

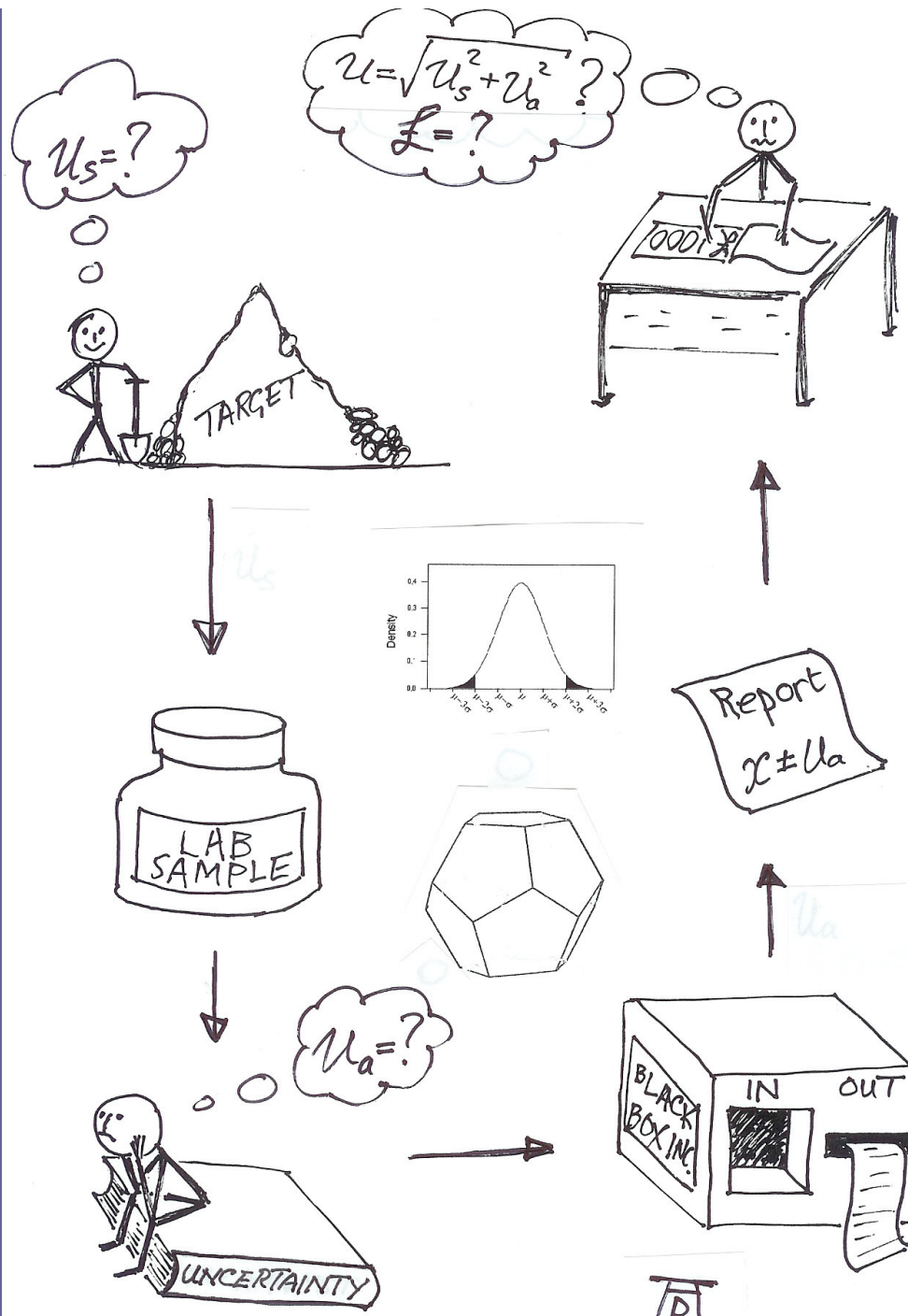
The Quality of Sampling in Context

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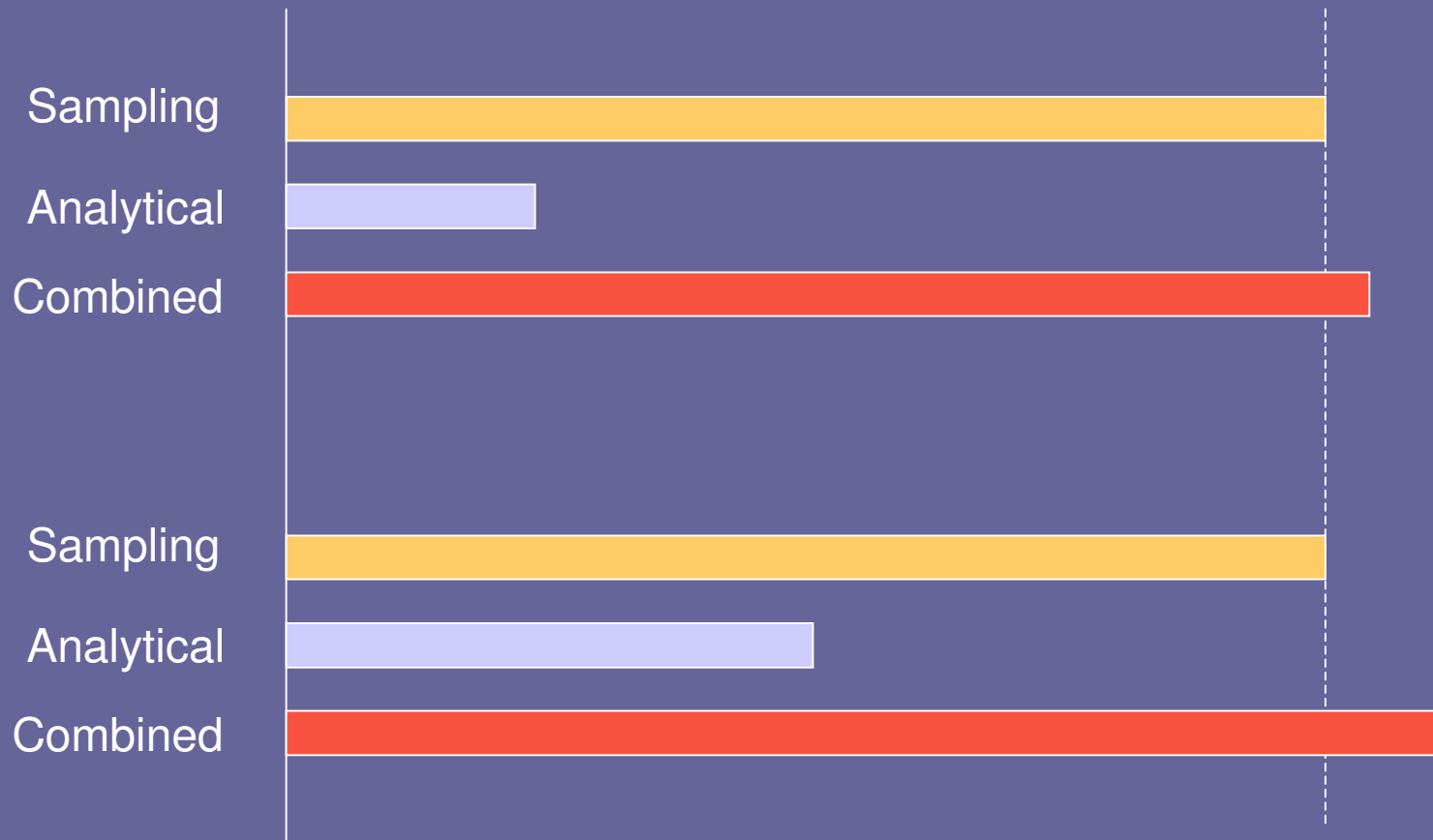
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Combining uncertainties

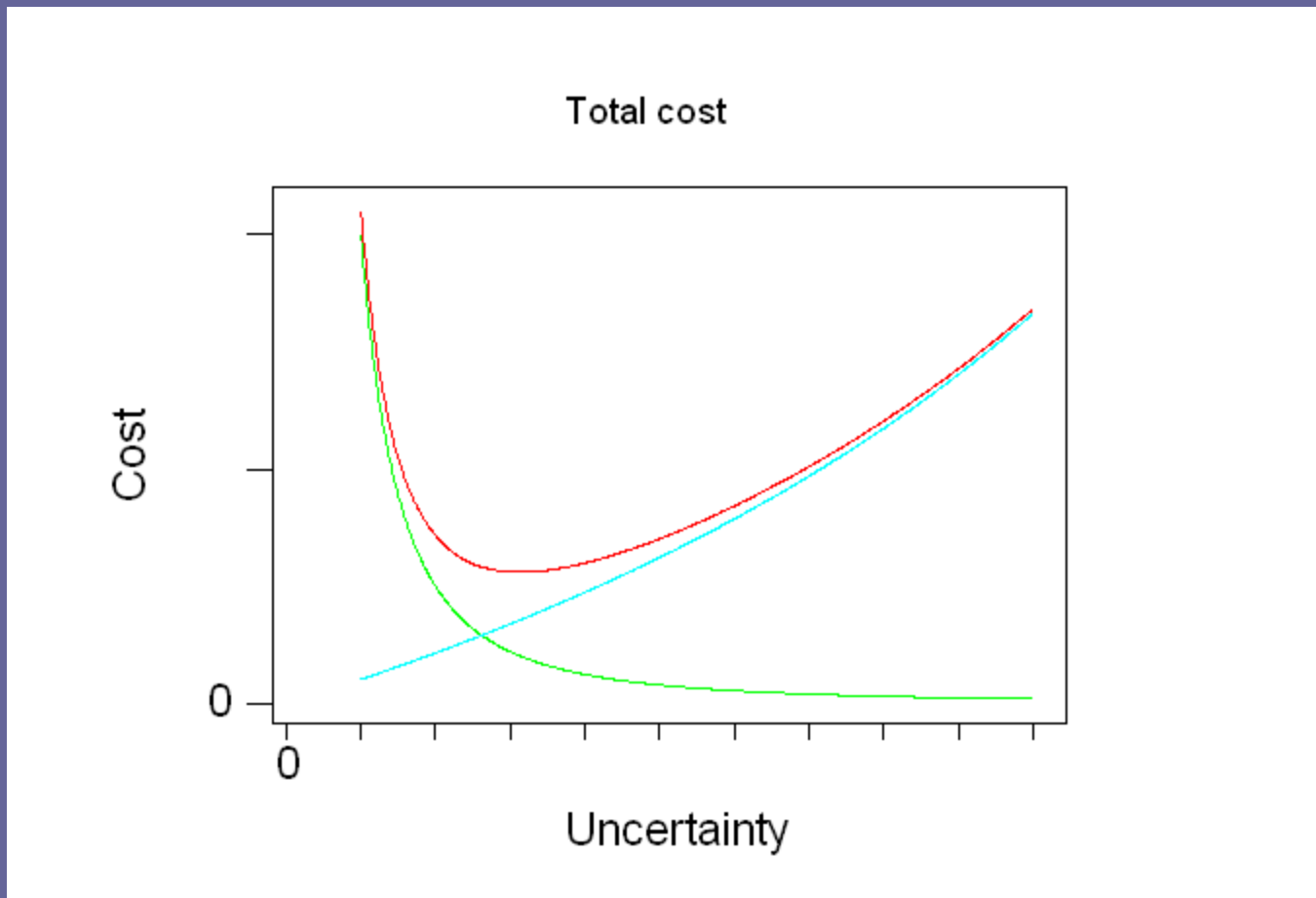
$$u = \sqrt{u_s^2 + u_a^2}$$



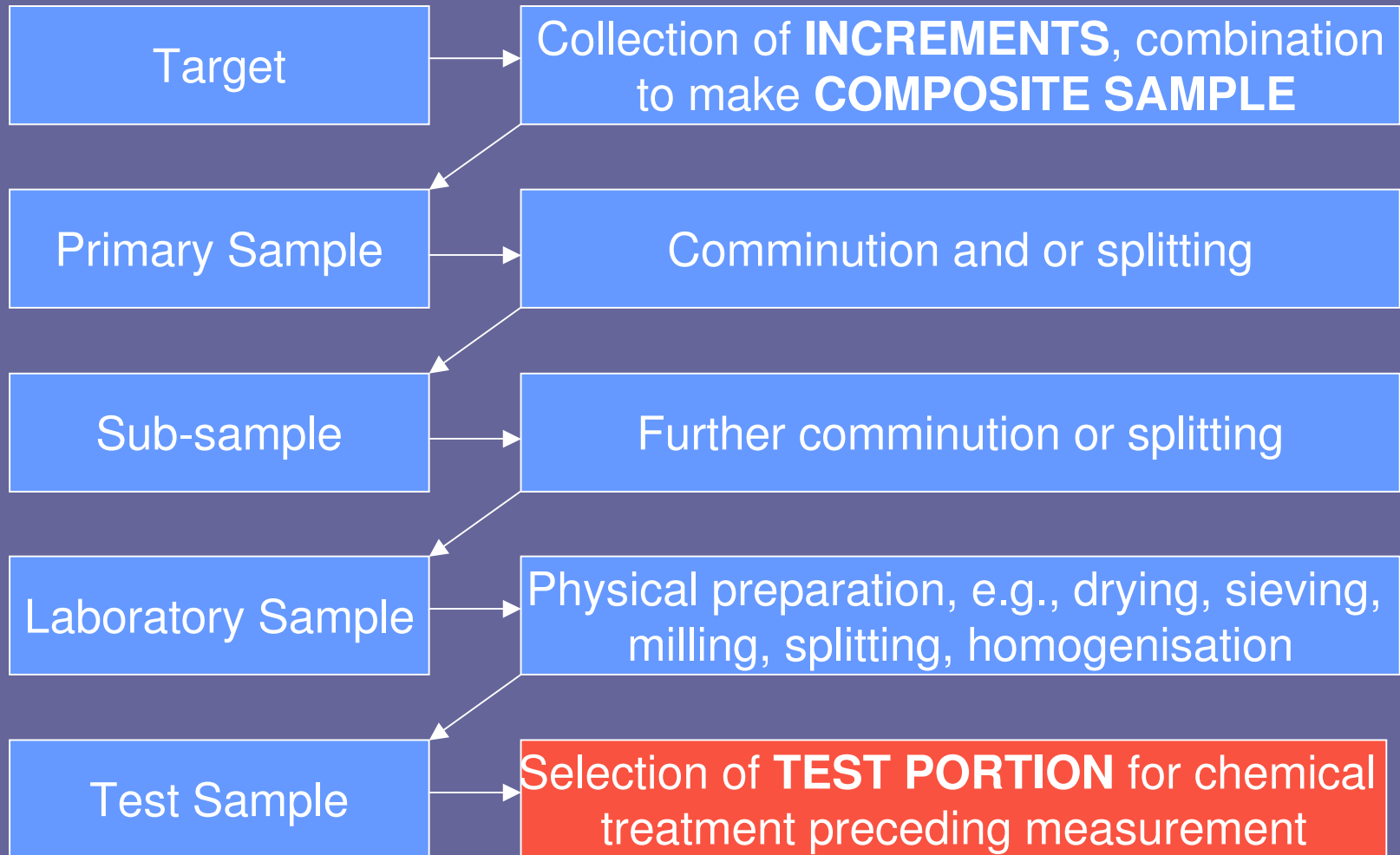
Fitness for purpose

- A result is fit for purpose when it maximises its expected utility.
- This means roughly that we need to minimise expected costs in the long term.
- There are operational costs of sampling and analysis.
- There are potential costs resulting from incorrect decisions based on the result.
- Both of these costs depend on uncertainty.

Long-term loss



Terminology



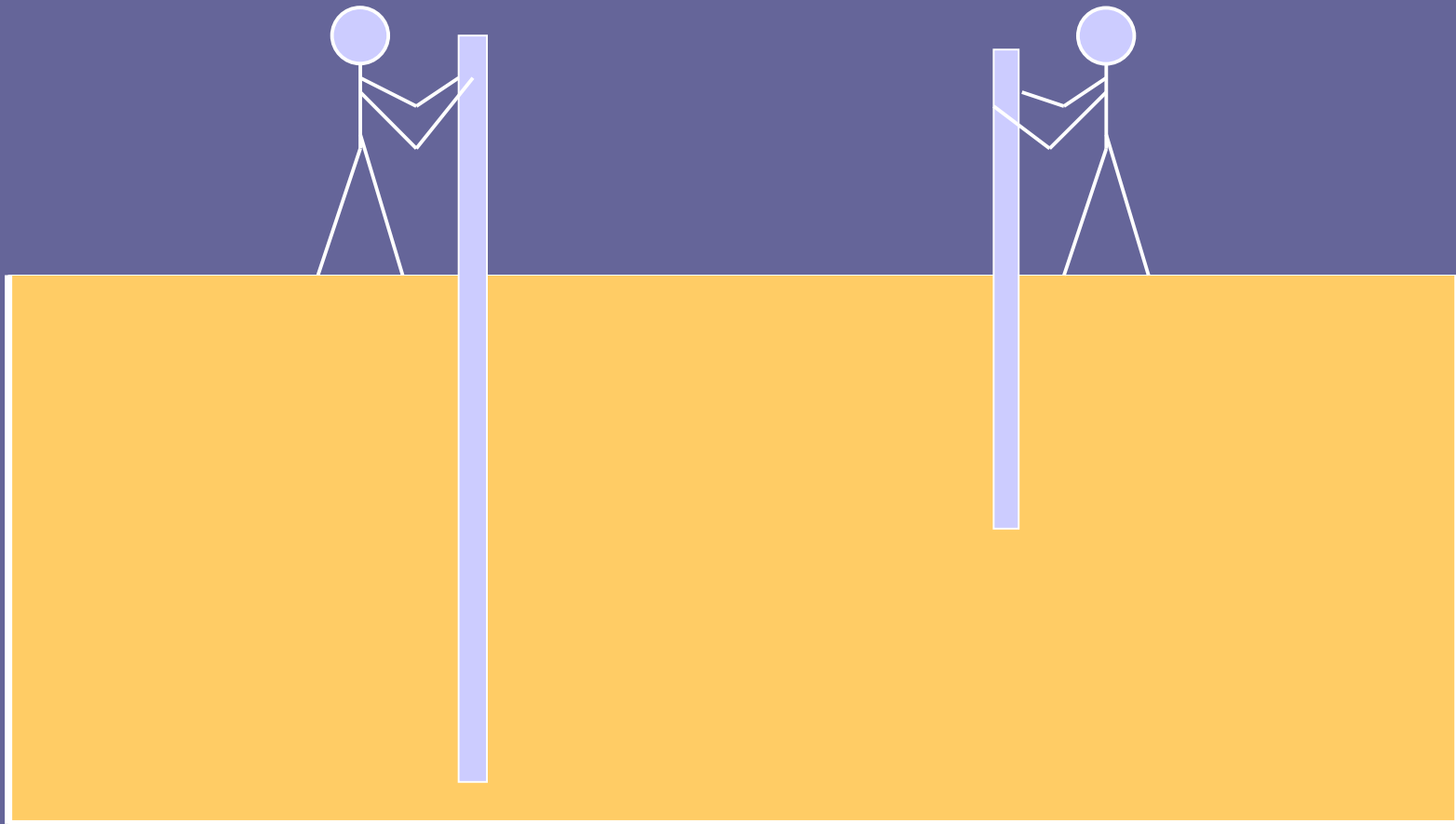
Components of sampling uncertainty

- **Bias**—difficult, often impracticable to address.
- **Precision**—Easy to address so long as a random element can be introduced into replicating the procedure.

Sampling bias

- Some experts think that sampling bias does not exist.
- Essentially they hold that sampling methods are empirical, *i.e.*, give an unbiased sample by definition.
- That is not generally correct—it is easy to see how sampling bias could arise in practice.

One way of taking a biased sample!



Addressing bias

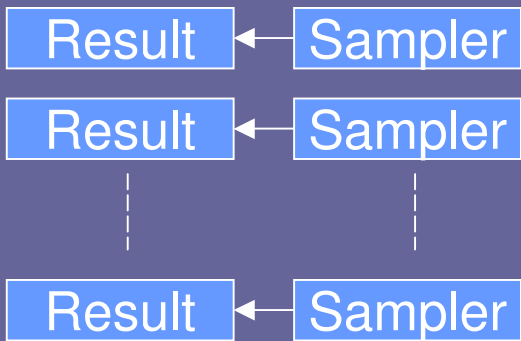
Analytical	Sampling
Reference material	Reference target (Severe problems with cost, stability)
Reference method and candidate method	Reference method and candidate method?

Comparison of paired methods

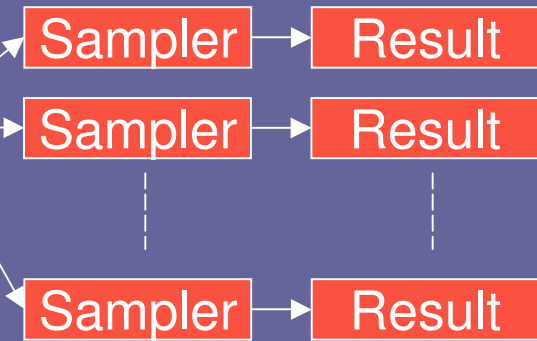
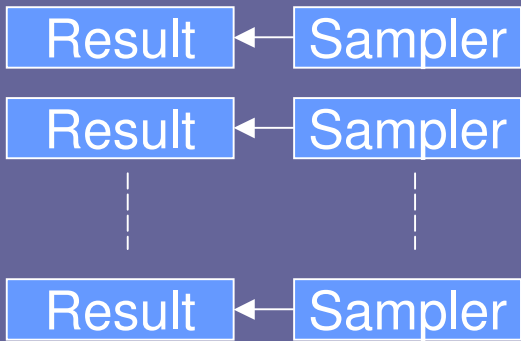
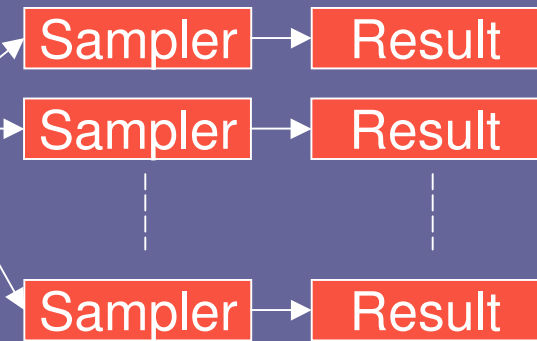
Two methods with:

- One target, one sampler?
- One target, multiple samplers?
- Multiple targets, one sampler?
- Multiple targets, multiple samplers?

Method A



Method B



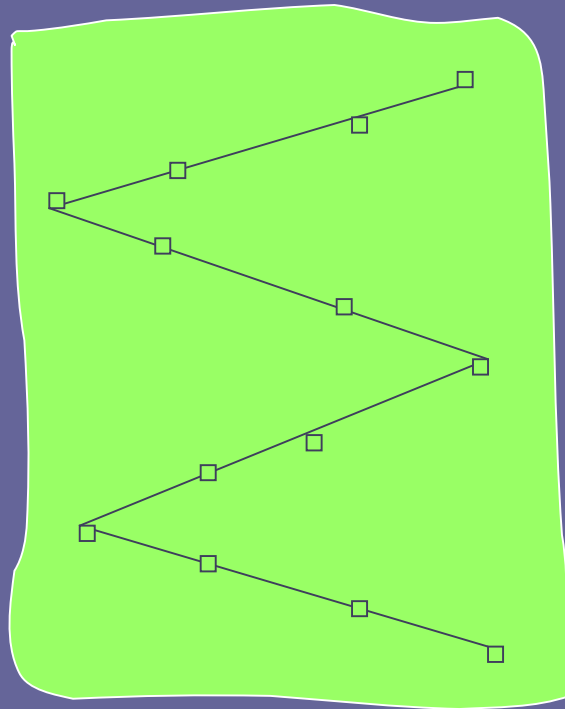
Targets 2,..., n > 10

Sampling precision

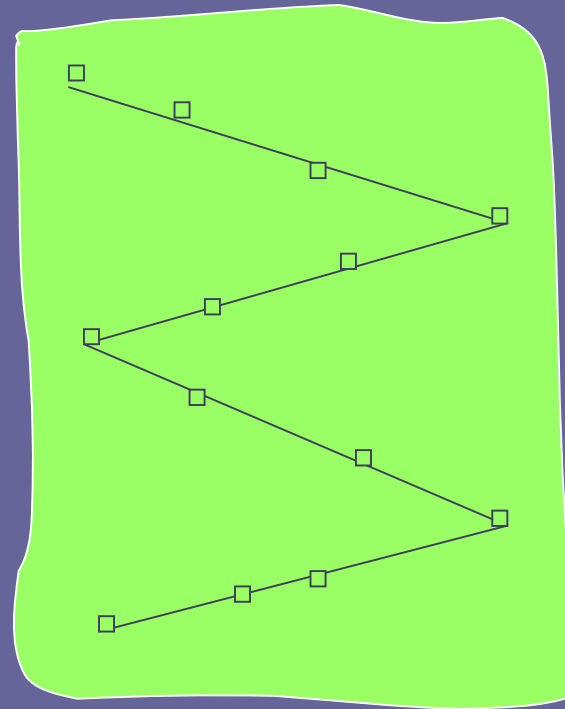
- Variations in execution of procedure.
- Variations in composition (heterogeneity) of target.
 - Sampling precision may vary from target to target of the same nominal type.
 - Initial validation of the sampling protocol needs to be supported by ongoing checks (internal quality control).
- Good estimation of precision needs ***RANDOM REPLICATION*** of sampling.

Random duplication—sampling to a pattern

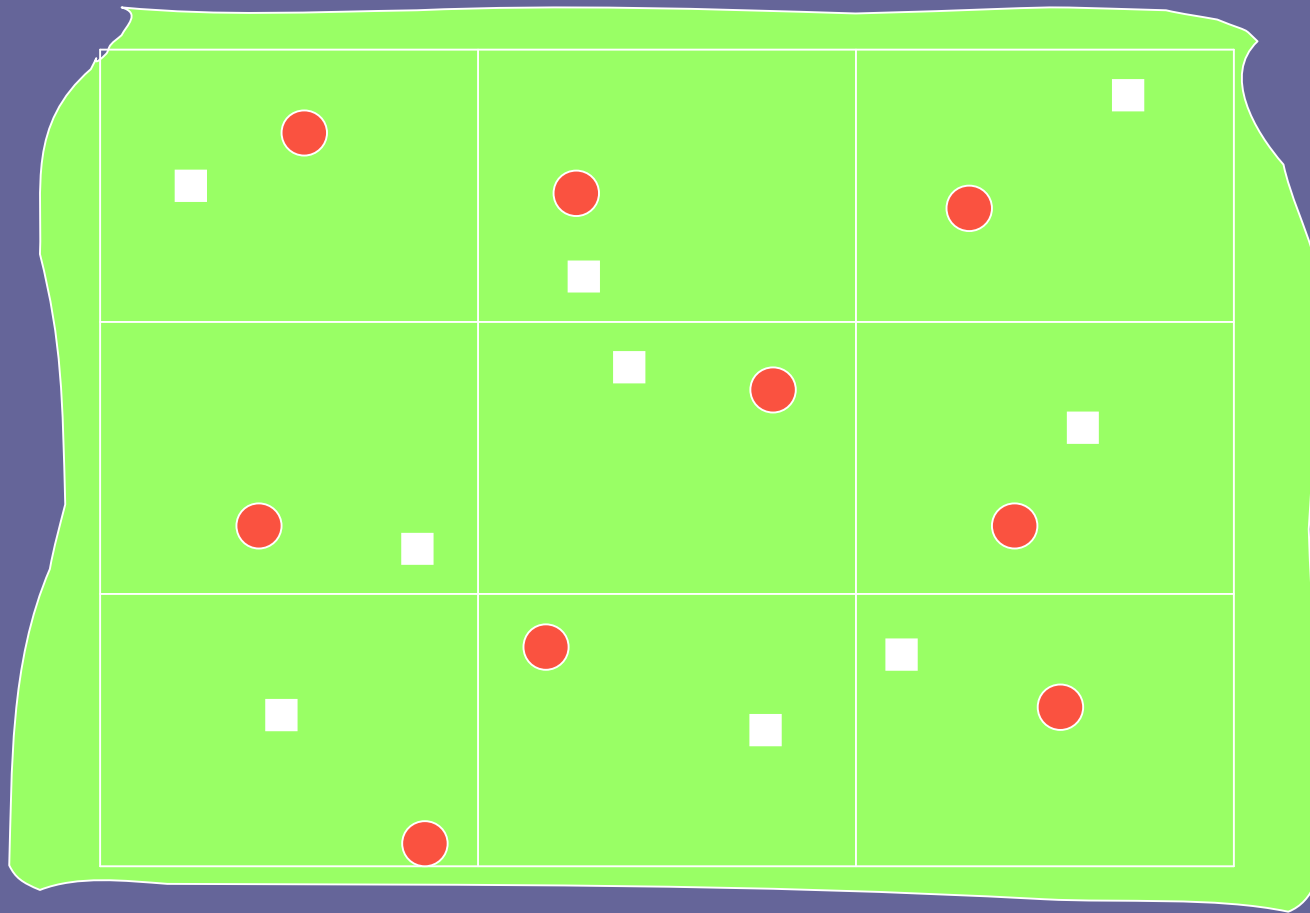
Composite Sample A



Composite Sample B

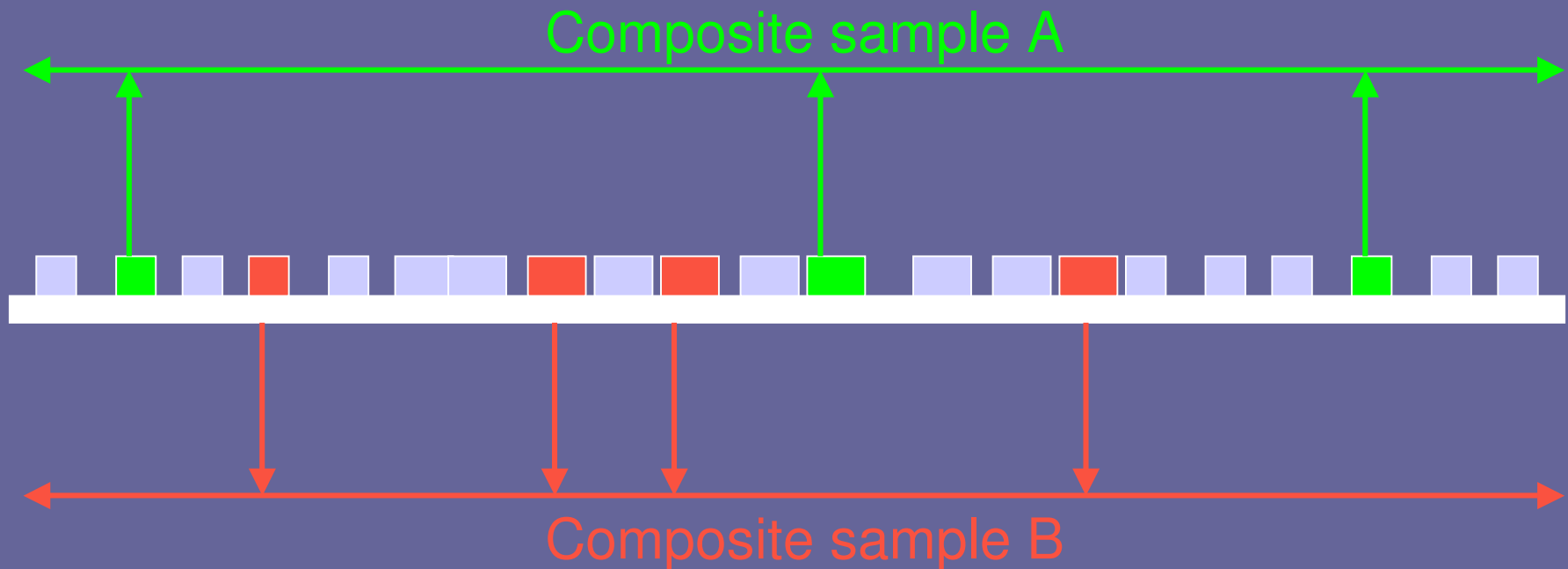


Stratified random design



- Composite sample A
- Composite sample B

Sampling from a conveyor belt



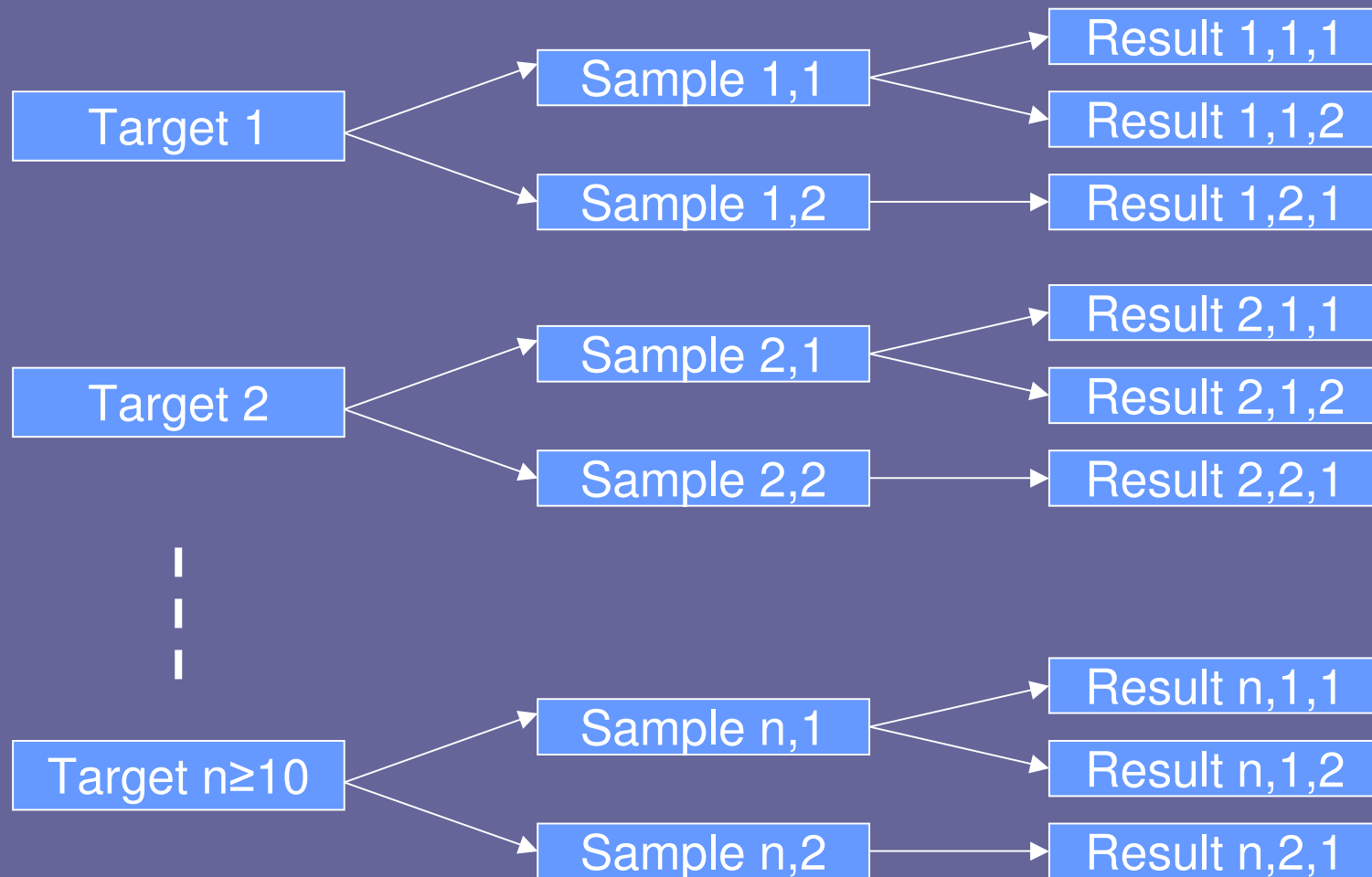
Precision-related activities

- Collaborative trial.
- “In-house” validation.
- Internal quality control.
- Proficiency test.

Collaborative trial

- **Requires:**
multiple targets, multiple samplers, duplicate samples, duplicate analysis (random repeatability conditions).
- **Provides:**
analytical repeatability variance,
between-sample (repeatability) variance,
between-SAMPLER (reproducibility) variance.
- **Drawbacks:**
VERY expensive.
- **Current usage:**
research only.

“In-house” validation

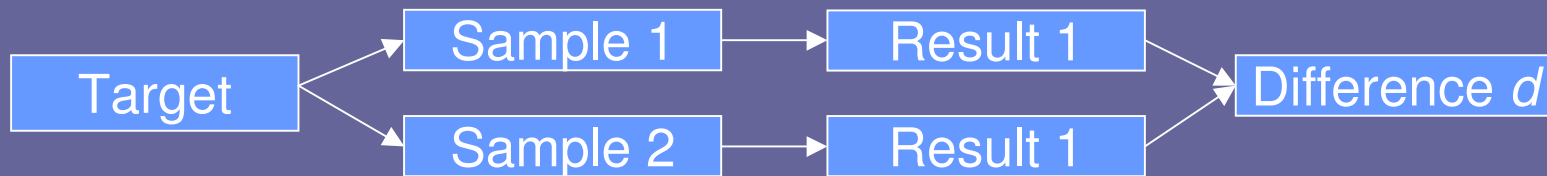


Note: unbalanced design with multiple targets is optimal

“In-house” validation

- Inexpensive to execute.
- Assumptions: (i) zero method bias; (ii) zero sampler bias.
- ANOVA gives $s_{s(r)}$ and s_a .
- Sampling precision \equiv sampling uncertainty (under assumptions).

Internal quality control

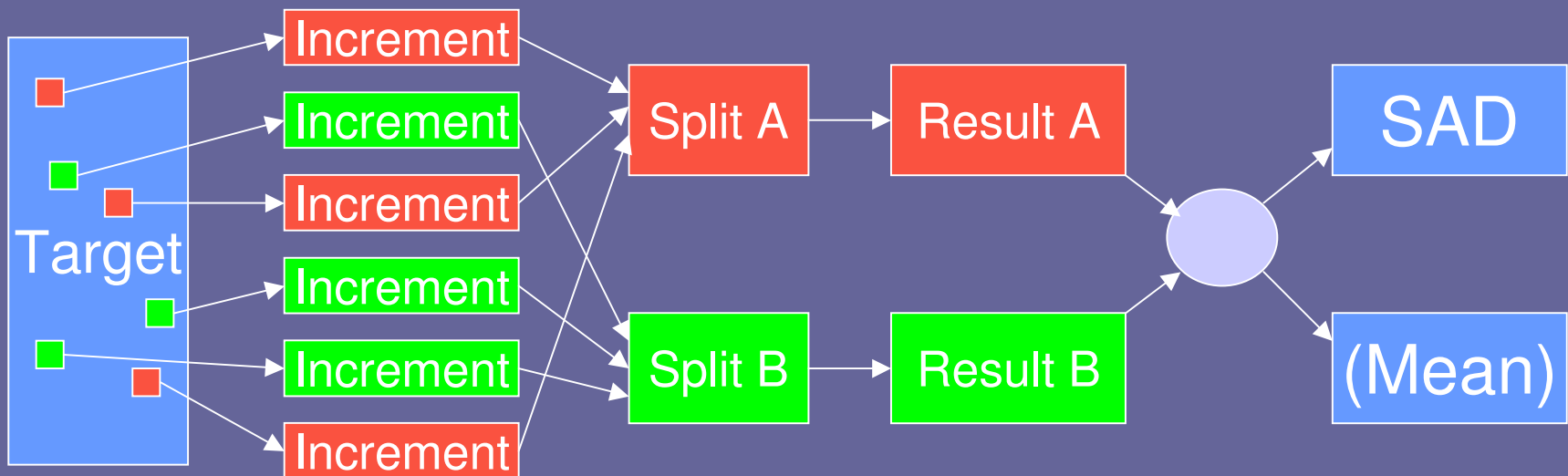


- Set up control chart for d (Shewhart or J-chart) using control lines at 0 , $\pm 2s$, and $\pm 3s$, where

$$s = \sqrt{2(s_a^2 + s_s^2)}$$

- For routine or occasional use (for sampling and analysis combined).
- Note: a result may be unfit for purpose, even if the error is due to heterogeneity and not the method.

IQC using the SAD protocol (Split Absolute Difference)

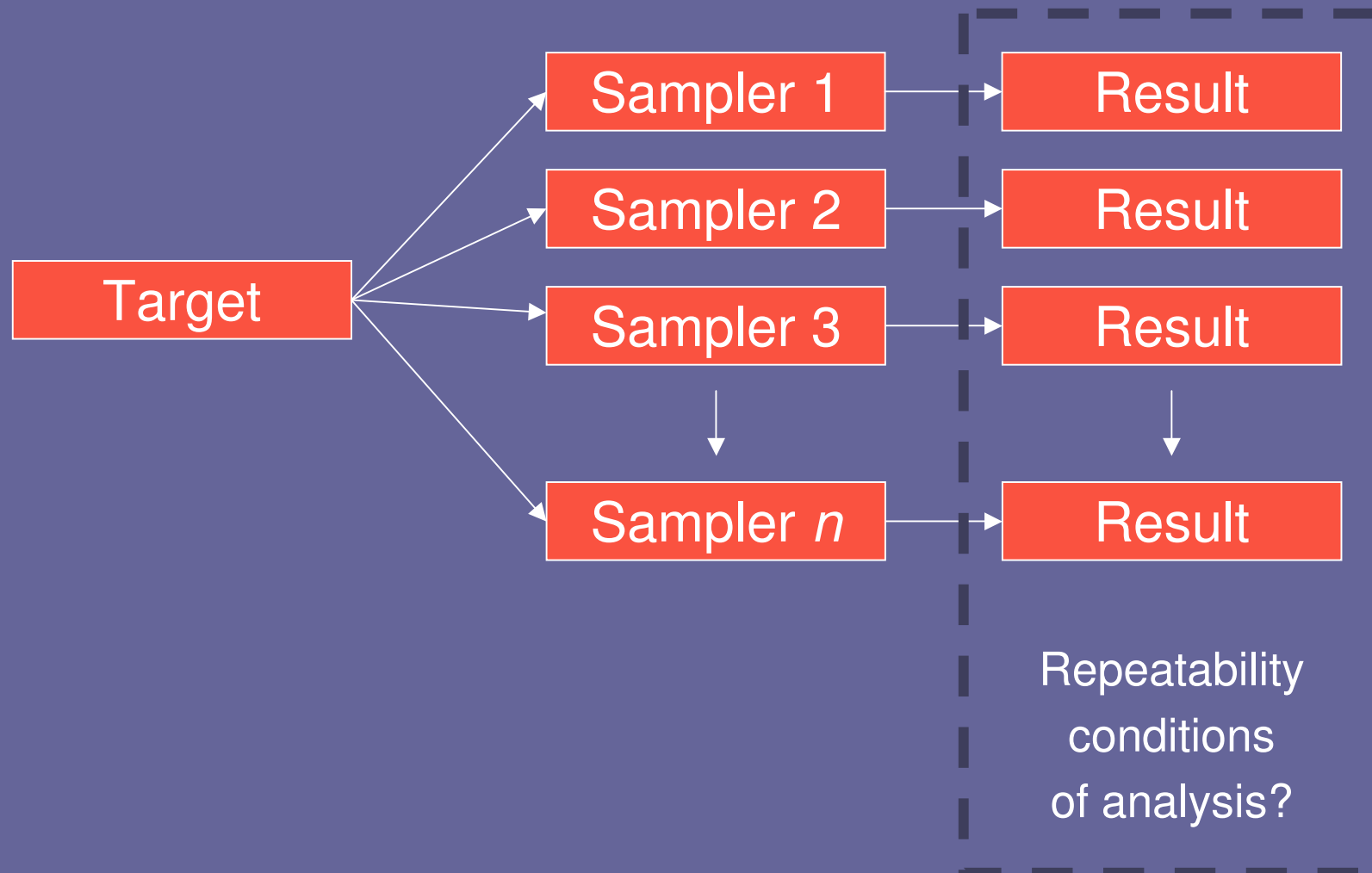


Increments divided between splits equally and at random.

Rationale of SAD

- $d = \text{Result A} - \text{Result B}$
- $\text{var}(d) = 2(2\sigma_s^2 + \sigma_a^2) = \sigma^2; \quad E(d) = 0$
- $\text{SAD} = |d|$
- Set up a one-sided chart with control lines at 0, 2σ and 3σ .
- *Analyst*, 2002, **127**, 174-177; 2004, **129**, 359-363.

Proficiency test in Sampling



Proficiency testing

- Samplers use their own preferred sampling protocol.
- Scheme provider conducts analysis under repeatability conditions (with $\sigma_a \ll \sigma_{s(R)}$).
- Provider specifies a fitness-for-purpose criterion.
- Provider calculates a z-score.
- **Practical difficulties.** Sampling must be “replicable” and “unobserved”. There may be overall target-specific bias.
- **Expensive.**
- **Usage:** research only at present

