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Abstract: Laboratory activities are focused on analytical methods, and often insufficient consideration is given to the selection of the test portion. Equal attention should be paid to the selection of the test portion, as it generally introduces substantially greater error than analytical error. Representative sampling requires control of all errors. The types and sources of error in laboratory sampling, as well as approaches for mitigating the errors, are addressed in “Guidance on Obtaining Defensible Test Portions” or “GOOD Test Portions.” Laboratory sampling should also not be overlooked in the in the laboratory quality system. In some cases, quality assurance and quality control will be similar to what is incorporated for analytical methods, and in other cases, it will be fundamentally different. Approaches for validation and verification of sampling protocols and appropriate quality control events can also be found in “GOOD Test Portions.”

Key Concepts for Laboratory Sampling

Sample quality criteria (SQC): A series of statements that clarify program technical and quality requirements to support defensible decisions. These statements include 1) the question to be answered, 2) definition of the decision unit, and 3) desired confidence in the inference.

Theory of sampling (TOS): A set of principles that describe all errors contributing to total sampling error as well as techniques for estimation and mitigation of error to an acceptable level.

Decision unit: The material from which a primary sample is collected and to which an inference is made.

Laboratory sampling: All manipulations performed on the laboratory sample after receipt and acceptance through selection of the test portion. The **Laboratory sampling protocol** is a detailed procedure(s) for obtaining a test portion from a laboratory sample. The protocol includes appropriate mass, number of increments, sample correctness, equipment, quality control, and procedures for maintaining evidentiary integrity necessary to meet the sample quality criteria.

Selection process: There are two types of selection processes: mass reduction and splitting.

Mass reduction process: Selection of a smaller mass or volume of material from a larger mass or volume.

Splitting: The division of a mass or volume of material into two or more equal portions.

Nonselection process: Manipulation of a sample (e.g., comminution, removal of extraneous material, removal of water), usually performed before a selection (e.g., mass reduction) process.

Sample: A mass or volume of a material selected from a larger mass or volume using principles of Theory of Sampling (TOS). The word *sample* should be used with a modifier as follows:

Primary sample: The material selected from a decision unit.

Laboratory sample: The material received by the laboratory.

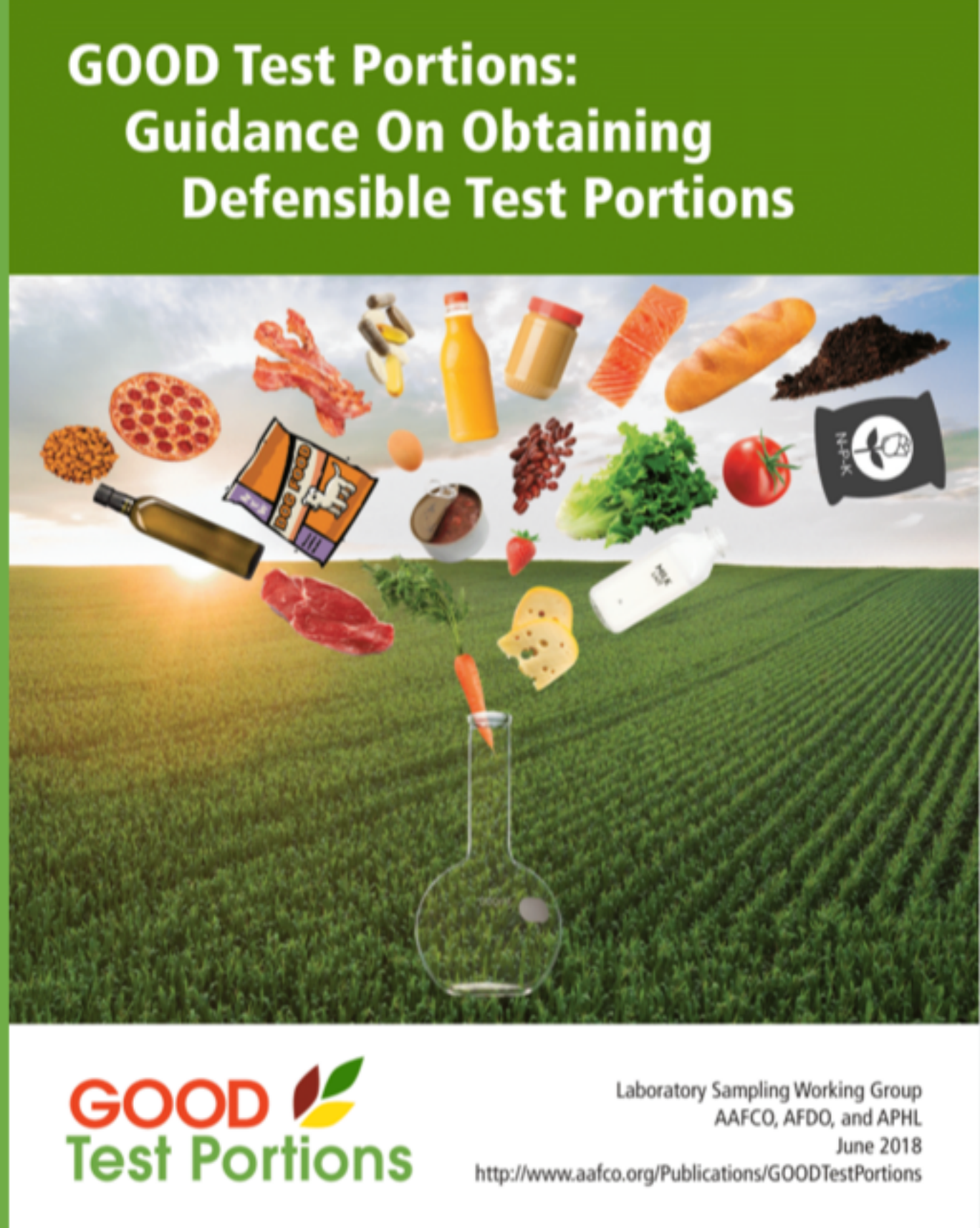
Analytical sample: The material from which the test portion is selected.

Replicate samples: Multiple samples selected under comparable conditions.

Split samples: Equal portions obtained by dividing a primary, laboratory, or analytical sample in its entirety.

Composite sample: Multiple laboratory samples, multiple analytical samples, or multiple test portions combined for analytical efficiency.

Test portion: The mass or volume of material selected from an analytical sample for a single test.

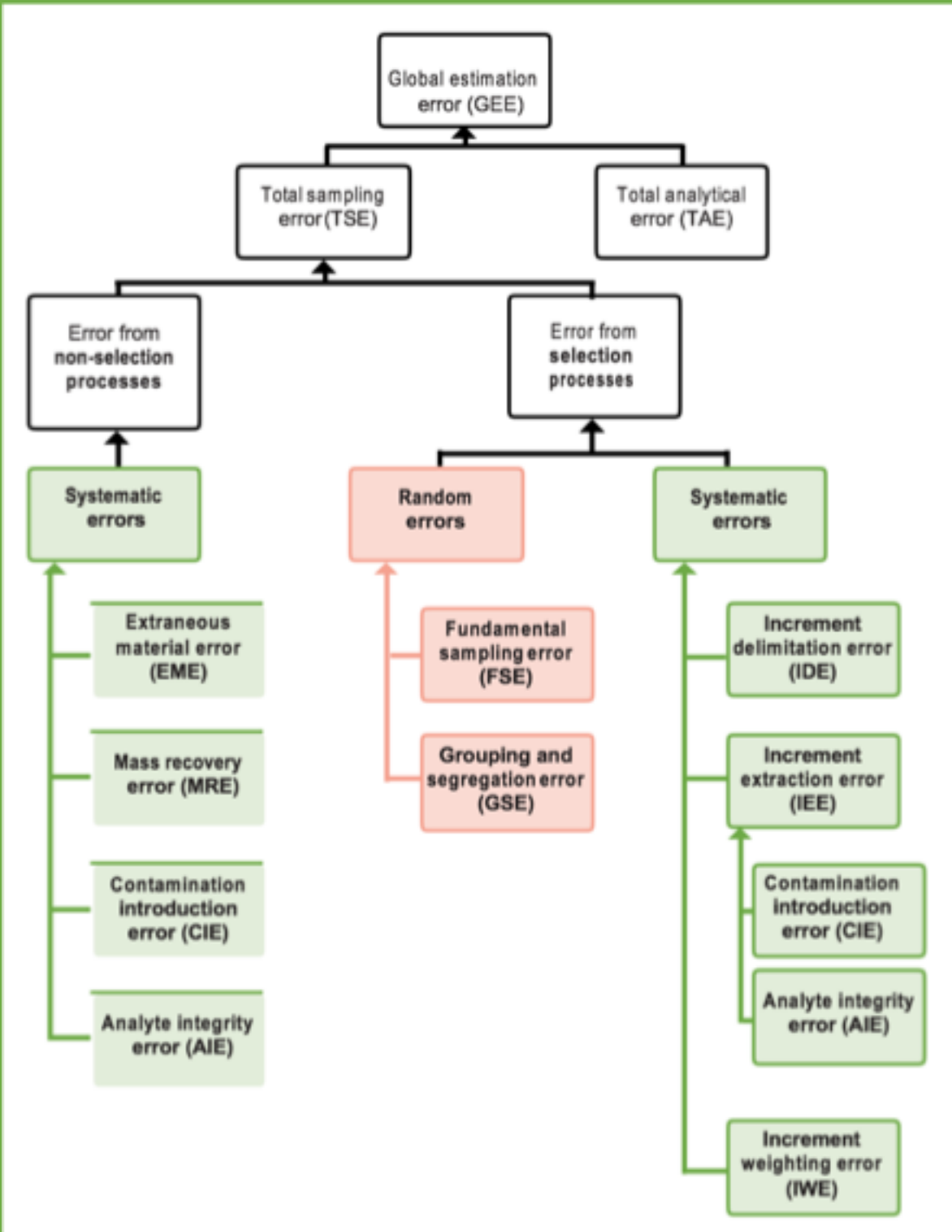
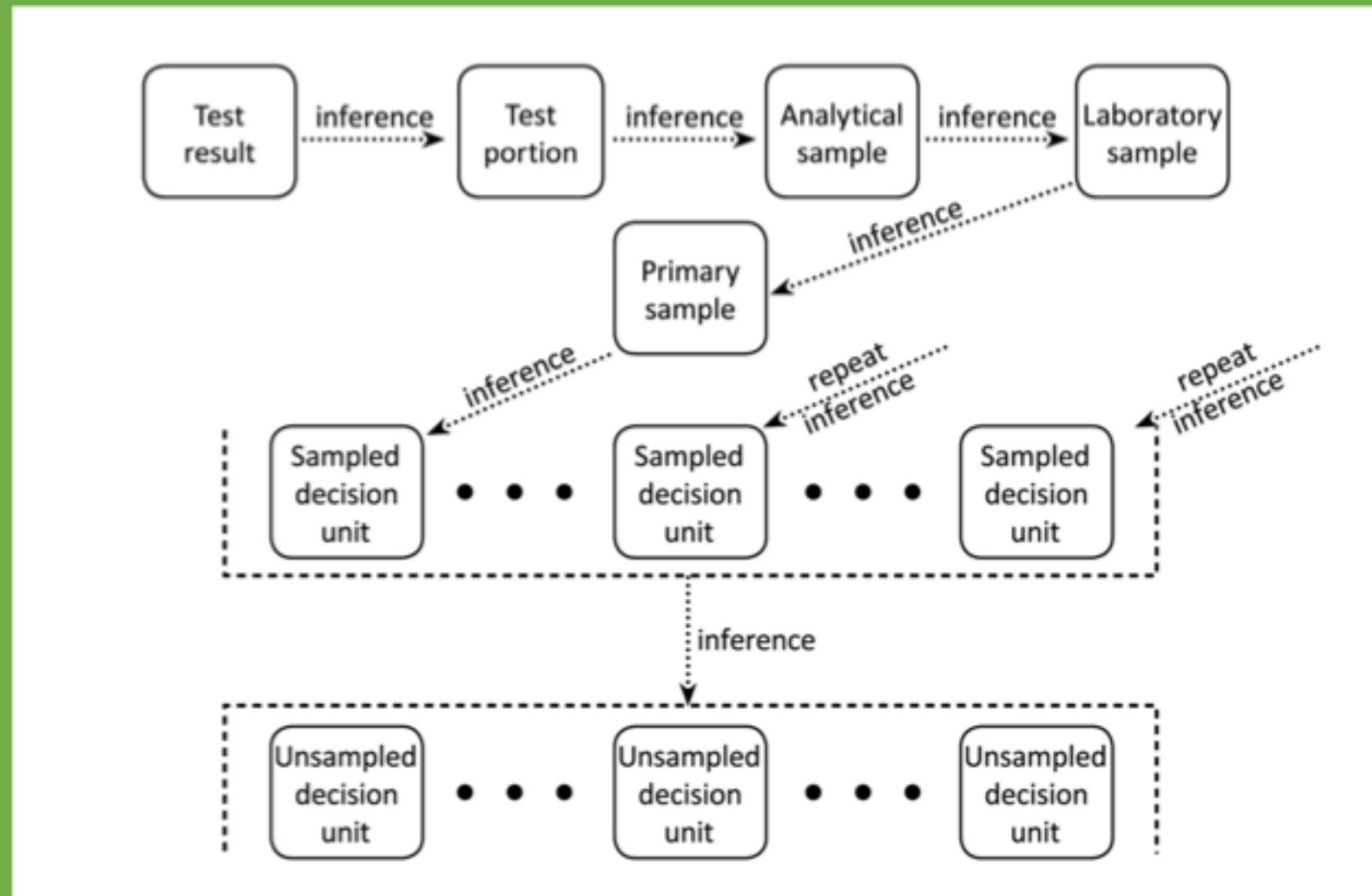


Increment: A group of elements collected by a single operation of a sampling device and combined with other increments to form a sample. For some finite element materials, an increment may consist of a single element.

Comminution: Reduction of particle size by crushing, chopping, grinding, etc.

Extraneous material: Material in the laboratory sample that is not part of the decision unit and must be eliminated or accounted for (i.e., removed at a nonselection process, avoided at a selection process and/or compensated by mathematical correction).

Inference: The estimation of a concentration or characteristic of a larger amount of material from data derived from testing a smaller amount of material.



Errors in Laboratory Sampling

Global estimation error (GEE): Estimate of the total error in the entire process from primary sampling through final measurement. Global estimation error comprises total sampling error (TSE) and total analytical error (TAE).

Laboratory sampling consists of:

- nonselection processes (e.g., comminution, removal of extraneous material, removal of water, use of a comminution aid such as dry ice
- selection processes (i.e., selecting a smaller mass from the larger mass).

Obtain a test portion that is representative of the decision unit by adhering to the principles of Theory of Sampling (TOS). TOS defines the following relationships:

- the relationship of error to mass,
- the relationship of error to increments, and
- the relationship of error to sample correctness

Total sampling error (TSE): Error from all nonselection and selection processes that causes the concentration or characteristic of the test portion to deviate from the true concentration or characteristic of the decision unit.

Random Errors in Selection Processes

Fundamental Sampling Error—Fundamental sampling error (FSE) is random error due to compositional heterogeneity (CH) and is controlled through the selection of an adequate mass.

Grouping and Segregation Error—Grouping and segregation error (GSE) is random error due to distributional heterogeneity (DH) and is controlled through the selection of a sufficient number of random increments. Note: Increments must always be selected at random locations.

Systematic Errors (see Figure at bottom of first column)

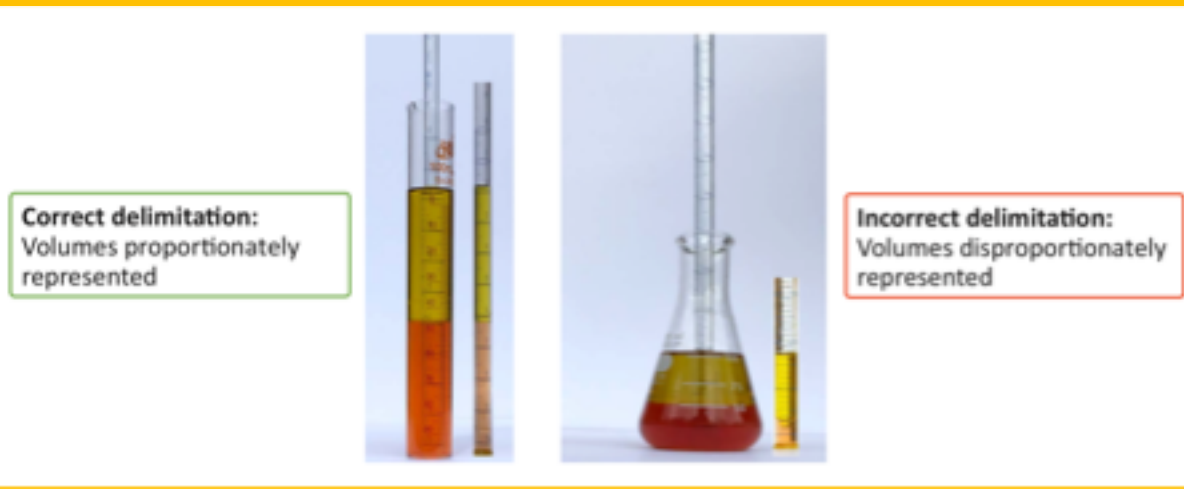
Increment Delimitation Error—Increment delimitation error (IDE) is systematic error due to incorrect shape of the volume delimiting the increment resulting in nonequiprobable selection of elements. IDE occurs when all the elements of a material do not have an equal probability of being selected due improper tool design.

Increment Extraction Error—Increment extraction error (IEE) is systematic error due incorrect increment extraction. It is a result of improper removal of an increment such that, even if the volume delimiting the increment is correct, not all elements are selected. An example is material falling out of a cylindrical probe as the increment is being removed.

Contamination Introduction Error (CIE)—Systematic error due to unintended contamination introduced into the material from external sources (e.g., the environment, the container, tools and equipment, or the analyst) results in CIE.

Analyte Integrity Error (AIE)—Analyte integrity error is systematic error and results in changes to chemical, biological, radiological, or physical characteristics from those of the decision unit. Analyte integrity error typically is controlled by appropriate sampling and handling techniques. Examples of introduction of AIE include loss of viability of the microbiological target, and volatilization, adsorption, or oxidation of the analyte during the selection process.

Increment Weighting Error (IWE)—Increment weighting error is systematic error due to inconsistent or disproportional increments (in mass or volume) resulting in over- or underrepresentation of certain portions of the material being sampled.



Additional Systematic Errors

Extraneous Material Error (EME) and Mass Recovery Error (MRE). See QA/QC column.

Relationship of Error to Mass

FSE is related to the magnitude of CH, the mass selected, and the particle size distribution of the material. To control FSE for a given state of CH, the diameter of the particles must be reduced, the mass increased, or a combination of both.. The relationship of error to CH, mass, and the maximum particle size is given by:

$$s_{FSE}^2 \propto \frac{CH \times diameter_{max}^3}{mass}$$

Relationship of Error to Increments

GSE is related to the magnitude of DH and the number of increments selected. As a general practice, sufficient increments are selected to reduce GSE until its contribution to GEE is negligible. The relationship of error to DH and number of increments is as follows:

$$s_{GSE}^2 \propto \frac{DH}{number\ of\ increments}$$

Relationship of Error to Sample Correctness

Control of IDE and IEE are collectively referred to as *sample correctness*. Achieved when all elements of the material being sampled have equal probability of selection.

QA/QC for Laboratory Sampling

Validation of a Laboratory Sampling Protocol

The validation of a new laboratory sampling protocol must:

- demonstrate that the protocol meets the desired scope of application
- demonstrate that the protocol meets the agreed upon SQC
- confirm sample correctness
- validate sufficient mass to meet the error criteria
- validate sufficient number of increments to meet the error criteria.

There are two approaches for validation: 1) determine error utilizing TOS equations, or 2) determine error experimentally from test results. Experimental validations for laboratory sampling can be designed in several ways:

Whole sample extraction—An option for validation of laboratory sampling protocols is to compare the result obtained from testing the selected portion to the result obtained when testing the entire unselected (remaining) portion. If two results compare, the selection process is valid. If the unselected portion is too large for a single extraction process, multiple extractions may be performed and the multiple extracts proportionately combined to obtain a single test result to represent all the unselected material.

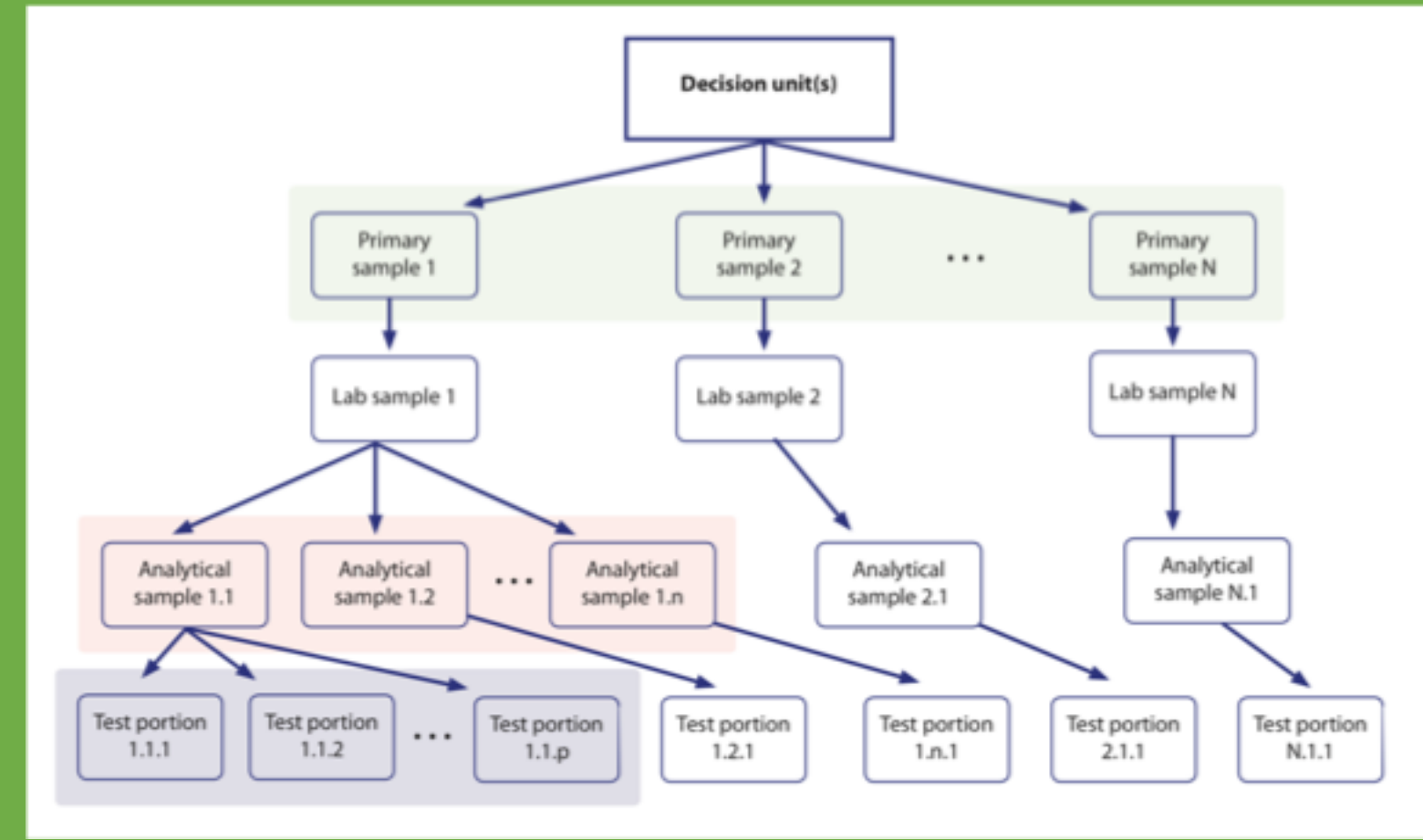
Materials with a known amount of analyte of interest or surrogate—A second option is to perform the protocol to be validated on known materials containing the analyte of interest. These materials can be certified reference, fortified, or incurred. When using certified reference or fortified material, it is critical that the materials mimic routine samples. Surrogates that mimic the behavior of the analyte of interest (e.g., radiolabeled compounds, isotopes) are an alternative to the analyte of interest to facilitate measurement.

Tracers—A third option is the use of tracers that are unrelated to the analyte of interest (e.g., sand; Microtracers™ (a trademark of Micro-Tracers Inc., San Francisco, CA) but that can provide useful information. The limitation for this option is that the analyte of interest may or may not behave as the tracer behaves and caution needs to be used when extrapolating results to routine sampling.

Once validated, a sampling protocol can be periodically verified through performance tests, which can be devised to verify a nonselection or selection process, including carryover, final particle size distribution, and contamination and cleaning procedures.

Quality Control for Random Error

Quality control replicates are used to monitor random error. Using more replicates improves the error estimation. The error can be monitored at any selection process to provide an estimate of the random error from that point forward. By performing replication at multiple selection processes, it is possible to isolate error from an individual process through subtraction (see Figures below). The error contribution from any selection process equals the random error starting from that process forward minus the random error starting from the subsequent process forward.



Error estimate	Relative standard deviation (RSD) calculation ^a	Error calculation ^a
Estimate of overall GEE (TSE + TAE)	RSD of 1,1,1,2,1,1,...,N,1,1 = RSD _T	$GEE = RSD_T$
Estimate of overall TSE	RSD of 1,1,1,2,1,1,...,N,1,1 = RSD _T	$TSE = \sqrt{RSD_T^2 - TAE^2}$
Error contribution from selection of the primary sample (ps)	RSD of 1,1,1,2,1,1,...,N,1,1 = RSD _T	$E_{ps} = \sqrt{RSD_T^2 - RSD_{ps}^2}$
Error contribution from selection of the analytical sample (as)	RSD of 1,1,1,1,2,1,1,...,1,n,1 = RSD _{ps}	$E_{as} = \sqrt{RSD_{ps}^2 - RSD_{as}^2}$
Error contribution from selection of the test portion (tp)	RSD of 1,1,1,1,1,2,...,1,1,p = RSD _{as}	$E_{tp} = \sqrt{RSD_{as}^2 - TAE^2}$

^aRSD is expressed as a decimal (part of 1) for all error calculations.

^bTo express calculated error as %RSD, multiply calculated GEE, TSE, E_{ps}, E_{as}, and E_{tp} by 100.

Quality Control for Systematic Error

Extraneous material error: A qualitative measure may be to compare, either visually or by weighing, the separated extraneous material as performed by multiple analysts.

Contamination introduction error: Contamination introduction error from equipment and the environment can be evaluated by processing material that contains no analyte and interpreted as QC blanks. Swabs and swipes of equipment can be processed as QC blanks.

Mass recovery error: Mass recovery error can be determined by visual inspection of equipment for incomplete removal of material or weighing of material before and after processing.

Analyte integrity error: A technique is to measure splits at multiple points in time and observe for trends. Use of radiolabeled compounds, use of fortified or known incurred materials, or comparison with a previously validated protocol may also provide opportunities to monitor analyte integrity error.

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