STATISTICAL ANALYSIS of UL LTTA data

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1. Current Procedure for Analyzing LTTA data

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- Test samples are received from both the candidate product and the reference product, the reference having a certified RTI performance

- Test samples are annealed for 2 days at the lowest temperature used in the test protocol

- Test data (Toughness, Tensile Strength and Dielectric Strength) are generated at Time 0 on 10 samples. Average value at Time 0 is calculated.

- Test samples are aged at 4 temperatures, with 10 degC intervals, for prolonged times. Test temperatures are (have to be) defined by the Applicant.

- At intermediate intervals, 5 samples are removed from the oven and tested. Average values are calculated for this residence time (Time xxx)

Current Procedure for Analyzing LTTA data

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- This procedure is continued till the values have dropped to below 50% of the value at Time 0

- Average values are plotted vs Time and the best fitting model is calculated. From this, a f_{50} value is obtained (f_{50} is the time at which the property has decreased to 50% of its original value)

- The f_{50} values are plotted as a function of 1/T for both products. The data points should (are expected to) fit a linear relationship (according to Arrhenius)

- These linear fits should be parallel for both products.

- From these linear fits and the known RTI for the reference product, the RTI for the candidate product can be calculated.

Current Procedure for Analyzing LTTA data

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EXAMPLE

MATERIAL :	REFERENCE		COND:	40/23/50	COLOR:	NC	
PROPERTY:	Izod Impact	UNITS:	kj / sq m		TEMP (C):	160	
CONTROL	THICKNESS:	3.00			Rough F50 Point:	1469	

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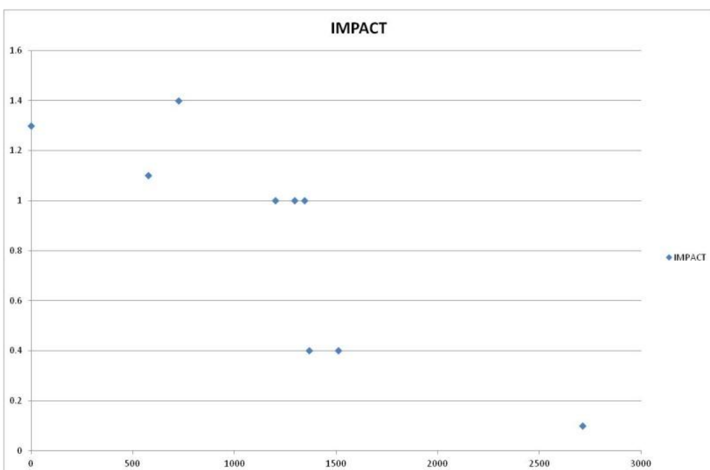
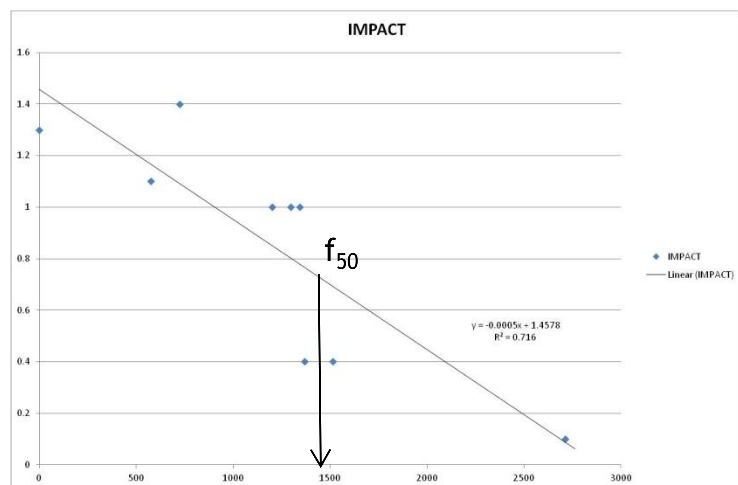
SET ID:	17	ANNEAL:	140	DATE COMPLETED:

HOURS	SAMPLES 1	2	3	4	5	6	7	8	9	10	AVG. VALUES	% OF A/R
0	1.4	1.1	1.0	1.5	0.9	1.2	1.4	1.8	1.9	1.1	1.3	100
576	1.5		1.5	0.2							1.1	83
724	1.9	1.2	0.9	2.9	0.3						1.4	108
1200	1.3	0.1	1.2	0.5	1.7						1.0	73
1296	2.4	0.3	0.3	1.6	0.2						1.0	72
1344	2.0	0.1	1.0	1.0	0.8						1.0	76
1368	0.2	0.3	0.4	0.1	1.2						0.4	33
1512	1.0	0.4	0.1	0.0	0.3						0.4	27
2712	0.2	0.1	0.1	0.2	0.1						0.1	9
											0.0	0
											0.0	0
											0.0	0
											0.0	0





Current Procedure for Analyzing LTTA data

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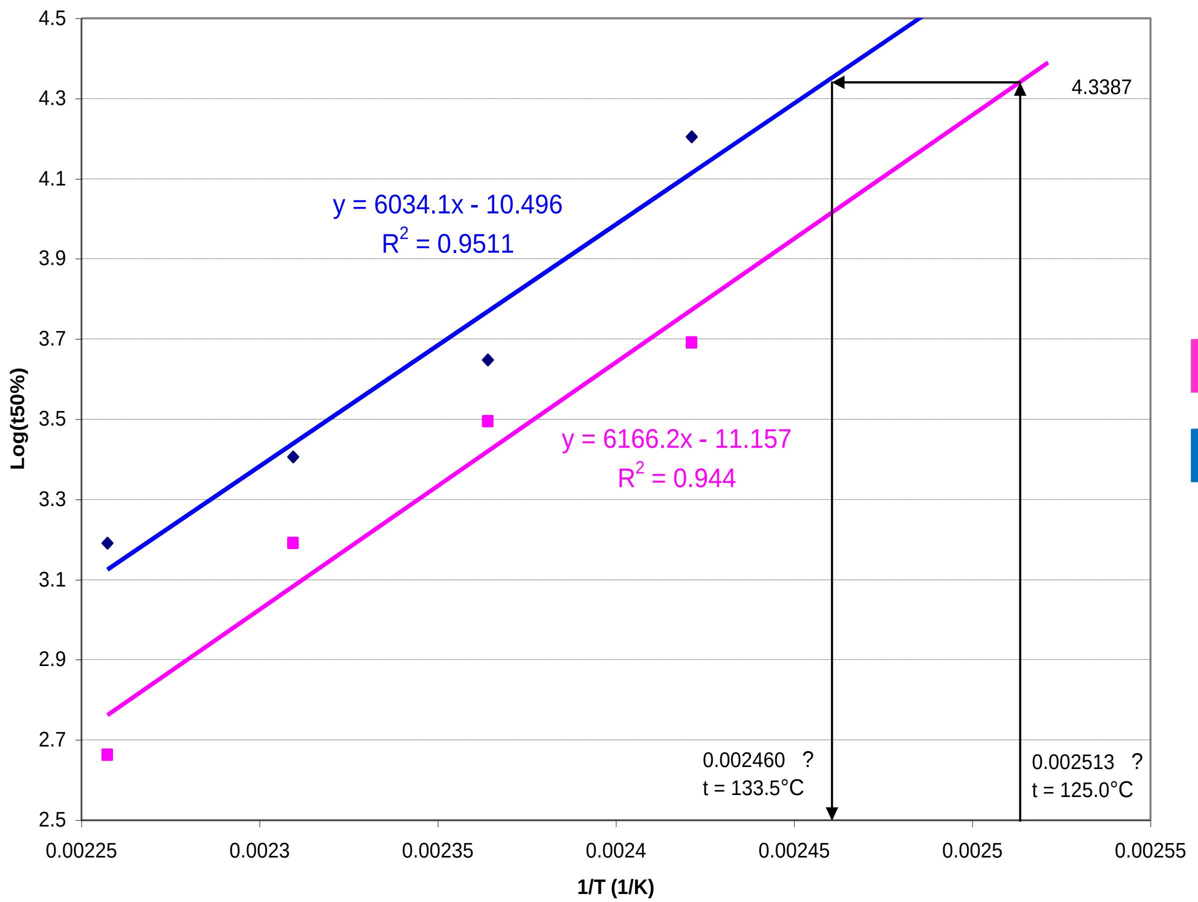
TENSILE STRENGTH of Candidate vs Reference products



Pink : Ref
Blue: Cand

2. Issues with Current Procedure for Analyzing LTTA data

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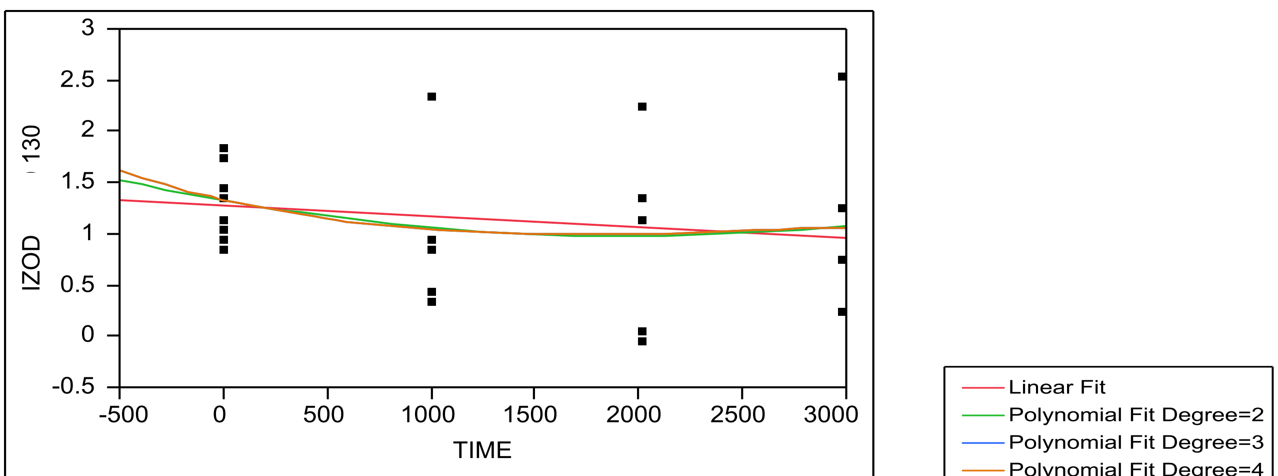
Example

MATERIAL :	REFERENCE			COND:	40/23/50	COLOR:	NC
PROPERTY:	Izod Impact		UNITS:	kj / sq m		TEMP (C):	130
CONTROL	THICKNESS:	3.00				Rough F50 Point:	2767

SET ID: 33 | ANNEAL: 140 | DATE COMPLETED:

HOURS	SAMPLES 1	2	3	4	5	6	7	8	9	10	AVG. VALUES	% OF A/R
0	1.4	1.1	1.0	1.5	0.9	1.2	1.4	1.8	1.9	1.1	1.3	100
1008	0.9	0.5	1.0	2.4	0.4						1.0	78
2016	1.2	0.1	1.4	0.0	2.3						1.0	75
2976	0.3	1.3	0.3	0.8	2.6						1.1	81
4536											0.0	0
											0.0	0
											0.0	0
											0.0	0
											0.0	0
											0.0	0
											0.0	0
											0.0	0
											0.0	0

Bivariate Fit of IZOD REFERENCE at 130C By TIME at 130C



Issues with Current Procedure for Analyzing LTTA data

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Are these calculated models meaningful and/or accurate?

How do we pick the best model?

Can this model be used to calculate the f_{50} value?

It is proposed to use Statistical Analyses to define a Statistically Significant model using ALL datapoints (and not only the averages)

3. Statistical Analysis

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a. WHAT?

Build a Statistically Significant Model correlating the Dependent Variable (property) to the Independent Parameter (Aging Time) to calculate therefrom the f_{50} value

Statistically Significant, what does that mean?

- A change of the Independent Parameter (Aging Time) causes a significant change to the Dependent Variable (Property)

- The calculated model does not show any LACK-of-FIT
  When there is LACK-of-FIT, there are other (unknown) parameters influencing the data more than the (known) independent parameters

Statistical Analysis

WHY?

To make sure that the calculated model contains parameters that contribute significantly, i.e. changes of the independent parameter cause changes of the independent variables which are not caused by other independent variables and/or by error (variability of the methodology)

and the observed changes in the dependent variables are caused by the changes in the independent parameter

in other words,

the oven aging time has a significant effect on the property changes

and there are no other independent parameters (including error) that have an even bigger effect on the property changes

Statistical Analysis

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HOW?

Statistical Analysis of the MEANS of the datapoints
also relevant for the shortened (2000 hrs) LTTA program

Calculation of empirical models
- only containing Contributing Parameters
- showing no LACK-of-FIT

Using a Statistical Analysis Software Program, such as JMP (SAS)

Statistical Analysis

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b. Statistical Analysis of the MEANS of the datapoints

Are the means of the data (statistically significantly) different from each other or not?

- are the differences between the means caused by a change of the independent parameter?

- comparison between the variability between the data of the same dataset and the differences of the means of these datasets

Clarified by an example

Statistical Analysis

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Example

Suppose we want to investigate the effects of three different fertilizers on the growth of some particular plant species. For that purpose, the three fertilizers are applied each to three plants (of same height at the start of the test) and height of the plants is recorded after 6 weeks. Results are shown below.

Individual HEIGHT measurements (cm)

Fertilizer	A	B	C
Plant 1	10	20	50
Plant 2	50	40	40
Plant 3	30	60	60
Average Height	30	40	50

Question: Which fertilizer has been most effective in growing the plant?

When considering only the average values, one would conclude that Fertilizer C is the most effective.

But, is this the correct conclusion?

Statistical Analysis

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Example

Suppose we had obtained the following test results.

Individual HEIGHT measurements (cm)

Fertilizer	A	B	C
Plant 1	28	42	52
Plant 2	32	38	48
Plant 3	30	40	50
Average Height	30	40	50

Question: Which fertilizer has been most effective in growing the plant?

When considering the average values, again one would conclude that Fertilizer C is the most effective.

Is this conclusion valid?

Statistical Analysis

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In order to come to the correct conclusion, one has to be sure that there is a significant difference between the calculated averages (means).

If the averages are significantly different, the variation measured (or sum of squares) between the Fertilizer Treatments would be large in comparison to the average variation within a Fertilizer treatment.

This can be done in an ANOVA Table (Analysis Of Variance),

Statistical Analysis

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ANALYSIS OF VARIANCE TABLE (ANOVA)				
Source of Variation	Sum of Squares	Degrees of Freedom (DF)	Mean Squares	F
Between Treatments (explainable)	A = m*(Sum of Squared Deviations of Treatment Means from the Overall Mean)	# of Treatments - 1	X1 = A/DF between	X1/X2
Within Treatments (errors)	B = Sum of Squared Deviations of Individual data from the respective Treatment Mean	(# of Treatments) * (# of data points per group - 1)	X2 = B/DF within	
TOTAL	SS of the Total Data Set	(Total# of Data Points - 1)		

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Making these calculations for dataset 1, brings us to an F value of 1.
For the second dataset, using the same methodology, o ne arrives at an F value of 75.

These calculated F values now have to be compared to tabled F values, which depend on the Degrees of Freedom of the dataset and on the desired confidence level (typically chosen at 0.95).
Hence, in our case we look for $F_{2,6,0.95} = 5.14$

Now, when the calculated F value is higher than the tabled F value, it means that the Treatments have a significant effect on the Data (with 95% certainty).

This means in our case that, for dataset 1, the Fertilizer Treatments did NOT have a significant effect on plant growth, despite the fact that the averages for each dataset were quite different.

This means that our conclusion, which was based on considering only the average values, that for the first data series, Fertilizer C is the most effective, is WRONG.

For dataset 2 however, the Fertilizer Treatments did show to have a statistically significant effect on plant growth. Calculated F value is larger than the Tabled F value (=5.14). Hence, here we can conclude that Fertilizer C indeed is the most effective.

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Statistical Analysis of the MEANS from the example from the UL LTTA TOOLS workgroup meeting, December 2012

- 2000 hrs LTTA program

- using JMP

- analysis can be done in two ways
    - using the absolute values of the data
    - using relative values (%Retention)

- what you get is
    - Quantiles, Means, Standard Deviations, ANOVA and Comparison of Means, typically Student's t tests and Tukey-Kramer
    - Also shown in graphical form

Analysis at 2000 hours

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- Assuming the following data is produced "As Received" and at "2000 hours"

This is only an example! The statistics that follow are correct, but for impact strength each set should be 10 specimens per the proposal

Set Number	Control - As Received	Candidate - As Received	Control - 2000 hours	Candidate - 2000 hours
1	3.1	4.3	2.6	3.4
1	4.9	5.1	4.2	4.1
1	5.2	4.3	4.4	3.4
1	3.9	3.1	3.3	2.5
1	4.1	4.2	3.5	3.4
2	4.9	3.0	4.2	2.4
2	5.3	4.3	4.5	3.4
2	4.4	4.8	3.7	3.8
2	4.3	4.9	3.6	3.8
2	4.1	5.3	3.5	4.2
3	4.7	3.1	4.0	2.5
3	3.5	4.5	3.0	3.6
3	4.4	4.8	3.7	3.8
3	4.9	4.7	4.2	3.8
3	4.3	5.1	3.7	4.1
4	4.9	4.9	4.2	3.9
4	3.8	3.3	3.2	2.6
4	2.7	3.0	2.3	2.4
4	5.3	4.9	4.5	3.9
4	4.8	5.4	4.1	4.3

Statistical Analysis

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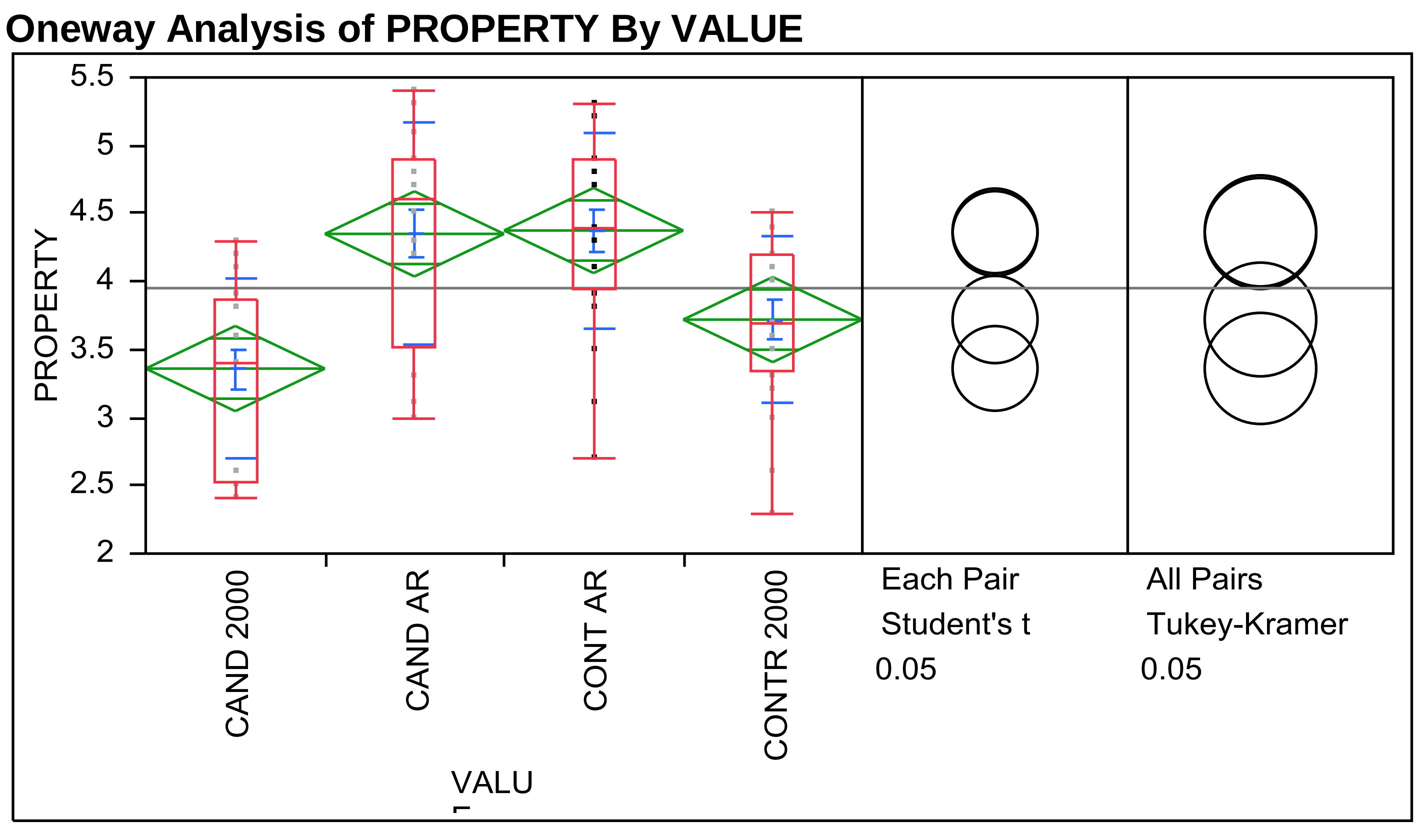

Quantiles
Means
Sdev

Comparison
of Means

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Comparisons for all pairs using Tukey-Kramer HSD

q*	Alpha
2.62680	0.05

Abs(Dif)-HSD	CONT AR	CAND AR	CONTR 2000	CAND 2000
CONT AR	-0.58386	-0.55886	0.07114	0.43114
CAND AR	-0.55886	-0.58386	0.04614	0.40614
CONTR 2000	0.07114	0.04614	-0.58386	-0.22386
CAND 2000	0.43114	0.40614	-0.22386	-0.58386

Positive values show pairs of means that are significantly different.

Level			Mean
CONT AR	A		4.3750000
CAND AR	A		4.3500000
CONTR 2000		B	3.7200000
CAND 2000		B	3.3600000

Levels not connected by same letter are significantly different.

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CONCLUSION

Retained properties (after 2000 hrs aging) of CONTROL and CANDIDATE material are NOT statistically different.

Hence, the CANDIDATE material should receive the same RTI as the CONTROL material

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c. 4 point LTTA program

- Are the means of the data (statistically significantly) different from each other or not? COMPARISON of MEANS

- Data fit to various Polynomial models

  Property = f(x)

  with f(x) = linear n=1

  quadratic n=2

  cubic n=3

  polynomial n=4

- Plot with data points and fitted models (visual assessment)

- Per model
  - Lack-of-Fit
  - parameter estimates with SIGNIFICANCE

Therefrom, the 'best' model is maintained for f_{50} calculation
  - NO Lack-of-Fit
  - only SIGNIFICANTLY contributing parameters

Statistical Analysis

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EXAMPLE 1

MATERIAL :	REFERENCE		COND:	40/23/50	COLOR:	NC
PROPERTY:	Izod Impact	UNITS:	kj / sq m		TEMP (C):	160
CONTROL	THICKNESS:	3.00			Rough F50 Point:	1469

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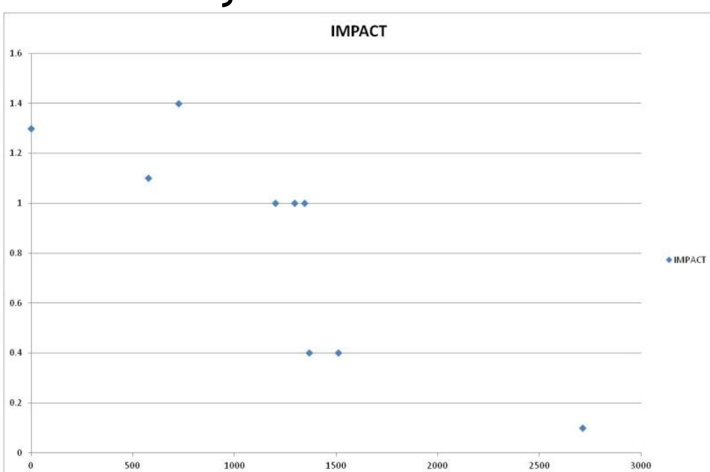
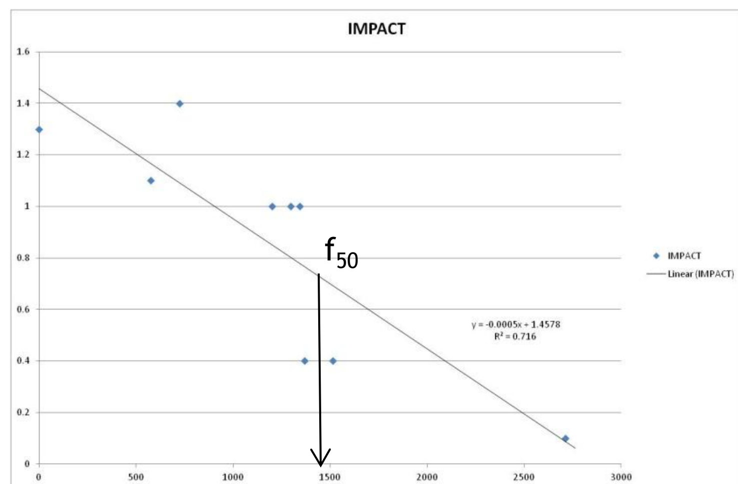
1512	1.0	0.4	0.1	0.0	0.3						0.4	27
2712	0.2	0.1	0.1	0.2	0.1						0.1	9
											0.0	0
											0.0	0
											0.0	0
											0.0	0

Current analysis





Statistical Analysis

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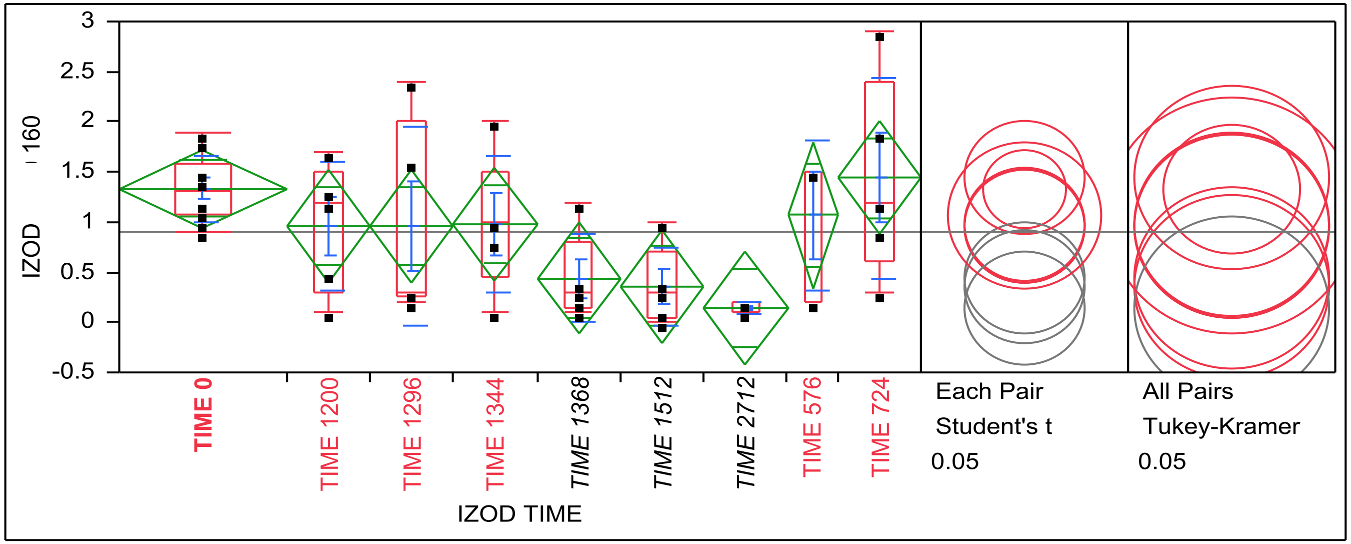
Comparison of Means

Oneway Analysis of IZOD REFERENCE at 160C By TIME at 160C



Statistical Analysis

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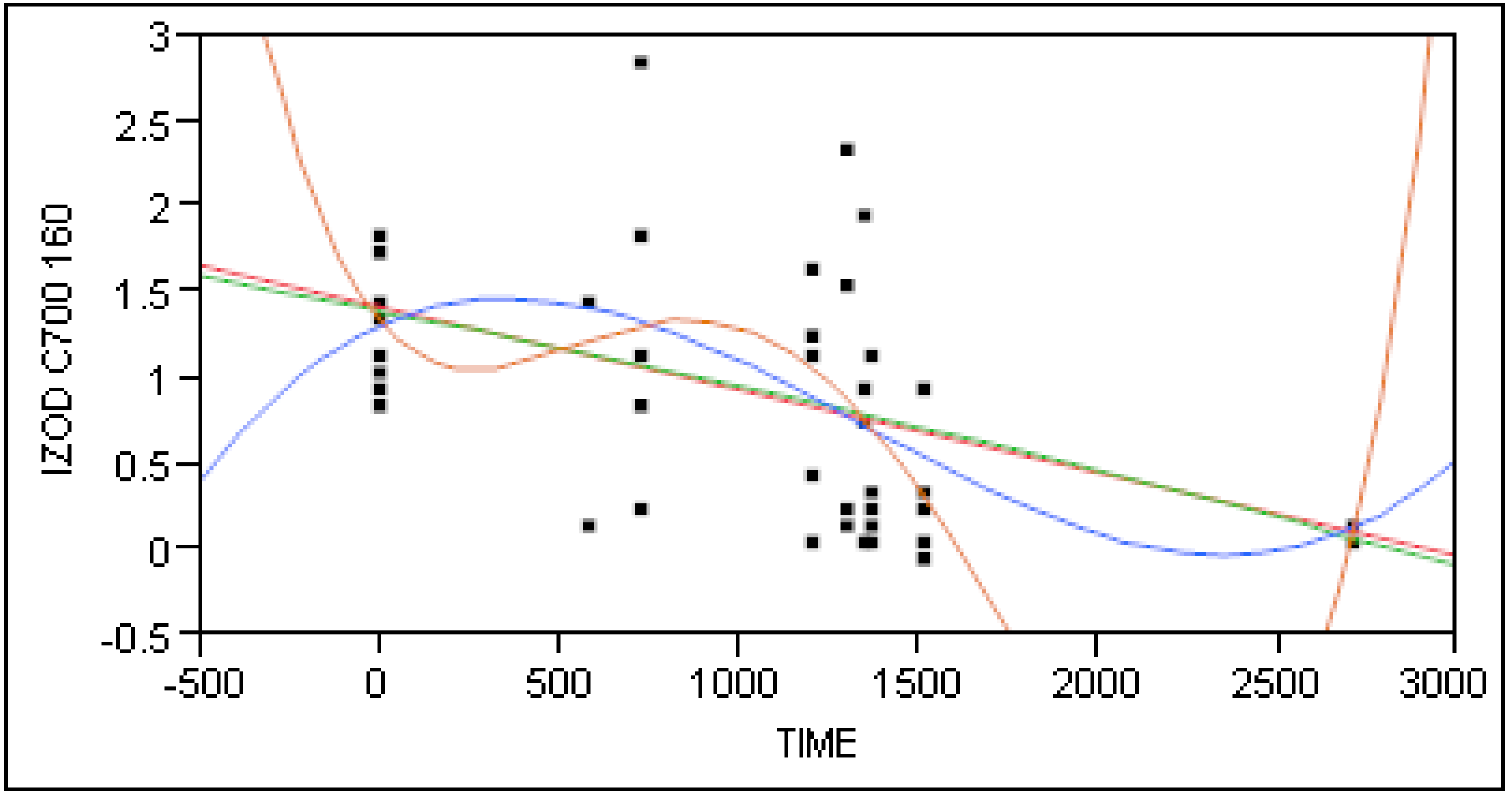
Bivariate Fit of IZOD REFERENCE at 160C By TIME at 160C



Statistical Analysis

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Linear Fit

IZOD REF 160 = 1.4211371 - 0.0004821*TIME

Summary of Fit

RSquare	0.276724
RSquare Adj	0.261001
Root Mean Square Error	0.612094
Mean of Response	0.89375
Observations (or Sum Wgts)	48

Lack Of Fit

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack Of Fit	7	2.266641	0.323806	0.8437
Pure Error	39	14.967667	0.383786	**Prob > F**
Total Error	46	17.234307		0.5584
				Max RSq
				0.3718

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	1	6.593818	6.59382	17.5995
Error	46	17.234307	0.37466	**Prob > F**
C. Total	47	23.828125		0.0001*

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	1.4211371	0.153652	9.25	<.0001*
TIME	-0.000482	0.000115	-4.20	0.0001*

There is No Lack-of-Fit and TIME is a significant variable in the model.

Statistical Analysis

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Polynomial Fit Degree=2

IZOD REF 160 = 1.4292182 - 0.000474*TIME - 2.8663e-8*(TIME-1093.92)^2

Summary of Fit

RSquare	0.277761
RSquare Adj	0.245662
Root Mean Square Error	0.618414
Mean of Response	0.89375
Observations (or Sum Wgts)	48

Lack Of Fit

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack Of Fit	6	2.241927	0.373654	0.9736
Pure Error	39	14.967667	0.383786	**Prob > F**
Total Error	45	17.209593		0.4559
				Max RSq
				0.3718

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	2	6.618532	3.30927	8.6531
Error	45	17.209593	0.38244	**Prob > F**
C. Total	47	23.828125		0.0007*

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	1.4292182	0.15846	9.02	<.0001*
TIME	-0.000474	0.00012	-3.94	0.0003*
(TIME-1093.92)^2	-2.866e-8	1.128e-7	-0.25	0.8005

There is No Lack-of-Fit, but still, only TIME is a significant variable in the model.

Statistical Analysis

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EXAMPLE 2

MATERIAL :	REFERENCE	COND:	40/23/50	COLOR:	NC
PROPERTY:	Izod Impact	UNITS:	kj / sq m	TEMP (C):	130
CONTROL	THICKNESS:	3.00		Rough F50 Point:	2767

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SET ID:	33	ANNEAL:	140	DATE COMPLETED:

	SAMPLES										AVG.	% OF
HOURS	1	2	3	4	5	6	7	8	9	10	VALUES	A/R
0	1.4	1.1	1.0	1.5	0.9	1.2	1.4	1.8	1.9	1.1	1.3	100
1008	0.9	0.5	1.0	2.4	0.4						1.0	78
2016	1.2	0.1	1.4	0.0	2.3						1.0	75
2976	0.3	1.3	0.3	0.8	2.6						1.1	81
4536											0.0	0
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											0.0	0
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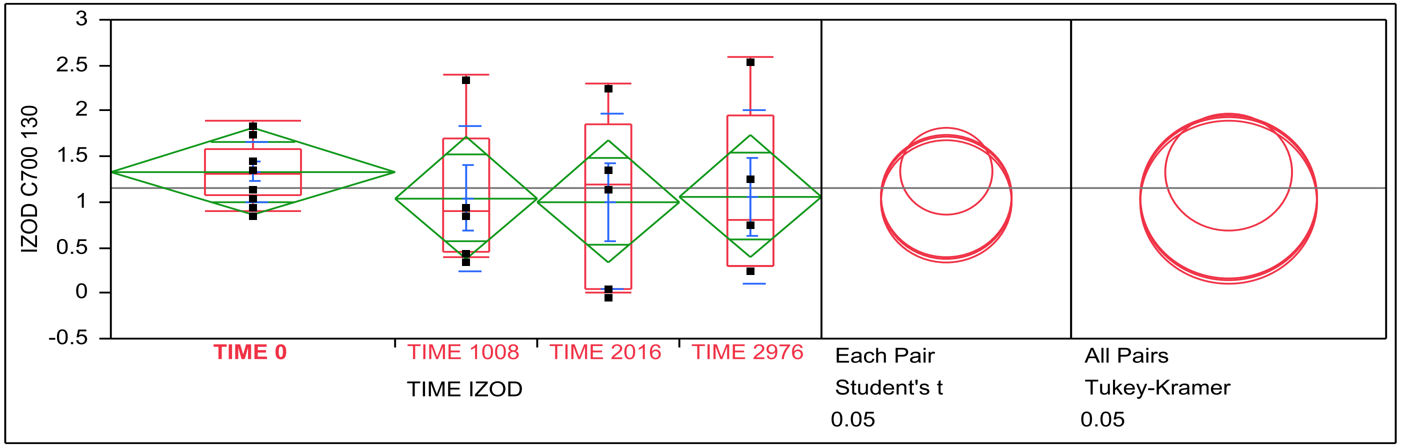
Oneway Analysis of IZOD REFERENCE at 130C By TIME at 130C



Statistical Analysis

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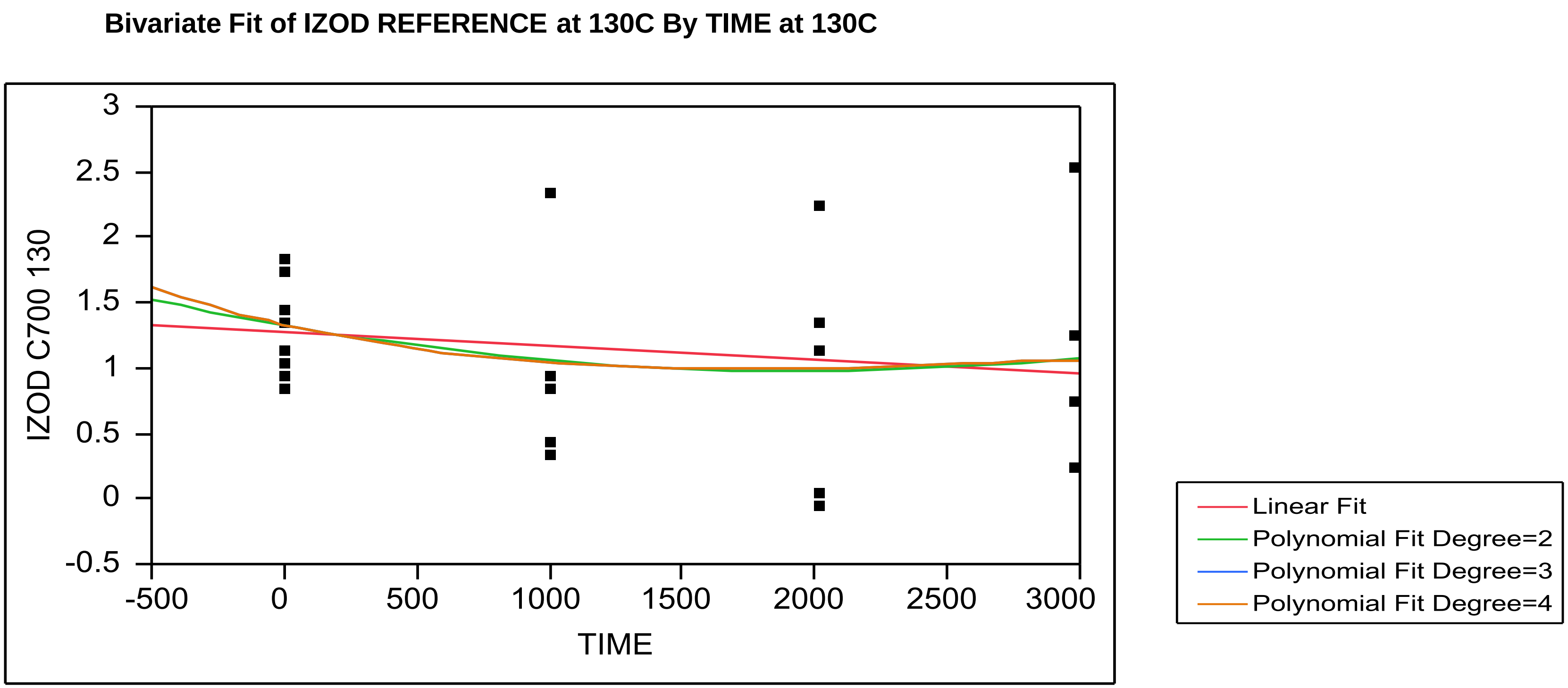

Statistical Analysis

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Linear Fit

IZOD REF 130 = 1.275461 - 0.0001029*TIME

Summary of Fit

RSquare	0.031107
RSquare Adj	-0.01102
Root Mean Square Error	0.694883
Mean of Response	1.152
Observations (or Sum Wgts)	25

Lack Of Fit

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack Of Fit	2	0.180845	0.090422	0.1738
Pure Error	21	10.925000	0.520238	**Prob > F**
Total Error	23	11.105845		0.8417
				Max RSq
				0.0469

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	1	0.356555	0.356555	0.7384
Error	23	11.105845	0.482863	**Prob > F**
C. Total	24	11.462400		0.3990

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	1.275461	0.199892	6.38	<.0001*
TIME	-0.000103	0.00012	-0.86	0.3990

There is No Lack-of-Fit, but TIME is NO significant variable to the model.

Statistical Analysis

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CONCLUSIONS from Statistical Analysis of 4 point LTTA program

-For EXAMPLE 1: LINEAR MODEL is maintained, as higher order models have no additional significantly contributing parameters

- For EXAMPLE 2: NO MODELS are maintained, as no significantly contributing parameters are found

- From the 8 datasets, only 5 are maintained for f_{50} calculation and subsequent RTI determination

Statistical Analysis

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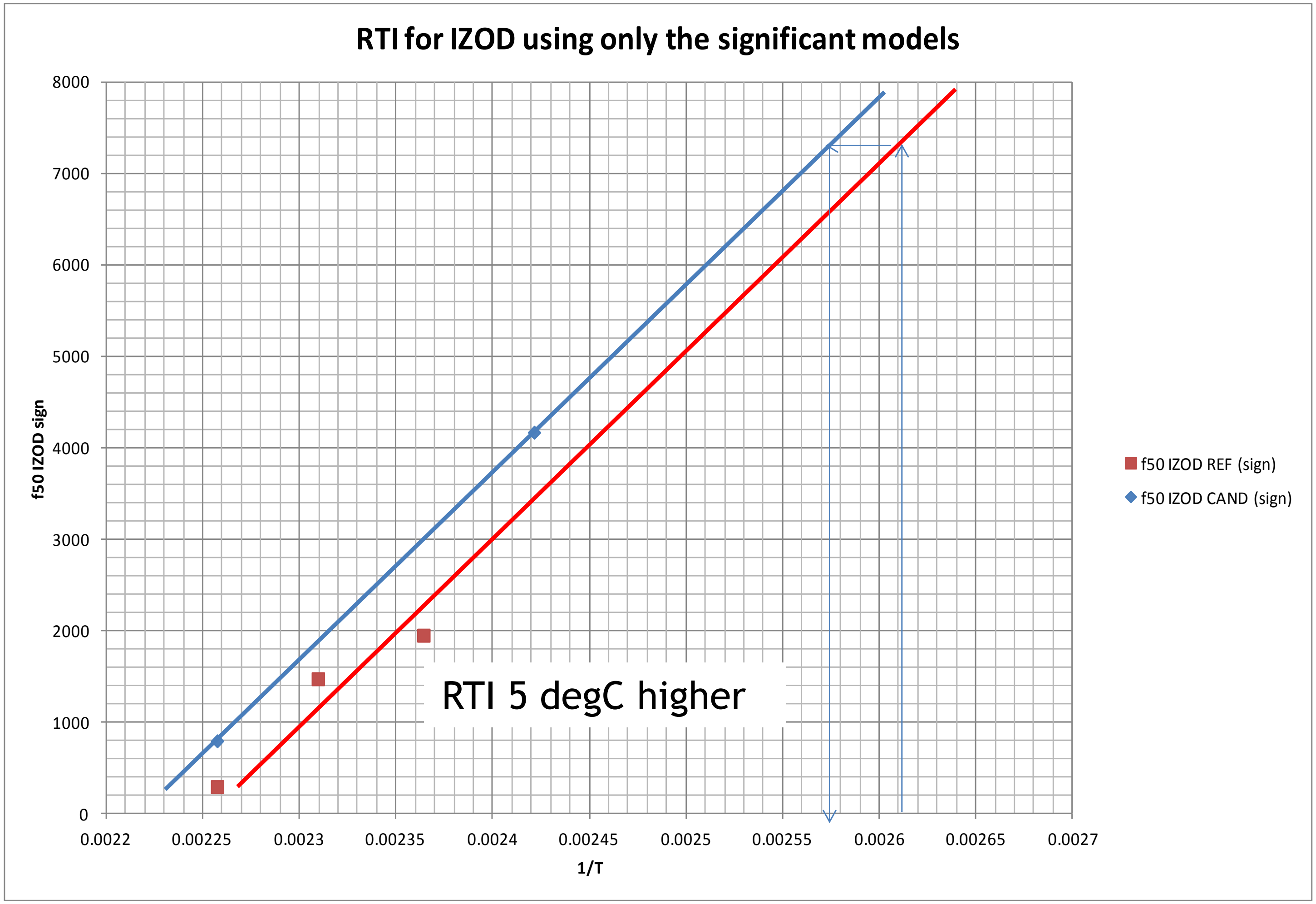

Statistical Analysis

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4. CONCLUSIONS & PROPOSALS

STATISTICAL ANALYSIS is an essential tool for analysis of LTTA data

Both for

COMPARISON of MEANS and

Defining MODELS for f_{50} (or any f_x)

- uses all datapoints
- takes into account the variability of the methodology
- decision criteria taken on the basis of statistics

It is proposed to introduce STATISTICAL ANALYSIS in the UL LTTA procedures

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THANK YOU

QUESTIONS?