



Diene Value by Maleic Anhydride Addition Reaction

UOP Method 326-17

Scope

This method is for determining maleic anhydride reactivity with a wide variety of oils, ranging from debutanized light hydrocarbon distillates to heavy drying oils, using titration.

The method gives a measure of the *conjugated diolefin* content of the sample. The determination is somewhat empirical since some conjugated diolefins may not react completely, while certain compounds other than conjugated diolefins also may be reactive. For example, anthracene, along with many of its homologs and corresponding alkylated compounds, as well as certain vinyl aromatics, react as dienes with maleic anhydride. Therefore, the results obtained by this method must be carefully interpreted in the light of these specified limitations.

The range of quantitation for diene value is from 1.2 to over 100. A modified procedure can be used to estimate diene values less than 1.2.

If the average molecular weight of the conjugated diolefins is known or can be estimated, the mass-% concentration of conjugated diolefins can be calculated.

References

AOCS Official Method Th 1a-64, "Diene Value," www.aocs.org

Ellis, B. A. and Jones, R. A., *Analyst* **61**, 812 (1936)

McKinney, R. S., Hallbrook, N. J., and Rose, W. G., *Oil and Soap* **19**, 141-143 (1942)

Norton, J. A., *Chem. Rev.* **31**, 319 (1942)

UOP Method 999, "Precision Statements in UOP Methods," www.astm.org

Outline of Method

Maleic anhydride is refluxed with the sample in boiling toluene for 3 hours. The unreacted maleic anhydride is hydrolyzed to maleic acid, extracted from the reaction mixture, and titrated with sodium hydroxide. A blank is run using the same amount of maleic anhydride as charged to the reaction flask. The amount reported as having reacted with the sample is the net volume obtained by potentiometric titration difference, and from this data the diene value and/or the percent dienes can be calculated. An alternative titration technique, using a manual (colorimetric) procedure, is described in the *Appendix*. Additional information regarding this technique is provided in *References*.

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Definition

Diene value, the number of grams of iodine equivalent to the amount of maleic anhydride that reacts with 100 g of sample (based on 2 atoms of iodine per mole of maleic anhydride) under the specified reaction conditions.

Apparatus

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

Balance, readability 0.01 g

Beaker, 250-mL, tall, without spout, borosilicate glass, Reliance Glass, Cat. No. G-9906-002, three required

Bottle, polyethylene, 1000- mL, Fisher Scientific Co., Cat. No. 03-313-5D

Condenser, Liebig, with Ts 24/40 ground-glass joint, Fisher Scientific, Cat. No. 07-721C, at least two required

Crucible, high form, 10- mL, porcelain, Fisher Scientific, Cat. No. FB965C, with cover, Fisher Scientific, Cat. No. FB965S

Cylinders, graduated, 10- and 25- mL, Class B, Fisher Scientific, Cat. Nos. 08-549-5B and -5C, respectively

Desiccator, 150- mm ID, and *porcelain plate*, Fisher Scientific, Cat. Nos. 12-141-433 and 08-641A, respectively

Electrode, iEcotrode Plus, combination glass, with sleeve diaphragm, double junction, Metrohm AG, Cat. No. 6.0280.300. Store in water when not in use.

Flask, Erlenmeyer, 250- mL, Fisher Scientific Co., Cat. No. 10-040F

Flask, Erlenmeyer, 250- mL, with Ts 24/40 ground-glass joint, Fisher Scientific, Cat. No. 10-047C, at least two required

Flask, Erlenmeyer, 500- mL, borosilicate glass, heavy walled, with side arm, Fisher Scientific, Cat. No. 10-180K, optional, see *Standardization of Sodium Hydroxide*

Flask, volumetric, 1000- mL, Class A, Fisher Scientific, Cat. No. 10-210-5G

Funnel, filter, Fisher Scientific, Cat. No. 10-326-2C

Funnel, separatory, 250- mL, Fisher Scientific, Cat. No. 10-437-5C

Hot plate, Thomas Scientific, Cat. No. 5983C06

Magnetic stir bar, Fisher Scientific, Cat. No. 14-511-64, three required

Mortar, porcelain, 130- mm OD, with *pestle*, porcelain, Fisher Scientific, Cat. Nos. FB961E and FB961O, respectively

Oven, drying, capable of operation at 120°C, Fisher Scientific, Cat. No. 15-103-0508

Pipet filler, Fisher Scientific, Cat. No. 13-681-102A

Pipet, Mohr, 25- mL, Fisher Scientific, Cat. Nos. 13-665-100F

Pipets, volumetric transfer, 2-, 3-, 5-, 10-, and 20- mL, Class A, Fisher Scientific, Cat. Nos. 13-650-2C, -2D, -2F, -2L, and -2N, respectively

Regulator, nitrogen, two-stage, high purity, delivery pressure range 15-200 kPa (2-30psig), Matheson Gas Products, Model 3121-580

Ring stands and clamps, to hold apparatus, local supply

Stirrer, magnetic, Fisher Scientific, Cat. No. 14-493-120S

Stirring rod, glass, Fisher Scientific, Cat. No. 11-380D

Titration, potentiometric, recording, ± 2000 - mV range, 1- mV resolution, capable of reducing the titration rate to a minimum in the vicinity of the endpoint, with dispenser having a volume readout of 0.00 - 99.99 mL, 0.0001 of the buret volume resolution, Metrohm Model 905 Titrando system with 801 Stirrer, Metrohm AG

Tongs, stainless steel, crucible, Fisher Scientific, Cat. No. 15-186

Tubing, thick walled, rubber, for vacuum use, Fisher Scientific, Cat. No. 14-173D, optional, see *Standardization of Sodium Hydroxide*

Vacuum pump, Precision Model No. DD-20, Fisher Scientific, Cat. No. 01-182, optional, see *Standardization of Sodium Hydroxide*

Reagents and Materials

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used. References to water mean deionized water.

Absorbent, carbon dioxide, Ascarite II, 20 to 30-mesh, Fisher Scientific, Cat. No. A184-500

Boiling chips, silicon carbide, Fisher Scientific, Cat. No. NC9063828

Desiccant, 8 mesh, indicating, Fisher Scientific, Cat. No. 07-578-3A

Electrolyte, 3 mol/L potassium chloride, Fisher Scientific, Cat. No. 01-917-103

Filter paper, qualitative, medium, acid-free, non acid-washed, Whatman No. 1, Fisher Scientific, Cat. No. 09-805F

1,3 Cyclohexadiene, with 0.05% BHT (Butylated Hydroxy Toluene) as inhibitor, Purity 97%, Sigma Aldrich Cat. No C100005

Maleic anhydride [108-31-6], 99%, mp 52-55°C, Acros Organics, Fisher Scientific, Cat. No. AC125240010

Maleic anhydride in toluene. Dissolve 60 g of maleic anhydride in warm toluene. Cool, transfer to a one-liter volumetric flask, and dilute to the mark with toluene. Allow the solution to stand at least one day, and filter through a qualitative-grade filter paper before using.

Methyl-tert-butyl ether [1634-04-4], (MTBE), or *tert-butyl methyl ether*, 3 degree boiling range, Fisher Scientific Co., Cat. No. E127-4, or equivalent

1,3 Cyclohexadiene reference standard solution – Standard A (for DV more than 1.2). Weigh to the nearest 0.1 mg, 2 g of 1,3 Cyclohexadiene into a 250- ml volumetric flask, tared to nearest 0.01 g. Dilute the mark with Toluene, mix well and re-weigh. Record the total weight. Calculate Theoretical Diene value by Equation 2. Store the solution in refrigerator (stable for six months).

1,3 Cyclohexadiene reference standard solution – Standard B (for DV less than 1.2). Weigh to the nearest 0.01 g, 50 g of 1,3 Cyclohexadiene reference standard (for DV more than 1.2) into a 250- ml volumetric flask, tared to nearest 0.01g. Record the weight. Dilute to the mark with Toluene, mix

well and re-weigh. Record the total weight. Calculate the Theoretical Diene value by Equation 3. Store the solution in refrigerator (stable for six months).

Nitrogen, 99.999% minimum purity

PTFE Sleeve, ST/NS 24/40, Sigma Aldrich, Cat No. Z104884 or *Pencil*, soft lead, local supply, source of graphite lubricant

Phenolphthalein indicator solution, 1% w/v, Fisher Scientific, Cat. No. SP62-500

Potassium hydrogen phthalate, primary standard, Fisher Scientific, Cat. No. P243-100

Sodium hydroxide, 0.1M, Certified, Fisher Scientific, Cat. No. SS276-1, for low diene value analysis only

Sodium hydroxide, 1.0M, Certified, Fisher Scientific, Cat. No. SS266-1

Toluene, 99.8%, HPLC grade, Fisher Scientific, Cat. No. T290-1

Water, carbon dioxide free, see *Standardization of Sodium Hydroxide*

Water, deionized

Procedure

The analyst is expected to be familiar with general laboratory practices, the technique of potentiometric titration, and with the equipment being used.

Standardization of Sodium Hydroxide

1. Assemble and operate the titrator and electrodes as per the manufacturer's instructions.
2. Fill the dispenser reservoir of the titrator with the 1.0 M sodium hydroxide solution.
 - If a diene value less than 1.2 is to be determined, standardize the 0.1 M sodium hydroxide solution in the same manner.
 - The solution must be protected from atmospheric carbon dioxide by attaching a guard tube containing an absorbent, such as Ascarite, to the dispenser reservoir.
3. Crush approximately 3 g of potassium hydrogen phthalate using a mortar and pestle.
4. Transfer the potassium hydrogen phthalate to a clean crucible and dry at 120°C for 2 hours in a drying oven.
5. Remove the crucible from the oven using tongs, place it in a desiccator, cover it, and allow it to cool to ambient temperature.
6. Place a stirring bar into each of three 250- mL beakers.
 - The standardization is performed in triplicate.
7. Weigh approximately 0.5 g of dried potassium hydrogen phthalate, to the nearest 0.1 mg, into each of the three 250- mL beakers and record the masses in each beaker.
 - If the 0.1-M sodium hydroxide solution is being standardized, weigh in approximately 0.1 g of the dried potassium hydrogen phthalate, to the nearest 0.1 mg.
8. Add, by graduated cylinder, 100 mL of carbon dioxide free water to each beaker.
 - The water must be carbon dioxide free. Prepare immediately before use by boiling deionized water for approximately 10 minutes to expel carbon dioxide and then cooling while purging with nitrogen, or by placing the water under vacuum for sufficient time to degas. For example, 500 mL of water requires approximately 90 minutes under vacuum to fully degas.

9. Place one of the beakers on the titration stand, immerse the electrodes and buret tip, start a slow flow of nitrogen to the headspace of the beaker to expel air, and stir.
 - Adjust the stirring speed to create a vortex in the solvent such that bubbles do not develop at its center.
 - Obtain a stable reading before proceeding to the next step.
10. Adjust the titration parameters so that the initial titration rate in the plateau region is 0.3 mL/min and the titration rate in the region of the endpoint is reduced to 0.1 mL/min. Titrate the potassium hydrogen phthalate solution with the 1.0M sodium hydroxide. Record, to the nearest 0.001 mL, the volume of titrant used to reach the endpoint of the titration.
 - The endpoint is the midpoint of the inflection; the point at which the curve changes from concave to convex.
11. Titrate the contents of the other two beakers in the same manner.
12. For each titration, calculate the molarity of the sodium hydroxide to three decimal places, using Equation 1:

$$M = \frac{10^3 A}{204.2B} \quad (1)$$

where:

- A** = mass of potassium hydrogen phthalate weighed into beaker, g
- B** = volume of sodium hydroxide solution used to reach the endpoint, mL
- M** = molarity of the 1.0M sodium hydroxide, moles/L
- 204.2** = molecular mass of potassium hydrogen phthalate, g/mole
- 10³** = factor to convert moles/mL to moles/L

13. Average the results of the three determinations to three decimal places.
 - Results from each of the triplicate runs should not deviate by more than 0.001 M. If greater deviations occur, make certain that there are no problems with the equipment or the procedure; then repeat the procedure until the required repeatability is obtained on three consecutive runs.
 - The sodium hydroxide solution must be standardized at least weekly to detect changes in molarity. A reference quality assurance sample may be run daily to confirm the stability of the titrant between standardizations.

Standardization with 1,3 Cyclohexadiene

1. Calculate the theoretical Diene value (Standard A) reference standard to one decimal place using Equation 2.

$$\text{Theoretical Diene Value} = \frac{(253.8)(XP)}{(80.13)T} \quad (2)$$

where:

- 253.8** = Molecular Mass of Iodine
- X** = Mass of 1,3 Cyclohexadiene, g
- P** = percentage Purity of 1,3 Cyclohexadiene
- 80.13** = Molecular Mass of 1,3 Cyclohexadiene
- T** = Total Mass of 1,3 Cyclohexadiene plus Toluene diluent, g

2. Calculate the theoretical Diene Value (Standard B) reference standard to two decimal place using Equation (3)

$$\text{Theoretical Diene Value} = \frac{\text{Value from eqn (2) (Y)}}{T_1} \quad (3)$$

where:

- Y** = Mass of 1,3 Cyclohexadiene reference standard in Toluene, g
- T₁** = Total Weight of Y plus Toluene diluent, g

For more than 1.2 DV, take aliquot size between 5-10 g and for less than 1.2 DV take aliquot of 20 g. For rest of procedure follow from step 2 in “Sample Analysis” section. If determined Diene value is not within 10% of calculated theoretical Diene Value, then re-standardize Sodium Hydroxide solution and verify critical process step like reflux and Maleic acid recovery stage.

Sample Analysis

1. Weigh a sample of appropriate size, usually 5-20 g, into the dry 250- mL Erlenmeyer flask with a ground glass joint.
 - If a diene value greater than 1 is expected, use 5-10 g; if a diene value less than 1 is expected use 20 g.
2. Using a volumetric pipet, add 20 mL of the filtered maleic anhydride-toluene solution and a few boiling chips to prevent bumping.
 - If the measured diene value of the sample was previously determined to be less than 1.2, and an estimate of the value below 1.2 is desired, pipet only 2 mL of the filtered maleic anhydride-toluene solution into the flask containing 20 g of the sample. With a Mohr pipet (or individual volumetric pipets), add 18 mL of toluene and a few boiling chips to prevent bumping.
3. Pipet the same amount of filtered maleic anhydride-toluene solution used for the samples to an empty 250- mL Erlenmeyer flask with a ground glass joint. This will be the blank, and should be treated in the same manner as the samples.
4. Lubricate the joint on the condensers with a PTFE Sleeve or a thin layer of graphite using a soft pencil.
5. Fit the Erlenmeyer flasks to the condensers and suspend the assemblies over a hot plate. Adjust the temperature of the hot plate to achieve a mild boiling condition. Reflux for three hours.
6. Allow to cool to ambient temperature.
7. Using a graduated cylinder, add 5 mL of water into the flask through the top of the condenser; then gently boil the contents for an additional 15 minutes.
8. Allow to cool to ambient temperature.
9. Using a graduated cylinder, add 5 mL of MTBE through the top of the condenser, followed by 20 mL of water.
10. Remove the condenser and carefully transfer the contents of the flask into a 250- mL separatory funnel. Wash the flask with a total of 20 mL of MTBE divided into 3 portions, then wash with 25 mL of water, also added in 3 increments. In each case, add the washings to the separatory funnel.
 - In some cases an insoluble substance forms which makes the recovery of the maleic acid difficult. In the event this has occurred, break up the insoluble compound with a stirring rod and extract with hot water:
 - a. Using a graduated cylinder, add 15 mL of water to the reflux flask, heat to boiling and continue boiling for several minutes.
 - b. Cool and transfer the water extract to the separatory funnel.
 - c. Repeat Steps a and b at least twice more, adding each extract to the separatory funnel.
 - d. Continue to Step #11.
11. Shake the contents of the separatory funnel 4-5 minutes with occasional venting. Allow the two phases to separate.
12. Place a stirring bar into a titration beaker. Draw off the aqueous layer into a titration beaker.

Extract the residual liquid in the separatory funnel, as described in Step 11, three times with successive 25-, 10- and 10- mL portions of water, in each case adding the water extracts to the titration beaker containing the aqueous layer drawn off previously.

13. Position the beaker on the titration stand, start a slow flow of nitrogen to the headspace of the beaker to expel air, and stir.
 - Adjust the stirring speed to create a vortex in the solvent such that bubbles do not develop at its center.
 - Continue applying a nitrogen blanket throughout the titration.
14. Immerse the electrodes into the solution and wait for a stable reading.
15. Titrate the solution with the 1.0M sodium hydroxide using the following conditions. Adjust the titration parameters so that the initial titration rate in the plateau region is 0.3 mL/min, and the titration rate in the region of the endpoint is reduced to 0.1 mL/min.
 - One drop of phenolphthalein indicator may be used to help determine whether the potentiometric titration is complete, as indicated by the phenolphthalein color change from colorless to pink. This is especially helpful where the titration proceeds through two inflections. Note, however, that the potentiometric endpoint may occur slightly after the phenolphthalein color change is observed. Also, care must be taken that the amount of phenolphthalein added is minimal. If more than one drop is added, a false high endpoint may result.
16. Record, to the nearest 0.001 mL, the volume of titrant needed to reach the endpoint of the titration.
 - The endpoint is the midpoint of the inflection; the point at which the curve changes from concave to convex.
 - If the titration curve has two inflections, the total volume of titrant needed to reach the second inflection is recorded for use in the calculations.
 - After each titration, rinse the electrodes and the dispenser tip with water.
 - Colorimetric titration may also be used, see Appendix.
 - If the measured diene value of the sample was previously determined to be less than 1.2, and an estimate of the value below 1.2 is desired, titrate the combined aqueous extracts with the 0.1M sodium hydroxide solution in place of the 1.0M sodium hydroxide solution.

Calculations

Calculate the diene value using Equation 4.

$$\text{Diene value} = \frac{(B - A)(M)(12.69)}{W} \quad (4)$$

where:

A = volume of sodium hydroxide solution required to titrate sample, mL
B = volume of sodium hydroxide solution required to titrate blank, mL
M = molarity of the sodium hydroxide solution, mol/L
W = mass of sample, g

$$12.69 = \frac{(126.9)(100)}{1000}$$

where:

100 = from definition of diene value, 100 g of sample
126.9 = molecular weight of iodine/2, see definition of diene value
1000 = converts L to mL

Report the diene value to the nearest 0.1, or to three significant figures, whichever is less.

If the average molecular weight of the conjugated dienes is known, the concentration of the conjugated dienes can be calculated using Equation 5.

$$\text{Conjugated dienes, mass-\%} = \frac{CD}{253.8} \quad (5)$$

where:

C = average molecular weight of conjugated dienes, g/mol

D = diene value, from Equation 1

$$253.8 = (2)(126.9)$$

where:

2 = moles of caustic per mole of maleic anhydride

126.9 = previously defined

Report the concentration of the conjugated dienes to the nearest 0.1 mass-%.

Precision

Precision statements were determined using UOP Method 999, from precision data obtained using a potentiometric titrator.

Repeatability and Intermediate Precision

A nested design was carried out for determining diene value with two analysts in one laboratory. Each analyst carried out two tests on two samples on two separate days for a total of sixteen analyses. Using a stepwise analysis of variance procedure, the within-day estimated standard deviation (esd) was calculated for the concentration and is listed in Table 1. Two tests performed by the same analyst on the same day should not differ by more than the repeatability allowable difference shown in Table 1 with 95% confidence. Two tests performed in one laboratory by different analysts on different days should not differ by more than the intermediate precision allowable difference shown in Table 1 with 95% confidence.

Table 1
Repeatability and Intermediate Precision, Diene Value

<u>Diene Value</u>	<u>Mean</u>	<u>Repeatability</u>		<u>Site Precision</u>	
		<u>Within Day esd</u>	<u>Allowable Difference</u>	<u>Within Lab esd</u>	<u>Allowable Difference</u>
1.8 DV	1.8	0.08	0.3	0.09	0.3
3.67 DV	3.5	0.07	0.3	0.12	0.5

There is insufficient data to calculate the reproducibility of the test at this time. The data in Table 1 are a short-term estimate of repeatability. When the test is run routinely, a control standard and chart should be used to develop a better estimate of the long-term repeatability.

Time for Analysis

The elapsed time for one determination is 5 hours. The labor requirement is one hour.

Suggested Suppliers

Fisher Scientific Co., 711 Forbes Ave., Pittsburgh, PA 15219-4785 (412-490-8300)
www.fishersci.com

Matheson Gas Products Inc., 166 Keystone Drive, Montgomeryville, PA 18936 (215-641-2700)
www.mathesontrigas.com

Metrohm, AG 6555 Pelican Creek Circle, Riverview, FL 33578, (866-638-7646) www.metrohm.com

Reliance Glass Division, Wilmad/Lab Glass, 1455 Elmhurst Road, Elk Grove Village, IL 60007
(847-228-2851) www.wilmad-labglass.com

Appendix

Analysis Using Colorimetric Titration

If a potentiometric titrator is not available, the procedure can be performed using colorimetric titration as described below.

Apparatus

The following items are required in addition to, or as an alternative to, those listed in the body of the method. References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

Buret, Blaubrand automatic burette, 10 ml with 0.02 ml graduation, Sigma Aldrich, Cat. No. Z 323306.

Procedure

The analyst is expected to be familiar with general laboratory practices, the technique of colorimetric titration, and with the equipment being used.

Standardization of Sodium Hydroxide

Standardize the 1.0-*M* sodium hydroxide as follows. If an estimation of the diene value below 1.2 is desired, standardize the 0.1-*M* sodium hydroxide in the same manner.

- Follow Steps 3 through 7 under *Standardization of Sodium Hydroxide* in the body of the method.
- Position one of the beakers on the magnetic stirrer, and stir.
 - Stir at a rate sufficient to form a vortex, but not to create bubbles.
- Purge the headspace of the beaker with nitrogen to expel air.
 - Continue applying a nitrogen blanket throughout the titration.
- Add about 10 drops of phenolphthalein indicating solution to the contents of the titration beaker.
- Fill the 5- mL buret with the 1.0*M* sodium hydroxide and lower the buret tip into the beaker.
 - If titrating with the 0.1*M* sodium hydroxide solution, use the 10-mL buret.
- Titrate the solution to the pink phenolphthalein endpoint.
 - The endpoint color should remain unchanged for 10 seconds.
- Record, to the nearest 0.01 mL, the volume of titrant needed to reach the endpoint of the titration.
- Titrate the contents of the other two beakers in the same manner.
- Calculate the molarity of the sodium hydroxide, to three significant figures, using Equation A1.

$$M = \frac{10^3 A}{204.2B} \quad (A1)$$

where:

A = mass of potassium hydrogen phthalate weighed into beaker, g

B = volume of sodium hydroxide solution used to reach the endpoint, mL

M = molarity of the sodium hydroxide, moles/L

204.2 = molecular mass of potassium hydrogen phthalate, g/mole

10³ = factor to convert moles/mL to moles/L

- Average the results of the three determinations to three significant figures.

- Results from each of the triplicate runs should not deviate by more than 2% of the value. If greater

deviations occur, make certain that there are no problems with the equipment or the procedure; then repeat the procedure until the required repeatability is obtained on three consecutive runs.

- The sodium hydroxide solution must be standardized at least weekly to detect changes in molarity. A reference quality assurance sample may be run daily to confirm the stability of the titrant between standardizations.

Sample Analysis

1. Follow Steps 1 through 12 under *Sample Analysis* in the body of the method.
2. Position the titration beaker on the magnetic stirrer, start a slow flow of nitrogen to the headspace of the beaker to expel air and stir.
 - Adjust the stirring speed to create a vortex in the solvent such that bubbles do not develop at its center.
 - Continue applying a nitrogen blanket throughout the titration.
3. Add about 10 drops of phenolphthalein indicating solution to the contents of the titration beaker.
4. Titrate the combined aqueous extracts with the 1.0M sodium hydroxide solution, using the phenolphthalein indicator solution as the indicator (clear to pink).
 - If the measured diene value of the sample was previously determined to be less than 1.2, and an estimate of the value below 1.2 is desired, titrate the combined aqueous extracts with the 0.1-M sodium hydroxide solution in place of the 1.0-M sodium hydroxide solution, using phenolphthalein indicator solution as the indicator.
5. Calculate the diene value as described in the body of the method.

Precision

For colorimetric titration, the estimated standard deviation (esd) based on 10 duplicate analyses at each level is shown in Table A1. Duplicate results by the same operator should not differ by more than the allowable difference shown (95% probability).

Table A1

<u>Diene Value</u>	<u>esd</u>	<u>Allowable Difference</u>
<5	0.07	0.2
5-50	0.25	0.8
>50	0.40	1.3