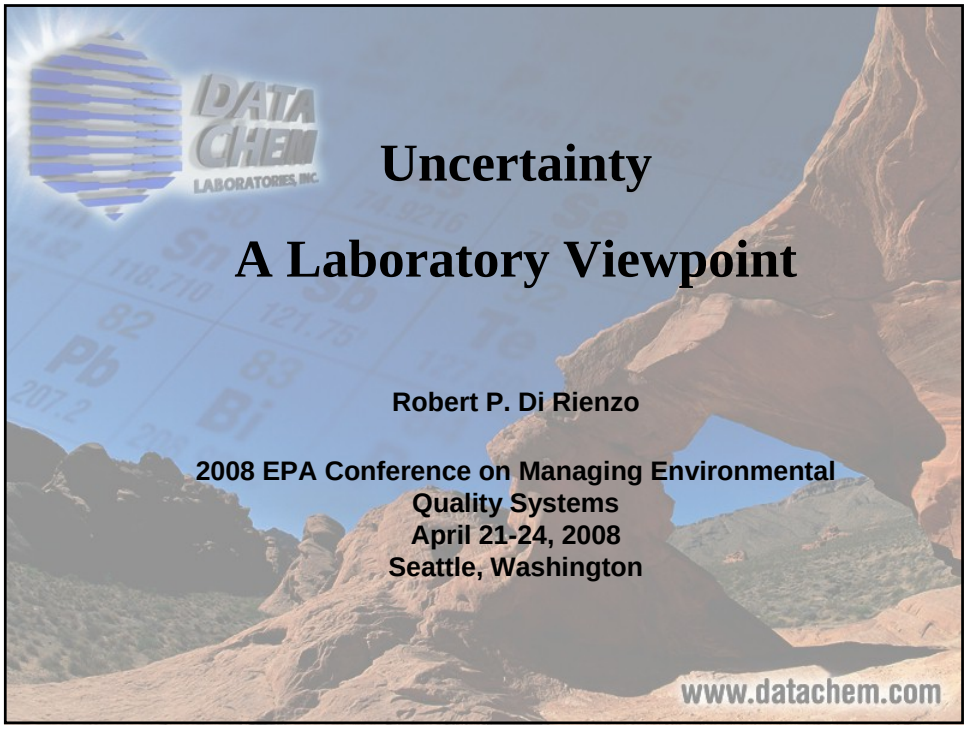
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Uncertainty
A Laboratory Viewpoint
Robert P. Di Rienzo
2008 EPA Conference on Managing Environmental Quality Systems
April 21-24, 2008
Seattle, Washington
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Overview
• Definitions
• Components of Uncertainty
• Analytical Testing Uncertainty
❖ References
❖ Sources of Error
❖ Estimation of Uncertainty
• Sample Preparation
❖ References
❖ Sources of Error
❖ Laboratory Procedures
• Conclusions
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**Measurement uncertainty narrows down the difference between the actually measured value and the true value. The result of a measurement comprises two parts: an estimate of the true value and the uncertainty of this estimate.**

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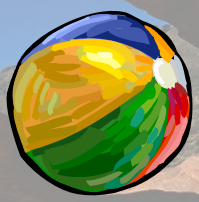

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Every measurement has a degree of uncertainty associated with it. The uncertainty derives from the measuring device and from the skill of the person doing the measuring.
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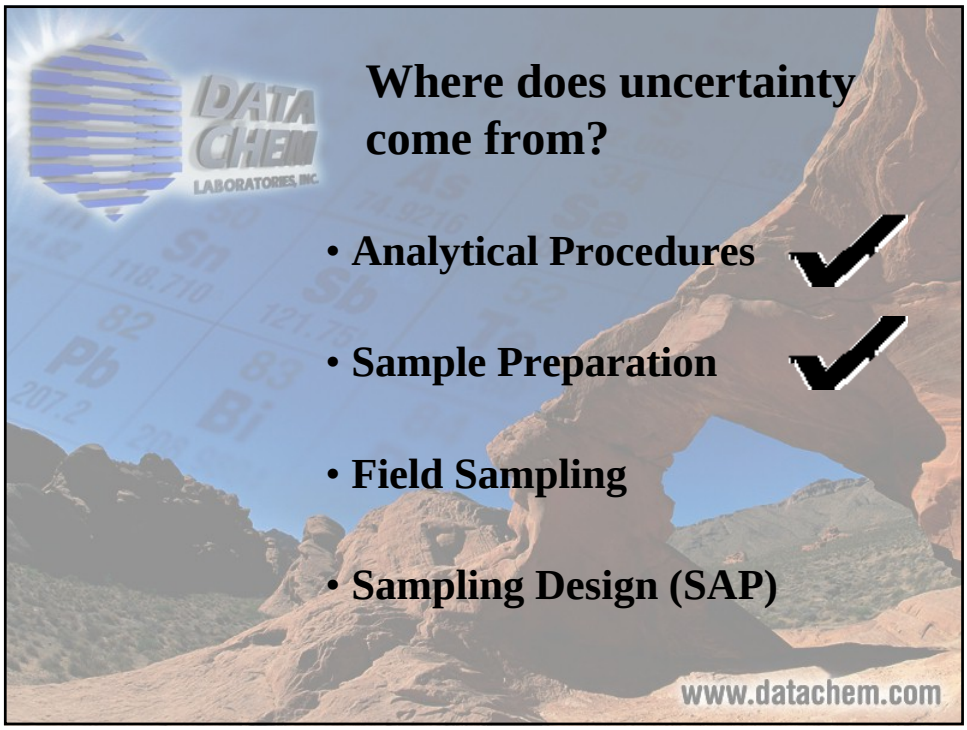
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Where does uncertainty come from?
• Analytical Procedures
• Sample Preparation
• Field Sampling
• Sampling Design (SAP)
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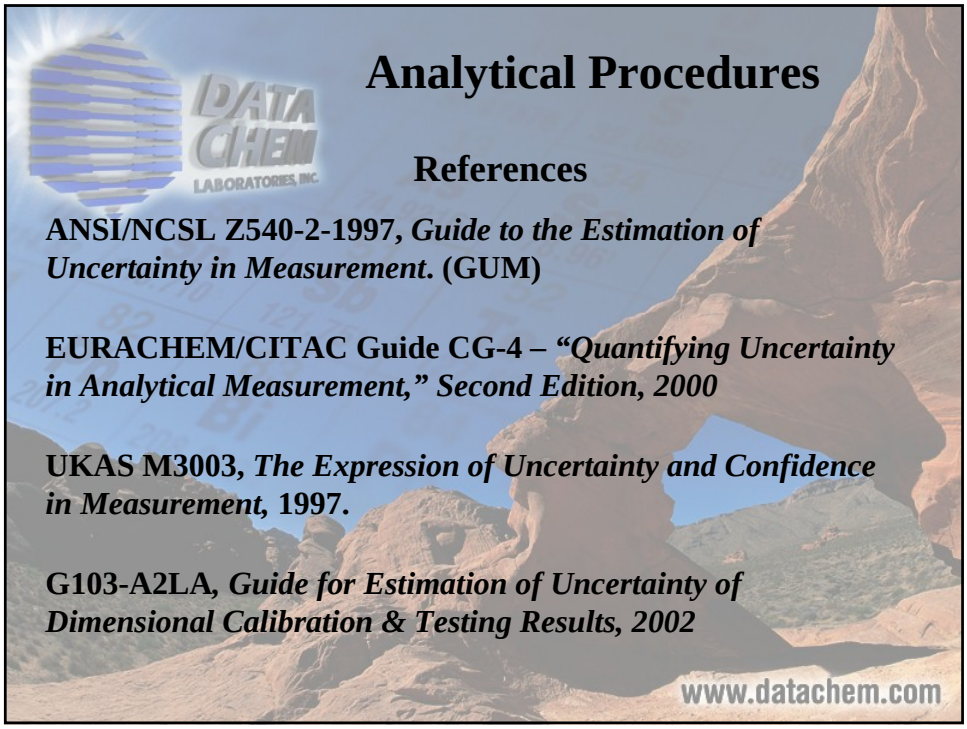
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ANSI/NCSL Z540-2-1997, Guide to the Estimation of Uncertainty in Measurement. (GUM)
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UKAS M3003, The Expression of Uncertainty and Confidence in Measurement, 1997.
G103-A2LA, Guide for Estimation of Uncertainty of Dimensional Calibration & Testing Results, 2002
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http://www.eurachem.org/
http://www.measurementuncertainty.org/
http://physics.nist.gov/cuu/Uncertainty/index.html
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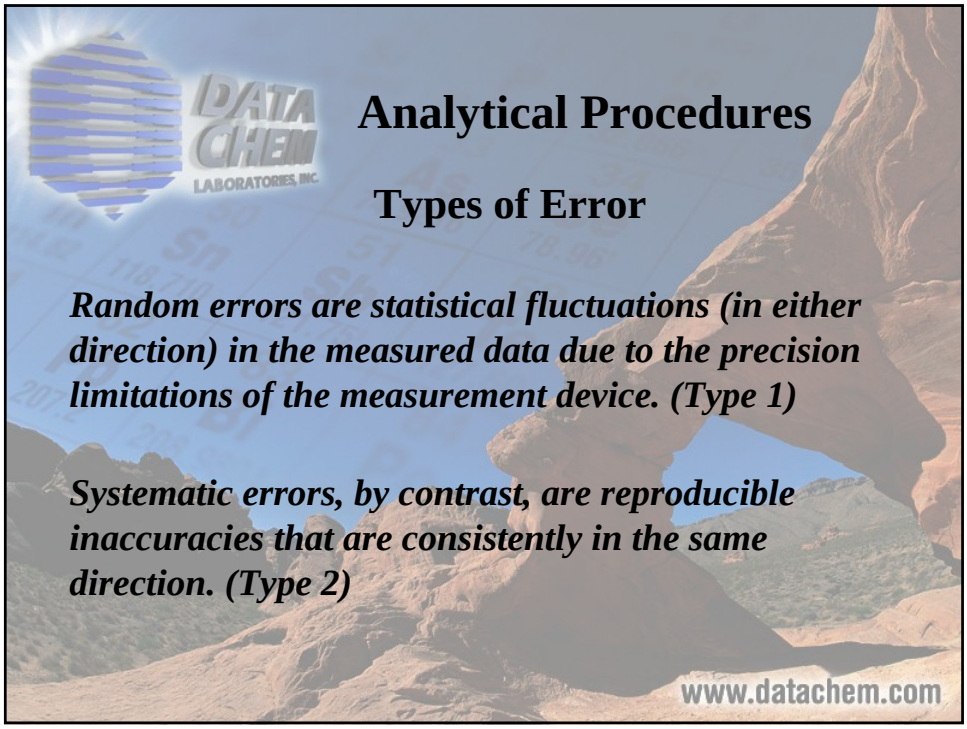
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Types of Error
Random errors are statistical fluctuations (in either direction) in the measured data due to the precision limitations of the measurement device. (Type 1)
Systematic errors, by contrast, are reproducible inaccuracies that are consistently in the same direction. (Type 2)
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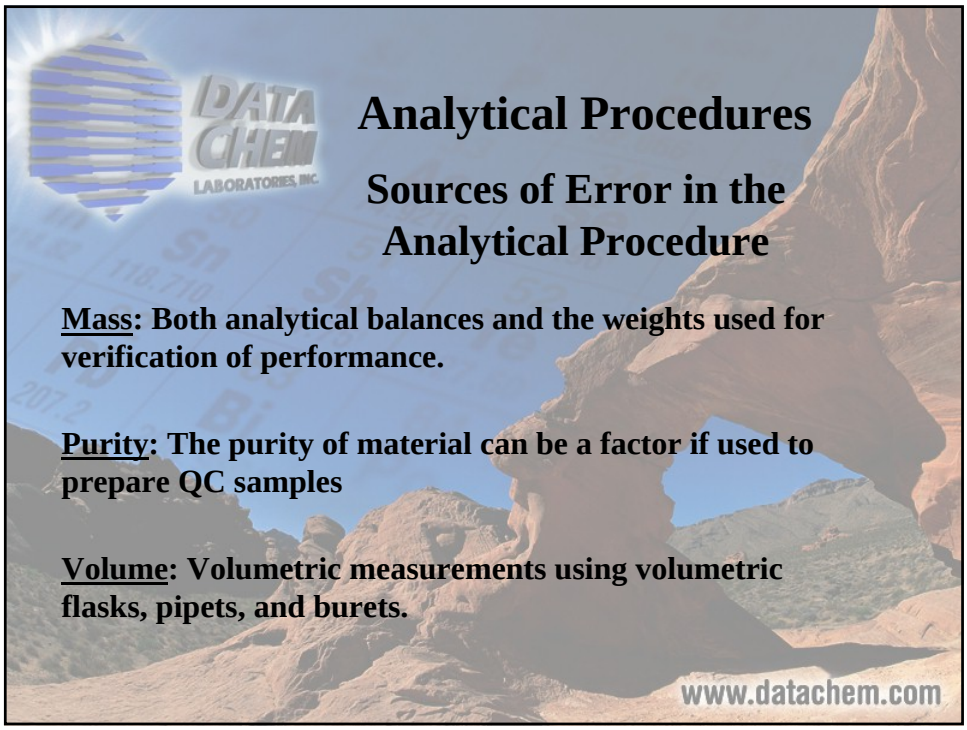
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Sources of Error in the Analytical Procedure
Mass: Both analytical balances and the weights used for verification of performance.
Purity: The purity of material can be a factor if used to prepare QC samples
Volume: Volumetric measurements using volumetric flasks, pipets, and burets.
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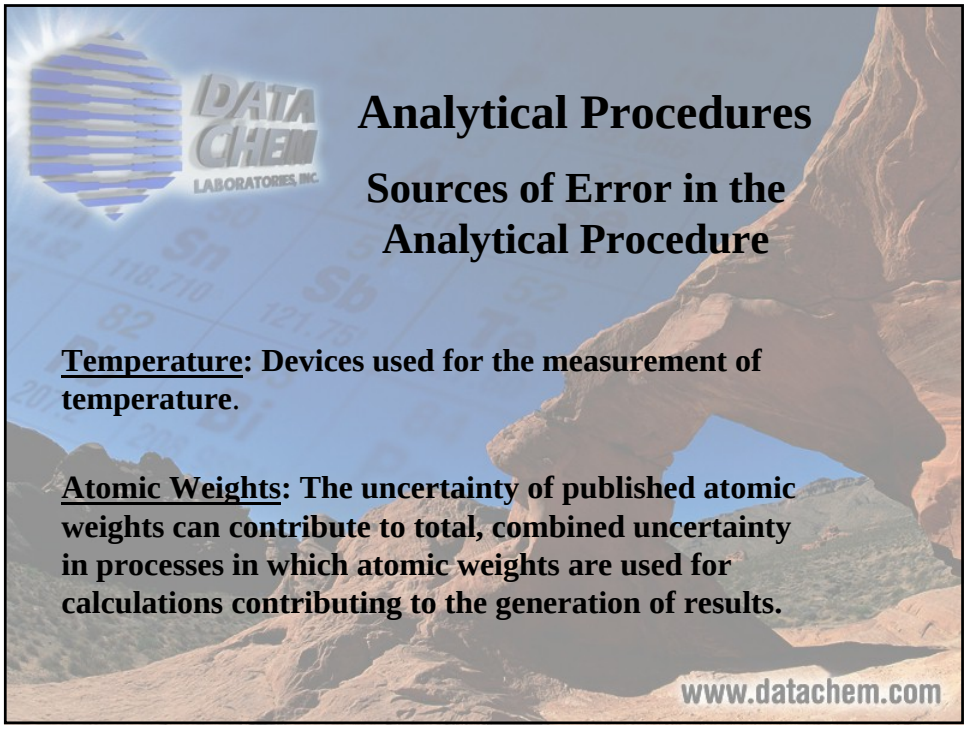
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Analytical Procedures
Sources of Error in the Analytical Procedure
Temperature: Devices used for the measurement of temperature.
Atomic Weights: The uncertainty of published atomic weights can contribute to total, combined uncertainty in processes in which atomic weights are used for calculations contributing to the generation of results.
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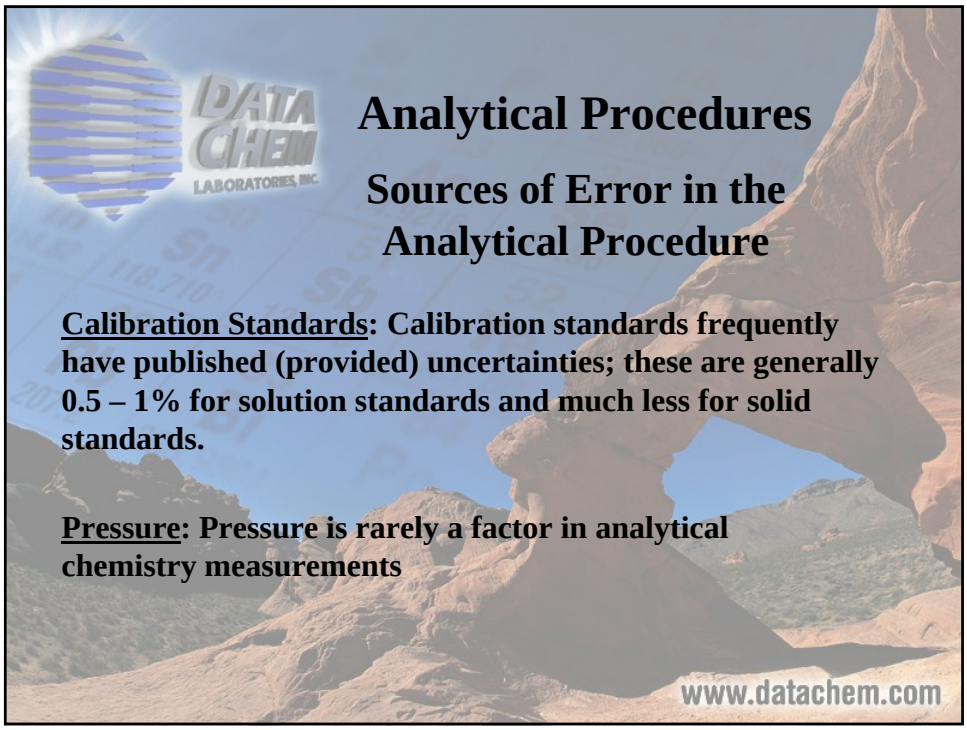
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Sources of Error in the Analytical Procedure
Calibration Standards: Calibration standards frequently have published (provided) uncertainties; these are generally 0.5 – 1% for solution standards and much less for solid standards.
Pressure: Pressure is rarely a factor in analytical chemistry measurements
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# Analytical Procedures

## Sources of Error in the Analytical Procedure

**Standardization Process: The standardization process for most instrumental analyses introduces uncertainty because of the inexact nature of the process.**

**Instrumentation Sensors: Sensors have uncertainty because of lack of stability.**

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# Analytical Procedures

## Estimation of Uncertainty

**Step 1 - Identification of major sources of uncertainty for applicable types of laboratory measurements**

**Step 2 - Determination of the type of the error associated with each major source of uncertainty**

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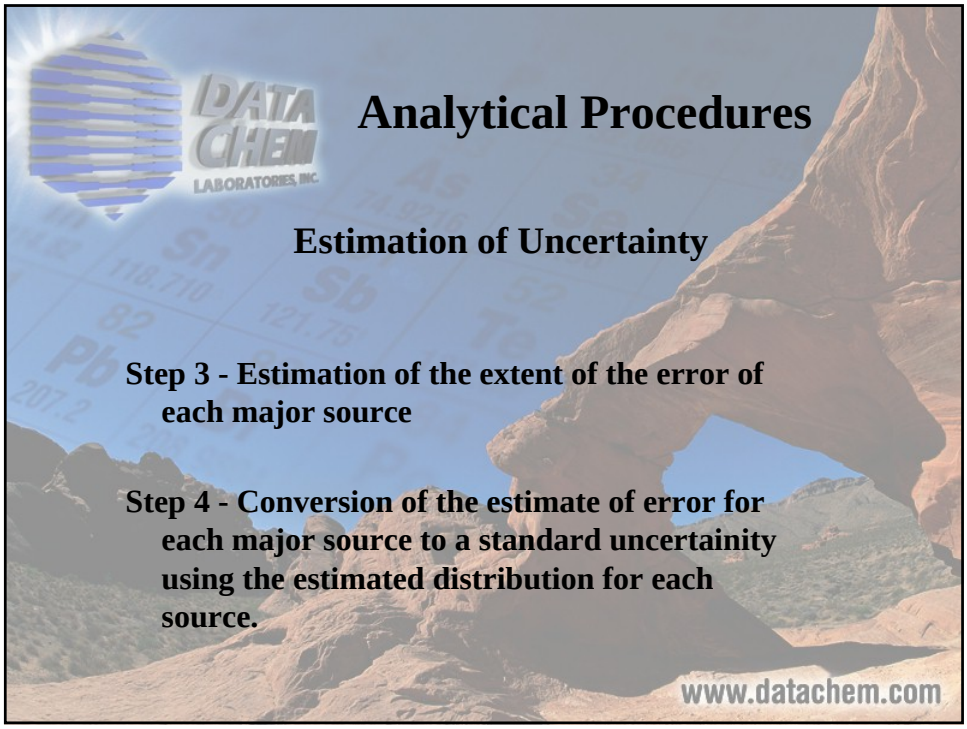
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Analytical Procedures
Estimation of Uncertainty
Step 3 - Estimation of the extent of the error of each major source
Step 4 - Conversion of the estimate of error for each major source to a standard uncertainity using the estimated distribution for each source.
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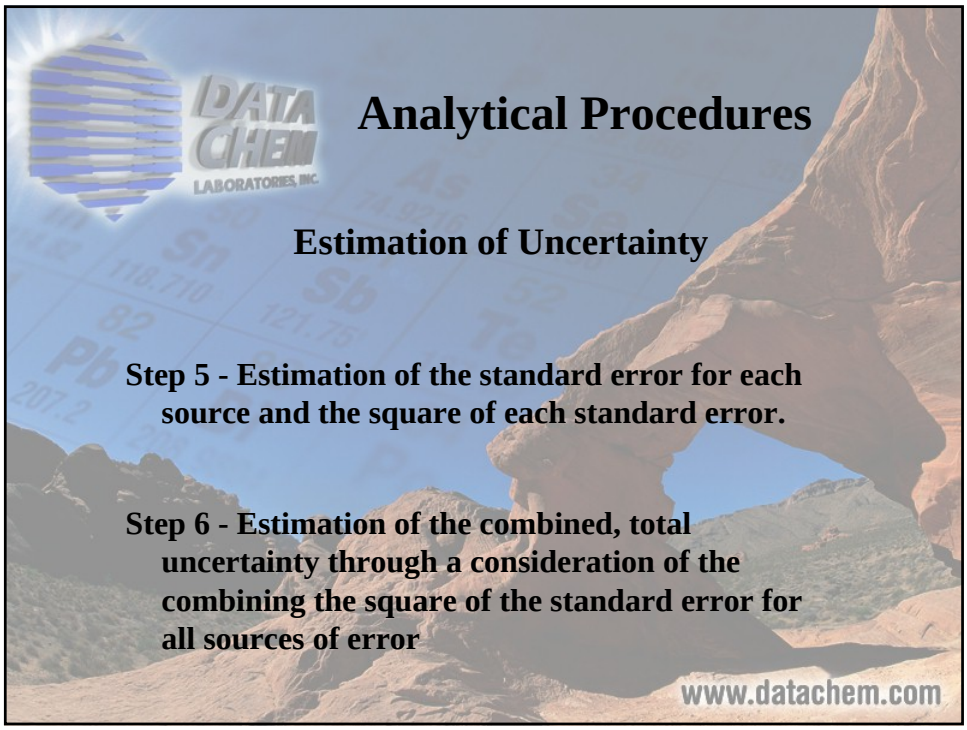
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Analytical Procedures
Estimation of Uncertainty
Step 5 - Estimation of the standard error for each source and the square of each standard error.
Step 6 - Estimation of the combined, total uncertainty through a consideration of the combining the square of the standard error for all sources of error
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## Analytical Procedures

| Source | Estimate of Error | Type of Error | Standard Error | Square of the Standard Error |
|---|---|---|---|---|
| Mass | 0.03 | 1 | 0.03 | 0.0009 |
| Volume | 0.05 | 1 | 0.05 | 0.0025 |
| Temperature | 0.012 | 1 | 0.012 | 0.0001 |
| Calibration Standards | 1 | 2 | 0.5 | 0.25 |
| Atomic Weights | 0.02 | 2 | 0.01 | 0.0001 |
| Standardization Process | 3 | 1 | 3 | 9.0 |
| Purity | 0.1 | 2 | 0.05 | 0.0025 |
| Combined Uncertainty: | | | | 9.26 |

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## Analytical Procedures

### Estimation of Uncertainty

**Step 7 - Identification of sources of uncertainty of significant importance and of insignificant importance**

**The Standardization process, which includes instrument calibration and measurement of samples, is the most significant factor contributing to error.**

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## Analytical Procedures

### Estimation of Uncertainty

**Step 8 - Estimation of error solely from significant sources (The insignificant sources of error are not included in this estimation.)**

**Estimation of error from the standardization process can be assessed using the Quality Control Samples (Historical Control Limits).**

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## Analytical Procedures

### Estimation of Uncertainty

**Step 9 - Calculation of expanded uncertainty based only on significant sources of error**

**Result(1 ± 2S*r*)**

**Note: S*r* is the relative standard deviation (expressed as a fraction) calculated from the pertinent quality control results.**

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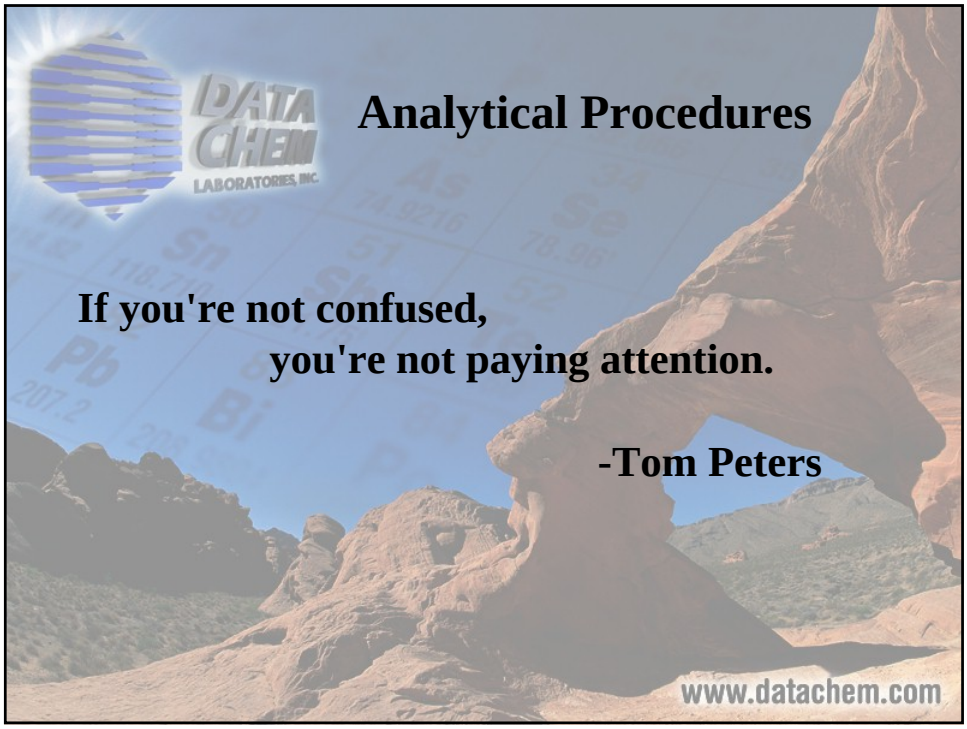
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Analytical Procedures
If you're not confused,
you're not paying attention.
-Tom Peters
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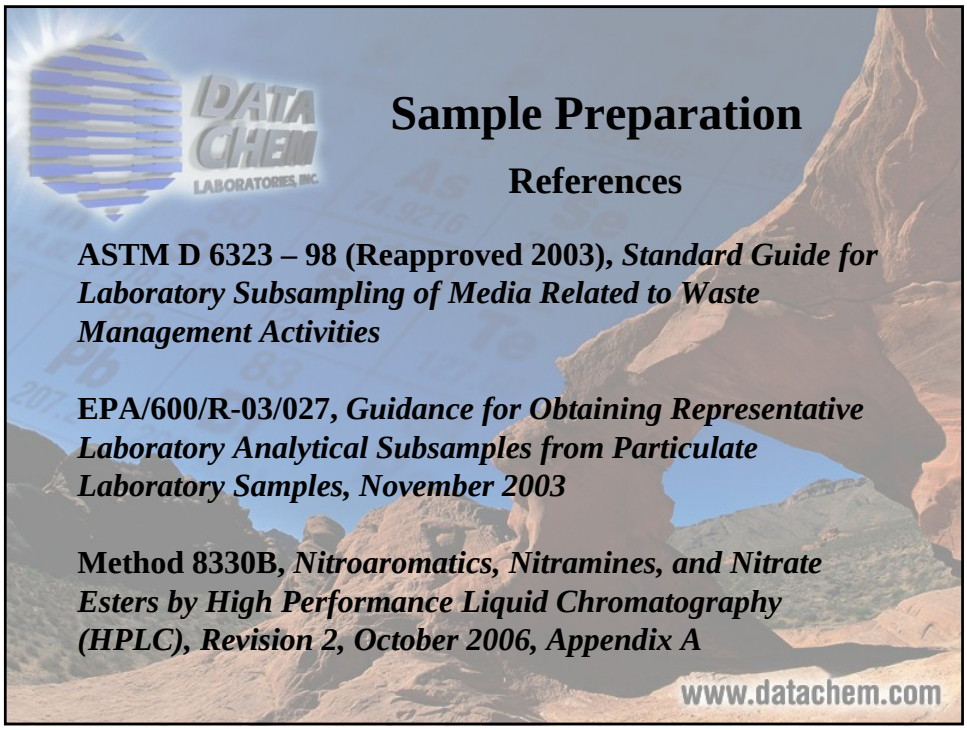
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Sample Preparation
References
ASTM D 6323 – 98 (Reapproved 2003), Standard Guide for Laboratory Subsampling of Media Related to Waste Management Activities
EPA/600/R-03/027, Guidance for Obtaining Representative Laboratory Analytical Subsamples from Particulate Laboratory Samples, November 2003
Method 8330B, Nitroaromatics, Nitramines, and Nitrate Esters by High Performance Liquid Chromatography (HPLC), Revision 2, October 2006, Appendix A
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# Sample Preparation

## Sources of Error in the Sample Preparation

- **Compositional Heterogeneity –Size, shape, physical/ chemical properties of particles**
- **Distributional Heterogeneity–Spatial grouping clumping of particles–Stratified segregation of Particles**

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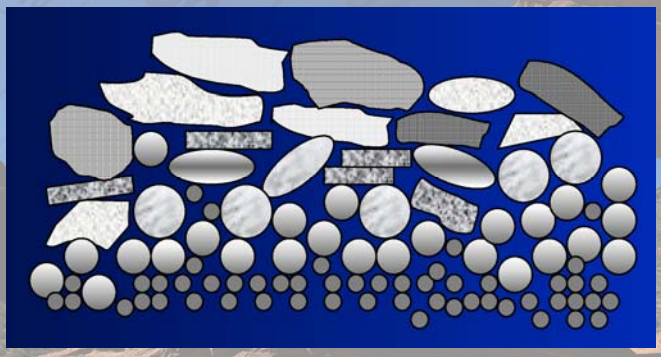
# Sample Preparation

## Compositional and Distributional Heterogeneity



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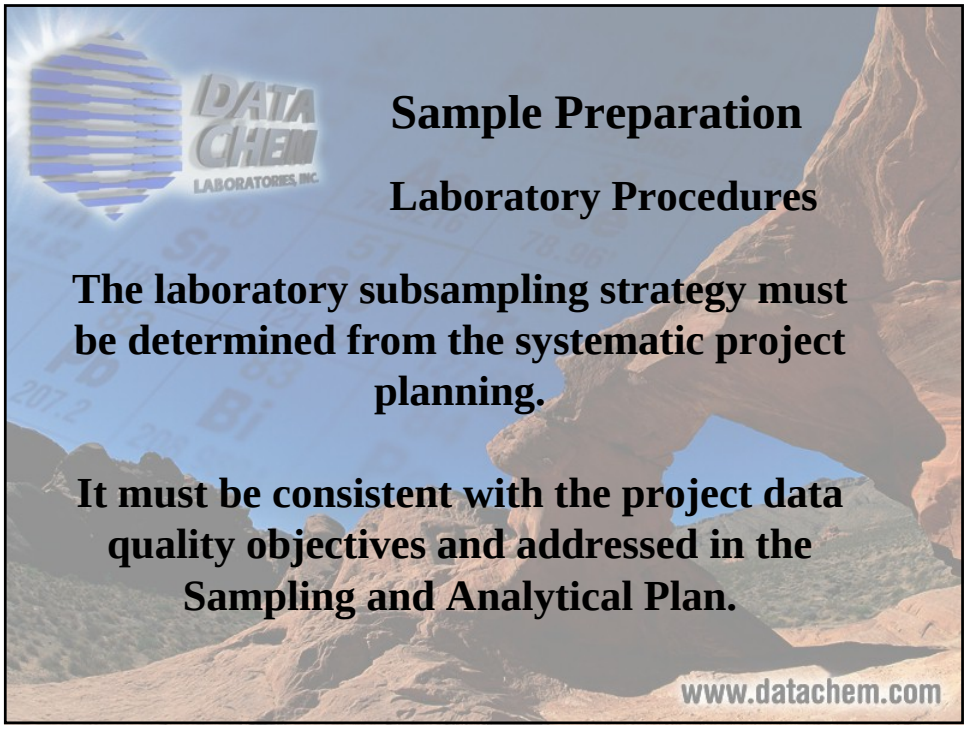
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Sample Preparation
Laboratory Procedures
The laboratory subsampling strategy must be determined from the systematic project planning.
It must be consistent with the project data quality objectives and addressed in the Sampling and Analytical Plan.
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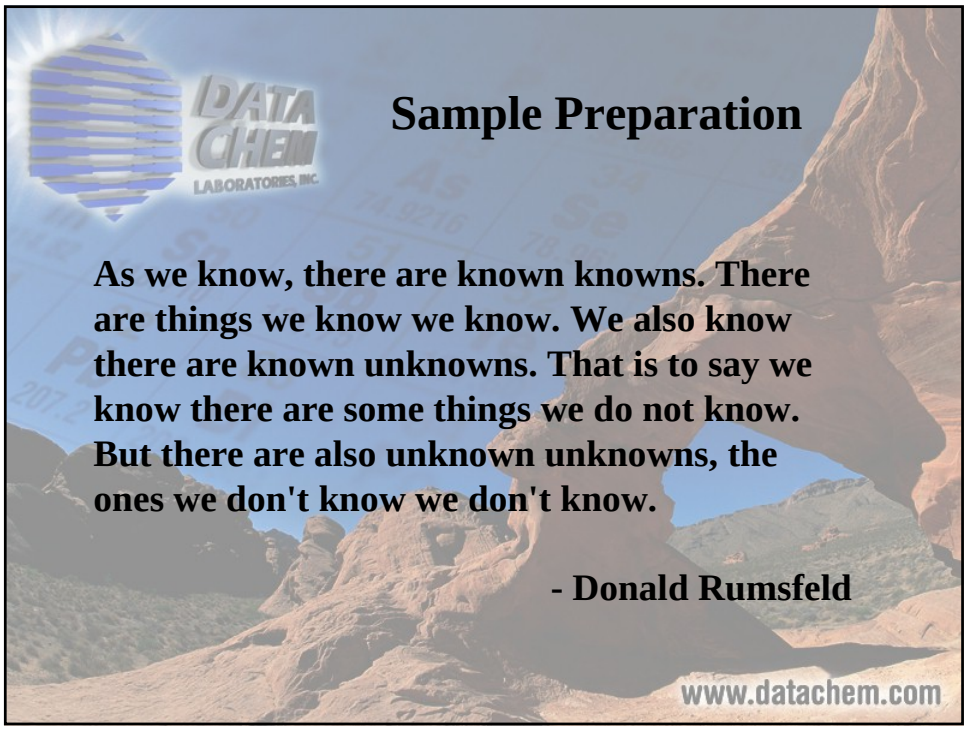
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Sample Preparation
As we know, there are known knowns. There are things we know we know. We also know there are known unknowns. That is to say we know there are some things we do not know. But there are also unknown unknowns, the ones we don't know we don't know.
- Donald Rumsfeld
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# Sample Preparation

## ASTM D 6323 Table 1 – Limitations and Advantages of Sample Preparation Options

| Instruction | Limitations | Advantages |
|---|---|---|
| Remove artifacts, such as rocks and twigs, from the sample prior to subsampling, | 1) May bias analytical results by altering contaminant concentration.<br>2) May bias sample if results are not properly weight averaged. | *1*) May be easier to subsample.<br>*2*) May be easier to analyze.<br>*3*) Appropriate if the target population is material minus artifacts. |

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# Sample Preparation

## ASTM D 6323 Table 1 – Limitations and Advantages of Sample Preparation Options

| Instruction | Limitations | Advantages |
|---|---|---|
| Dry sample | May alter chemistry or change stability of some compounds. | *1*) Allows for consistency of subsampling for liquid/solid mixtures.<br>*2*) Analytes reported unbiased by moisture content. |

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# Sample Preparation

**ASTM D 6323 Table 1 – Limitations and Advantages of Sample Preparation Options**

| Instruction | Limitations | Advantages |
|---|---|---|
| Reduce particle size | *1*) Increasing surface area may effect data in some procedure with particle digestion or extraction.<br>*2*) May be difficult, depending on matrix. | Allows for consistency of subsampling. |

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# Conclusions

**There are three kinds of lies: lies, damned lies and statistics.**

**- Benjamin Disraeli**

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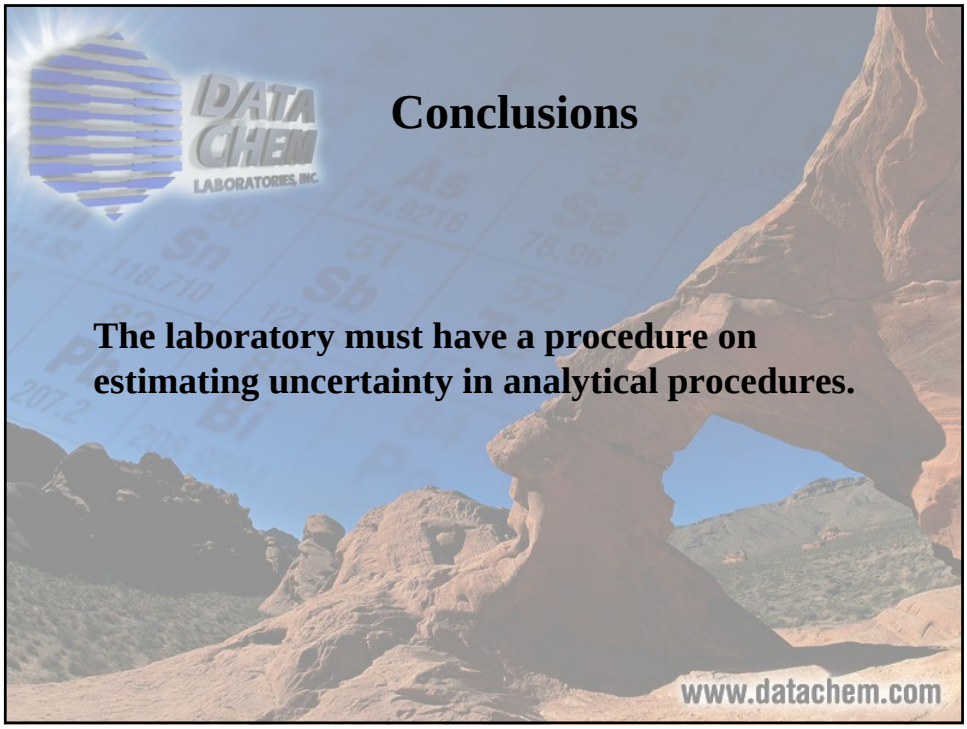
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Conclusions
The laboratory must have a procedure on estimating uncertainty in analytical procedures.
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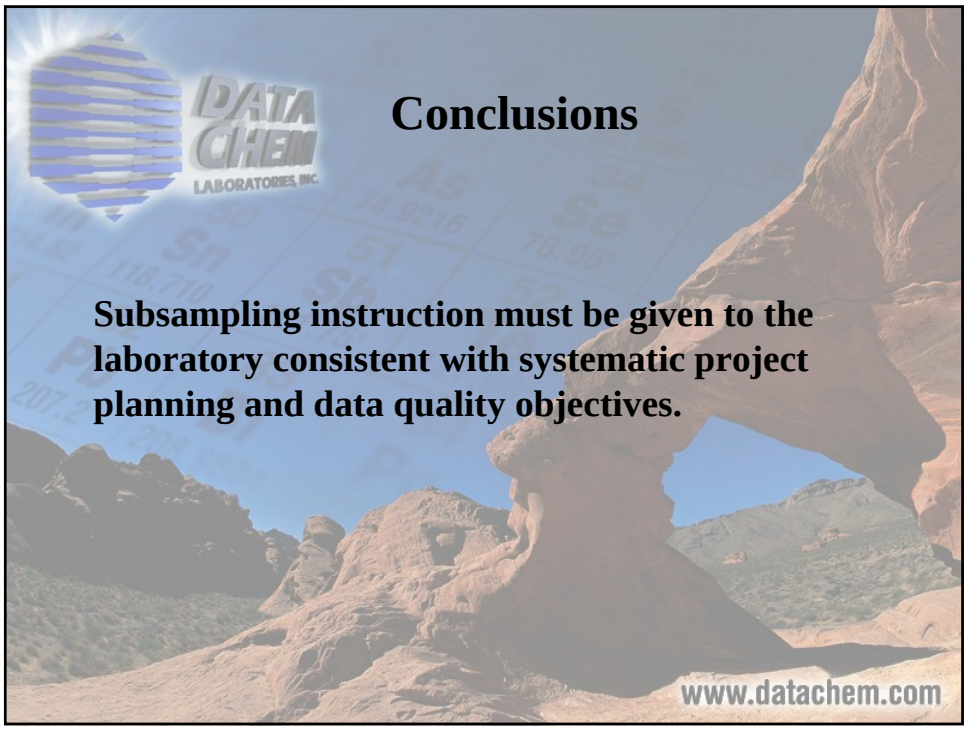
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Conclusions
Subsampling instruction must be given to the laboratory consistent with systematic project planning and data quality objectives.
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# Conclusions

## Sources of Error

| | |
|---|---|
| **Field Sampling and Sample Design** | **Up to 1000%[1]** |
| **Sample Preparation** | ***50%* of Sampling Error? Proportional** |
| **Analysis** | **2% to 20%[1]** |

**1** - Industrial Waste Dumps, Sampling and Analysis, Encyclopedia of Analytical Chemistry, 2000

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# Conclusions

**Up to now, the estimation of uncertainty efforts have been a laboratory issue and have helped to improve laboratory performance.**

**Analytical uncertainty is insignificant to the total measurement uncertainty.**

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