ASTM Standard Guide for Development and Optimization of D19 Chemical Analysis Methods Intended for EPA Compliance Reporting

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Catalyst Information Resources

The Method Development, Optimization and Validation Process

- Eureka! I have an idea, but no method yet
- Preliminary Test Method
- **Optimized Test Method**
- Validated Test Method

Related ASTM Documents

- E178 Dealing with Outlying Observations
- D2777 Determination of Precision and Bias of Applicable Test Method
- D4841 Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents
- D5847 Writing Quality Control Specifications for Standard Test Methods for Water Analysis
- E691 Conducting an Inter-laboratory Study to Determine the Precision of a Test Method
- E1488 Statistical Procedures to Use in Developing and Applying Test Methods
- E1169 Conducting Ruggedness Tests
- E1601 Conducting an Interlaboratory Study to Evaluate the Performance of an Analytical Method.
- E2857 Validating Analytical Methods

Reasons for a New or Modified Method

- New analyte of concern
- Improve sensitivity
- Improve precision/accuracy
- Reduce costs
- Reduce hazardous wastes
- Improve health and safety (e.g., diazomethane)

ASTM D-19 and the ATP Process

- D-19 has many volunteers from the vendor community who have great ideas
- D-19 has a good interlaboratory validation study practice, D-2777
- D-19 has no Standard Guide for optimizing a test method before the interlaboratory validation study

Assumptions in D2777

- The method has already been optimized in a pilot prior to conducting the interlaboratory study.
- An interlaboratory study is done only after the task group has assured itself that preliminary evaluation work is complete and the method has been written in its final form.
- The interlaboratory study corroborates the method write up within the limits of the test design.
- The interlaboratory study is a fair evaluation of the inter-laboratory variability when using the method to analyze the matrices, and concentration ranges specified in the method.

Scope of New Practice

...identifies procedures for use in developing and optimizing new or modified chemical methods intended for regulatory compliance reporting in US EPA drinking water and wastewater programs. This guide may also be useful for developing methods for emerging contaminants that may not yet have regulatory requirements.

... offers an organized collection of information or a series of options and does not recommend a specific course of action. This document cannot replace education or experience and should be used in conjunction with professional judgment.

Two Options

- **Modification** – Proof of Equivalence
  - must be the same analytical technique
  - All sample preservation, holding times, sample extraction apply to the new method
  - If the method is modified to overcomes an interference, updates apparatus or comprises a technical change, a limited single lab study comparing the modified method and a new collaborative study is required.
- **New** Method
  - Design Phase
  - Development Phase
  - Optimization Phase
  - Evaluation Phase (Interlaboratory Study)

Design Phase

- An ASTM member proposes new method
- ASTM creates a task group if the method is needed.
- A rationale for the method is prepared. The rationale should include:
  - The need for the method
  - The intended use of the method
  - A list of potential stakeholders
  - An invitation to all members to join and take part
- The methods performance characteristics are documented prior to commencing development.


Bob Beimer
Bill Telliard
Bruce Colby
Larry Keith
Somebody from Texas

Performance Characteristics

- **Sensitivity**
- **Precision**
- **Bias**
- **Comparability**
- Dynamic Range
- False Positive/Negative (Selectivity)

Desirable Features

- Cost
- Time
- Capacity
- Ruggedness
- Regulatory Acceptability
- Laboratory Preference

Establishing Performance Needs

1. Ideal – Measurement Quality Objectives (MQOs) established
2. Second best alternative– Compare to arbitrary limit
3. Third best alternative – Compare to reference method performance
4. Last – Document performance obtained

Development Phase

- Conduct studies to determine the appropriate operations, instruments, reagents and variables to study or not to study further on various matrices and concentration ranges as defined in the scope.
- These studies be may single lab studies consisting of a series of smaller experiments in sequential order. Or preferably, several members of the task group study and test available options.
- The draft test method is prepared in ASTM format with preliminary test results on samples reference materials presented at a meeting.

Optimization Phase

- Use statistically controlled procedures to systematically and progressively record and compare the outcome of experiments to create a series of operations.
  - sample collection and preservation,
  - holding time,
  - reagent preparation and shelf life,
  - contributions to variability,
  - interferences and interference checks,
  - calibration range, and
  - method detection limit studies.
- Perform repeatability tests consisting of seven spikes at a minimum of three concentrations in all applicable matrices.

Optimization Phase (Cont.)

- Conduct preliminary multiple laboratory variability studies.
- Prepare provisional precision and bias statements. Perform ruggedness testing, eliminating flexibility for a user to modify significant variables.
- Include a quality control section with acceptance limits based preliminary data.
- The draft method should now be of sufficient form for use in an inter-laboratory study.
- Ballot at sub-committee level to approve the draft method prior to conducting an inter-laboratory study.

One Example: Calibration

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

Determination of Bias

1. Certified Reference Material
2. Spiked samples
3. Comparison to fundamentally different technique
4. Comparison to reference method
5. Split samples with a referee lab
6. Professional judgment

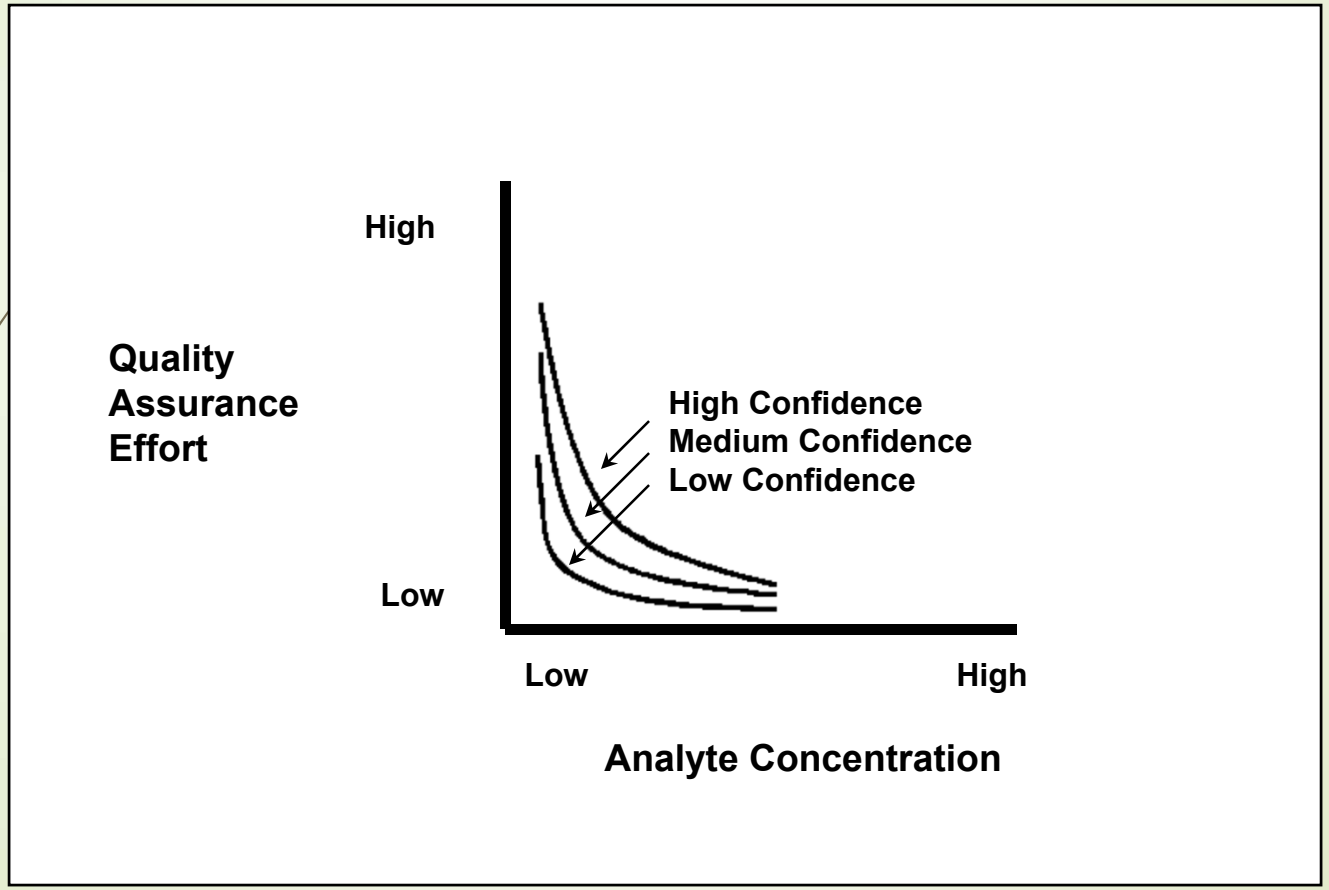
Determination of Precision

- Replicate measurements
- Split samples
- Field replicates
- Collaborative study
- Multiple samples over time or space
- Spike replicates

Determination of Sensitivity

1. EPA Method Detection Limit study

Relationship of Confidence, Concentration and QA Effort



ACS, 1983

Planning

- Defines and Details...
  - Analytes to be measured
  - Level of Confidence regarding identification
  - Concentrations to be measured
  - Accuracy (Precision and Bias)

The method, detection level and QC effort are outcomes from this process

Analyte Selection

Acceptable

- Regulation
- Scientific Literature
- Site History
- Professional Judgment
- Engineering Knowledge
- Review of Raw Materials and Chemistry
- Intuition

Inappropriate

- Method List

Confidence of Identification

- False positive / negative risk
- Survey
- Monitoring
- Pass / Fail

Detection Level Considerations

- **Acceptable**
  - Risk assessment
  - Regulation
  - Project objectives
    (e.g. treatment effectiveness, mass balance)
- **Inappropriate**
  - Method performance (unless MDL> desired level)
  - How low can I go!

Evaluation (Validation) Phase

- Conduct interlaboratory study per D2777

Why Validate?

- Get approval from EPA
- Assists in method selection
- Provides indication of potential utility
- Useful guide for best performance that can be expected
- Provides basis for comparison of alternative methods
- Helps establish legal standing
- Meets TNI accreditation requirements

Validation of Methods

- Validation is the confirmation by examination and the provision of objective evidence that the particular requirements for a specific intended use are fulfilled.

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Levels of Validation Effort

- Limited matrix, single facility;
  - Industrial discharger
- Limited matrices; multiple facilities
  - Commercial laboratory analyzing wastewater
- Unlimited matrices and facilities
  - **ASTM and other CSB Methods**

Outcome from Validation Process

- Statements of precision, bias, sensitivity, range

"Such statements are often misinterpreted; they merely describe the results of the exercise and are, at best, estimates of typical performance expectations for the method. However, such information should be obtained to the extent possible since it provides a quantitative basis for judging performance capability."

Taylor 1983

Misuse of Validation Data

- Quality of all future measurements

Daubert vs. Merrell Dow Pharmaceuticals (1993)

Federal Rules of Evidence, not Frye, provide the standard for admitting expert scientific testimony

"The most influential Supreme Court case you've never heard of."

Daubert Foundation Principles

- Whether a theory or technique can be (and has been) tested (method validation)
- Whether it has been subjected to peer review and publication (reference method)
- Whether there is a high known or potential rate of error(PT and QC samples)
- Whether there are professional standards controlling the technique's operation(TNI standard)


thank you
danke
謝謝
ngiyabonga
teşekkür ederim
рахмат
Баярлалаа
спасибо
faafetai lava
gracias
dank je
merci
obrigado
dziękuję
bedankt
go raibh maith agat
mochchakkeram
sukriya
kop khun krap
terima kasih
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