Specimen Heterogeneity Analysis : Revisited

F. Meisenkothen
Air Force Research Laboratory | AFRL
Materials Characterization Facility | MCF
Operated by UES, Inc. at
Wright Patterson Air Force Base, Ohio

J. J. Donovan
University of Oregon
Department of Chemistry
Eugene, OR

The following presentation was cleared for public release by WPAFB Public Affairs.
Document #'s RX-08-057 and WPAFB 08-0310 (abstract and conference proceedings)
Document #'s RX-08-503 and WPAFB 08-4705 (brief and presentation)

UNIVERSITY OF OREGON

UES

Acknowledgements

The authors would like to thank the following people for many helpful discussions related to the investigation of this topic :

Dale Newbury of N.I.S.T.
Ryna Marinenko of N.I.S.T.
Eric Lifshin of S.U.N.Y., Albany
Paul Shade of the Ohio State University
Robert Wheeler of UES, Inc.
Michael Uchic of the Air Force Research Laboratory
Dan Kremser of Battelle
Jared Shank of UES, Inc.

Work for this project was done under the support of AFRL Contract # F33615-03-C-5206

UNIVERSITY OF OREGON

UES

Motivation

$$\delta\overline{C} = \overline{C}\,\frac{t_{\nu,P}\sigma_N}{\left(\sqrt{n}\right)\left(\overline{N}\right)}$$

Question : Is the homogeneity range equation doing what we think it is doing ?
(Scanning Electron Microscopy and X-ray Microanalysis, by Goldstein, et al)

Compare Different Methods for quantifying specimen heterogeneity:

1) NIST-ANOVA (benchmark)
2) Weight Percent
3) Goldstein, et.al.
4) Lifshin, et.al. (generalized)

Probability and Statistics

"Identical" engineering measurements show variations

Quantify :

1) ***Mean Value*** -- the best estimate of the true value

2) ***Standard Deviation*** -- a measure of the point to point variation in the measured data (StDev)

3) ***Standard Deviation of the Mean*** -- uncertainty in the measurement of the mean (SDoM)

Different Heterogeneity Methods – Differ in how we evaluate StDev & SDoM

Finite Datasets – Single Specimen

Mean

$$\bar{x} = \frac{\sum x_i}{n}$$

Our best estimate of the quantity x

Sample Standard Deviation

$$\sigma_x = \sqrt{\frac{1}{n-1}\sum (x_i - \bar{x})^2}$$

σ_x of the measurements is estimate of the average uncertainty of the individual measurements.

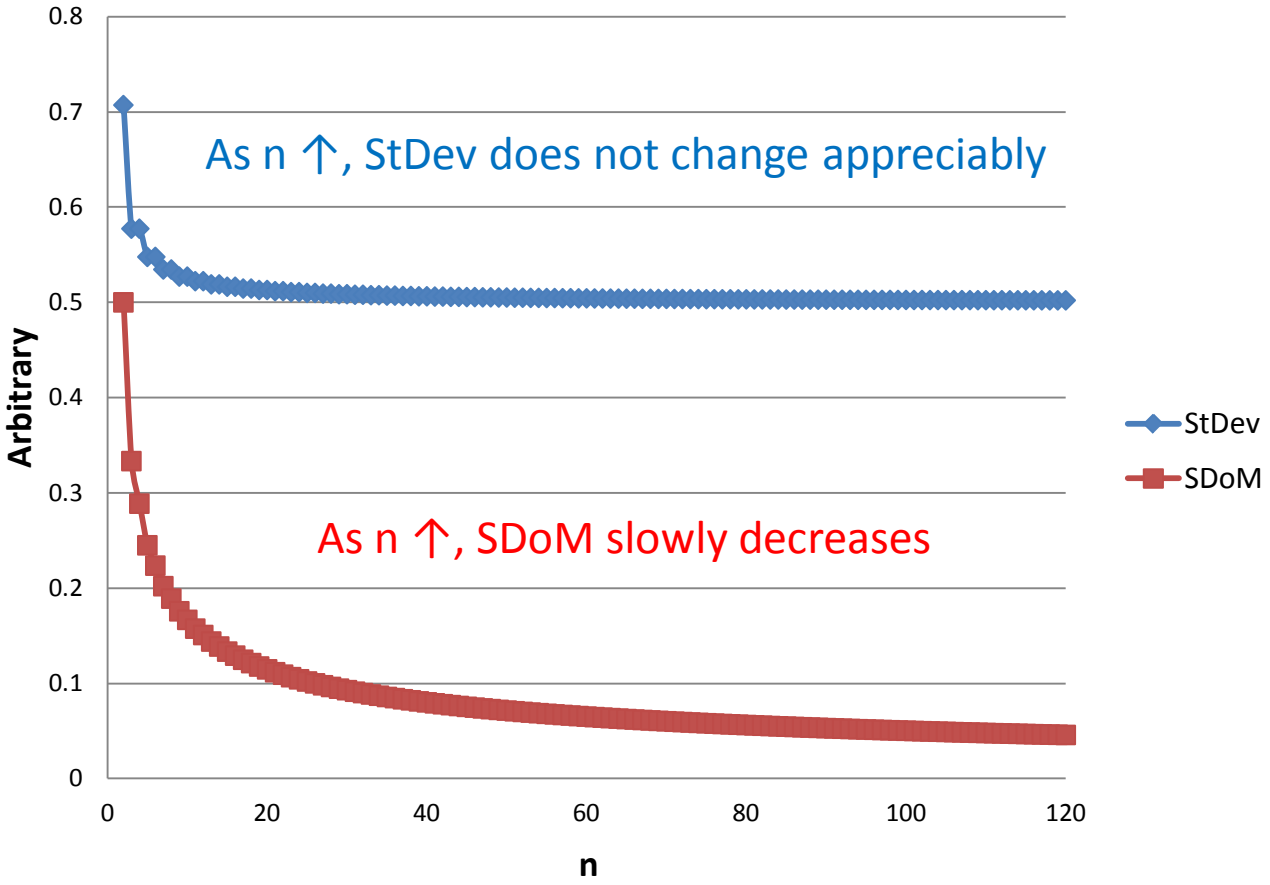
**Counting Experiments* : events occur at random, but with a definite average rate, the uncertainty is the square root of the counted number (Poisson).

Standard Deviation of the Mean

$$\sigma_{\bar{x}} = \frac{\sigma_x}{\sqrt{n}}$$

Also called “Standard Error” and “Standard Error of the Mean”

StDev vs. SDoM



- The mean represents the combination of all n measurements.

- Make more measurements before computing the average, the result is more reliable.

Finite Data Sets – Single Specimen

Large Data Sets :

• The sampling distribution is approximately a normal distribution around the true value (the familiar bell curve).

• As n increases, the approximation improves.

• The z term, used in defining the confidence interval of large datasets, provides a reliable weight estimate of the true probability

For a normal distribution :

$\pm 1\sigma_x$ is approx. 68 % probability (z=1)
$\pm 2\sigma_x$ is approx. 95.4 % probability (z=2)
$\pm 3\sigma_x$ is approx. 99.7 % probability (z=3)

Finite Data Sets – Single Specimen

Small Data Sets (Students t distribution):

• Approximation of sampling distribution as normal distribution is poor

• Approximation becomes worse as n decreases

• The z term, used in defining the confidence interval of large datasets, does not provide a reliable weight estimate of the true probability

• A new variable, the “t estimator” can be used to compensate for the difference.

• The t estimator is a function of the probability and the degrees of freedom in the standard deviation.

Finite Datasets – Single Specimen

Student t Distribution			
ν	$t_{68.27}$	$t_{95.45}$	$t_{99.73}$
1	1.84	13.97	235.78
2	1.32	4.53	19.21
5	1.11	2.65	5.51
10	1.05	2.28	3.96
20	1.03	2.13	3.42
50	1.01	2.05	3.16
300	1.00	2.01	3.03
∞	1.00	2.00	3.00

As $\nu \rightarrow \infty$

- Student's t distribution approximates the normal distribution
- $t \rightarrow z$

UNIVERSITY OF OREGON

UES

Finite Datasets – Single Specimen

Uncertainty in an individual measurement

(large dataset)

$$x_i = \bar{x} \pm \underbrace{z\sigma_x}_{\text{Confidence Interval}} \quad \text{(P \%)}$$

(small dataset)

$$x_i = \bar{x} \pm \underbrace{t_{\nu,P}\sigma_x}_{\text{Confidence Interval}} \quad \text{(P \%)}$$

Relative uncertainty = quality of the measurement (%)

$$RU = \frac{z\sigma_x}{\bar{x}}$$

$$RU = \frac{t_{\nu,P}\sigma_x}{\bar{x}}$$

For example :

Measure distance of 1 mile with uncertainty of 1 inch = good

Measure distance of 3 inches with uncertainty of 1 inch = bad

Finite Datasets – Single Specimen

Uncertainty in our best estimate of the true value

(large dataset)

$$x_{best} = \bar{x} \pm \underbrace{z\sigma_{\bar{x}}}$$

Confidence Interval

(small dataset)

$$x_{best} = \bar{x} \pm \underbrace{t_{\nu,P}\sigma_{\bar{x}}}$$

Confidence Interval

Relative uncertainty = quality of the measurement (%)

$$RU = \frac{z\sigma_{\bar{x}}}{\bar{x}}$$

$$RU = \frac{t_{\nu,P}\sigma_{\bar{x}}}{\bar{x}}$$

Defining a Heterogeneity "Range" and "Level"

Heterogeneity Range = range of concentrations that will characterize the point to point variation within the specimen, at a particular confidence level (use StDev)

Heterogeneity Range = (t)*(StDev) = C.I.

$$\overline{N} \pm 3\sqrt{\overline{N}}$$ (e.g. Yakowitz, et.al)

Heterogeneity Level = Quality of the Measurement = Relative Uncertainty

Heterogeneity Level (%) = (100)*(C.I.) / (Mean)

$$\frac{3\sqrt{\overline{N}}}{\overline{N}} \times 100$$ (e.g. Yakowitz, et.al)

NIST-ANOVA (Analysis of Variance)

- The Bench Mark

- Multiple specimens, multiple analysis points, and multiple replicates

- Each component of variance can be evaluated individually.

  S, macroheterogeneity (between specimens)
  P, microheterogeneity (between points)
  E, measurement error (between replicates)

- Rigorous and complicated.

- Details will not be described here.

Marinenko, et al, Microscopy and Microanalysis, August 2004

NIST-ANOVA (Analysis of Variance)

The Grand Mean

$$\overline{W} = \frac{1}{(n_S n_P n_E)} \sum_{i=1}^{n_S} \sum_{j=1}^{n_P} \sum_{k=1}^{n_E} W_{ijk}$$

The variance of the grand mean (SDoM)

$$\sigma_{\overline{W}}^2 = \frac{\sigma_{S_W}^2}{n_S} + \frac{\sigma_{P_W}^2}{n_S n_P} + \frac{\sigma_{E_W}^2}{n_S n_P n_E}$$

Approximate 99% confidence interval for the mean micrometer scale concentration

$$\overline{W} \pm 3 \underbrace{\left[\frac{\sigma_{S_W}^2}{n_S} + \frac{\sigma_{P_W}^2}{n_S n_P} + \frac{\sigma_{E_W}^2}{n_S n_P n_E} \right]^{1/2}}_{Standard\ Deviation\ of\ the\ Mean}$$

(the uncertainty in the measurement of the mean)

UNIVERSITY OF OREGON

UES

NIST-ANOVA (Analysis of Variance)

The overall variance of the measurement, W

$$\sigma_W^2 = \sigma_{S_W}^2 + \sigma_{P_W}^2 + \sigma_{E_W}^2 \qquad \text{(StDeV)}$$

Approximate 99% confidence interval for a concentration measurement, W, at the micro-scale is

$$\overline{W} \pm 3\underbrace{\left[\sigma_{S_W}^2 + \sigma_{P_W}^2 + \sigma_{E_W}^2\right]^{1/2}}_{S\,\mathrm{tan}\,dard\,Deviation}$$

(the uncertainty associated with the measurement of W)

UNIVERSITY OF OREGON

UES

Goldstein, et.al. Heterogeneity Equations

$$\delta C = \overline{C}\,\frac{t_{\nu,P}\sigma_N}{\left(\sqrt{n}\right)\left(\overline{N}\right)}$$

(Heterogeneity Range)

$$\frac{\delta C}{\overline{C}} = \frac{t_{\nu,P}\sigma_N}{\left(\sqrt{n}\right)\left(\overline{N}\right)}$$

(Heterogeneity Level)

- Easy to use
- Quick to apply
- Results in concentration units, not counts
- Does not include terms for standards
- Does not include terms for composition dependence of ZAF correction

Revised Goldstein, et.al. Equations

The confidence interval for the mean concentration would thus be

$$\delta\overline{C} = \overline{C}\,\frac{t_{\nu,P}\sigma_N}{\left(\sqrt{n}\right)\left(\overline{N}\right)} \qquad \text{(SDoM)}$$

(Original Goldstein, et.al. Eqn.)

Revised Goldstein Eqn. (Heterogeneity Range)

$$\delta C = \overline{C}\,\frac{t_{\nu,P}\sigma_N}{\overline{N}} \qquad \text{(StDev)}$$

Revised Relative Uncertainty (Heterogeneity Level)

$$\frac{\delta C}{\overline{C}} = \frac{t_{\nu,P}\sigma_N}{\overline{N}}$$

UNIVERSITY OF OREGON

UES

Heterogeneity Range : A Short Example

- Peak counts not shown here to save space.
- 95% confidence (small dataset, 20 points).

- Use Revised Goldstein, et al Eqn., all data fits within the calculated range.

- Use Original Goldstein, et al Eqn., >50% of the data falls outside of the calculated range. (red)

Al	Ti	Zr	Mo	Sn	Total
6.09	85.45	4.28	1.92	2.06	99.81
6.24	84.83	4.14	1.91	2.05	99.16
6.18	85.24	4.10	1.96	1.98	99.46
6.21	85.44	4.00	1.88	2.08	99.61
6.22	85.22	3.85	2.00	2.06	99.35
6.09	85.93	4.12	2.05	2.09	100.28
6.18	85.22	4.10	1.90	1.98	99.37
6.15	86.07	4.22	1.86	2.10	100.41
6.28	85.33	3.98	2.05	2.06	99.70
6.17	86.05	3.96	1.99	2.09	100.26
6.15	85.49	3.99	1.93	2.06	99.62
6.20	86.13	4.14	1.91	1.98	100.37
6.16	85.49	3.96	1.94	2.09	99.63
6.13	85.32	4.08	1.94	2.15	99.61
6.09	85.63	4.16	1.89	2.13	99.91
6.06	85.65	4.05	2.02	2.07	99.86
6.18	85.28	3.99	1.96	2.15	99.56
6.11	85.56	4.02	1.98	2.11	99.79
6.23	85.77	4.26	1.98	1.99	100.23
6.25	85.23	3.95	1.88	2.04	99.35

Average	**6.17**	**85.52**	**4.07**	**1.95**	**2.07**
Revised Goldstein HeteroRange	***0.12***	***0.78***	***0.23***	***0.11***	***0.09***
Min	**6.05**	**84.74**	**3.84**	**1.84**	**1.98**
Max	**6.29**	**86.30**	**4.29**	**2.05**	**2.16**
Revised Goldstein HeteroLevel	***1.9***	***0.9***	***5.5***	***5.4***	***4.3***
Revised Goldstein HeteroLevel (Poisson)	***1.6***	***0.7***	***6.2***	***6.6***	***4.2***
Goldstein HeteroRange	***0.03***	***0.17***	***0.05***	***0.02***	***0.02***
Min	**6.14**	**85.34**	**4.02**	**1.92**	**2.05**
Max	**6.20**	**85.69**	**4.12**	**1.97**	**2.09**
Goldstein HeteroLevel	***0.4***	***0.2***	***1.2***	***1.2***	***1.0***
Goldstein HeteroLevel (Poisson)	**0.4**	**0.2**	**1.4**	**1.5**	**0.9**

UNIVERSITY OF OREGON

UES

Lifshin, et.al. Equation

Specifying the mean concentrations, and the uncertainty in these mean values, is a great way to look for subtle variations in concentration when comparing multiple specimens.

- Results in concentration units (Ziebold eqn.)
- Calculates the SDoM concentration for a given element
- Assumes unknown and standard were collected under identical conditions (i,t)
- Assumes ideal Poisson distribution for uncertainty of the measurements

$$\sigma_{\overline{C}}^2 = \overline{C}^2 \left[\frac{\overline{N} + \overline{N}(B)}{n\left(\overline{N} - \overline{N}(B)\right)^2} + \frac{\overline{N}_S + \overline{N}_S(B)}{n'\left(\overline{N}_S - \overline{N}_S(B)\right)^2} \right] \left[1 - \frac{(a-1)\overline{C}}{a} \right]^2 \qquad \text{(SDoM)}$$

Lifshin, et al, Microscopy and Microanalysis, Nov./Dec. 1998
Ziebold, Analytical Chemistry, July 1967

Generalized Lifshin Equation

- Following derivation methods used in original Lifshin eqn.
- Calculates the StDev and SDoM for a given element
- Removes requirement that unknown and standard be collected under identical conditions
- Uses actual data variations rather than Poisson assumption

$$\sigma_{\overline{C}}^2 = \overline{C}^2\left[\frac{S^2 + S(B)^2}{n\left(\overline{N} - \overline{N}(B)\right)^2} + \frac{F^2\left(S_S{}^2 + S_S(B)^2\right)}{n'\left(\overline{N}_{SF} - \overline{N}_{SF}(B)\right)^2}\right]\left[1 - \frac{(a-1)\overline{C}}{a}\right]^2 \qquad \text{(SDoM)}$$

$$\sigma_C^2 = C^2\left[\frac{S^2 + S(B)^2}{\left(\overline{N} - \overline{N}(B)\right)^2} + \frac{F^2\left(S_S{}^2 + S_S(B)^2\right)}{\left(\overline{N}_{SF} - \overline{N}_{SF}(B)\right)^2}\right]\left[1 - \frac{(a-1)C}{a}\right]^2 \qquad \text{(StDev)}$$

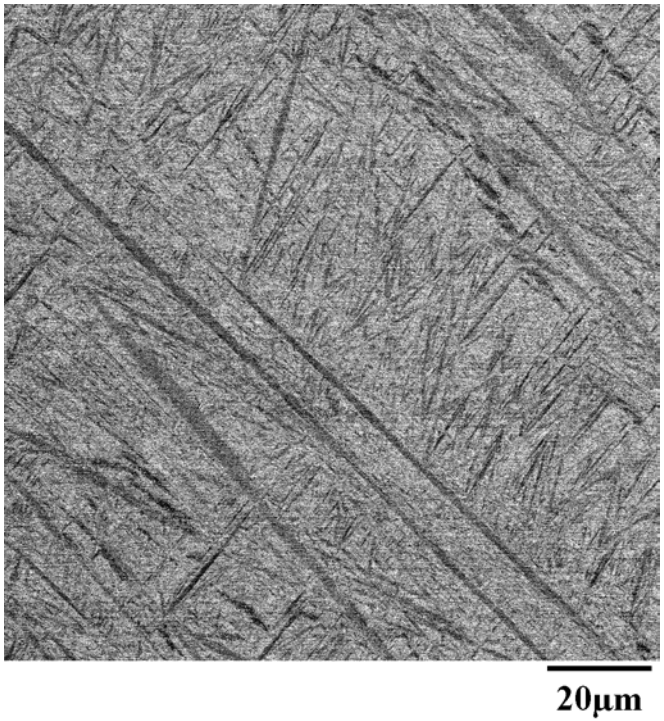
$$F = \frac{i * t}{i_s * t_s}$$

UNIVERSITY OF OREGON

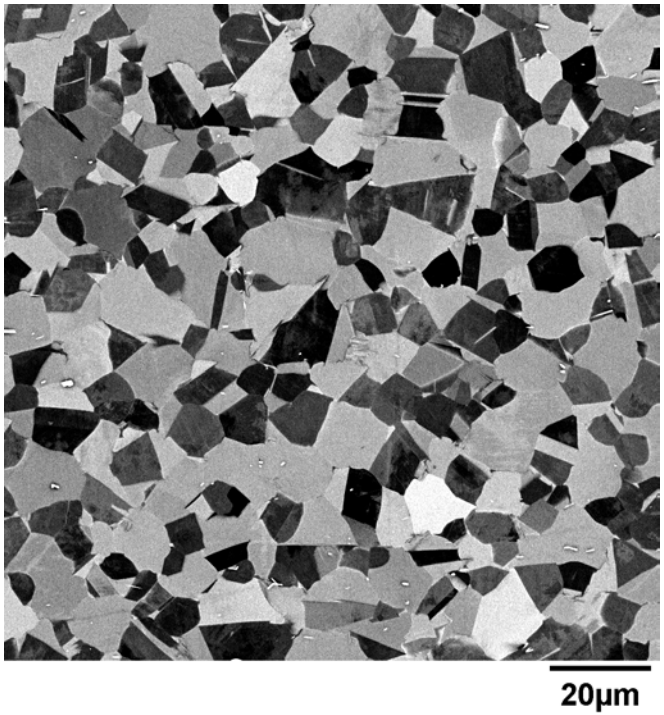
UES

Experimental

Cameca SX-100 EPMA-WDS, PAP matrix correction, 15 keV



Ti-6Al-2Mo-4-Zr-2Sn
(homogeneous)



Ti-31Al-3Mn-13Nb
(heterogeneous)

Each alloy was analyzed at 300 points (ANOVA - 10 regions, 6 locations, 5 replicates).

Results- Homogeneous Alloy

TABLE 1. Alloy 1 Mean Composition (3-Sigma Confidence Interval)

(Mean Concentration)	Al *(6.11)*	Ti *(85.93)*	Zr *(3.92)*	Mo *(2.02)*	Sn *(2.02)*	*(% wt.)*
Weight Percent DataSet	± 0.01	± 0.04	± 0.01	± 0.003	± 0.002	***(% wt.)***
Marinenko-ANOVA	± 0.02	± 0.07	± 0.04	± 0.01	± 0.009	***(% wt.)***
Revised Goldstein, et al	± 0.01	± 0.04	± 0.01	± 0.002	± 0.002	***(% wt.)***
Lifshin-Generalized	± 0.01	± 0.06	± 0.01	± 0.003	± 0.003	***(% wt.)***

TABLE 2. Alloy 1 Homogeneity Range (3-Sigma Confidence Interval)

(Mean Concentration)	Al *(6.1)*	Ti *(85.9)*	Zr *(3.9)*	Mo *(2.02)*	Sn *(2.02)*	*(% wt.)*
Weight Percent DataSet	± 0.1	± 0.6	± 0.2	± 0.04	± 0.04	***(% wt.)***
Marinenko-ANOVA	± 0.1	± 0.7	± 0.2	± 0.05	± 0.04	***(% wt.)***
Original Goldstein, et al	± 0.01	± 0.04	± 0.01	± 0.002	± 0.002	***(% wt.)***
Revised Goldstein, et al	± 0.1	± 0.6	± 0.2	± 0.04	± 0.03	***(% wt.)***
Lifshin-Generalized	± 0.1	± 0.6	± 0.2	± 0.04	± 0.04	***(% wt.)***

TABLE 3. Alloy 1 Homogeneity Level (3-Sigma Relative Uncertainty)

(Mean Concentration)	Al *(6.11)*	Ti *(85.93)*	Zr *(3.92)*	Mo *(2.02)*	Sn *(2.02)*	*(% wt.)*
Weight Percent DataSet	2%	1%	5%	2%	2%	
Marinenko-ANOVA	2%	1%	5%	2%	2%	
Original Goldstein, et al	0.1%	0.04%	0.3%	0.1%	0.1%	
Revised Goldstein, et al	2%	1%	5%	2%	2%	
Lifshin-Generalized	2%	1%	5%	2%	2%	

UNIVERSITY OF OREGON

UES

Results- Heterogeneous Alloy

TABLE 4. Alloy 2 Mean Composition (3-Sigma Confidence Interval)

	Al	Ti	Mn	Nb	
(Mean Concentration)	*(31.1)*	*(53.5)*	*(2.71)*	*(12.95)*	*(% wt.)*
Weight Percent DataSet	± 0.3	± 0.2	± 0.07	± 0.07	*(% wt.)*
Marinenko-ANOVA	± 0.2	± 0.2	± 0.06	± 0.1	*(% wt.)*
Revised Goldstein, et al	± 0.3	± 0.3	± 0.06	± 0.07	*(% wt.)*
Lifshin-Generalized	± 0.3	± 0.3	± 0.07	± 0.07	*(% wt.)*

TABLE 5. Alloy 2 Homogeneity Range (3-Sigma Confidence Interval)

	Al	Ti	Mn	Nb	
(Mean Concentration)	*(31)*	*(53)*	*(3)*	*(13)*	*(% wt.)*
Weight Percent DataSet	± 5	± 4	± 1	± 1	*(% wt.)*
Marinenko-ANOVA	± 6	± 4	± 1	± 1	*(% wt.)*
Original Goldstein, et al	± 0.3	± 0.3	± 0.06	± 0.07	*(% wt.)*
Revised Goldstein, et al	± 6	± 4	± 1	± 1	*(% wt.)*
Lifshin-Generalized	± 5	± 4	± 1	± 1	*(% wt.)*

TABLE 6. Alloy 2 Homogeneity Level (3-Sigma Relative Uncertainty)

	Al	Ti	Mn	Nb	
(Mean Concentration)	*(31.06)*	*(53.50)*	*(2.71)*	*(12.95)*	*(% wt.)*
Weight Percent DataSet	17%	7%	45%	9%	
Marinenko-ANOVA	19%	8%	45%	9%	
Original Goldstein, et al	1%	0.5%	2%	1%	
Revised Goldstein, et al	18%	8%	39%	9%	
Lifshin-Generalized	17%	7%	45%	9%	

UNIVERSITY OF OREGON

UES

Conclusions

- Sqrt (n) term should be removed from denominator of Goldstein, et al Eqn.

- Lifshin equation can be generalized (use heterogeneity studies, remove the Poisson assumptions)

- The new equations are in agreement with the bench marks (NIST-ANOVA, Weight %)