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A new Standard Guide for the development and Optimization of chemical methods for compliance reporting

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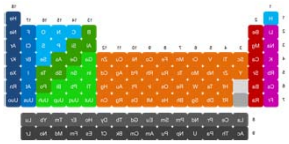
ASTM D8272 is a new guide to provide guidance to method developers



Analyte Selection and Scope

Sampling and Sample Preservation

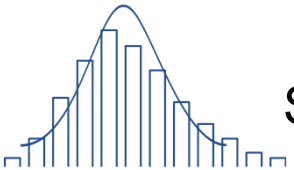
Digestion and Extraction

Calibration and Linearity

Holding time and shelf life studies

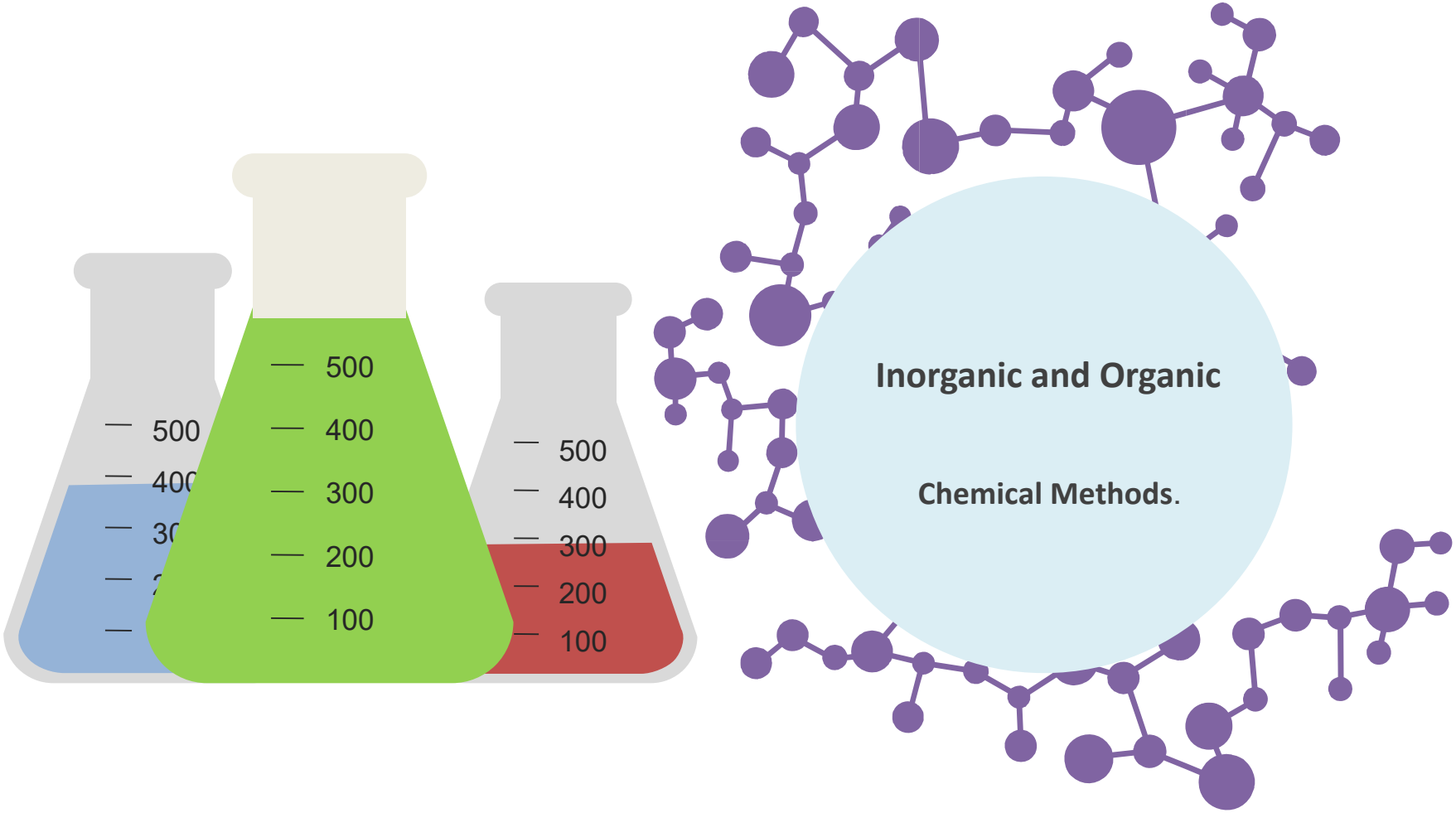
Interferences

Quantitation and Quality Control



Single lab validations

The guide is limited to ASTM Subcommittees D19.05 and D19.06



Definitions specific to the guide

development (of a method), n –an empirical series of steps that determine how to set up and run a chemical operation.

optimization (of a method), n- a series of experiments consisting of systematic variations in an attempt to define critical steps of a new or modified test method in which important errors can be made.
Discussion – Optimization helps define the exact steps an analyst should take to ensure data obtained meets the accuracy and precision requirements of the method.

validation (of an analytical method), n—confirmation, by the provision of objective evidence and examination, that a method meets performance requirements and is suitable for its intended use. .
Discussion – Method validation is a practice performed by laboratories to demonstrate their capability of obtaining results that meet the specifications of the method. In environmental testing, method validation usually consists of establishing the calibration range, determination of minimum detectable concentration, and determination of precision and bias.

Development and Optimization → happens before a method is published
Validation → happens before a lab runs a published method

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All ASTM Methods are required to have a precision and bias statement

- Statements of precision and bias in test methods are required by the Form and Style for ASTM Standards, Section A21. Precision and Bias (Mandatory).

- Section A21.2.2 states “Precision shall be estimated in accordance with the interlaboratory test program prescribed in Practice E691, Conducting an Interlaboratory Study to Determine the Precision of a Test Method, or by an interlaboratory test program that yields equivalent information, for example, a standard practice developed by an ASTM technical committee”.

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ASTM Committee D19 uses Practice D2777 for conducting inter-laboratory studies

- Practice D2777, Section 1.2, requires a task group proposing a new method to carry out a collaborative study from which concentration limits, repeatability and reproducibility precision and bias statements are developed.
- Practice D2777 Section 6.1 assumes the method has already been optimized prior to conducting the collaborative study.
- Practice D2777 Section 4, Summary of Practice, requires a collaborative study only after the task group has assured itself that preliminary evaluation work is complete and the method has been written in its final form.

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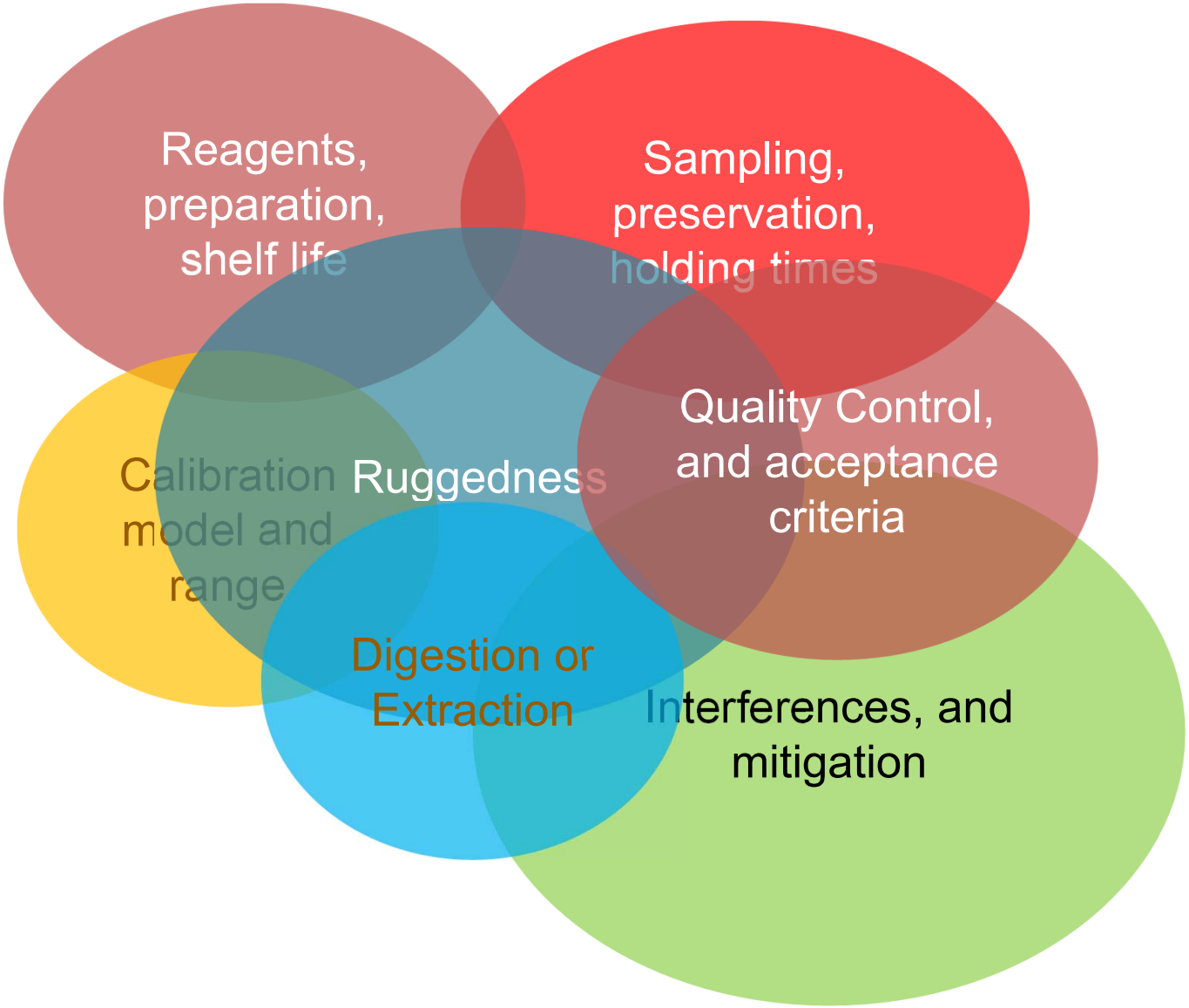
Practice D2777 requires considerable pilot work on variables, such as:



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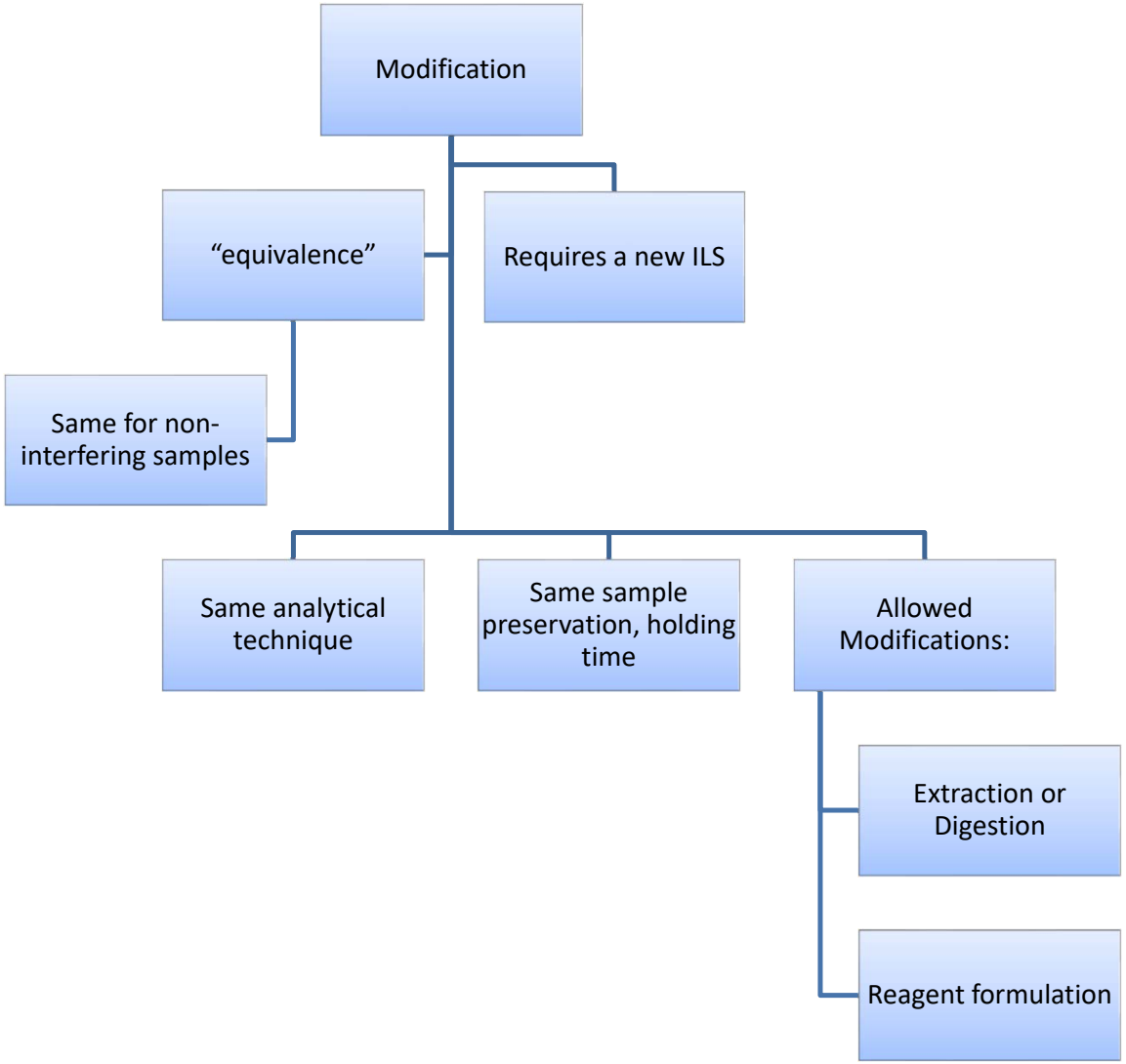
Modification of an existing method still requires a single lab study and ILS



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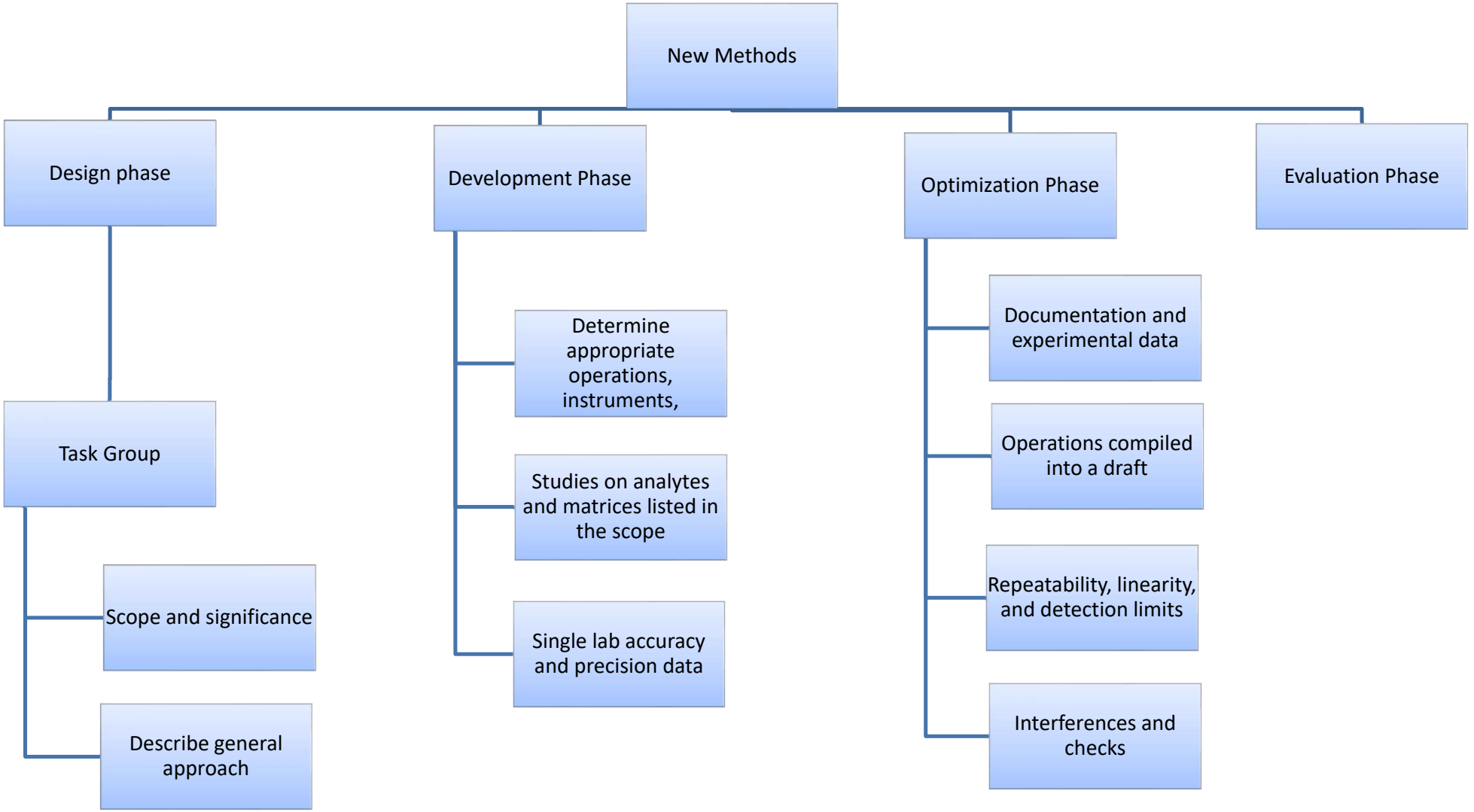
New methods require extensive development and optimization



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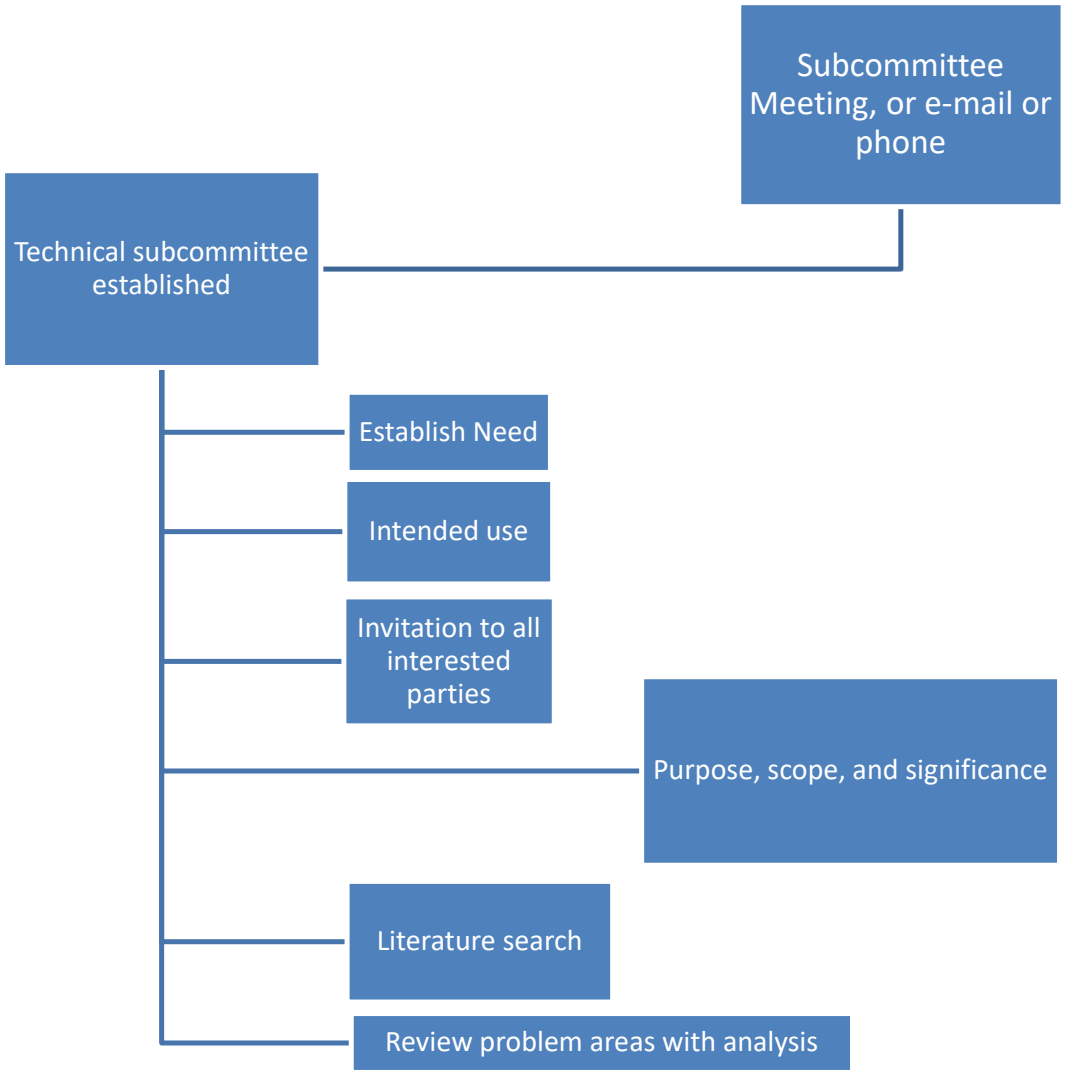
Design Phase – Beginning a new method



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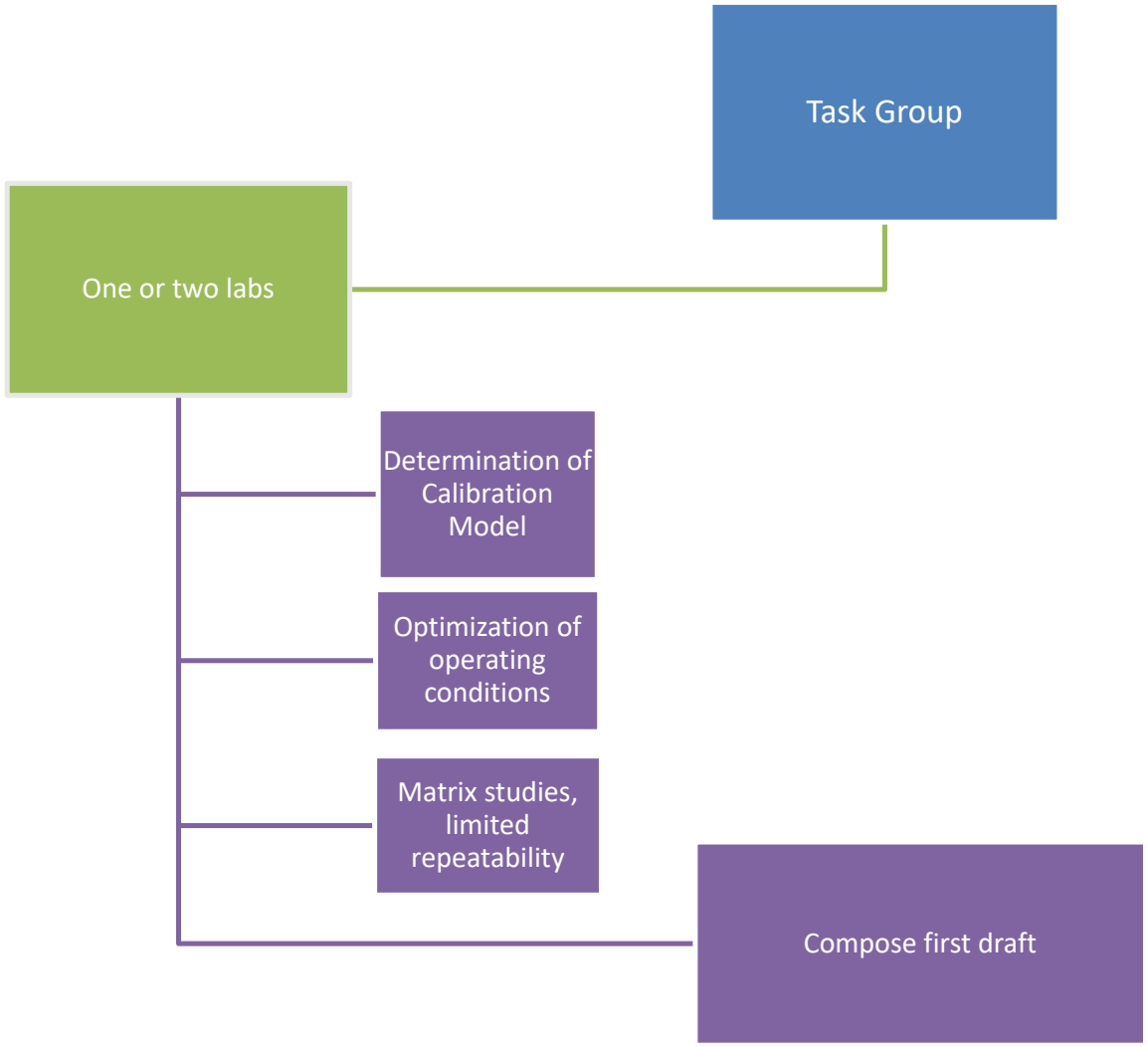
Development phase – Determine appropriate matrices, calibration, limited studies



Optimization Phase - develop the method and determine performance characteristics

Selectivity

Calibration

Bias

Repeatability

Quantitation Limits

Sample Collection and Preservation

Reagent preparation and storage

Ruggedness

Selectivity are other constituents that may also respond

- Test matrix blanks and fortified matrix blanks preferably at three or more different concentrations spanning the expected range of the method.
- Repeat with synthetic or actual matrices containing expected interferences.
- If possible, devise spot tests enabling rapid checks for interferences.
- Use Table 1 and Table 2 for examples of matrices
- Document any interference and their upper concentration limits
- Analyze any available Certified Reference Materials (CRM)

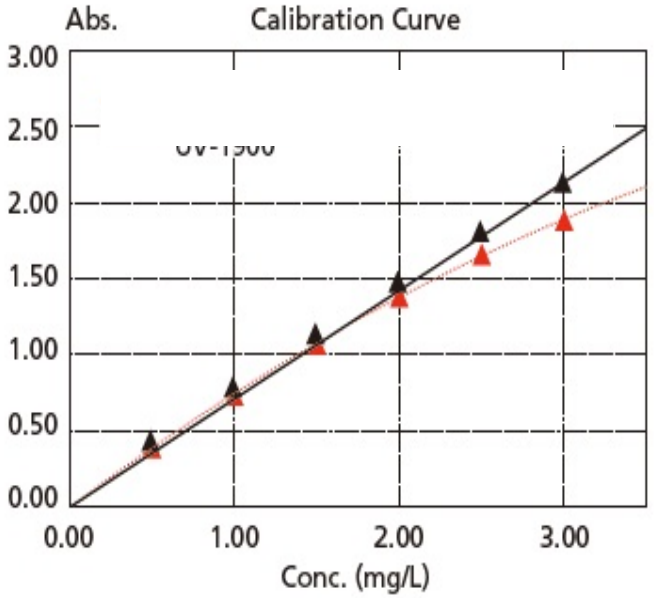


Table 1 – Examples of Representative Wastewater Matrices

POTW effluent
Synthetic Ocean Water (Practice D1141)
Soil Extract (if soil extracts may be analyzed by the method or else add another POTW)
Groundwater (> 500 ppm TDS), may be 500 mg/L TDS of Synthetic Ocean Water in Reagent Water
Surface water (> 2 ppm TOC), may be reagent water with 2 ppm TOC from humic acid
Drinking Water
Municipal POTW pretreatment
Industrial effluent - treated
Industrial effluent - treated

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Table 2 – Representative Matrices for Drinking water testing

Finished tap water
Surface water (containing about 2 mg/L organic matter as humic acid). Assumes target analyte not a constituent of humic acid.
Ground water (containing about 500 mg/L TDS)

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Calibration – Determine the appropriate calibration or standardization model

- **Define the calibration technique and calibration model.**
- **Allow the calibration model to fit the data.**
- **If feasible, measure each calibration level in triplicate (replicated) to evaluate random error associated with instrument response.**

- **If a titration or gravimetric method, describe necessary steps to standardize reagents, or obtain accurate weights on the balance.**
  - For example, the average of four replicate determinations of Normality results in a value with ½ the random error of a single titration.
  - In addition, test different volumes of sample to document effect on sample size.

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Guidelines for determination of the appropriate calibration model, based on single lab study

Recovery of mid range Spikes (all evaluated matrices)	RSD	Calibration Model
70 – 130 %	≤ 20%	External Standard
< 70 %	≤ 20%	External Standard [1]
> 130 %		Reject the analyte or modify the extraction
70 – 130 %	> 20%	Use internal standard calibration, or isotope dilution (if isotopes are available)

[1] External Standard Calibration is appropriate, however, consider rejecting the analyte or modifying the extraction

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Bias – Evaluate systematic errors comparing replicates with known values

- Plot method results of up to nine different matrices analyzed at up to five different concentrations against known spiked values.
- Prepare a scatter plot for each matrix, and insert a regression line with equations (Practice E3080-17).
- Slopes should be normally distributed with no outliers (E178).
- Another option is to overlay each regression line in one plot.
- The lines from each matrix should overlay within the precision of replicates from a clean matrix.
- An outlying slope is easily detected visually.

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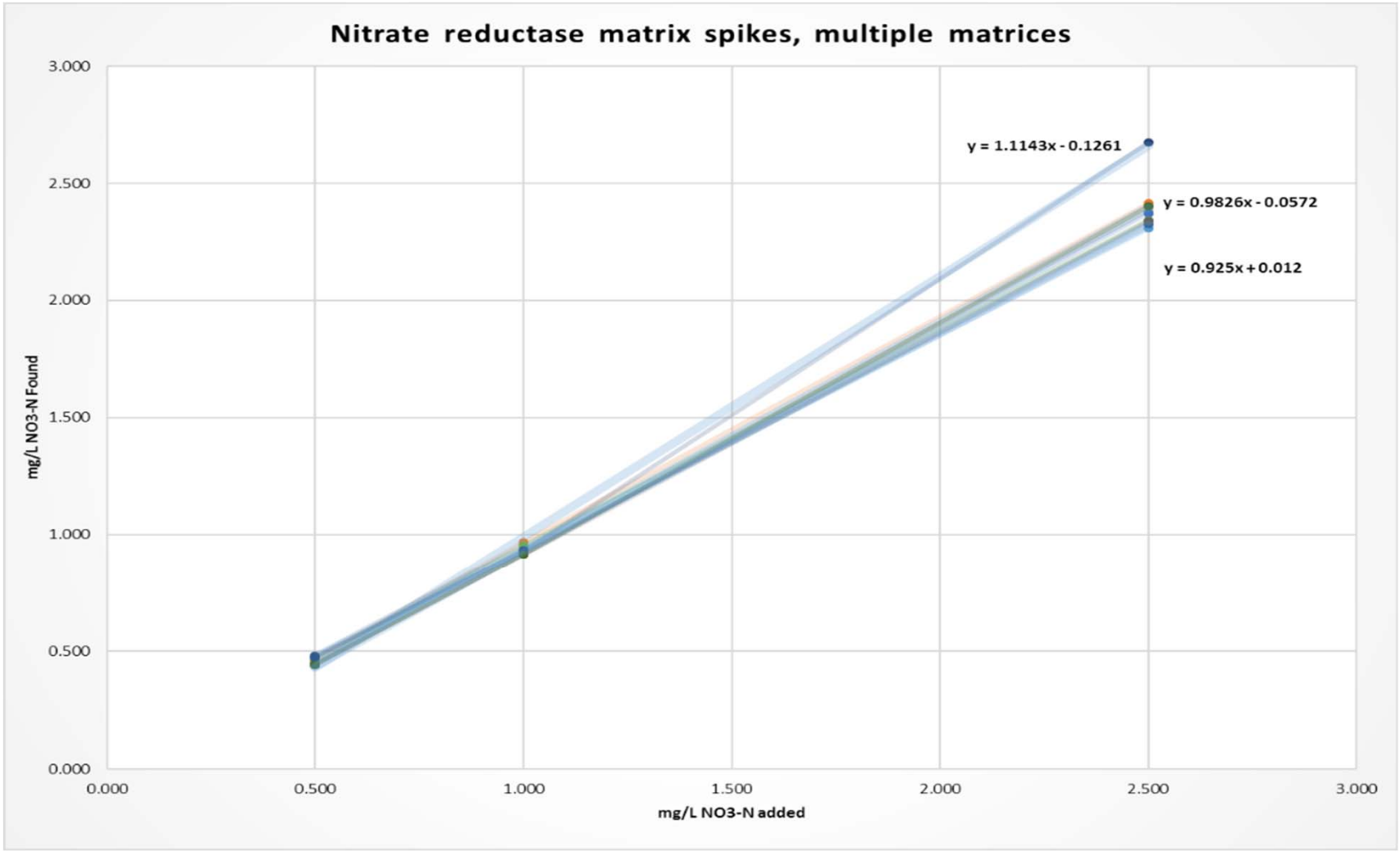
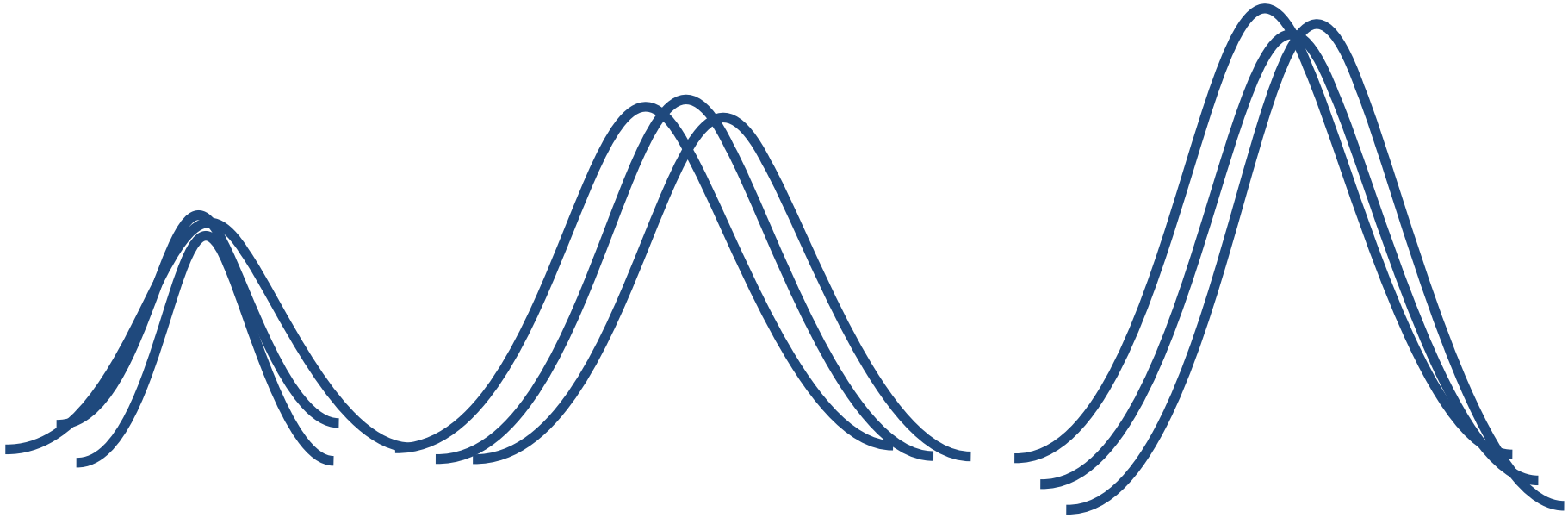
Overlay plot of nitrate spikes of three concentrations in eleven matrices



Repeatability – analyze consecutive replicates of each calibration standard

- Encompassing the entire range of the method and expressed as standard deviation or percentage relative standard deviation
- Evaluate the repeatability of the method in an interference free matrix.
- Then analyze three to eight consecutive measurements (same as used for bias determination) of up to nine different representative matrices to evaluate repeatability in real samples.
- Use an F-Test to compare standard deviations between matrices.
- For a better comparison, use as many replicates as possible.



Determine the LOQ and MDL

- ASTM validation for methods intended for EPA compliance monitoring should define the MDL (if applicable) according to the EPA definition.
- Follow the 40 CFR Part 136 Appendix B procedure for determining the MDL,
- or using the detection limit procedure for the applicable regulatory program.

Sample Collection and Preservation

- Conduct studies to determine minimum sample size required,
- sample container and container materials,
- preservatives,
- and holding time.
- Describe checks in the procedure for verification that preservation criteria were met.
- Follow Practice D4841 to determine holding time using different sample containers, preservatives, and storage temperatures

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Reagent Preparation and Storage

- **Conduct literature research or, preferably, shelf life studies to determine**
  - reagent containers,
  - container materials,
  - and storage temperature.
  - Note in the procedure when reagents change color,
    - a precipitate forms,
    - or when analyte response falls above or below acceptable limits.

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Perform ruggedness testing according to D1169 or similar

- **Pinpoints the variables that are associated with the performance of a standard test method and that impact the variability of the precision.**
- **If a ruggedness test is not performed prior to the actual interlaboratory study, the participants in the study may not be aware of the variables that directly impact the results of performing the method.**
- **The ruggedness test should be confined to a single laboratory in order to maximize the visibility of any variables.**
- **Examples of variables to consider include:**
  - Sampling and subsampling sample mass or volume,
  - Extraction or digestion times and solvent
  - Temperature of digestion,
  - Dilution volumes and diluents
  - Aspiration times or injection volumes

Evaluation phase = Inter-lab study

- **Draft standard should now be of sufficient form for use in an inter-laboratory study.**
- **Often balloted the draft at sub-committee level first**
- **the inter-laboratory study is to measure**
  - how well the new method operates at different laboratories/locations
  - and how large a difference in results using the method in two labs is acceptable.
  - The data collected provides guidance to users of the method on how well different instrument setups and/or users function on various materials.
  - Include a wide range of reproducible matrices, and analyte concentrations.

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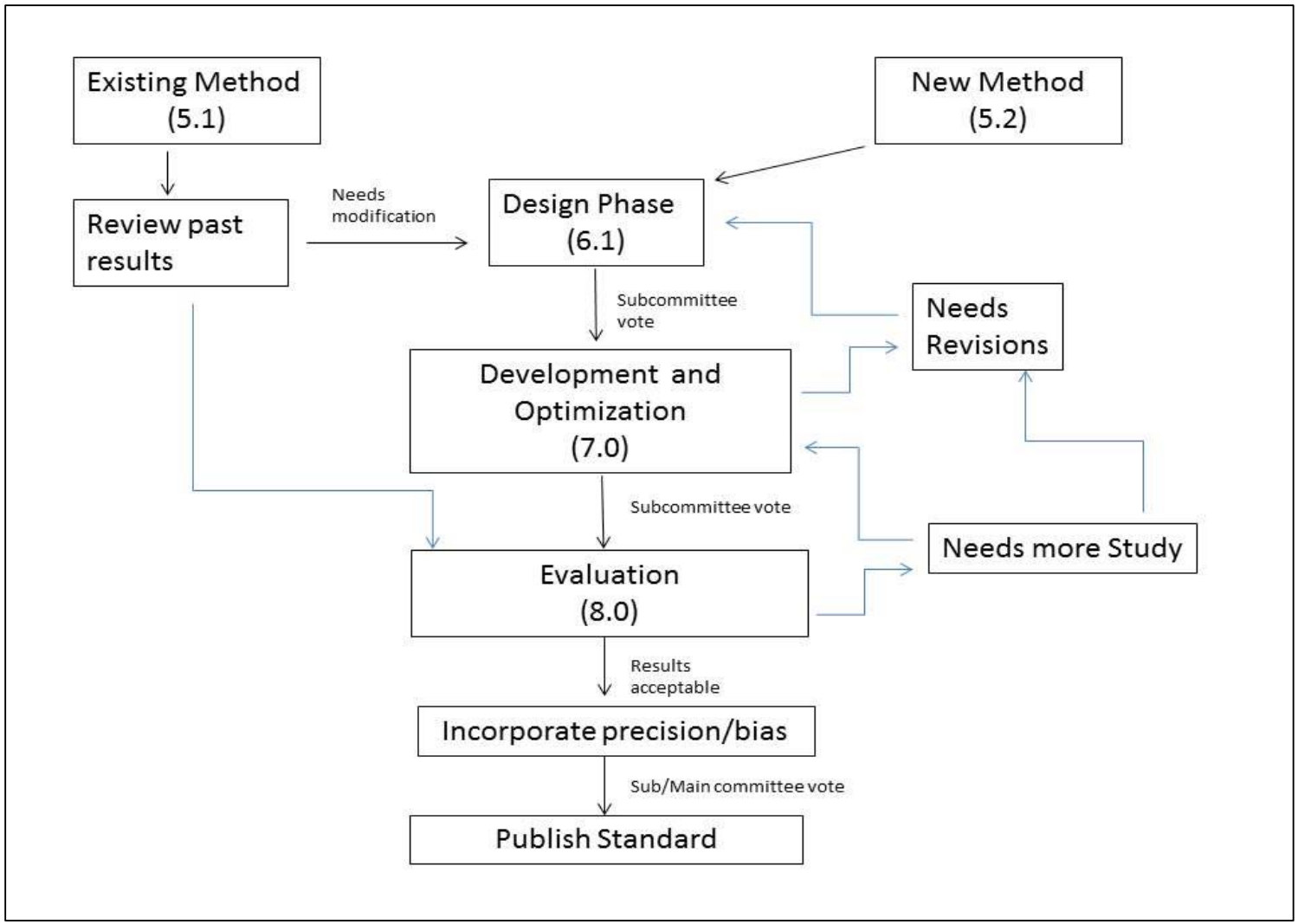
A summary of the steps, showing balloting as included in the guide



Any Questions?

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