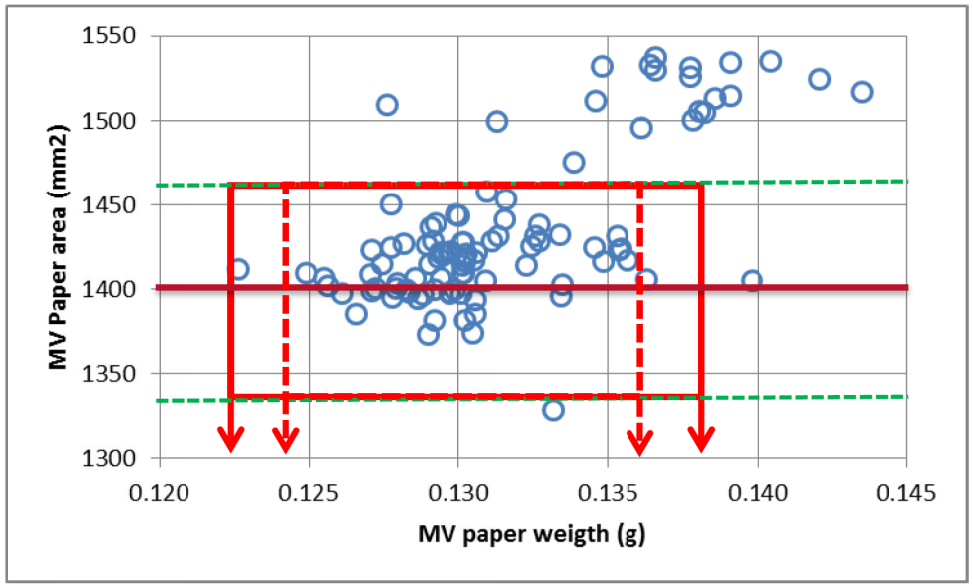
Average weight	0.1315	
StDev	0.0040	
2 x StDev	0.0081	
% (2xStDev)	6.1	19 time out of 20

A typical variation of approximately ± 6% to 7% is to be expected based on weight variation of the MV papers

(variation in paper + content of indicator)

Recommended modifications to the method
Certification of MV paper

Reference : USN NSW MVP lot IH-10K001-368



Average: 0.130 g ± 0.008g → ± 6.2%

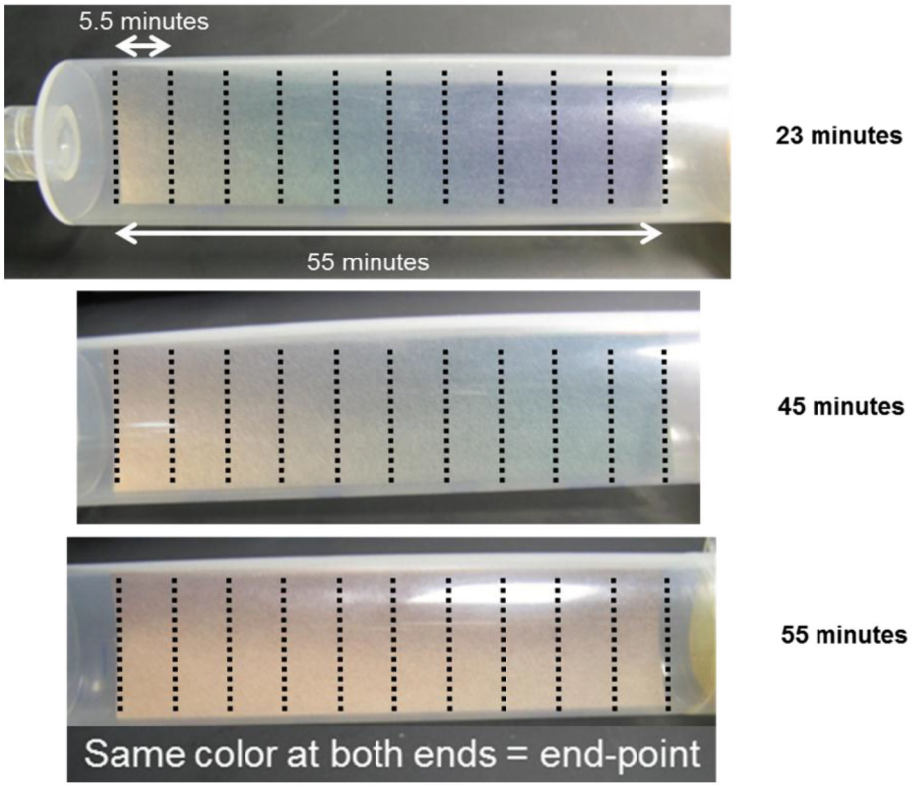
Taking into consideration the MV papers with optimum surface areas still produce a fairly wide weight distribution from about 0.124g to 0.136 g

Or
Average: 0.130 g ± 0.006g → ± 4.6%

Recommended modifications to the method
Certification of MV paper

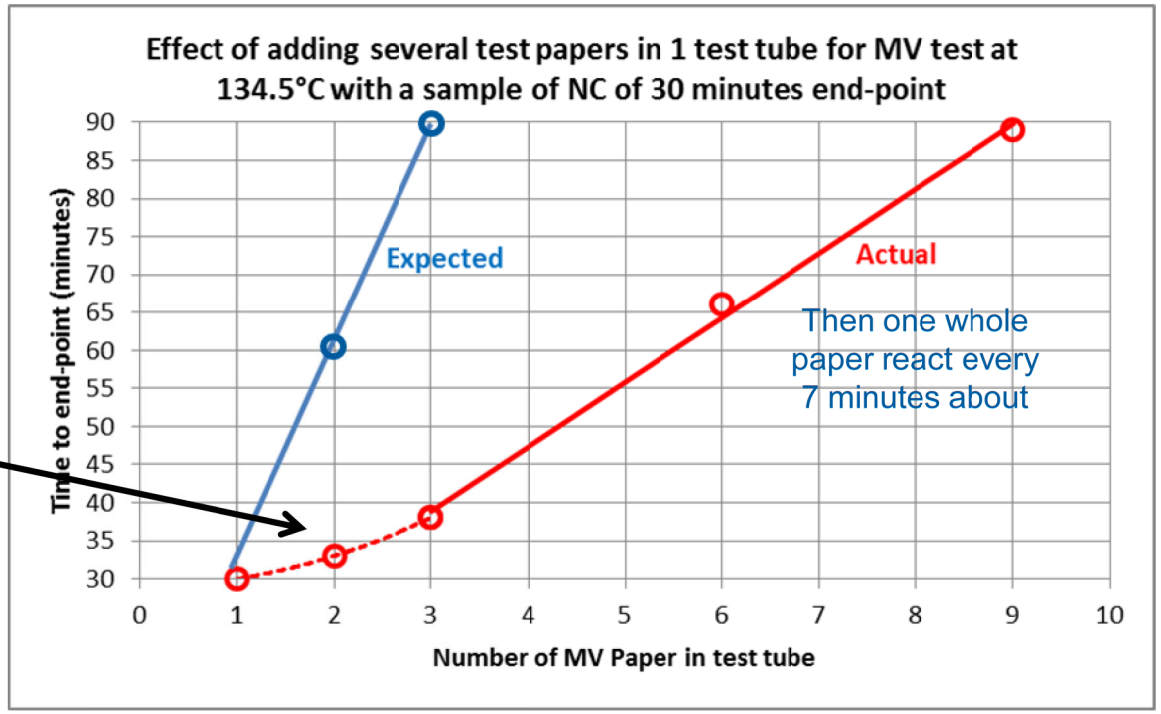
Changes in color of MV paper during certification using standard NO_2 gas:

What is the precision of determination of the end-point?



MV papers in an actual stability test with NC

If more than 1 paper is added per test tube, the reaction time is delayed…
… however, it is not delayed as much as expected.



The NOx generated near end point will flood several papers.

Number of MVP	Time to end-point
1	30
2	33
3	38
6	66
9	88

The MV test is not mainly affected by the amount of indicator on each paper

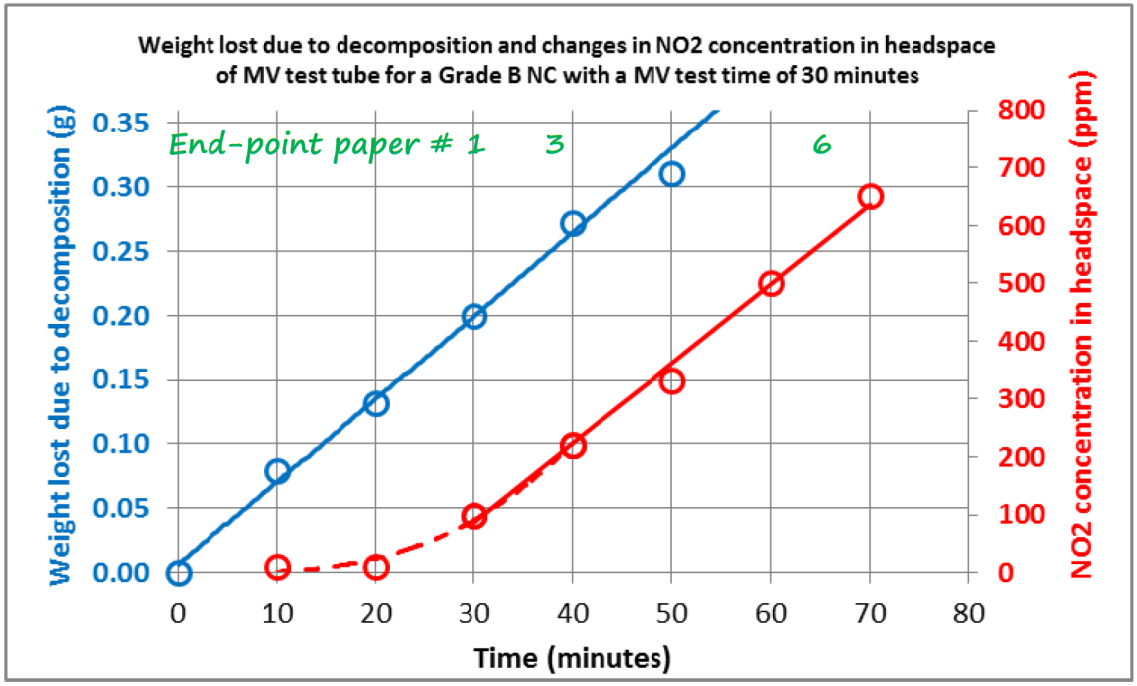
MV papers in an actual stability test with NC

Approximated values of weight lost due to decomposition and increase in NO_2 content in the MV test tube during a stability test

Basically, nothing happens for the first 20 minutes. The NOx (measured by Draeger tubes)is generated rapidly after 20 minutes and the end-point is expected (for the NC tested) at about 30 minutes. The MV paper then reacted completely in a few minutes.

For fast MV test (End-point near tolerance limit):
The MV test is mainly affected by the reaction time of the MV paper which is strongly affected by the moisture content in the MV paper.

For slow MV test (end-point far from tolerance limit):
The content in indicator becomes more important but still not critical. Then one whole paper reacts every 7 minutes or about.



MV papers in an actual stability test with NC

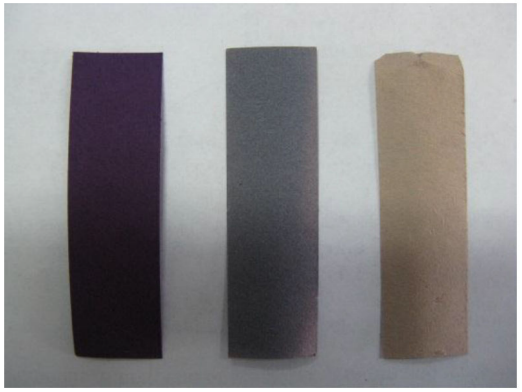
In a fast test, the MV paper changes color rather rapidly and the change of color is nearly simultaneous at both end of the paper (bottom and top of the MV paper).

In a slow test, the MV paper changes color gradually from the bottom to the top of the MV paper.

For the certification using standard NO_2 gas, the paper is subjected to a steady concentration of NO_2 for 55 minutes.

Note: The use of diluted NO_2 in nitrogen will affect the colour of the end-point of the MV paper (greyish-blue instead of salmon-pink) but not the time. The end-point is more difficult to perceive. Use of NO_2 in nitrogen is not recommended.

The greyish-blue fades to salmon-pink when paper is left standing in air for a few hours



Recommended modifications to the method
Shelf-life of the MV indicator papers

Certification of the methyl violet paper.

The paper shall be stored at room temperature and in the shade. The maximum shelf-life of the indicator papers in a sealed bottle is **5 years**. Once the bottle is open, the shelf-life of the bottle's contents **is reduced to 1 year**. After 1 year, the moisture content of the paper shall be verified and adjusted, if necessary. The bottle containing the verified indicator papers shall be given another 1 year of shelf-life. Under no circumstances shall the indicator paper shelflife be extended beyond 5 years after manufacture.

The cost of preparing and certifying MV about 500 papers:

Chemicals (including std gas):	*56.20 $*
5 hrs tech time (about 85$/hrs):	*425.00 $*
Manufacturing cost:	*about 0.95$ / paper*

Cutting papers is the most time consuming and account for about 50-60% of technician time. If a more efficient cutting instrument is available, the manufacturing cost can be reduced to about 0.50-0.60$ per paper.