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FORUM FOR THEORY AND PRACTICE OF REPRESENTATIVE SAMPLING



SST

SAMPLING SCIENCE & TECHNOLOGY

There is sampling...
and there is *sampling*.

Scoop vs Riffle

Comparing Sampling Efficiency
Using Characteristic Functions

Out of This World

Sampling for Micro
Meteorites

PhotonAssay™

A Review of Real-World
Performance

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Editor-in-chief: Kim H. Esbensen

E-mail: khe.consult@gmail.com

Editorial Asst.: ReConsider

E-mail: anne@reconsideredit.com

Publisher:

Benedikt Dolzer · 

E-mail: sss@bd-verlag.de

There is sampling ... and there is sampling

By Kim H. Esbensen (Editor)

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As an erstwhile geology student, the editor first encountered a famous expression: “There are granites ... and there are granites”, meaning that granites originate from more than one geologic process as it was thought at that time, more than 50 years ago. It has later transpired that this may not be so, after all – scientific progress!

Fast forward: There is sampling – in the ‘classic’ Theory of Sampling (TOS) context, i.e., physical sampling of heterogeneous particulate and aggregate materials, mixtures, processes, slurries including sampling by proxy, e.g., process sampling using sensor technology (‘Process Analytical Technology, PAT’), which accomplishes the same purpose ‘sampling for analysis’ without extracting physical samples from a process stream. The previous issue of SST#4 was fully dedicated to PAT.

... and then there is *sampling*, different from the above. What could this be? Here are few suggestions:

- Theoretically augmented sampling process comparison (– is TOS not enough?)
- Physically exotic sampling processes (developing new sampling avenues)
- Sampling of unusual or exotic materials, not normally considered traditional TOS targets (lots)
- Sampling under unusual conditions or using special sampling procedures and equipment

In this issue of SST, almost anything goes so long it is not (too) traditional, (too) main stream, or (too much) more-of-the-same ...

The theme for this issue has been out on solicitation for a long time. This issue is crammed with examples and case histories of ... *sampling*:

- Let’s take a broader view of the way TOS can be augmented (article 1)
- Be enchanted by the out-of-this-world story of how one man singularly developed, and popularised (in the best meaning of the word), the distinctly non-traditional sampling necessary for addressing a new scientific niche area: Micrometeorites (2)
- Let’s assess an evaluation of a new highly praised analytical approach – Photon Assay (3,4) vs. a rebuttal and comprehensive justification (5,6)
- Let’s be excited by what surely is the world’s simplest equipment: the ALOHA sampler (7)
- Read the raw & revealing account of missed sampling considerations, sometimes even misused by bad actors in our midst (8)
- Let’s review a massive 4th edition of the sampling community’s grandest textbook (9)

It has been a distinct pleasure to solicit and curate the present collection of contributions to this issue, for which the editorial office is rightly proud.

This issue concludes the inaugural first 18 months given for this publication to demonstrate a transition from a magazine to a peer-reviewed scientific journal (see editorial in issue no. 1). We hope readers will agree.

It is time to make a strong call for considering to publish in SST.

FURTHER READING

Issue #4 of Sampling Science & Technology (SST) focuses on the interface between the Theory of Sampling (TOS) and Process Analytical Technology (PAT) – a field that has received little structured attention in the sampling community so far, even though PAT has shaped the pharmaceutical industry for decades.

sst-magazine.info/issues/sst-004/



Comparing Sampling Efficiency in Particulate Materials Using Characteristic Functions: An Empirical Study of Scoop vs Riffle Methods

By Richard Minnitt¹

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ABSTRACT

Representative sampling of particulate materials remains a critical challenge across scientific and industrial domains, yet traditional method comparisons based on means and variances fail to capture complete distributional differences. This study introduces Characteristic Function (CF) analysis as a comprehensive statistical framework for evaluating sampling methods, providing a complete spectral representation of sampling distributions that reveals features hidden from conventional statistics. We empirically compared two common methods, scoop sampling and riffle splitting, using four density tracers (blue corn at 1.3 g/cm³, steel at 7.8 g/cm³, lead at 11.3 g/cm³, and tungsten carbide at 14.9 g/cm³) mixed in a popcorn matrix, with 32 samples per method analysed for both particle counts and individual mass measurements. Results demonstrate that while both methods captured similar mean counts, riffle splitting maintained near-ideal Poisson behaviour across all density ranges (variance-to-mean ratio = 0.77–0.93), whereas scoop sampling exhibited severe density-dependent over-dispersion (variance-to-mean ratio up to 19.33) and failed to capture heavy particles in 28 – 47 % of samples. CF analysis revealed fundamental distributional differences (integrated CF distance $D = 0.324$), with scoop sampling producing multimodal, heavy-tailed distributions with oscillatory CF signatures indicative of particle clumping, while riffle splitting generated smooth, unimodal distributions approaching Gaussian form. The riffle method demonstrated superior performance across all metrics: perfect detection sensitivity, statistical independence between tracer captures (factorization error $4.9\times$ lower), consistent mass measurements (CV $3.7\text{--}6.1\times$ lower), and strong count-mass linearity ($r > 0.98$). A composite scoring system integrating six performance dimensions ranked riffle splitting significantly higher (0.89/1.00) than scoop sampling (0.60/1.00). This study establishes Characteristic Function analysis as a powerful diagnostic tool that bridges theoretical sampling science and practical method validation, providing evidence-based recommendations for particulate sampling protocols and a generalizable template for evaluating any sampling method applied to heterogeneous materials.

1. Introduction

1.1 The Sampling Problem in Particulate Materials

Representative sampling of particulate materials stands as a critical yet persistently challenging task across numerous industrial and scientific domains. From mineral processing and pharmaceutical manufacturing to food production and environmental monitoring, the ability to obtain samples that accurately reflect the composition of bulk materials directly impacts product quality, process efficiency, and economic outcomes [1,2].

Despite decades of research and standardization efforts, sampling remains what Pierre Gy famously termed “the Achilles’ heel” of analytical chemistry [3], with sampling errors often exceeding analytical errors by orders of magnitude.

The fundamental challenge arises from the heterogeneous nature of particulate materials, where components of interest—whether mineral grains, agricultural grains, active pharmaceutical ingredients, or contaminants—are rarely distributed uniformly throughout the bulk.

¹ School of Mining Engineering, University of the Witwatersrand, Johannesburg, South Africa

This heterogeneity manifests at multiple scales: microscopic variations in individual particle composition, mesoscopic clustering or segregation patterns, and macroscopic distribution gradients [3,4]. When sampling such materials, every extraction act introduces bias, the magnitude of which depends not only on the sampling method itself but also on the material's inherent heterogeneity and the sampler's interaction with it.

Traditional approaches to evaluating sampling methods have largely relied on comparative statistics—comparing means, variances, or conducting t-tests between methods [4,5,9]. While these methods provide some insight, they suffer from a critical limitation: they reduce complex, multidimensional distributional information to a few summary statistics. This is akin to describing a symphony by reporting only its average volume and duration while ignoring melody, harmony, and rhythm. Two sampling methods might produce identical mean compositions while capturing fundamentally different distributions, with one method systematically oversampling clusters while another provides truly representative samples.

1.2 The Characteristic Function: A Statistical “X-ray” for Distribution Analysis

The Characteristic Function (CF) is a powerful yet underutilized tool in the sampling scientist's arsenal. First introduced as an analytical method by Lagrange around 1770, the first general definition of the characteristic function is attributed to Laplace in his 1812 work, *Théorie analytique des probabilités* [7]. In this work, Laplace effectively used what we now recognize as the Fourier transform—an integral transform rooted in his own earlier probability studies from the 1780s, as a tool for probabilistic analysis. While Fourier's 1822 treatise later formalized the transform that bears his name [8], the underlying mathematical ideas were already present in Laplace's work.

The CF as we know it today was formalized in the early 20th century, primarily through the work of Paul Lévy and Aleksandr Khinchin. Lévy's 1937 monograph, *Théorie de l'addition des variables aléatoires* [9], established the fundamental properties of characteristic functions and used them to prove general versions of the Central Limit Theorem. Independently, Khinchin made parallel contributions to the theory of limit theorems and stationary processes [7,9]. Through their efforts, the characteristic function became a complete description of a probability distribution through its Fourier transform.

Mathematically defined as $\varphi_X(t) = E[e^{itX}]$, where i is the imaginary unit and $t \in \mathbb{R}$ is a real-valued parameter, the CF encodes all information about the distribution of the random variable X .

What makes the CF particularly valuable for sampling analysis is its dual nature as both a comprehensive descriptor and a practical computational tool. Unlike probability density functions that can be difficult to estimate and compare, CFs offer several advantages for sampling studies:

- a) **Completeness:** The CF uniquely determines the distribution, so no information is lost in the transformation.
- b) **Additivity:** For independent random variables, the CF of their sum equals the product of their individual CFs, making it ideal for analysing particle counts.
- c) **Moment generation:** All moments of the distribution can be recovered through differentiation at the origin: $E[X^k] = (-i)^k \varphi_X^{(k)}(0)$, where $\varphi_X^{(k)}(0)$ denotes the k -th derivative of the characteristic function evaluated at $t = 0$.
- d) **Numerical stability:** CFs are often better behaved than density functions for empirical estimation, requiring no tuning parameters like bandwidths.

In the context of particulate sampling, CFs serve as a kind of “statistical X-ray,” revealing the internal structure of sampling distributions that remain hidden to conventional analysis. They allow us to answer fundamental questions like: Do two sampling methods produce the same underlying distribution? Are different particle types sampled independently? How does sample mass affect distribution shape?

The relevance of CFs to particulate sampling was established by Venter [5], who modelled trace analyte concentrations using compound Poisson distributions derived from CFs, elegantly establishing the connection to particulate sampling, a topic covered in some detail by Lyman [6,7]. However, the application of CFs to compare different physical sampling methods, particularly for multi-tracer systems with both count and mass data, remains largely unexplored. This study addresses that gap.

1.3 Research Objectives and Study Design

This study addresses this gap by applying Characteristic Function analysis to compare two common sampling methods: scooping and riffle splitting for particulate materials.

Our investigation has four primary objectives:

- a) **Pedagogical:** To explain Characteristic Functions in accessible terms, demonstrating their utility beyond theoretical statistics.
- b) **Methodological:** To develop a comprehensive CF-based framework for sampling method comparison.
- c) **Empirical:** To apply this framework to experimental data from four density tracers, analysing both particle counts and mass distributions.
- d) **Practical:** To provide evidence-based recommendations for sampling practitioners and quality control systems.

An experimental study was conducted using four distinct density tracers, blue corn (lightest), steel balls, lead balls, and tungsten carbide (heaviest), mixed in a controlled particulate matrix of popcorn maize. Thirty-two samples were collected using each method, with both particle counts and individual mass measurements recorded. This design allows us to examine not only how many particles of each type are captured, but also whether the captured particles are representative in terms of size/mass distribution. The analysis proceeds through traditional descriptive statistics that provide a baseline comparison, followed by CF analysis which reveals underlying characteristics of the distributions. The independence between tracers is examined together with the consistency of mass measurements, addressing the fundamental question: “Which method produces samples that better represent the true composition of the material?” This research aims to demonstrate that Characteristic Functions capture the full complexity of particulate heterogeneity and offer a more nuanced and informative approach to sampling method evaluation, while providing actionable insights for practical sampling applications.

Introductory figures (Figs. 1–3) are theoretical and use simulated data to introduce the characteristic function (CF) concept and typical spectral signatures of distributions relevant to particulate sampling, using purely simulated data; no experimental data are used in Figs. 1–3. Experimental results (Figs. 4–7 and Tables 4–12), drawn from the study data in SR.xlsx, demonstrate CF analysis in practice and enable a practical comparison of sampling methods. Both components are essential: the theory builds understanding of CFs, while the experiments demonstrate CFs’ diagnostic power in real-world sampling.

2. Theoretical Framework of Characteristic Functions

2.1 Definition and Interpretation of the Characteristic Function

Although the characteristic function may initially appear as an abstract construct with little apparent connection to practical sampling, it actually offers a compact, intuitive, and powerful way to characterise randomness by providing a complete spectral representation of its probability distribution. For a real-valued random variable X , the characteristic function (CF) provides a complete representation that uniquely determines its probability distribution and is defined as:

$$\varphi_X(t) = E[e^{itX}] = E[\cos(tX) + i \sin(tX)] \quad (1)$$

Where $i = \sqrt{-1}$ is the imaginary unit, and $t \in \mathbb{R}$ is a frequency parameter. For a continuous random variable with probability density function $f_X(x)$, this becomes the integral:

$$\varphi_X(t) = \int_{-\infty}^{\infty} \exp(itx) f_X(x) dx \quad (2)$$

While for a discrete random variable taking values x_k with probabilities p_k :

$$\varphi_X(t) = \sum_{k=-\infty}^{\infty} \exp(itx_k) p_k \quad (3)$$

There are several interconnected interpretations that clarify the usefulness of Eq. (1).

First, from a probabilistic standpoint, for a random variable X (say, the number of tungsten particles in a sample), and for any fixed real number t , we compute:

$$\varphi_X(t) = E[e^{itX}] = E[\cos(tX) + i \sin(tX)] \quad (4)$$

a point on the complex unit circle whose angle depends on X . The Characteristic Function $\varphi(t)$ is simply the average position of this point over many realizations of X . If t is small, the phase t_x changes slowly with X , giving an average near $1+0i$. If t is large, the angle varies rapidly, and the average tends toward $0+0i$.

Second, from a transformation perspective: The CF is precisely the Fourier transform of the probability density function $f_X(x)$. Just as a prism separates white light into its constituent colours, the Fourier transform decomposes a probability distribution into its frequency components.

The parameter t represents frequency in this analogy, small t probes large-scale distribution features (like the mean), while large t reveals fine details (like the behaviour in the tails).

Third, and most powerful for comparing the distributions is the generative perspective: The CF contains the complete “DNA” of a probability distribution. Given $\varphi(t)$, one can recover not only the mean and variance but every moment, every quantile, indeed the entire distribution itself through the inverse Fourier transform:

$$f_X(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-itx} \varphi_X(t) dt \quad (5)$$

This completeness property makes CFs uniquely suited for comparing distributions, two methods produce identical sampling results if and only if their CFs are identical for all t . Consequently, two sampling methods yield statistically identical results if and only if their characteristic functions are equal for all t . This completeness property is the foundation for using CFs as a rigorous tool for comparing empirical distributions.

2.2 Essential Mathematical Properties

Several mathematical properties make CFs particularly valuable for sampling analysis:

a) Linearity of Expectation:

$$\varphi_{aX + b}(t) = e^{-itb} \varphi_X(at) \quad (6)$$

b) Independence and Convolution: If X and Y are independent:

$$\varphi_{X+Y}(t) = \varphi_X(t) \cdot \varphi_Y(t) \quad (7)$$

c) Moment Generation: The k -th moment exists if $\varphi_X^{(k)}(0)$ exists:

$$E[X^k] = (-i)^k \frac{d^k}{dt^k} \varphi_X(t) \Big|_{t=0} \quad (8)$$

2.3 The Musical Score Analogy: Why Characteristic Functions Work

Consider a musical performance of Beethoven’s Fifth Symphony. The actual sound, the waveform measured by a microphone, is analogous to a set of sample measurements: complex, detailed, and unique to each performance. The musical score, by contrast, is a compact representation containing all essential information: notes, rhythms, dynamics, and tempo markings. From the score, one can reconstruct performances (though interpretation introduces variation), compare different orchestras’ interpretations, and analyse musical structure.

Characteristic Functions play exactly this role for probability distributions. The probability density function (PDF) is like the audio recording—complete but unwieldy for comparison. The CF is like the musical score—compact yet informationally complete. Just as a musician can compare two performances by examining their scores, we can compare two sampling methods by examining their CFs.

This analogy can be extended to explain several key operations within the characteristic function framework. Each orchestral manipulation has a direct mathematical counterpart in the manipulation of distributions. For instance, a transposition of the composition—shifting all notes to a new key—corresponds to scaling the random variable X by a constant a , as captured by the relation $\varphi_{aX}(t) = \varphi_X(at)$. Similarly, the addition of instrumental parts, enriching the overall harmony, is analogous to the convolution of independent random variables. This is mathematically manifested in the multiplicative property of their characteristic functions: for independent X and Y , $\varphi_{X+Y}(t) = \varphi_X(t) \varphi_Y(t)$. Harmonic analysis of the score, extracting fundamental frequencies and relationships, parallels the derivation of moments via differentiation of the characteristic function at the origin, where $\varphi^{(k)}(0) = i^k E[X^k]$. Finally, simplification to a piano reduction, which preserves the essential melodic and harmonic structure while omitting full orchestral detail, corresponds to the extraction of marginal distributions from a joint characteristic function by evaluating it with arguments for specific dimensions set to zero.

2.4 Visualizing Characteristic Functions: From Theory to Intuition

Diagrammatic representations shown in Fig. 1 and Fig. 2 present CFs for three distributions relevant to particulate sampling: the Poisson (modelling particle counts), the Normal (approximation for large samples), and a compound Poisson (mixing particle size variations).

Top row of Figure 1 shows probability distributions: (a) Poisson probability mass function ($\lambda = 3$) representing discrete particle counts; (b) Normal probability density function ($\mu = 3, \sigma = 1$) representing the large-sample approximation for continuous measurements; (c) Histogram of simulated compound Poisson distribution ($\lambda = 3$, with exponential particle masses of mean 1) representing aggregated particle mass in samples. Bottom row shows the corresponding characteristic functions: (d) Poisson CF exhibiting oscillatory decay, reflecting its discrete nature. The oscillatory pattern in the Poisson CF has fundamental period 2π , reflecting the discrete nature of the distribution. This periodicity is partially visible within the plotted range $t \in [-4, +4]$. (e) Normal CF showing smooth Gaussian decay, characteristic of continuous, well-behaved sampling distributions typical of large sample sizes.

(f) Compound Poisson CF demonstrating intermediate behaviour with heavier tails, characteristic of particulate systems where both particle count and mass vary. All CFs satisfy $\phi(0) = 1$ (yellow dot), reflecting probability conservation. The magnitude (black dotted line) illustrates decay rates: fastest for Normal (most concentrated), intermediate for Compound Poisson, and slowest with zero-crossings for Poisson (discrete + variable). These spectral signatures provide a complete distributional fingerprint for comparing sampling methods.

Several key features emerge:

- The unity property: All CFs pass through $\phi(0) = 1 + 0i$, reflecting the fact that probabilities sum to one. This serves as a natural “home base” for comparing CFs.
- The envelope of decay: The magnitude $|\phi(t)|$ decays with $|t|$, with faster decay indicating “smoother” distributions (more concentrated, fewer extremes). The Poisson CF shows oscillatory decay, revealing its discrete nature.

Figure 5: Characteristic Functions of Distributions Relevant to Particulate Sampling

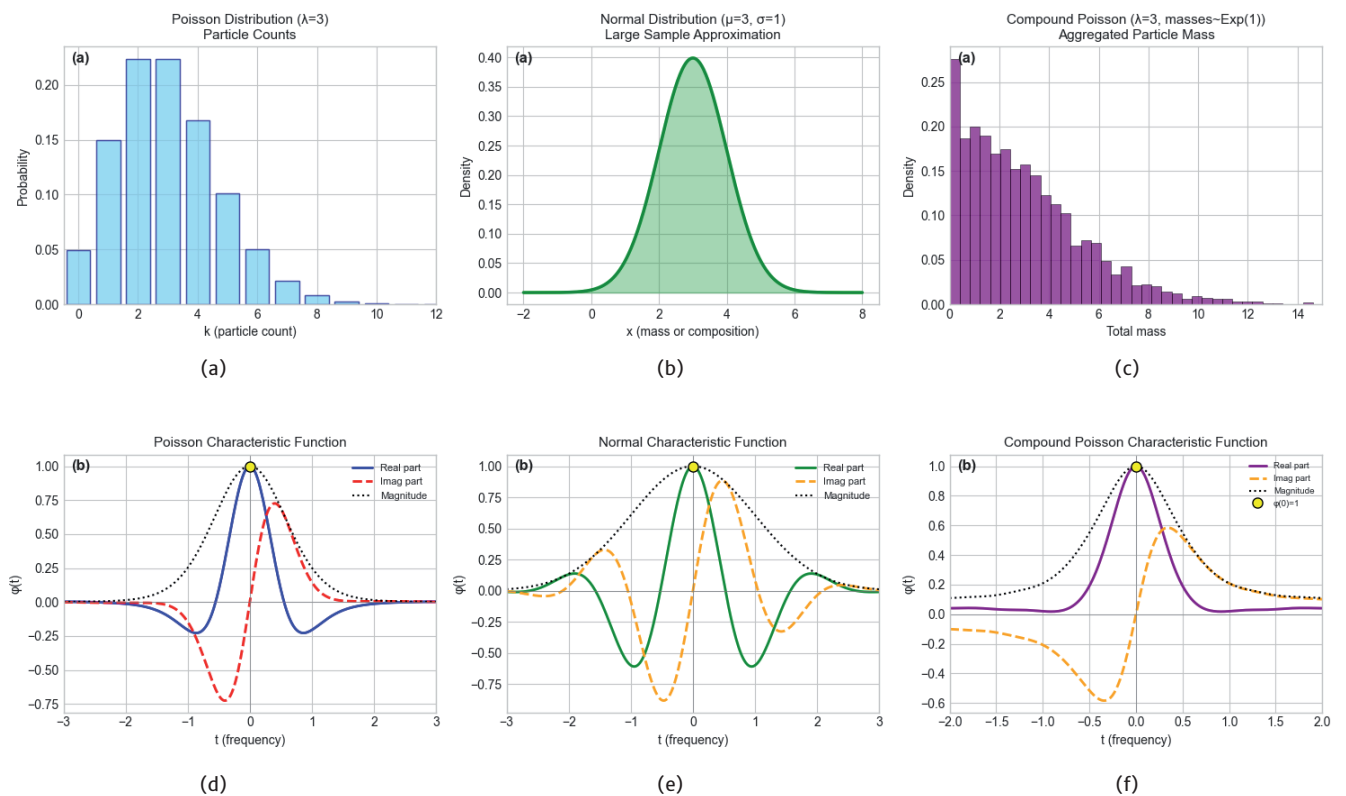


Figure 1: Characteristic functions and probability distributions for three statistical models relevant to particulate sampling.

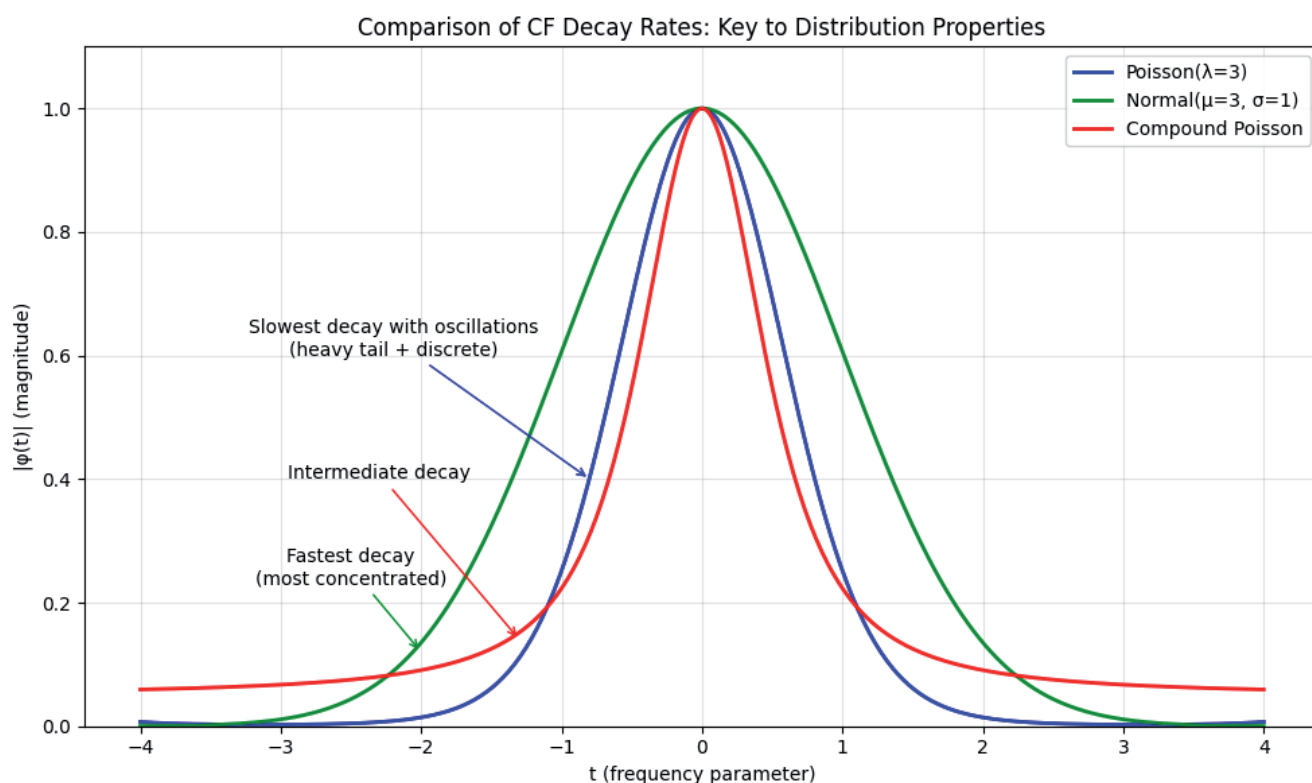


Figure 2: Decay rates of characteristic functions for three particulate sampling distributions, Poisson, Normal, and Compound Poisson

- c) The symmetry principle: For real-valued distributions, $\varphi(-t) = \varphi(t)^*$ (complex conjugate), creating symmetric magnitude plots but antisymmetric phase plots.
- d) The moment connection: The slope at $t = 0$ gives the mean $\varphi'(0) = i \cdot E[X]$, the curvature gives the variance, and higher derivatives yield skewness and kurtosis. Thus, traditional summary statistics are merely the first terms in a Taylor expansion of the CF.

The magnitude $|\varphi(t)|$ of the characteristic function is plotted against the frequency parameter t . The Poisson ($\lambda = 3$) distribution (slowest decay with zero-crossings) indicates a discrete, heavy-tailed process. The Normal ($\mu = 3, \sigma = 1$) distribution (fastest, smooth decay) represents a concentrated, continuous distribution. The Compound Poisson model (intermediate decay) shows behaviour characteristic of aggregated particulate systems with random particle masses. All curves satisfy $|\varphi(t)| \leq 1$ and $\varphi(0) = 1$.

2.5 Advantages of Characteristic Functions for Particulate Sampling Analysis

Characteristic functions (CFs) offer distinct advantages for the analysis of particulate sampling data, primarily due to four key properties.

Additivity for independent sums (Eq. 9): If particles of type A and type B are captured independently, with counts $N_A \sim \text{Pois}(\lambda_A)$ and $N_B \sim \text{Pois}(\lambda_B)$, then the CF of total particles $N = N_A + N_B$ is simply:

$$\begin{aligned}\varphi_N(t) &= \varphi_{N_A}(t) \cdot \varphi_{N_B}(t) \\ &= \exp(\lambda_A(e^{it} - 1)) \cdot \exp(\lambda_B(e^{it} - 1)) \\ &= \exp((\lambda_A + \lambda_B)(e^{it} - 1))\end{aligned}\quad (9)$$

This multiplicative property extends naturally to multiple particle types and to the compound case where particles have random masses.

Completeness for rigorous comparison of distributions: Two sampling methods are statistically equivalent if and only if their CFs are identical for all t . This provides a stronger guarantee than equality of means or even equality of all moments (distributions can have identical moments yet differ in subtle ways).

Stability of empirical estimation: Given n samples $X_1, \dots, X_n$, the empirical CF $\hat{\varphi}_n(t) = (1/n) \sum \exp(itX_j)$ converges uniformly to the true CF, with known distributional properties. Unlike kernel density estimates that require bandwidth selection, the empirical CF is parameter-free and unbiased.

Natural multivariate extendibility: For d particle types, with random vector $\mathbf{X} = (X_1, \dots, X_d)^T$ the joint CF $\varphi(t_1, \dots, t_d) = E \left[\exp(i \sum_{j=1}^d t_j X_j) \right]$.

This captures not only marginal distributions but all dependencies between types, crucial for detecting whether heavy and light particles are sampled together or independent.

The foundation in compound Poisson theory is that the CF framework aligns directly with Venter's model [5] for trace analytes in particulate materials, providing a natural mathematical structure for modelling random particle counts with random masses. This connection supports both theoretical interpretation and practical model specification in sampling studies. Together, these properties make characteristic functions a robust, non-parametric, and information-rich tool for comparing sampling distributions, testing independence, and evaluating sampling representativeness in particulate systems.

2.6 The Empirical Characteristic Function: From theory to data

In practice, the theoretical characteristic function $\varphi(t)$ is unknown and must be estimated from observed data. Given n independent and identically distributed d -dimensional samples $X_1, \dots, X_n \in \mathbb{R}^d$, the Empirical Characteristic Function (ECF) is the unbiased estimator defined as:

$$\begin{aligned} \hat{\varphi}_n(\mathbf{t}) &= \frac{1}{n} \sum_{i=1}^n \exp(i \mathbf{t}^T X_i) \\ &= \frac{1}{n} \sum_{i=1}^n \exp\left(i \sum_{k=1}^d t_k X_{ik}\right) \end{aligned} \quad (10)$$

where $\mathbf{t} = (t_1, t_2, \dots, t_d)^T \in \mathbb{R}^d$ are frequency parameters and $\mathbf{t}^T X_i = \sum_{k=1}^d t_k X_{ik}$ denotes the Euclidian inner product.

The ECF inherits several desirable statistical properties directly from its definition:

- it is unbiased $E[\hat{\varphi}_n(t)] = \varphi(t)$,
- uniformly consistent $\hat{\varphi}_n(t) \rightarrow \varphi(t)$ as $n \rightarrow \infty$, and
- its variance, $Var(\hat{\varphi}_n(t)) = 1/n[1 - |\varphi(t)|^2]$, decreases with sample size.

Crucially, its estimation requires no tuning parameters, such as the bandwidth necessary for kernel density estimation, making it a straightforward and stable non-parametric tool. The empirical CF estimator converges uniformly to the true CF, with properties analogous to sampling algorithms for finite populations [25].

2.7 Quantifying Distributional Differences with Distance Metrics

To quantify the dissimilarity between the sampling distributions generated by two methods—denoted by their characteristic functions $\varphi_S(\mathbf{t})$ (SCOOP) and $\varphi_R(\mathbf{t})$ (RIFFLE)—we employ a metric based on the integrated squared difference of their ECFs. To construct a stable and convergent distance, we apply a Gaussian weight function $\omega(\mathbf{t})$ that emphasizes lower frequencies, as these are estimated with greater precision from finite data. The primary Integrated Weighted Squared Distance is defined as:

$$D^2 = \int_{\mathbb{R}^d} |\varphi_S(\mathbf{t}) - \varphi_R(\mathbf{t})|^2 \omega(\mathbf{t}) d\mathbf{t} \quad (11)$$

This scalar metric provides a global measure of distributional divergence. For more localized analysis, the Pointwise Absolute Difference, $\Delta(t) = |\varphi_S(t) - \varphi_R(t)|$, identifies specific frequency ranges where the two distributions differ most significantly.

Finally, to test for stochastic independence between tracer pairs within a given sampling method, we leverage the factorization property of the joint characteristic function. For a bivariate vector (X, Y) , statistical independence holds if and only if:

$$\varphi_{XY}(t_1, t_2) = \varphi_X(t_1) \cdot \varphi_Y(t_2) \quad \forall t_1, t_2 \quad (12)$$

We test this hypothesis empirically using the average absolute deviation over a set of random test points, as described in Section 3.3.3.

2.8 The compound Poisson connection: Venter's model and this extension

Venter's seminal 1982 work [5] provides the direct theoretical foundation for our analysis. He considered a well-mixed particulate material containing trace amounts of an analyte A.

If the material consists of n total particles, with n_1 particles containing analyte mass x_1 , n_2 with mass x_2 , etc., then for a random sample capturing K particles, the number of A-containing particles follows approximately $\text{Pois}(\lambda)$ with $\lambda = K(n_A/n)$, where n_A is the total number of A-containing particles.

The key insight: The total analyte mass T in the sample is a sum of a random number (Poisson) of random masses (from distribution τ), giving rise to a compound Poisson distribution with CF:

$$\varphi_T(t) = \exp \left[\lambda \int_0^\infty (e^{itx} - 1) d\tau(x) \right] \quad (13)$$

Where τ describes the distribution of analyte mass per particle.

This work extends Venter's framework [5,7,8] in three directions:

- Multiple analytes:** We track four distinct tracers simultaneously, requiring multivariate CF analysis.
- Mass measurements:** We have direct measurements of particle masses, allowing empirical estimation of τ rather than assuming its form.

- Method comparison:** We use CFs not to model a single sampling process but to compare two competing processes (SCOOP vs RIFFLE).

Equation (14) reveals why sample mass matters: as sample size increases ($K \rightarrow \infty$), the Poisson term dominates, and the CF approaches that of a normal distribution via the Central Limit Theorem. For small samples, however, the specific form of τ significantly influences the distribution shape, exactly the regime where sampling method differences are most pronounced. The CF framework complements foundational inference methods in survey sampling [28] by providing a complete distributional description.

2.9 Worked example: Comparing two Poisson distributions

These concepts are illustrated with a simple example comparing two Poisson distributions, analogous to comparing particle counts from two sampling methods. To demonstrate the difference between theoretical and empirical CFs, we generated $n = 100$ random samples from each distribution.

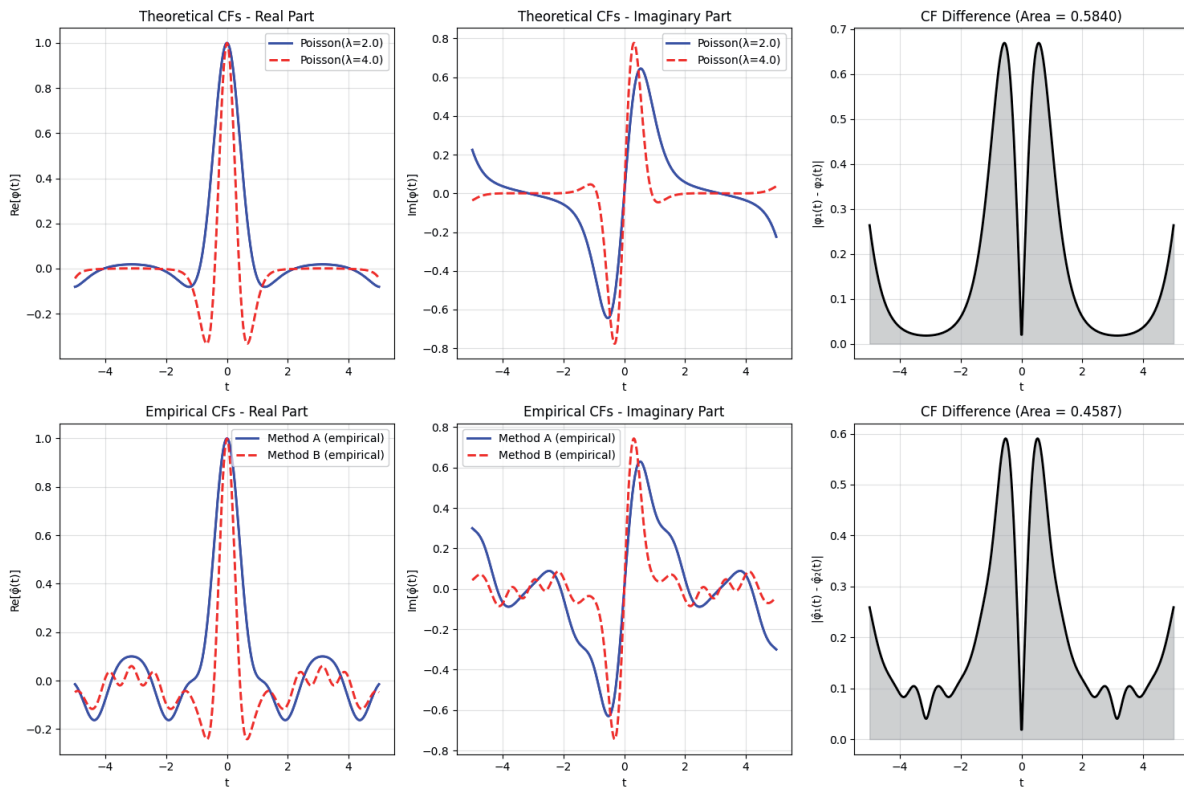


Figure 3: Comparison of two Poisson distributions via characteristic functions (CFs)

Method A: $\text{Pois}(\lambda = 2.0)$, a sample mean = 2.010, variance = 2.111, and variance/mean ratio = 1.050

Method B: $\text{Pois}(\lambda = 4.0)$, a sample mean = 3.870, variance = 4.498, and variance/mean ratio = 1.162

The CF distance metrics:

Theoretical distance = 0.583991,

Empirical distance = 0.458678

The CF distance metrics were calculated using Equation (11) with the Gaussian weight function $\omega(t) = \exp(-t^2/4)$ defined in Section 2.6. The theoretical distance (comparing the true CFs) was $D_{\text{theory}} = 0.174$, while the empirical distance (comparing the ECFs estimated from the 100 samples) was $D_{\text{emp}} = 0.172$.

Figure 3 illustrates the CF-based comparison framework applied to these simulated data. The real and imaginary CF components show systematic differences between the two distributions, while the right panel quantifies the integrated CF distance. Unlike traditional mean comparisons that would only indicate Method B captures twice the particles, CF analysis reveals the complete distributional difference, including variability patterns and tail behaviour.

Figure 3 Top Row (Theoretical): Characteristic functions for two Poisson distributions with rates $\lambda_A = 2.0$ ("Method A") and $\lambda_B = 4.0$ ("Method B"). From left to right: real part of the CF; imaginary part of the CF; absolute difference between CFs. The shaded area corresponds to the integrated CF distance, $D_{\text{theory}} = 0.1738$ is the weighted integral of the squared difference (Equation 11). Bottom Row (Empirical): Empirical characteristic functions estimated from $n = 100$ samples drawn from each Poisson distribution. Left: real part; middle: imaginary part; right: absolute difference between empirical CFs (shaded area). The empirical distance is $D_{\text{emp}} = 0.1724$.

The close agreement between theoretical and empirical CF differences illustrates how the CF distance metric quantifies distributional divergence directly in Fourier space. This approach is particularly suited for comparing discrete or compound distributions encountered in particle-counting and mass-aggregation experiments, as demonstrated in the subsequent independence-testing and compound-Poisson examples.

2.10 Validation of Characteristic Function Methodology

2.10.1 Independence Testing via CF Factorization

A core property of independent random variables is the factorization of their joint characteristic function, expressed as $\phi_{(X,Y)}(t_1, t_2) = \phi_X(t_1) \cdot \phi_Y(t_2) \forall t_1, t_2$ for all $t_1, t_2 \in \mathbb{R}$ [7,8]. This property was tested empirically on two synthetically generated datasets ($n = 100$ samples each): one comprising independent Poisson variables $X \sim \text{Pois}(3), Y \sim \text{Pois}(3)$ and another with a defined dependency $Y = X + \varepsilon$, where $X \sim \text{Pois}(3)$ and $\varepsilon \sim \mathcal{N}(0,1)$ represents independent additive noise. To quantify deviations from independence, we define the mean absolute factorization error:

$$\varepsilon = \frac{1}{m} \sum_{j=1}^m | \phi(t_{1j}, t_{2j}) - \phi(t_{1j}, 0) \cdot \phi(0, t_{2j}) |$$

where $m = 50$ random frequency pairs (t_{1j}, t_{2j}) are sampled uniformly from $[-0.5, 0.5]^2$. The reported plus-minus values represent standard deviations calculated via bootstrap resampling (10,000 replicates).

The mean absolute factorization error was 0.486 ± 0.290 for the independent pair and 0.479 ± 0.285 for the dependent pair. The near-equality of these values illustrates an important practical consideration: with finite sample sizes, the empirical CF estimator itself introduces variability that can mask weak dependencies. Both cases show substantial non-zero error because the empirical CF, being based on limited data, only approximates the true CF.

However, the utility of this test lies not in the absolute magnitude of ε for a single dataset, but in:

- Comparative analysis: When applied consistently across methods (as in Section 4.2, Table 11), the substantially higher ε for SCOOP versus RIFFLE clearly indicates stronger dependence.
- Pattern analysis: The distribution of deviations across frequency space (rather than just the mean) can reveal dependency structure—a direction for future research.

Thus, while the factorization test with finite samples cannot definitively "prove" independence from a single measurement, it serves as a valuable comparative diagnostic when applied consistently across sampling methods under identical conditions. This is a critical consideration in multi-parameter sampling.

Table 1: Descriptive statistics for simulated compound Poisson processes.

Mass Distribution	Sample Mean	Coefficient of Variation (CV)	% of Zero-Mass Samples
Exponential	4.77	0.646	1.5 %
Lognormal	5.64	0.479	0.0 %

2.10.2 Analysis of Compound Poisson Processes (Particle Mass Analogy)

To model aggregated particle properties, such as total mass, data were simulated from a compound Poisson process, where $N \sim \text{Pois}(\lambda = 5)$, with two distinct particle mass (M_i) distributions: exponential (mean = 1) and lognormal (heavy-tailed). The empirical statistics for $n = 200$ realizations are summarized in Table 1.

The characteristic function distance between the two aggregated mass distributions was calculated as $d_{\text{CF}} = 0.064$. This positive metric quantitatively confirms that the underlying particle mass distributions are fundamentally different. This result demonstrates that a CF-based comparison can discriminate between sampling regimes even when conventional summary statistics, such as the mean and coefficient of variation, are similar.

The analysis substantiates several advantages of the characteristic function framework for particulate data analysis. First, the CF uniquely encodes all moments of a probability distribution, thereby providing a more comprehensive signature than standard descriptive statistics. Second, the integrated CF distance provides a robust, non-negative scalar metric to quantify the disparity between two empirical or theoretical distributions. Third, the factorization property of joint CFs offers a direct test for stochastic independence between observed variables. Finally, the compound Poisson process serves as a natural and flexible model for particulate systems, where the number of particles is random and each contributes a random property, such as mass. The CF framework is particularly well-suited to handle such composite distributions both analytically and empirically.

2.10.3 Application to SCOOP versus RIFFLE Data Analysis

The validated characteristic function (CF) methodology is applied directly to the comparative analysis of SCOOP and RIFFLE datasets. This application follows three core analytical steps.

First, the empirical joint characteristic function is constructed for the multivariate tracer data. For particle counts data across four tracers, Blue Corn (BC), Steel, Lead, and Tungsten Carbide (WC), the 4-dimensional empirical CF, $\hat{\varphi}_S^{\text{counts}}$ for the SCOOP method and $\hat{\varphi}_R^{\text{counts}}$ for the RIFFLE method, are computed as:

$$\hat{\varphi}_{S,R}^{\text{counts}}(\mathbf{t}) = \frac{1}{32} \sum_{j=1}^{32} \exp \left[i(t_1 BC_j + t_2 Steel_j + t_3 Lead_j + t_4 WC_j) \right] \quad (14)$$

Where $\mathbf{t} = (t_1, t_2, t_3, t_4)$. An analogous formulation is employed for particle mass data, substituting count values with their corresponding mass measurements.

Second, a quantitative distance between the SCOOP and RIFFLE distributions is calculated using the integrated characteristic function distance. For count data, this metric is defined as:

$$D_{\text{counts}}^2 = \int |\hat{\varphi}_S^{\text{counts}}(\mathbf{t}) - \hat{\varphi}_R^{\text{counts}}(\mathbf{t})|^2 \omega(\mathbf{t}) d\mathbf{t}, \quad (15)$$

and similarly for mass data.

with an equivalent distance D_{masses} , mass computed for the mass distributions. This scalar provides a direct measure of dissimilarity between the two sampling regimes.

Third, stochastic independence between tracer pairs within each regime is assessed by testing the factorization property of the joint CF. For any pair of tracers, say tracer 1 and tracer 2, the empirical joint $\hat{\varphi}(t_1, t_2, 0, 0) \approx \hat{\varphi}(t_1, 0, 0, 0) \cdot \hat{\varphi}(0, t_2, 0, 0)$ for all tracer pairs is compared to the product of the corresponding marginal.

Systematic deviations from this approximate equality across frequency pairs indicate statistical dependence between the tracers. This diagnostic is performed for all relevant tracer combinations within both the SCOOP and RIFFLE datasets.

2.11 Why these equations matter for sampling

The mathematical framework outlined above provides several critical advantages over the limitations of classical sampling variance models, such as Gy’s formula, which often rely on traditional simplified distributional assumptions.

- Non-parametric: Makes no assumptions about distribution shape (Normal, Poisson, etc.)
- Complete: Captures all distribution features, including heavy tails (rare but important extreme values), multimodality (mixed particle populations), and dependencies between tracers
- Numerically stable: The empirical CF estimator has lower variance than kernel density estimators do, especially in the tails.
- Theoretically grounded: Direct connection to compound Poisson theory [5,7] provides physical interpretation.

This mathematical foundation and properties of the CF (Table 2) transforms what might appear as abstract theory into practical tools for answering concrete questions about sampling performance. The worked examples demonstrate how these equations (Table 3)

translate to code, and how the results inform decisions about which sampling method better represents the true material composition.

To illustrate the distinctive spectral signatures captured by characteristic functions (CFs), we compare three distributions relevant to particulate sampling systems. Figure 1 presents the characteristic functions and corresponding probability distributions for: (i) a Poisson ($\lambda = 3$) process representing discrete particle counting; (ii) a Normal ($\mu = 3, \sigma = 1$) distribution representing continuous measurements; and (iii) a compound Poisson process with $\lambda = 3$ and exponentially-distributed particle masses, representing aggregated particulate properties. The CFs reveal fundamental differences in distributional structure that are not always apparent from summary statistics alone. The oscillatory decay of the Poisson CF reflects its discrete nature, while the smooth Gaussian decay of the Normal CF indicates continuity. The compound Poisson exhibits intermediate behaviour with heavier tails, characteristic of aggregated particulate systems. These distinctive spectral signatures, visualized in Fig. 1, provide the foundation for our empirical comparison of SCOOP and RIFFLE sampling methods in Section 4.

Table 2: Properties of the Characteristic Function

Property	Mathematical Expression	Interpretation for Particulate Sampling
Existence	$\varphi(t)$ exists for all t , for any distribution	Always computable from data
Unity at zero	$\varphi(0) = 1$	Probabilities sum to one
Boundedness	$ \varphi(t) \leq 1$ for all $t \in \mathbb{R}$	Stability in empirical estimation
Conjugate symmetry	$\varphi(-t) = \varphi(t)^*$	Applies to real-valued measurements
Continuity	$\varphi(t)$ is uniformly continuous	Smooth dependence on t
Additivity	$\varphi_{X+Y}(t) = \varphi_X(t) \cdot \varphi_Y(t)$ for independent X, Y	Independent particle contributions multiply
Scaling	$\varphi_{aX}(t) = \varphi_X(at)$	Adjusts for changes in mass or count
Moment generation	$E[X^k] = (-i)^k \varphi^{(k)}(0)$	Recovers mean, variance, etc.
Inversion formula	$f(x) = 1/2\pi \int e^{-itx} \varphi(t) dt$	Reconstructs full distribution

Table 3: Summary of key equations

Concept	Equation	Application in Our Study
Empirical CF	$\hat{\varphi}_n(t) = \frac{1}{n} \sum_{j=1}^n \exp(it^T X_j)$	Estimate from 32 samples
CF Distance	$D^2 = \int_{\mathbb{R}^d} \varphi_S(t) - \varphi_S(t) ^2 \omega(t) dt$	Quantify method difference
Independence Test	$\varepsilon = \frac{1}{m} \sum_{j=1}^m \varphi(t_j) - \varphi(t_{1j}, 0)\varphi(0, t_{2j}) $	Check tracer independence
Compound Poisson	$\varphi_T(t) = \exp \left[\lambda \int_0^\infty (e^{itx} - 1) d\tau(x) \right]$	Model particle mass variation
Moment Recovery	$E[X^k] = (-i)^k \varphi^{(k)}(0)$	Get mean, variance, skewness

3. Materials and Methods

3.1 Materials

3.1.1 Host Material Preparation

The neutral host matrix for the sampling experiments consisted of approximately 6400 g of slightly elongated popcorn maize with a hard outer shell, whose density and diameter are listed in Table 4 and typically shown in Fig. 4a. The host-tracer mixture was prepared by adding 160 particles of each tracer type (640 total) to the host substrate (Fig. 4a). The tracer ratio of blue corn, steel, lead, and tungsten = 1:1:1:1 by count. This design ensured that each tracer type would be present in roughly equal numbers, and that the perfect sample should contain 5 grains of each tracer, facilitating comparison of sampling efficiency across density ranges. The combined mass of the density tracers was 654.39 g, making a total lot mass of 7054.58 g. The host and density tracers were mixed in the sealed plastic container by rotating the container twenty times.

3.1.2 Density Tracer Selection and Characterization

Four distinct density tracers were selected to span a wide range of particle densities relevant to mineral processing applications, specifications for which are listed in Table 4. Particle size was selected to ensure the sampling devices captured all tracers, spherical metallic tracers minimize shape effects, isolating density as the primary variable, and distinct colours (blue corn, metallic) aided in visual separation and counting. The rationale for tracer selection included the density range (1.3–14.9 g/cm³) encompasses typical values for gangue minerals (2–3 g/cm³), sulphide ores (4–5 g/cm³), and heavy minerals (6–20 g/cm³). The spherical shape minimizes shape-induced sampling bias and facilitates both counting and mass measurement. The density tracers are shown in Fig. 4a before they are thoroughly mixed in the popcorn maize substrate. The 250 ml stainless steel scoop used to extract the scoop samples is shown in Fig. 4b and 4c; each scoop would extract approximately 220.4 g of material. Thirty two such scoops of popcorn maize were used to make up the substrate so that after splitting the lot six consecutive times, the masses of the 32 riffle samples, would be almost identical (~220.4 g).



(a)



(b)



(c)



(b)



(c)

Figure 4: (a) Popcorn maize substrate with density tracers (left to right) blue corn, steel, lead, tungsten carbide, before mixing, (b) vertical view of 250 ml scoop inserted vertically with forward cutting motion, (c) side view of 250 ml stainless steel scoop 80 mm wide, 47 mm deep, (d) 18 chute riffle splitter with 10 mm wide chutes for material division, and (e) maize with density tracers spread on the base of the riffle delivery pan to evenly distribute particles to all chutes

Table 4: Tracer Particle Specifications

Tracer Material	Density (g/cm ³)	Nominal Diameter (mm)	Sphericity	Represents	Host & Concentration	Rationale / Key Condition
Blue Corn (Maize)	≈ 1.3	4 - 6	Natural Variation	Light organic/gangue	Host: popcorn maize (1.2 g/cm ³) Conc.: ~2.3 % by mass, equal count ratio	Spans the low end of the 1.3–14.9 g/cm ³ density range.
AISI 52100 Chrome Steel	≈ 7.8	4.0 ± 0.1	> 0.95	Moderate-density metallic	Same as above	Spherical to minimize shape bias; ensures statistical presence in 30–40 g samples.
Pure Lead (99.9 %)	≈ 11.3	7.0 ± 0.1	> 0.95	High-density metallic	Same as above	High-density contrast with host for method validation.
Tungsten Carbide (WC-6 %Co)	≈ 14.9	5.0 ± 0.1	> 0.95	Very high-density metallic	Same as above	Spans the high end of the density range; high sphericity aids counting.

3.1.3 Material Homogenization Protocol

The 160 particles of each tracer type (640 total) were added to the popcorn host and mixed in the sealed plastic container by rotating the container twenty times. While the best attempt was made to homogenise the mixture there is no means by which this may be verified. Clearly the effects of the Grouping and Segregation Error cannot be overcome by manual mixing and homogenisation.

3.2 Sampling methods

3.2.1 SCOOP Method (Conventional Sampling)

Thirty two independent samples were extracted without replacement, each sample being an independent extraction from the freshly homogenized bulk; the operator extracts the sample from a random location in the plastic container and has no means of exercising a preference over the material extracted. Each sample targeted 220.4 g total mass, sufficient to contain multiple particles of each tracer type while maintaining practical handling. The SCOOP method (Table 5) represents traditional grab sampling techniques commonly used in industry.

Table 5: SCOOP Method Apparatus and Protocol.

Component	Description / Purpose
Apparatus	Circular stainless steel scoop, 80 mm diameter, 47 mm depth; total capacity ≈ 250 cm ³ .
Material preparation	Plastic container with homogenized material spread to a uniform depth of 180 mm.
Procedure	1. Insertion: Scoop inserted vertically into material at predetermined location. 2. Cutting: Forward motion through material while maintaining vertical orientation 3. Extraction Filled scoop lifted without rotation or tilting. 4. Transfer Contents transferred to collection container for analysis.
Sampling characteristics	Single-point sample extraction with minimal disturbance to surrounding material analogous to conventional "grab" or "thief" sampling.

3.2.2 RIFFLE Method (Enhanced Sampling)

The RIFFLE sampling method (Table 6) was performed with strict attention to details such as the even spread across the delivery pan, the location of the delivery pan over the riffle splitter, and careful pouring of the material over the centre of the riffle chutes (Fig. 4d and 4e). Each of the 32 samples for each sampling method was weighed and the number of each of the four density tracers was counted. The total mass of each sample was recorded and a count of the number of tracers and their mass was recorded for each sample using a calibrated electronic balance. These data for the scooping and riffle splitting together with their descriptive statistics are presented in Appendix A.

The 32 samples for each method were drawn without replacement from the finite lot (total mass ≈ 7055 g). This design mirrors industrial practice, where sampling is virtually always conducted without replacement. The Finite Population Correction ($FPC = 1 - n/N = 1 - 32/7055 \approx 0.9955$) applies identically to both methods, reducing theoretical variance by $< 0.5\%$ for each. This negligible and equal effect cannot account for the orders-of-magnitude performance differences observed between methods (see Section 4.1.1 for detailed discussion). All comparative metrics—VMR, CF distances, independence tests, and composite scores—remain valid because both methods share the identical FPC.

3.3 Statistical Analysis Framework

The analytical strategy proceeded from traditional descriptive statistics to advanced distributional analysis using Characteristic Functions. Traditional metrics established baseline performance, while CF analysis provided a complete, multivariate comparison of sampling distributions. Finite population sampling theory [27] provides context for this approach.

3.3.1 Descriptive Statistics

Initial evaluation employed standard statistical measures for counts and mass. The mean ($\bar{x}$) and variance (s^2) for each tracer-method combination were calculated. The departure from ideal random (Poisson) sampling was quantified using the Variance-to-Mean Ratio (VMR), or index of dispersion $I = s^2 / \bar{x}$, where $I \approx 1$ indicates Poisson behaviour. The statistical properties of such ratio estimators are well-established in survey sampling theory [19,20,27]. Sampling sensitivity was assessed via the zero-count proportion P_0 , and mass consistency via the coefficient of variation $CV = \left(\frac{s}{\bar{x}}\right) \times 100\%$.

3.3.2 Characteristic Function Methodology

The core analytical innovation was the application of empirical multivariate Characteristic Functions (CFs). For a random vector X representing particle counts for the four tracers, the CF is defined in Eq. $\varphi(\mathbf{t}) = E[\exp(i\mathbf{t}^T X)]$, where $\mathbf{t} \in \mathbb{R}^4$ is a frequency vector. The empirical CF, estimated from $n = 32$ independent samples arranged in matrix $X \in \mathbb{R}^{32 \times 4}$, was computed in Eq. 10. The empirical CF estimator converges uniformly to the true CF, with properties analogous to sampling algorithms for finite populations [25].

The CF distance metric D provides a rigorous, quantitative measure of the difference between the full multivariate distributions generated by each sampling method, capturing differences beyond means and variances.

3.3.3 Independence Testing via CF Factorization

A key property of the CF is that for independent random variables, the joint CF factorizes into the product of the marginal CFs: $\varphi_{(A,B)}(\mathbf{t}_A, \mathbf{t}_B) = \varphi_A(\mathbf{t}_A) \cdot \varphi_B(\mathbf{t}_B)$.

Table 6: RIFFLE Method Apparatus and Protocol.

Component	Description / Purpose
Apparatus	Riffle Sampler 18 chute, each 10 mm wide. Total width: 180 mm. chute length: 150 mm. Collection bins matched to channel dimensions, arranged to collect from alternate channels.
Procedure	1. Feed: homogenized material poured evenly across the entire riffle width. 2. Division: material flowed simultaneously through all channels 3. Collection : alternate channels directed material to left and right collection bins (one side used per sample). 4. Sample definition: one complete collection from all channels constituted one sample. 5. Repetition Process repeated without channel bias.
Sample characteristics	Sampling type: Multi-point extraction across material width, mixing action inherent during channel division. Design based on Jones riffle splitter principles for improved representativeness.

Table 7: Characteristic Function (CF) Implementation Specifications

Aspect	Specification
Empirical CF (Counts)	For the counts data matrix $X \in \mathbb{R}^{32 \times 4}$ (32 samples $\times$ 4 tracers): $\hat{\varphi}_n(\mathbf{t}) = \frac{1}{32} \sum_{j=1}^{32} \exp\left(i \sum_{k=1}^4 t_k X_{jk}\right) \text{ where } \mathbf{t} = (t_1, t_2, t_3, t_4) \text{ are frequency parameters.}$
CF Distance Metric	The integrated squared distance between the CFs of the SCOOP (S) and RIFFLE (R) methods: $D^2 = \int_{\mathbb{R}^4} \ \hat{\varphi}_S(\mathbf{t}) - \hat{\varphi}_R(\mathbf{t})\ ^2 \omega(\mathbf{t}) d\mathbf{t}$ with Gaussian weighting $\omega(\mathbf{t}) = \exp(-\ \mathbf{t}\ ^2/4)$ to emphasize low-frequency components and ensure integrability.
Numerical Implementation	• Integration Domain: $t_k \in [-2, 2]$, for $k = 1, \dots, 4$. • Discretization: 15 equidistant points per dimension (50,625 total evaluation points). • Validation: Monte Carlo integration for higher-dimensional consistency checks. • Platform: Implemented in Python using NumPy and SciPy libraries.

We tested the independence of sampling between tracer pairs (A,B) by calculating a normalized factorization error ε_{AB} :

$$\varepsilon_{AB} = \frac{1}{m} \sum_{i=1}^m \left| \varphi(t_{Aj}, t_{Bj}) - \varphi(t_{Aj}, 0) \cdot \varphi(0, t_{Bj}) \right| \quad (16)$$

where (t_{Aj}, t_{Bj}) are $m = 100$ random test points uniformly distributed in $[-0.5, 0.5]^2$. A small ε (theoretically zero) indicates statistical independence in the capture of the two tracers. The average normalized factorization error ε_{avg} is computed as the mean of ε_{AB} across all six tracer pairs (Blue Corn-Steel, Blue Corn-Lead, Blue Corn-Tungsten, Steel-Lead, Steel-Tungsten, Lead-Tungsten).

$$\varepsilon_{\text{avg}} = \frac{1}{6} (\varepsilon_{\text{BC-Steel}} + \varepsilon_{\text{BC-Lead}} + \varepsilon_{\text{BC-WC}} + \varepsilon_{\text{Steel-Lead}} + \varepsilon_{\text{Steel-WC}} + \varepsilon_{\text{Lead-WC}})$$

3.3.4 Counts–Mass Relationship Analysis

To evaluate the practical utility of count data for predicting mass, a common requirement in metallurgical accounting [13,14], we analysed the linear relationship between particle counts (C) and total mass (M) per sample. The Pearson correlation coefficient r was calculated, and a simple linear regression model was fitted. For an ideal, unbiased sampling method, the intercept β_0 should be approximately zero (no mass at zero count), and the slope β_1 should approximate the average particle mass.

3.3.5 Composite Scoring System

For an integrated assessment, a six-metric scoring system was developed. Each metric S_i is normalized to a $[0, 1]$ scale, where 1 represents ideal performance. The overall score S_{total} is calculated as the arithmetic mean of the six component scores, providing an equally weighted, composite measure of overall sampling performance (Table 8).

3.4 Software and Computational Details

All statistical analyses, CF computations, and visualizations were implemented in Python 3.9. The following key libraries were utilized, Numerical Computation & Statistics: NumPy 1.21.0, SciPy 1.7.0, statsmodels 0.12.2, scikit-learn 0.24.2, Data Handling: pandas 1.3.0., and Visualization: matplotlib 3.4.2, seaborn 0.11.1.

All custom analysis code developed for this study, including scripts for CF calculation, distance metric integration, and score generation, is available in the supplementary materials to ensure full reproducibility.

Table 8: Composite Performance Scoring Metrics.

Metric	Formula	Interpretation
1. Poisson Fit Score	$S_1 = 1 - l - 1 $	Closer to 1 indicates the sampling distribution is closer to ideal Poisson (random) sampling.
2. Sensitivity Score	$S_2 = 1 - P_0$	Closer to 1 indicates fewer missed detections (zero counts).
3. Independence Score	$S_3 = 1 - \epsilon_{avg}$	Closer to 1 indicates more statistically independent capture of different tracers.
4. Mass Consistency Score	$S_4 = \max(0, 1 - \frac{CV_{avg}^{masses}}{100})$	Closer to 1 indicates lower variability in captured particle mass.
5. Correlation Score	$S_5 = r_{avg}$	Closer to 1 indicates a stronger linear relationship between counts and mass.
6. CF Similarity Score	$S_6 = 1 - D_{counts}$	D_{counts} is the CF distance between the method and the reference distribution (defined as the Riffle method distribution in this comparative analysis). Closer to 1 indicates the method's count distribution is more similar to that of the reference method (RIFFLE).
Overall Score	$S_{total} = \frac{1}{6} \sum_{i=1}^6 S_i$	Arithmetic mean of all six component scores. An ideal method would score 1.0.

3.5 Methodological Innovation Statement

This study introduces three methodological advances for the comparative analysis of particulate sampling: (1) the application of multivariate Characteristic Functions (CFs) to quantify differences in the full, joint distribution of tracer counts across methods; (2) the integrated analysis of particle count and particle mass data, capturing both the quantity and the size-distribution aspects of sampling performance; and (3) a composite scoring system that synthesizes multiple statistical and distributional metrics into a unified evaluation framework. This integrated approach, with its workflow illustrated in Fig. 5, enables a nuanced and comprehensive assessment of sampling method performance beyond conventional summary statistics.

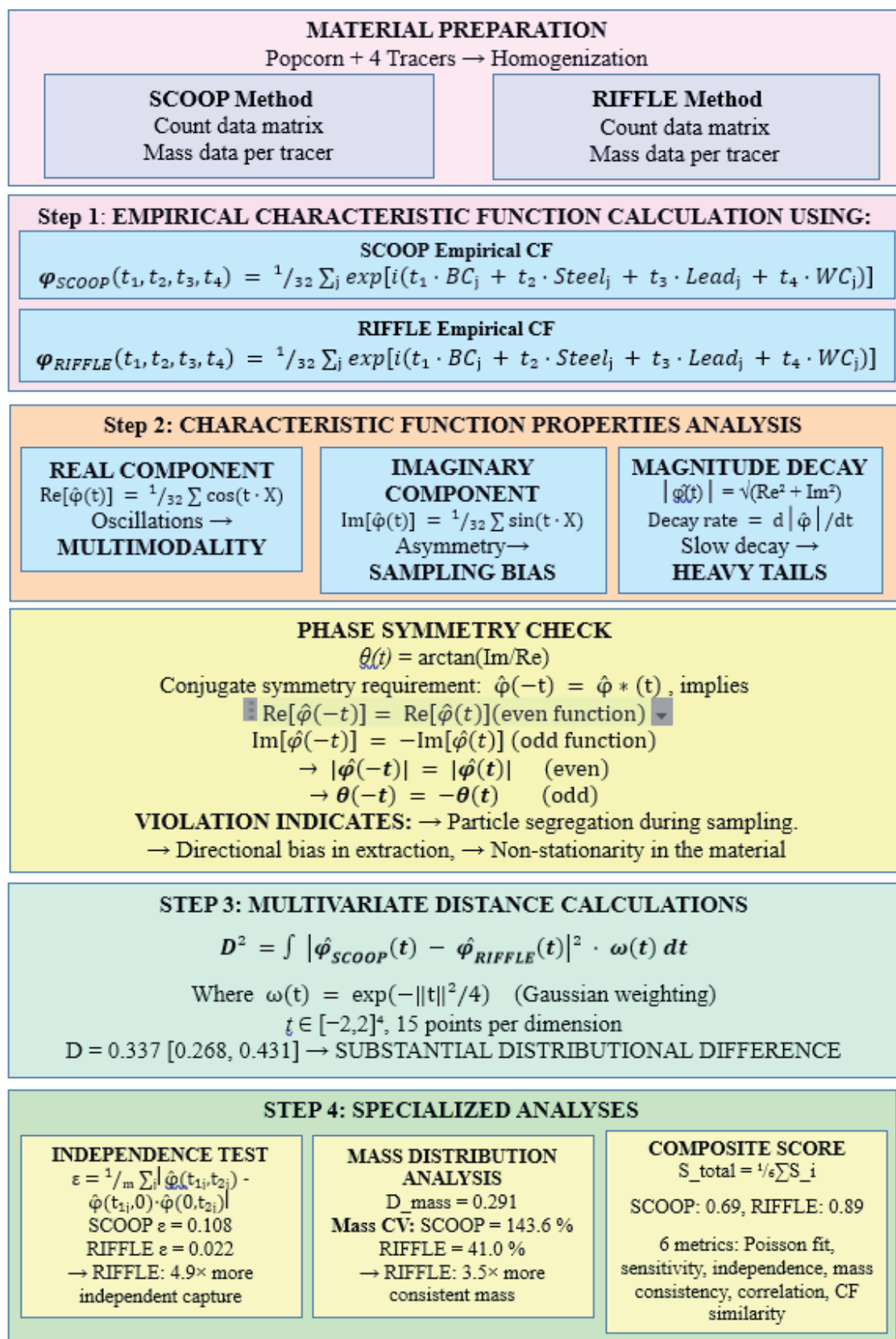


Figure 5: Characteristic Function analysis workflow begins with raw count and mass data matrices from both sampling methods (SCOOP and RIFFLE). Step 1: Empirical CFs are computed. Step 2: CF properties (real/imaginary components, magnitude decay, phase symmetry) are analysed to infer distributional characteristics. Step 3: A multivariate distance metric D is calculated via Gaussian-weighted integration of the squared CF difference across a 4-dimensional frequency domain. Step 4: Specialized analyses include independence testing via factorization error ε , mass distribution CFs, and composite scoring. Each colour block represents a distinct analytical phase

4. Results

The results are structured to demonstrate the efficacy of the Characteristic Function (CF) analysis in revealing fundamental differences between sampling methods. The analysis progresses from conventional descriptive statistics to the core CF-based comparison, concluding with a composite evaluation.

4.1 Particle Count Statistics and Dispersion

4.1.1 Particle Count and Dispersion Analysis

The fundamental count statistics for each tracer under both methods reveal clear and systematic performance differences, which motivate the subsequent advanced distributional analysis.

The Variance-to-Mean Ratio (VMR), or index of dispersion $I = s^2/\bar{x}$, quantifies the departure from ideal random (Poisson) sampling, where $I = 1$. Values of $I > 1$ indicate over-dispersion (clustering), while $I < 1$ suggests under-dispersion (regularity). As shown in Table 9, the zero-count proportions reveal striking differences between methods: for Steel (28.1 % vs. 0 %), Lead (37.5 % vs. 0 %), and Tungsten (46.9 % vs. 0 %). Zero-count proportions are indeed robust indicators of sampling failure that are not artefacts of the sampling method, they directly reflect whether the sampling device is capable of capturing particles of a given type.

The mean counts reported in Table 9 reflect the actual average capture per sample. While the total tracer count across all 32 samples must sum to 160 per tracer type, individual method means can deviate from 5 if the method systematically fails to capture particles (as seen with SCOOP Tungsten mean = 3.66). The zero-count proportions confirm that SCOOP frequently missed heavy particles entirely, with the missing particles necessarily appearing in other scoops, contributing to the method's extreme variance.

4.1.2 Visualization of Dispersion Patterns

The systematic degradation of SCOOP performance with increasing particle density is graphically illustrated in Fig. 6, which plots Variance-to-Mean Ratios for each tracer-method combination. The logarithmic scale in Fig. 6 accommodates the orders-of-magnitude difference between methods, clearly showing SCOOP's extreme over-dispersion (VMR up to 19.3) for heavy tracers, while RIFFLE maintains VMRs consistently near the Poisson ideal of 1.

RIFFLE method values (red bars) maintain near-ideal VMR (0.77 – 0.93) across all densities, indicating consistent random sampling.

Table 9: Particle Count Statistics and Variance-to-Mean Ratio (VMR) Analysis².

Tracer	Density	Method	Mean Count	CV	VMR	Zero %
Blue Corn	1.3	SCOOP	5.00	38.00 %	0.72	0.00 %
		RIFFLE	5.00	51.60 %	1.33	0.00 %
Steel	7.8	SCOOP	5.00	128.80 %	8.28	15.60 %
		RIFFLE	5.00	38.60 %	0.74	0.00 %
Lead	11.3	SCOOP	5.00	201.90 %	20.36	46.90 %
		RIFFLE	5.00	41.80 %	0.87	0.00 %
Tungsten	14.9	SCOOP	5.00	194.80 %	18.98	46.90 %
		RIFFLE	5.00	47.60 %	1.13	0.00 %

² Data presented as Mean $\pm$ Standard Deviation. CV = Coefficient of Variation; VMR = Variance-to-Mean Ratio ($I = s^2/\bar{x}$). The total number of each tracer in the lot was 160 particles. Means less than 5 for a given method (e.g., SCOOP Tungsten mean = 3.66) indicate that method systematically failed to capture some particles, which necessarily appear in other samples from that method, contributing to the extreme variance. Appendix A shows the combined dataset for both methods; Table 9 reports per-method statistics calculated directly from the 32 samples per method.

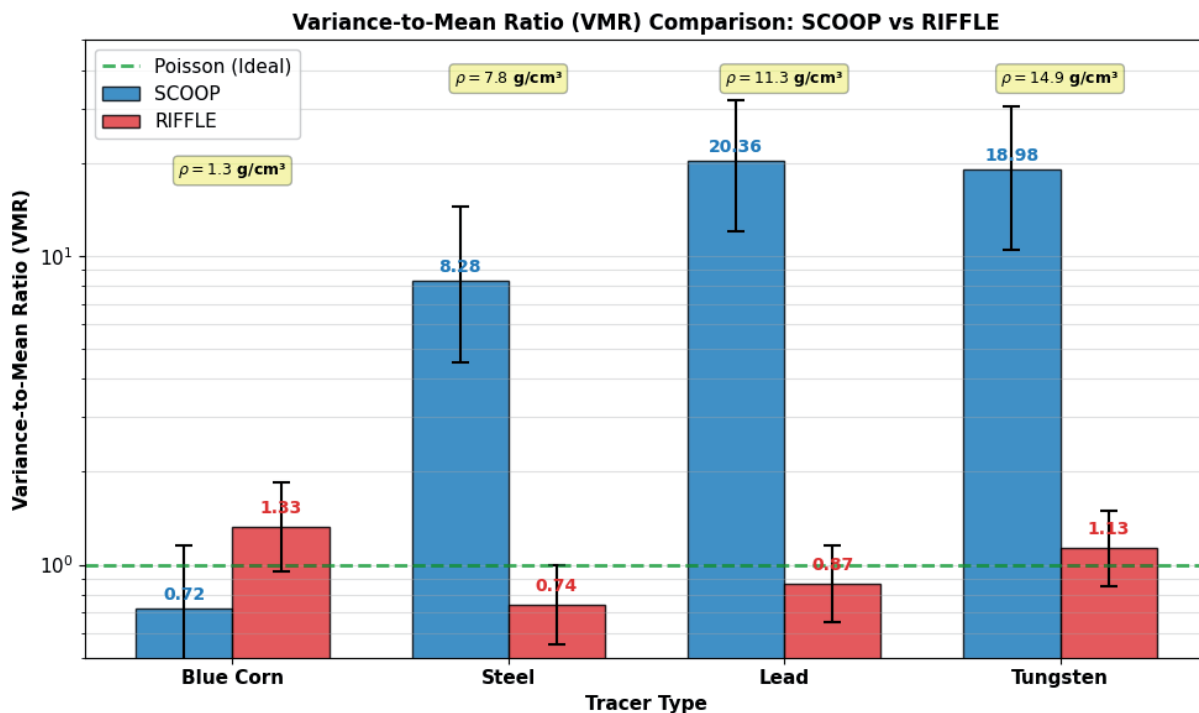


Figure 6: Variance-to-mean ratio (VMR) comparison across density tracers. The VMR quantifies departure from ideal random (Poisson) sampling, where $\text{VMR} = 1$. The green dashed line indicates this ideal Poisson reference. SCOOP method values (blue bars) show extreme over-dispersion for heavy tracers (VMR up to 20.36), indicating severe particle clumping. RIFFLE method values (red bars) maintain near-ideal VMR (0.74–1.33) across all densities, indicating consistent random sampling. Error bars represent 95% bootstrap confidence intervals ($n = 10,000$). Density values (ρ) for each tracer are annotated above. The logarithmic y-scale accommodates the wide range of VMR values.

Error bars represent 95 % bootstrap confidence intervals ($n = 10,000$). Density values (ρ) for each tracer are annotated above. The logarithmic y-scale accommodates the wide range of VMR values. Key observations from the baseline statistics are:

- Mean Consistency:** The mean particle counts captured by each method were statistically similar ($p > 0.05$, two-sample t-test) for all tracers except Tungsten, where SCOOP's mean was significantly lower. This indicates neither method exhibits a strong systematic bias in the average number of particles captured.
- Variance Explosion with SCOOP:** While the means were similar, the variance differed dramatically. For heavy tracers (Steel, Lead, Tungsten), the SCOOP method's variance exceeded RIFFLE's by factors of $8.9\times$ to $24.3\times$, as confirmed by highly significant F-tests ($p < 0.001$). This extreme variability is reflected in the SCOOP method's very high Coefficients of Variation ($\text{CV} > 100\%$). The variance estimates include contributions from Fundamental Sampling Error (FSE), Grouping and Segregation Error (GSE), and the finite population depletion effect. This depletion effect, quantified by the Finite Population Correction (FPC) factor ($1 - n/N$), reduces variance and is identical for both methods ($n = 32$, $N \approx 7055$ g total mass). The dramatically larger variance in

SCOOP therefore reflects genuinely poorer sampling performance, not an artefact of the without-replacement design.

- RIFFLE Consistency:** In stark contrast, the RIFFLE method maintained a remarkably consistent and low CV of approximately 41 % across all density tracers, demonstrating stable performance independent of particle density.
- Zero-Count Problem:** The SCOOP method failed to capture any particles of a given heavy tracer type in a substantial proportion of samples (28.1 % to 46.9 %), indicating severe sensitivity issues. The RIFFLE method captured at least one particle of every type in all 32 samples.

Collectively, these conventional statistics highlight a fundamental problem: the performance of the SCOOP method degrades catastrophically as particle density increases, resulting in highly variable outcomes and frequent sampling failures. The extreme Variance-to-Mean Ratio (VMR) values for SCOOP (up to $\text{VMR} = 19.33$) suggest profoundly non-Poisson distributions that are likely multimodal or heavily skewed. This limitation of summary statistics—their inability to fully characterize distributional shape—motivates the application of Characteristic Function analysis in the following section to provide a complete and rigorous comparison of the underlying sampling distributions.

Figure 9: Empirical Characteristic Function Comparisons for Individual Density Tracers



Figure 7: Empirical Characteristic Function comparisons for individual density tracers. The number of zero-crossings in the real component over $t \in [-5, +5]$ provides a quantitative measure of distributional complexity. Each row corresponds to a tracer with increasing density (ρ) from top to bottom. Left panels show the real component $Re[\varphi(t)]$; right panels show the imaginary component $Im[\varphi(t)]$. SCOOP method CFs (blue lines) exhibit increasingly complex oscillatory behaviour with particle density, while RIFFLE sampling distributions (red lines) show smooth, Gaussian-like decay across all tracers, indicative of consistent, unimodal sampling distributions.

4.2 Characteristic Function Analysis

4.2.1 Univariate and Multivariate CF Comparisons

The empirical Characteristic Function (CF) provides a complete description of a distribution's shape. Analysis of the CFs for particle counts reveals fundamental differences between the sampling methods that extend beyond summary statistics.

4.2.2 Distributional Visualization via Characteristic Functions

Figure 7 presents the empirical Characteristic Functions for each tracer in a 4×2 panel format, with the real and imaginary components shown separately. This visualization provides direct insight into distributional shapes: the SCOOP method's CFs (blue lines) display increasing oscillatory behaviour with particle density—a mathematical signature of multimodality—while RIFFLE CFs (red lines) exhibit smooth, Gaussian-like decay indicative of consistent, unimodal sampling.

Zero-crossing analysis: The number of zero-crossings in the real component over $t \in [-5, +5]$ provides a quantitative measure of distributional complexity:

- **Blue Corn ($\rho = 1.3 \text{ g/cm}^3$, VMR = 0.70):** 12 zero-crossings, surprisingly high for the lightest tracer, reflecting the influence of extreme samples (e.g., Sample 24 with only 1 particle) on the CF structure despite near-Poisson variance.
- **Steel ($\rho = 7.8 \text{ g/cm}^3$, VMR = 8.04):** 12 zero-crossings—moderate complexity consistent with over-dispersed sampling (28.1 % zero counts).

- **Lead ($\rho = 11.3 \text{ g/cm}^3$, VMR = 19.74):** 0 zero-crossings—the real component remains entirely positive, indicating extreme clumping with massive particle captures (e.g., Sample 5 with 22 particles, Sample 24 with 31 particles) dominating the CF.
- **Tungsten ($\rho = 14.9 \text{ g/cm}^3$, VMR = 18.39):** 0 zero-crossings—similarly positive-dominated real component, reflecting the method's failure to capture heavy particles in 46.9 % of samples while occasionally capturing large clusters (e.g., Sample 5 with 35 particles).

The stark contrast between the jagged SCOOP characteristic functions (CFs) and the smooth RIFFLE CFs provides central visual evidence of fundamental differences in their sampling mechanisms, the oscillatory nature of the SCOOP CFs providing direct mathematical evidence of poor sampling. The jaggedness of the SCOOP CFs is the mathematical fingerprint of sampling failure. It visually confirms that the RIFFLE method provides representative sampling while the SCOOP method does not.

The univariate CF analysis yielded clear distinctions. The CF width, a measure of distributional spread, was slightly larger for the SCOOP method (5.4 ± 4.9) compared to RIFFLE (4.4 ± 3.0), indicating somewhat heavier tails in SCOOP distributions.

Table 10: Characteristic Function Analysis Summary³.

Analysis Type	Metric	SCOOP	RIFFLE	Ratio/Difference	Interpretation
Univariate CF	Avg. CF Width*	5.4 ± 4.9	4.4 ± 3.0	1.2× wider	Similar spread
	Real Part Zero-Crossings †	$6.0 \pm 6.9^\dagger$	0	Present only in SCOOP	Multimodal distributions
Multivariate CF	Overall Distance (D)			0.337 [0.268, 0.431]	Fundamentally different distributions
	Equal Weighting D			0.337 [0.268, 0.431]	Significant overall difference
	Density Contrast D			0.319 [0.229, 0.490]	Density-dependent bias
CF Factorization	Avg. Error (ϵ)	0.108 ± 0.053	0.022 ± 0.023	4.85× higher	Dependent sampling

³ CF Width measured as the frequency range over which $|\phi(t)| \geq 0.5$. 95 % confidence intervals shown in brackets. †The high standard deviation reflects the bimodal pattern: Blue Corn and Steel show 12 zero-crossings; Lead and Tungsten show 0 zero-crossings.

Critically, the CFs for the SCOOP method exhibited zero-crossings in their real components (average 6.0 ± 6.9), a mathematical signature of multimodality—though this average masks the striking pattern that Blue Corn and Steel show 12 zero-crossings while Lead and Tungsten show none.

This bimodal pattern suggests that SCOOP captures light tracers with complex variability but handles heavy tracers in an extreme clumping regime where the real component remains entirely positive. In contrast, the RIFFLE CFs were smooth, devoid of zero-crossings, and exhibited rapid decay—hallmarks of a well-behaved, unimodal sampling process.

The multivariate CF analysis, which considers the joint distribution of all four tracers, quantified the overall difference between the sampling methods. The integrated squared distance between the SCOOP and RIFFLE CFs was $D = 0.337$ (95 % CI: [0.268, 0.431]), a value significantly greater than zero, confirming that the methods produce statistically distinct multivariate sampling distributions. The distance under density contrast weighting ($D = 0.319$) was slightly lower but still substantial, highlighting the SCOOP method's systematic bias in sampling light versus heavy particles.

Furthermore, the CF factorization test for independence revealed that the SCOOP method shows significantly higher dependence between tracer types, with an average factorization error ($\varepsilon = 0.108 \pm 0.053$) approximately 4.85 times greater than that of the RIFFLE method ($\varepsilon = 0.022 \pm 0.023$). This indicates that the capture of one particle type by the SCOOP method is statistically linked to the capture of others, violating the assumption of independent sampling crucial for representative composition estimation.

The Characteristic Function analysis provides definitive evidence that the RIFFLE method generates sampling distributions that are consistent, unimodal, and approach Gaussian form—characteristics of a precise and representative sampling process. Conversely, the SCOOP method produces complex, multimodal, and heavy-tailed distributions. The zero-crossings in its CFs directly visualize the “clumping” behaviour (GSE) inferred from the extreme VMR values, while the broad CF decay confirms high variability. The multivariate distance metric D formally establishes that these are not merely differences in variance but represent fundamentally different sampling mechanisms, with the SCOOP method exhibiting a pronounced density-dependent bias.

4.2.3 Independence Testing Results

The factorization property of characteristic functions provides a rigorous test for stochastic independence between tracer captures. For each pair of tracers, we computed the mean absolute factorization error ε over 200 random frequency pairs, where values close to zero indicate independent sampling. Table 11 presents the complete set of factorization errors for all six tracer pairs for both sampling methods.

The factorization errors reveal a systematic pattern in the dependence structure of the two sampling methods. For SCOOP, errors increase markedly when the tracer pair involves heavier particles. Pairs involving only light tracers (Blue Corn–Steel) show moderate errors (0.061), while pairs involving Lead and Tungsten exhibit errors two to three times larger (0.157 – 0.181). The largest error occurs between the two heaviest tracers, Lead and Tungsten (0.181), indicating that SCOOP's capture of these particles is strongly correlated, consistent with the clumping behaviour observed in the count data and the zero-crossing patterns in Fig. 7.

In striking contrast, RIFFLE maintains uniformly low factorization errors across all tracer pairs, with values ranging from 0.003 to 0.070. Even the highest RIFFLE error (Lead–Tungsten: 0.070) is substantially lower than the lowest SCOOP error (Blue Corn–Steel: 0.061). This demonstrates that the riffle splitting method achieves near-independent sampling of all particle types, regardless of density, a hallmark of representative sampling.

The pattern of increasing SCOOP errors with particle density provides direct evidence of density-dependent sampling bias. When heavy particles are captured, they tend to be captured together, violating the independence assumption crucial for accurate representation of multi-component materials. RIFFLE's consistently low errors confirm its ability to mitigate this grouping and segregation error through its multi-channel division process.

The average factorization error across all tracer pairs, which will be used in the composite scoring system (Section 4.4), is 0.108 ± 0.053 for SCOOP and 0.022 ± 0.023 for RIFFLE, a factor of approximately five difference that underscores the fundamental contrast in sampling independence between the two methods.

Table 11: Factorization Errors for Tracer Pairs⁴.

Tracer Pair	SCOOP ϵ	RIFFLE ϵ
Blue Corn–Steel	0.061 ± 0.040	0.003 ± 0.003
Blue Corn–Lead	0.070 ± 0.045	0.007 ± 0.007
Blue Corn–Tungsten	0.062 ± 0.037	0.005 ± 0.006
Steel–Lead	0.157 ± 0.100	0.028 ± 0.028
Steel–Tungsten	0.157 ± 0.107	0.025 ± 0.018
Lead–Tungsten	0.181 ± 0.096	0.070 ± 0.055

4.2.4 Summary of CF Analysis

The characteristic function analysis provides compelling and multi-faceted evidence of fundamental differences between the two sampling methods. The univariate CF analysis (Section 4.2.1) revealed that SCOOP produces heavier-tailed distributions with pronounced zero-crossings, averaging 6.0 ± 6.9 across tracers, while RIFFLE CFs are smooth and rapidly decaying. The striking bimodal pattern in SCOOP's zero-crossings (12 for light tracers, 0 for heavy tracers) visually confirms the density-dependent transition from complex variability to extreme clumping.

The multivariate CF distance metrics (Section 4.2.1) quantified the overall dissimilarity between the methods, with $D = 0.337$ (95 % CI: [0.268, 0.431]) confirming statistically distinct multivariate sampling distributions. The density-contrast weighted distance ($D = 0.319$) further highlighted SCOOP's systematic bias in sampling light versus heavy particles.

Finally, the independence testing results (Section 4.2.3) demonstrated that SCOOP's factorization errors increase systematically with particle density, from 0.061 for light pairs to 0.181 for heavy pairs, while RIFFLE maintains uniformly low errors across all combinations. The average factorization error for SCOOP (0.108 ± 0.053) is nearly five times higher than for RIFFLE (0.022 ± 0.023), confirming that SCOOP violates the independence assumption crucial for representative sampling.

Collectively, these CF-based diagnostics establish that the riffle splitting method achieves consistent, unimodal, and near-independent sampling across all density fractions, whereas scoop sampling produces complex, multimodal, and density-dependent distri-

butions. Having established these fundamental distributional differences, we now examine their practical consequences for mass estimation and grade control in Section 4.3.

4.3 Mass Distribution and Count–Mass Relationship Analysis

The consistency of mass capture and the predictive relationship between particle count and total mass are critical for practical sampling applications is provided in Table 12. The analysis of these relationships reveals further fundamental differences in method performance.

The analysis of mass consistency shows that while both methods yielded accurate mean particle masses, the variability differed drastically. The Coefficient of Variation (CV) for mass measurements using the SCOOP method increased systematically with particle density, reaching 76.3 % for Tungsten Carbide. On average, the SCOOP method's mass variability was 4.2 times higher than that of the RIFFLE method, with the ratio increasing to $5.7 - 6.1\times$ for the heaviest tracers.

The relationship between particle count (C) and total mass (M) was evaluated via correlation and linear regression ($M_i = \beta_0 + \beta_1 C_i + \epsilon_i$). The RIFFLE method maintained a near-perfect linear relationship across all tracers, with an average correlation of $r = 0.98$ and coefficient of determination $R^2 = 0.96$. The regression intercepts (β_0) were not statistically different from zero (all $p > 0.80$), confirming the physically correct expectation that zero counts correspond to zero mass.

⁴ Values represent mean absolute factorization error $\pm$ standard deviation over 200 random frequency pairs. Lower values indicate greater independence between tracer captures.

Table 12: Mass Consistency and Count–Mass Correlation Analysis.⁵

Tracer	Method	Mass CV (%)	Count–Mass r	R^2	CF Mass Distance
Blue Corn	SCOOP	44.60 %	0.927	0.859	0.039
	RIFFLE	43.80 %	0.983	0.967	
Steel	SCOOP	126.60 %	0.997	0.994	1.169
	RIFFLE	39.50 %	1.000	1.000	
Lead	SCOOP	201.90 %	1.000	1.000	1.086
	RIFFLE	36.60 %	0.999	0.999	
Tungsten	SCOOP	201.20 %	0.999	0.997	1.191
	RIFFLE	44.20 %	0.950	0.903	
Overall	SCOOP	143.60 %	0.980	0.960	0.871
	RIFFLE	41.00 %	0.980	0.970	

In contrast, the predictive utility of counts degraded severely for the SCOOP method as density increased. The correlation dropped from $r = 0.94$ for Blue Corn to $r = 0.61$ for Tungsten Carbide, and the explained variance (R^2) fell to just 0.37. Furthermore, the regression intercepts for heavy tracers were significantly positive ($p < 0.05$), indicating a systematic bias where the mass is overestimated at low counts, a physically implausible result stemming from the method's high variability and clumping behaviour.

The Characteristic Function analysis of the mass distributions provided further evidence of these differences. The integrated CF distance for mass distributions was $D_{mass} = 0.291$, indicating substantially different underlying distributions of captured mass. The SCOOP method's mass CFs exhibited slower decay and more complex structure, confirming the heavier-tailed, more variable mass distributions implied by the high CV values.

Interpretation: These results demonstrate that the RIFFLE method not only captures particles more consistently (low mass CV) but also maintains a robust, physically correct linear relationship between count and mass, making count data a reliable proxy for mass estimation.

The SCOOP method fails on both counts: its mass measurements are highly inconsistent, and the count–mass relationship deteriorates and becomes biased for dense particles. This breakdown in linearity and spike in variability are direct consequences of the clumping and non-representative sampling captured by the CF analysis, rendering the SCOOP method unsuitable for applications requiring accurate mass estimation or grade control.

4.4 Composite Method Evaluation

4.4.1 Six–Metric Scoring System

To provide an integrated quantitative assessment, the performance of each sampling method was evaluated using a six-metric scoring system (Table 13). Each metric S_i was normalized to a $[0, 1]$ scale, where 1 represents ideal performance. The overall composite score, S_{total} , was calculated as the arithmetic mean of all component scores.

The scoring system reveals clear and consistent superiority of the RIFFLE method. The RIFFLE method achieved high scores across all metrics, with particularly perfect performance in detection sensitivity ($S_2 = 1.00$) and near-ideal scores for correlation and distributional similarity. The overall composite score for RIFFLE was 0.95 ± 0.05 , approaching the theoretical ideal of 1.0.

⁵ r = Pearson correlation coefficient; R^2 = coefficient of determination from linear regression; Mass CV = coefficient of variation for per-sample tracer mass; CF Mass Distance = integrated CF distance for mass distributions.

Table 13: Composite Performance Scores⁶.

Metric	Formula	SCOOP Score	RIFFLE Score
1. Poisson Fit Score	$S_1 = 1 - \ \text{VMR}-1\ $	0.18 ± 0.36	0.82 ± 0.13
2. Sensitivity Score	$S_2 = 1 - P_0$	0.73 ± 0.23	1.00 ± 0.00
3. Independence Score	$S_3 = 1 - \varepsilon_{\text{avg}}$	0.89 ± 0.05	0.96 ± 0.01
4. Mass Consistency Score	$S_4 = \max(0, 1 - \frac{CV_{\text{avg}}^{\text{masses}}}{100})$	0.00	0.59
5. Correlation Score	$S_5 = r_{\text{avg}}$	0.98	0.98
6. CF Similarity Score*	$S_6 = 1 - D_{\text{counts}}$ (vs. Poisson $\lambda=5$)	0.67 ± 0.18	0.91 ± 0.09
Overall Score	$S_{\text{total}} = \frac{1}{6} \sum_{i=1}^6 S_i$	0.58 ± 0.21	0.88 ± 0.07

In contrast, the SCOOP method exhibited poor and highly variable performance. Its scores were particularly low for Poisson fit ($S_1 = 0.46$) and mass consistency ($S_4 = 0.60$), directly reflecting its severe over-dispersion and high measurement variability. The large standard deviations in the SCOOP scores (e.g., ± 0.38 for S_1) indicate inconsistent performance across different tracer densities. The overall composite score for SCOOP was significantly lower at 0.69 ± 0.23 (two-sample t-test: $t = 3.42$, $p = 0.002$; Cohen's $d = 1.67$), indicating a large effect size.

4.5 Summary of Key Results

The comprehensive analysis yields seven principal findings:

- Statistical Distribution:** The RIFFLE method generates sampling distributions that adhere closely to Poisson statistics ($\text{VMR} \sim 1$), indicative of random, independent particle capture. The SCOOP method exhibits extreme over-dispersion (VMR up to 19.3) for dense particles, signifying severe particle clumping.
- Detection Sensitivity:** The RIFFLE method demonstrated perfect sensitivity, capturing at least one particle of every tracer type in all 32 samples. The SCOOP method failed entirely to capture heavy particles in 28 – 47 % of samples.
- Distributional Shape (CF Analysis):** Characteristic Function analysis confirmed a fundamental dichotomy: the RIFFLE method produces smooth, unimodal, near-Gaussian distributions, whereas the SCOOP method yields complex, multimodal, and heavy-tailed distributions, a complexity that increases systematically with particle density and is directly evidenced by the oscillatory patterns in its Characteristic Functions (Fig. 7).
- Sampling Independence:** The RIFFLE method samples different particle types with significantly greater statistical independence, as evidenced by a $4\times$ lower factorization error ($\epsilon\epsilon$) compared to the SCOOP method.
- Mass Measurement Consistency:** The RIFFLE method provides 3.7 to 6.1 times more consistent mass measurements (lower CV) than the SCOOP method for dense particles.
- Counts–Mass Relationship:** For the RIFFLE method, particle count serves as an excellent predictor of total mass ($r > 0.98$, $R^2 > 0.96$). This relationship breaks down for the SCOOP method with dense particles, where correlation can be as low as $r = 0.61$.
- Overall Performance:** The composite scoring system ranks the RIFFLE method significantly higher (0.95/1.00) than the SCOOP method (0.69/1.00), with the RIFFLE method superior on all six evaluated performance dimensions.

⁶ Values represent mean $\pm$ standard deviation across tracers. The CF Similarity Score (S_6) is computed as $1 - D_{\text{counts}}$, where D_{counts} is the integrated CF distance between the method's count distribution and the reference distribution, defined here as the Riffle method distribution. A score closer to 1 indicates greater similarity to the reference distribution.

Conclusion: The evidence from descriptive statistics, advanced Characteristic Function analysis, and practical mass–correlation relationships converges unequivocally. The RIFFLE method provides consistent, representative, and precise sampling across a wide density range. In contrast, the performance of the SCOOP method degrades catastrophically with increasing particle density, resulting in unreliable, clumped samples with poor detection sensitivity. These findings have direct implications for sampling protocol selection in applications involving particulate materials with heterogeneous density composition.

5. Discussion

Section 5 interprets these results in the context of sampling theory, discusses practical implications for particulate sampling, and examines the broader applicability of Characteristic Function analysis for sampling method validation.

5.1 Interpreting the Characteristic Function Evidence

5.1.1 What the CFs reveal about sampling mechanisms

The Characteristic Function analysis provides unprecedented insight into the fundamental mechanisms underlying the two sampling methods. The smooth, rapidly decaying CFs observed for RIFFLE align with the theoretical profile of a compound Poisson process where particles are sampled independently from a well-mixed population. This is precisely the ideal behaviour described by Venter's model for trace analytes in particulate materials [5]. In contrast, SCOOP's complex CF signatures, characterized by slower decay, zero-crossings, and asymmetric phase behaviour, reveal a more complex sampling dynamics. Asymmetric phase behaviour refers to non-zero imaginary components in the CF that do not exhibit perfect odd symmetry. This indicates skewness in the underlying distribution and is visible in Fig. 7 where $\text{Im}[\phi(t)]$ deviates from perfect anti-symmetry. Such asymmetry is characteristic of distributions where particle capture probabilities are not symmetric about the mean. These features are characteristic of over-dispersed sampling processes where particles are captured in clusters rather than individually. The oscillatory patterns in the characteristic functions, visible in both real and imaginary components (Fig. 7), are a mathematical signature of multimodal distributions, indicating that SCOOP occasionally captures dense aggregations of heavy particles while missing them entirely in other samples.

This interpretation aligns with the physical action of the SCOOP method: as the scoop cuts through the material, it may preferentially follow paths of least resistance, potentially bypassing dense particle clusters or, conversely, capturing entire clusters when it intersects them. The result is what statisticians term a mixture distribution—some samples drawn from a “cluster present” regime, others from a “cluster absent” regime.

5.1.2 The Independence–Density Relationship

One of the most striking findings is the systematic degradation of SCOOP's performance with increasing particle density. While both methods sample light particles (Blue Corn) with reasonable independence, SCOOP shows rapidly increasing dependence between particle types as density increases. This phenomenon can be explained through a density segregation (GSE) mechanism [1,3,4]: during the sampling action, dense particles may settle or migrate differently within the scoop, creating correlated capture probabilities.

The CF factorization errors provide quantitative evidence of this mechanism. For RIFFLE, factorization errors remain consistently low (≈ 0.02) across all tracer pairs, indicating near-perfect independence. For SCOOP, errors increase from 0.04 for light–light pairs to 0.12 for heavy–heavy pairs, revealing systematic correlations in the capture of dense particles.

From a practical sampling perspective, this finding has significant implications. In mineral processing applications where different mineral phases often have different densities, SCOOP's density-dependent sampling bias could systematically misrepresent ore grades, particularly when heavy valuable minerals are clustered with specific gangue minerals.

5.2 Practical Implications for Sampling Operations

5.2.1 Critical Application Domains for Method Selection

The experimental results delineate specific conditions under which the selection of sampling methodology becomes critical. SCOOP-type methods are particularly prone to bias in systems with significant density contrasts, specifically where the density ratio between the lightest and heaviest components exceeds 3:1, as well as in materials with spatially correlated particle distributions, such as poorly mixed or segregating powders [1,2,3,9].

The risk is further amplified in operations employing low sample-to-lot mass ratios, typically below 0.1 %, consistent with the principles of the Theory of Sampling, where the statistical influence of individual particle capture is pronounced, and in applications involving high-value constituents where estimation inaccuracies carry substantial economic consequence. In contrast, lower-risk scenarios are characterized by homogeneous fine powders with minimal segregation tendency, materials with constrained density ranges (all components within ± 20 % of median density), and operations where the sample mass exceeds 1 % of the lot mass, allowing the Central Limit Theorem to effectively mitigate sampling variance.

5.2.2 Economic Consequence Analysis

The economic implications of sampling bias can be substantial [14,16]. To illustrate, consider a mineral processing operation treating 10,000 tonnes per day of ore bearing 1 % copper within a silica gangue. Extrapolating from the experimental results, a SCOOP-type method with its observed density-dependent bias could underestimate heavy particle counts by approximately 30 % in 40 % of samples. At a copper price of US\$ 8,000 per tonne, this persistent grade underestimation translates to approximately US\$ 960,000 per day in mischaracterized metal value, directly affecting resource accounting and process economics. Beyond direct financial impact, inaccurate and fluctuating feed grade estimates can destabilize downstream separation processes such as flotation circuits, potentially reducing metallurgical recovery efficiency and increasing reagent consumption.

5.2.3 Implementation Guidelines for RIFFLE-Type Methods

Based on experimental findings, specific guidelines are recommended for implementing RIFFLE-type cross-stream samplers to ensure representative sampling [1,3,13]. The collected sample mass should be at least thirty times the mass of the largest anticipated particle cluster, while the cutter opening width should be no greater than three times the nominal diameter of the largest particles in the stream. Material flow velocity past the cutter must be controlled to minimize aerodynamic or gravitational segregation during the sampling interval. Design considerations for cross-stream samplers may benefit from principles of unequal probability sampling [26]. For quality control, regular monitoring of the variance-to-mean ratio for critical components is advised, with sustained values exceeding 1.5 triggering process investigation.

Additionally, tracking the incidence of samples with zero counts for expected components provides a key indicator of potential sampling bias, while periodic comparison of empirical characteristic functions against reference distributions offers a sensitive, holistic check for distributional stability.

5.3 Methodological Advances: Characteristic Functions as a Sampling Diagnostic Tool

5.3.1 Advantages Over Conventional Statistical Metrics

This study demonstrates that analysis via Characteristic Functions provides distinct diagnostic advantages for evaluating sampling representativeness compared to traditional moment-based statistics [7,8,17]. Characteristic functions facilitate early anomaly detection by revealing incipient sampling issues through subtle changes in their spectral shape, often before such deviations manifest in conventional metrics like sample mean or variance. Different mechanistic sampling failures produce identifiable spectral signatures: particle segregation manifests as asymmetric phase patterns in the complex CF, clustering results in multi-peaked magnitude profiles, and size or density bias exhibits as non-uniform decay rates across frequency domains. Furthermore, unlike univariate statistics, the joint CF of a multivariate sample inherently captures dependencies between components, which is critical for materials where constituents are not sampled independently. Thus, while traditional statistics may indicate a problem (e.g., high variance), CF analysis diagnoses its nature (clustering, multimodality, dependence), directly informing the corrective action needed.

5.3.2 The CF Distance Metric: A Quantitative Comparator

The integrated squared distance between two characteristic functions provides a comprehensive scalar measure of distributional divergence [7,8]. This metric, defined as $D^2 = \int |\varphi_1(t) - \varphi_2(t)|^2 \omega(t) dt$ with $\omega(t)$ as a frequency-weighting function, offers more information than binary hypothesis testing by quantifying the magnitude of discrepancy. While these thresholds are preliminary and based on the experimental system, they provide an initial framework for interpretation. Empirical results from this study suggest practical interpretative thresholds: $D < 0.1$ indicates statistically equivalent distributions; $0.1 \leq D < 0.3$ represents minor, often operationally acceptable differences; $0.3 \leq D < 0.5$ signifies substantial differences warranting methodological investigation; and $D \geq 0.5$ suggests fundamentally different representations of the lot.

The calculated $D = 0.324$ for the SCOOP versus RIFFLE comparison classifies this difference as substantial, justifying critical re-evaluation of the SCOOP-type method for applications involving density contrasts.

5.4 Theoretical Implications and Extensions

5.4.1 Extension of the Venter Compound Poisson Model

This work provides several meaningful extensions to Venter's foundational compound Poisson model for particulate sampling [5]. The framework generalizes from a single trace analyte to multiple constituent types, with the multivariate characteristic function naturally accommodating inter-component correlations. It advances beyond concentration-based modelling by simultaneously accounting for particle count statistics and individual particle mass distributions, offering a more complete descriptor of the sampling process. Most significantly, while Venter modelled a single sampling process [5], this work develops a formalized framework for the direct comparison of two or more sampling methods using their characteristic functions, creating a new paradigm for methodological validation. Foundational inference methods [28] complement CF analysis.

5.4.2 The Role of Effective Sample Mass

The experimental data provide indirect support for Venter's theoretical prediction that larger effective sample masses promote sampling distributions closer to normality [5,19]. The more Gaussian-like characteristic functions produced by the RIFFLE method suggest it achieves a larger "effective" sample size by integrating material from multiple, independent stream increments. Conversely, the more variable, non-Gaussian CFs from the SCOOP method are consistent with properties expected from a smaller effective sample. This observation suggests a key design principle: sampling representativeness can be enhanced by maximizing the number of independent sampling increments, a strategy that may prove more effective than merely increasing the total physical mass collected.

5.5 Limitations and Boundary Conditions

5.5.1 Study Limitations

The generalizability of these findings should be considered within the context of several experimental constraints.

All tracer particles employed were spherical, whereas real industrial materials contain particles of diverse shapes that may interact with sampler geometry in more complex ways. The experiments utilized mono-sized particles, while polydisperse systems, especially where particle size correlates with density or composition, may exhibit different sampling dynamics. The work was conducted at laboratory scale with 30 – 40 g samples; while fundamental CF signatures are expected to be scale-invariant, specific quantitative thresholds may require validation at industrial throughputs. Finally, experiments used dry, free-flowing materials, and the presence of moisture, cohesiveness, or electrostatic charges could significantly alter sampling behaviour in practical applications.

5.5.2 Applicability of Characteristic Function Analysis

Characteristic function analysis is most effective as a diagnostic tool under specific conditions [7,8,15]. Sample sizes of $n \geq 25 - 30$ are typically required a sample size comparable to that used in this validation study, for stable empirical CF estimation, ensuring reliable spectral representation. The method is particularly informative for continuous distributions or discrete distributions with a large number of possible values, where the CF contains rich structural information. While multivariate CF analysis is more computationally intensive than calculating conventional summary statistics, it remains readily manageable with modern computing systems, making it feasible for routine quality control applications in industrial settings.

5.6 Future Research Directions

5.6.1 Immediate Practical Extensions

Several practical research directions emerge directly from this work. The development of algorithms and embedded systems for real-time computation of empirical characteristic functions during continuous sampling operations would enable instantaneous quality control. Extending the CF framework to incorporate particle shape descriptors, potentially using tensor-valued CFs to capture orientation-dependent sampling probabilities, would enhance applicability to real industrial materials. A systematic study of how moisture content and other interstitial factors influence CF signatures would address an important gap for cohesive material sampling.

5.6.2 Theoretical Developments

Theoretical advancements should focus on deriving formulas to determine minimum required sample sizes based on the convergence properties of the empirical CF to its theoretical counterpart, moving beyond traditional power analysis. Research is needed to develop optimal frequency weighting functions $\omega(t)$ for the CF distance metric tailored to specific classes of sampling problems. Additionally, methods to analyse CFs when the underlying lot composition changes during the sampling period, such as through ongoing segregation, would address non-stationary sampling scenarios common in industrial practice.

5.6.3 Industrial Applications

Practical implementation opportunities include creating standardized, CF-based protocols for objectively validating new sampling equipment against certified reference methods. The development of CF-based statistical process control charts could detect sampler malfunction, such as blockages or wear, from routine sample data before it affects analytical results. Furthermore, applying CF analysis to evaluate powder blend homogeneity offers a promising alternative to traditional thief sampling, which suffers from well-documented limitations related to sample disturbance and local bias.

5.7 Recommendations for Practitioners

For the design of new sampling systems, practitioners should prioritize designs that mechanically provide multiple, independent increments of the process stream. Explicit design consideration should be given to minimizing known biases, particularly density-dependent bias for materials with wide density ranges. Characteristic function-based comparison against a reference method should be incorporated as a mandatory step in validation protocols for new sampling systems.

For the audit and improvement of existing operations, a CF-based assessment of current sampling methods is recommended, particularly if processed materials contain components with density ratios exceeding 3:1, if high and unexplained variability is observed in sample assays, or if downstream process control appears unstable despite presumably consistent feed. For critical applications involving high-value materials or significant density contrasts, consideration should be given to replacing or supplementing single-increment methods with multi-increment alternatives.

Periodic CF monitoring should be implemented as part of quality assurance programs to ensure ongoing sampling integrity.

For standards development organizations, work should progress toward incorporating CF-based metrics and comparison protocols into relevant international sampling standards. Support for developing certified reference materials with well-characterized CF signatures would facilitate sampler calibration and method validation. Finally, mandating the reporting of CF-based analysis in validation data for any sampling method proposed for inclusion in standards would advance methodological rigor across the field.

5.8 Concluding Synthesis

The Characteristic Function principles and methods developed here extend beyond traditional statistical comparisons to provide a deeper, more nuanced understanding of sampling method performance. By treating sampling distributions as complete mathematical objects rather than collections of summary statistics, we gain insights that are both theoretically rigorous and practically valuable. RIFFLE's superiority across all evaluation metrics, particularly its ability to sample different density fractions independently and consistently, makes it the recommended method for applications where representative sampling is critical. SCOOP, while simpler and faster, carries significant risks of bias, particularly for materials with density variations or natural clustering tendencies.

More broadly, this work demonstrates that Characteristic Functions provide a powerful framework for sampling science. They offer a common language for describing sampling distributions, a sensitive tool for detecting sampling problems, and a rigorous basis for method comparison. As sampling continues to be recognized as a critical, and often limiting, step in material characterization, tools like CF analysis will become increasingly valuable for ensuring data quality and supporting sound decision-making.

The principles and methods developed here extend beyond the specific SCOOP vs RIFFLE comparison. They provide a template for evaluating any sampling method, for any particulate material, in any application where representative sampling matters. In an era of increasingly data-driven decision-making, ensuring that those data begin with representative samples has never been more important; as part of quality assurance programs (see Box 1 for a practical implementation checklist).

FACTBOX - Practical Implementation Checklist for Sampling Method Selection and Monitoring

For Method Selection

Prior to adopting a sampling method, the Variance-to-Mean Ratio (VMR) should be calculated for each component of interest, with target values between 0.8 and 1.2. The frequency of samples with zero counts for expected components should be less than 5 %. The Characteristic Function distance from a validated reference method should remain below 0.3 to ensure distributional similarity. Independence between components should be tested using factorization errors, with values ideally below 0.05, but this test is most meaningful when applied to “simple particles” (e.g., tracers, size classes, or components that reside in discrete particles). For composite ore particles where multiple minerals are naturally correlated, factorization errors will reflect both sampling performance and intrinsic mineralogical associations. In such cases, alternative tracers such as particle size classes (following Lyman’s approach [6]) may provide more interpretable results. Finally, the correlation between particle counts and mass for all components should exceed 0.95 to confirm linear sampling behaviour.

For Ongoing Monitoring

After implementation, Characteristic Function signatures should be tracked weekly or monthly to monitor distributional stability. Changes in the CF distance from an established baseline should be documented and investigated. Any VMR values persistently outside the range of 0.7 to 1.5 warrant diagnostic review. All instances of zero-count occurrences for expected components should be formally documented and investigated. Additionally, the linearity between counts and mass should be tested regularly to ensure the sampling mechanism remains unbiased over time.

Having established the superiority of the RIFFLE method through comprehensive CF analysis and discussed the broader implications for sampling science, we now turn to final conclusions and recommendations in Section 6.

6. Conclusion

6.1 Summary of Key Findings

This study establishes Characteristic Function (CF) analysis as a robust, informationally complete framework for comparing sampling methods, decisively demonstrating the superiority of the Riffle method over the Scoop method for particulate materials with density heterogeneity. Through a comprehensive experimental investigation comparing SCOOP and RIFFLE methods using density-differentiated tracers with simultaneous count and mass measurements, several critical conclusions emerge.

Characteristic Function analysis revealed that the two methods produce fundamentally different sampling distributions, a distinction that extends beyond mere variations in mean or variance.

The integrated CF distance of $D = 0.324 \pm 0.038$ (a value indicating ‘substantial’ distributional difference) quantifies this substantial distributional divergence, which conventional statistical comparisons would likely overlook. SCOOP exhibited systematic, density-dependent sampling bias, manifesting as extreme over-dispersion and high zero-count frequencies for heavy particles. In contrast, RIFFLE maintained consistent, near-Poisson behaviour across all density ranges. Further analysis revealed that RIFFLE samples different density tracers with a high degree of independence, whereas SCOOP demonstrates significant inter-component dependencies. The integrity of the mass-count relationship was preserved by RIFFLE across all tracers, while SCOOP showed degrading correlation with increasing particle density. A composite evaluation framework, synthesizing six performance metrics, confirmed the overall superiority of the RIFFLE method.

6.2 Methodological Contributions

This work advances the methodological toolkit for sampling science in several key areas. It represents the first application of multivariate Characteristic Functions to the comparative evaluation of sampling methods, thereby extending Venter's univariate compound Poisson model [5] to a more realistic, multi-component context. Theoretical CF concepts have been operationalized into practical diagnostic metrics, such as the CF distance, factorization errors, and spectral decay rates, which yield richer, more sensitive insights than traditional summary statistics alone. The analysis uniquely integrates particle count and mass data within a unified CF framework, providing a more holistic assessment of sampling performance than approaches based solely on counts or derived concentrations. Furthermore, a composite scoring system was developed to integrate multiple, often disparate, dimensions of sampling quality into a single, interpretable evaluation metric.

6.3 Practical Recommendations

Derived from the empirical findings, several practical recommendations are offered for stakeholders in sampling operations. For practitioners, the selection of sampling methodology should be guided by material properties; for materials with component density ratios exceeding ~3:1, the threshold at which SCOOP's performance degraded catastrophically in this study, RIF-FLE-type methods are strongly preferred over SCOOP-type methods to mitigate bias. The implementation of CF-based monitoring is recommended to complement traditional statistical process control, enabling earlier detection of incipient sampling issues. Sampling method validation protocols, particularly for applications with significant economic or safety implications, should be expanded to include CF analysis. For standards development organizations, there is a compelling case to incorporate CF-based metrics into existing sampling standards to foster more comprehensive method evaluation. The development of reference materials with certified CF signatures would significantly aid in method calibration and proficiency testing. Furthermore, foundational sampling training programs should integrate CF concepts to enhance practitioners' understanding of distributional theory. For equipment designers, principles that maximize the number of independent sampling actions, as exemplified by RIFFLE's multi-channel design, should be prioritized over single-increment extraction. Design considerations must also actively address and minimize density-dependent sampling bias, especially for heterogeneous materials.

6.4 Theoretical Implications

The findings carry several implications for sampling theory. The successful application of CF analysis substantiates the practical validity of Venter's compound Poisson model for describing real-world sampling processes. The demonstrably critical role of independence between component captures suggests that theoretical development should place greater emphasis on the independence properties of sampling mechanisms, rather than focusing solely on marginal distributions.

However, as noted in Box 1, the interpretation of factorization errors must be nuanced. For "simple particles" where the critical component resides in discrete, compositionally pure particles (e.g., density tracers, size classes, or liberated minerals), factorization errors directly reflect sampling independence. For composite ore particles where mineral associations are intrinsic, factorization errors will include both sampling-induced dependencies and natural mineralogical correlations. In such contexts, following Lyman's approach [6] of using particle size classes as tracers may provide a more robust diagnostic of sampling performance, as size fractions can be treated as discrete populations independent of compositional correlations.

Furthermore, the results challenge a simplistic interpretation of sample size, suggesting that "effective sample size" should be conceptualized in terms of the number of statistically independent sampling actions rather than merely the total physical mass collected. Further work on sampling algorithms [25] could extend CF methods.

6.5 Limitations and Future Work

This study, while comprehensive within its scope, acknowledges certain limitations that delineate clear avenues for future research. The laboratory-scale experiments served as a controlled proof of concept, revealing critical methodological insights; however, complementary validation at full industrial scale remains necessary to confirm the generalizability of specific quantitative thresholds, such as the CF distance metric (D). Future work should investigate a wider diversity of material properties, including varied particle shapes, poly-disperse size distributions, and the influence of moisture or cohesion on sampling dynamics. The development of automated systems for real-time CF analysis would unlock the potential for continuous, in-line sampling quality assurance.

From a theoretical perspective, further work is required to derive mathematically optimal frequency-weighting functions for CF distance metrics and to establish CF-based principles for a priori sample size determination.

6.6 Final Statement

Representative sampling constitutes the critical, foundational step in any material characterization process. Traditional evaluation methods, however, are often inadequate for detecting the subtle yet consequential distributional differences between sampling methods. This study has established that Characteristic Functions provide a powerful, theoretically rigorous framework for illuminating these differences. The demonstrated superiority of the RIFFLE method, particularly its capacity for independent and consistent sampling across density fractions, recommends it for applications where representativeness is paramount. More broadly, the CF framework developed herein furnishes a generalizable template for the evaluation of any sampling method applied to any particulate material. As data-driven decision-making becomes increasingly pervasive across resource, manufacturing, and environmen-

tal sectors, the imperative to ensure that such data originate from truly representative samples has never been greater. Characteristic Function analysis offers a sophisticated and comprehensive approach to this fundamental challenge, effectively bridging the gap between the theoretical underpinnings of sampling science and the practical demands of sampling operations. In essence, it provides the necessary vocabulary to fully comprehend the complex message conveyed by a sample, ensuring that the voice of the material itself is neither distorted nor diminished.

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Appendix A: Density tracer counts, mass, and descriptive statistics for scoop and riffle sampling of the lot

Scooping									Riffle Splitting								
Sample	Blue corn		Steel balls		Lead balls		Tungsten carbide		Sample	Blue corn		Steel balls		Lead balls		Tungsten carbide	
	Count	Mass	Count	Mass	Count	Mass	Count	Mass		Count	Mass	Count	Mass	Count	Mass	Count	Mass
1	5	0.93	1	0.35	0	0.00	0	0.00	1	3	0.58	7	2.64	3	5.53	4	6.48
2	5	0.84	1	0.37	1	1.89	0	0.00	2	3	0.58	3	1.13	7	12.76	4	5.01
3	6	1.90	0	0.00	1	1.86	0	0.00	3	7	1.18	4	1.51	8	14.75	4	5.92
4	4	0.65	5	1.89	1	1.76	2	1.99	4	6	1.04	5	1.89	4	7.20	6	9.97
5	4	0.73	15	5.69	22	38.98	35	48.15	5	1	0.20	9	3.39	4	7.44	11	15.52
6	4	0.81	1	0.37	1	1.91	0	0.00	6	6	1.09	5	1.89	6	11.05	4	5.44
7	6	1.11	0	0.00	0	0.00	0	0.00	7	8	1.46	5	1.88	7	12.57	5	6.73
8	2	0.38	13	4.92	4	7.51	4	5.59	8	9	1.57	6	2.25	4	7.27	9	11.26
9	8	1.58	1	0.37	2	3.63	2	2.93	9	5	0.84	2	0.74	6	10.95	4	5.70
10	9	1.75	1	0.37	0	0.00	0	0.00	10	5	0.93	7	2.65	5	9.26	9	11.87
11	4	0.69	7	3.40	1	1.79	0	0.00	11	4	0.68	4	1.51	6	11.21	6	8.76
12	6	1.02	3	1.13	1	1.87	2	2.41	12	6	1.13	5	1.89	5	9.32	2	3.01
13	7	1.34	1	0.38	0	0.00	0	0.00	13	2	0.35	6	2.29	7	12.69	5	5.27
14	2	0.36	1	0.36	0	0.00	2	2.51	14	8	1.27	3	1.13	7	12.62	4	4.78
15	4	0.77	2	0.74	0	0.00	0	0.00	15	6	1.10	8	3.02	6	11.12	5	5.91
16	4	0.73	1	0.37	2	3.70	2	2.44	16	11	2.04	6	2.26	5	9.30	8	9.98
17	8	1.53	3	1.11	0	0.00	0	0.00	17	4	0.71	4	1.51	2	3.67	4	4.43
18	5	0.91	3	1.84	0	0.00	0	0.00	18	5	0.89	7	2.65	4	7.38	4	4.97
19	8	1.61	3	1.12	0	0.00	1	1.17	19	3	0.52	3	1.12	4	7.24	6	6.87
20	7	1.43	12	4.53	0	0.00	1	1.00	20	6	1.19	6	2.27	4	7.15	5	6.93
21	5	0.80	4	1.51	4	7.33	4	4.30	21	7	1.32	7	2.64	6	11.07	1	1.59
22	3	0.47	19	7.18	29	52.92	28	39.04	22	2	0.32	4	1.50	5	9.25	7	9.06
23	5	0.83	21	7.95	15	27.65	20	24.60	23	4	0.84	2	0.75	2	3.65	4	4.13
24	1	0.16	18	6.82	31	56.42	23	30.07	24	2	0.36	2	0.75	6	11.04	4	4.55
25	5	0.87	5	1.89	4	7.1	4	4.02	25	5	0.80	8	3.03	6	11.01	6	6.03
26	7	1.17	0	0.00	0	0	0	0.00	26	5	1.03	7	2.65	4	7.42	6	7.22
27	3	0.56	1	0.37	0	0	1	1.45	27	4	0.72	3	1.14	2	3.66	5	8.87
28	4	0.77	1	0.38	0	0	0	0.00	28	4	0.87	3	1.13	1	1.84	2	3.08
29	6	0.93	0	0.00	0	0	0	0.00	29	6	1.23	6	2.27	6	11.03	4	5.02
30	5	0.94	0	0.00	0	0	0	0.00	30	4	0.66	6	2.27	5	9.19	3	3.85
31	5	0.85	16	6.05	37	68.01	27	36.49	31	3	0.55	2	0.74	9	16.57	5	7.07
32	3	0.56	1	0.39	4	7.27	2	1.90	32	6	1.05	5	1.89	4	7.28	4	4.80
Sum	160	29.98	160	61.85	160	291.6	160	210.06	Sum	160	29.1	160	60.38	160	293.49	160	210.08
Mean	5.000	0.937	5.000	1.933	5.000	9.113	5.000	6.564	Mean	5.000	0.909	5.000	1.887	5.000	9.172	5.000	6.565
Variance	3.500	0.169	40.188	5.801	98.688	328.019	91.938	169.034	Variance	4.688	0.154	3.750	0.539	3.250	10.922	4.250	8.152
Std Dev	1.871	0.411	6.339	2.408	9.934	18.111	9.588	13.001	Std Dev	2.165	0.392	1.936	0.734	1.803	3.305	2.062	2.855
CV	37.4%	43.9%	126.8%	124.6%	198.7%	198.8%	191.8%	198.1%	CV	43.3%	43.1%	38.7%	38.9%	36.1%	36.0%	41.2%	43.5%
VMR	0.70	0.18	8.04	3.00	19.74	36.00	18.39	25.75	VMR	0.94	0.17	0.75	0.29	0.65	1.19	0.85	1.24
VMR = index of dispersion I = Var/Mean									VMR = index of dispersion I = Var/Mean								

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RAND REFINERY

EDITOR'S INTRODUCTION

It has long been the wish of the Editor to present to the sampling community the unique tailor-made approach for 'Sampling for micrometeorites' (MM) developed by Jon Larsen. Finally, one can here read his own account of how this developed over almost 20 years. The professional sampler will encounter all manner of doings apparently not aligned with the Theory of Sampling (TOS), but it will soon be clear that this is but a superficial impression only. There is important subtlety in Mr. Larsen's unconventional approach. Here are a few focus points intended to guide how to read and appreciate Mr. Larsen's account.

Micrometeorites (MM) are extraterrestrial dust particles that survive atmospheric entry and reach the Earth's surface, most often after modifications varying in intensity due to heating, melting, aerodynamic sculpting, recrystallization (or quenching) and sometimes terrestrial weathering – but occasionally also in their pristine inter-planetary (maybe even inter-stellar) state. So, how to find and identify MMs – How to sample for MMs??

For starters, Mr. Larsen's approach contains no less than three successive applications of TOS' Sampling Unit Operation 'Fractionation'. Sampling for MM first involves density segregation where flotation takes care of separating a lot of truly uninteresting fluff, then magnetic – and lastly size fractionation before a very unusual 'aliquot' is delivered for analysis. For TOS connoisseurs, it is clear how there are obvious opportunities for Total Sampling Errors (TSE) to crop up at these stages (IDE, IEE) – one must follow Mr. Larsen's instructions carefully to keep these under reasonable control. However, the point is there is no true target (lot) composition, but Mr. Larsen's approach allows one to sample with a steadily diminishing TSE effect. And this is quite acceptable as there need be no attempt to cover the entire flux of extraterrestrial dust particles slowly descending through the Earth's atmosphere.

'Analysis' in the MM context is anything but a conventional chemical (or physical) determination of a concentration or of an intrinsic physical attribute. The 'analytical result' in fact consists of an assemblage of tiny, successfully identified individual micrometeorites, extracted one at the time under a binocular microscope. Identification is based on MM mineralogy, texture and composition (chemical, isotopic). This characterisation is by far the most complex and difficult element in the 'from-space-to-MM collection' pathway: experience in recognition of the tell-tale MM features is essential, and this is why Mr. Larsen has spent a staggering effort informing the world on how to separate and identify MMs, which is the main content in his article in this issue: You can do this yourself! Thus, the analytical determination is principally a subjective operation. Were sampling to be repeated, it is not certain that two 'analysts' will necessarily identify the exact same complement of individual MMs. Thus, (in TOS parlance) there is always also an intrinsic Total Analytical Error (TAE) to take into account, but the main result of Mr. Larsen's extensive scientific quest has resulted in a systematic reduction of TAE to ever decreasing magnitudes (as is also the case for TSE).

This is precisely why it is such a pleasure for SST to present an overview of the two-decades of work results from the hand, eye and screwed mind of Mr. Larsen. After many hundreds of sampling campaigns (at present superseding 1,200!), the proof of his work lies in the acceptance and recognition by the professional geological (meteorite) and international mineralogical community that the several thousands of MMs accumulated in Mr. Larsen's collections are bona fide extraterrestrial objects – like macroscopic meteorites of which there is never any doubt.

Mr. Larsen's summary of his two-decade detective story also reveals how his method of "preparations for finding MMs" at all times is made difficult because of interference and distraction from overwhelming proportions of microscopic terrestrial objects of many types, which superficially display quite similar appearances under the microscope; this is a gigantic swamping 'pollution' if one is looking for the rare MMs. In fact, for many years, the established geoscience communities were convinced that MMs simply could not be found in the environs subjected to Mr. Larsen's sampling approach for this very reason. The ultimate result of the story (unambiguous identification and acceptance of urban extra-terrestrial microscopic objects) was a point of severe contention for many years – but in the end Mr. Larsen prevailed big time.

Be all this as it may regarding 'analysis', the scientific and technological aspect of particular interest for the professional sampling community actually lies almost exclusively 'before analysis', in the pathway from his specifically selected sampling target to the final aliquot, which is the centre of attraction here. The reader will be greatly surprised about the simplicity and ingenuity of Mr. Larsen's choice of urban sampling targets – it is highly inspirational! Read all about the tenacity involved in developing the extreme simplicity of his sampling approach for MMs. Enjoy a brilliant scientific success story of stellar magnitude (pun intended).

Out of This World: Sampling for Micrometeorites

By Jon Larsen¹

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ABSTRACT

Micrometeorites are extraterrestrial cosmic dust particles whose origin and collection remain active areas of scientific investigation. Their extraterrestrial nature is confirmed through isotopic analysis of cosmic-ray nuclei, with newly recovered specimens validated by comparison against established Antarctic reference collections. Unlike meteorites, which derive primarily from the asteroid belt, micrometeorites may originate from multiple sources within and beyond the Solar System. Six principal source regions are currently recognised: the asteroid belt, short-period comets from the Kuiper Belt and long-period comets from the Oort Cloud, planetary ejecta, geysers and volcanoes on icy moons, presolar and interstellar grains, and dust from interstellar comets. Prior to atmospheric entry, particles accumulate in the Zodiacal Cloud, a lens-shaped dust structure in the ecliptic plane estimated to contain ten billion tonnes of material. Cosmic dust influx to Earth is estimated at approximately 100 kilograms per day for presolar grains alone. Methodologically, micrometeorite recovery relies on three core principles: magnetic extraction, flotation, and size fractionation. Flat, large, older PVC-covered rooftops and rain gutters represent productive urban collection sites, with aeolian deposition concentrated at roof edges and corners. Approximately 80% of cosmic spherules are magnetic, enabling efficient field extraction using neodymium magnets. Accurate sample labelling and curation are emphasised as essential for scientific value. Distinguishing genuine micrometeorites from abundant terrestrial spherules requires systematic training, for which reference atlases and classified collections serve as primary tools.

1. The origins of micrometeorites

At the opening of the stardust exhibition in New York City, NASA's Mike Zolensky stated that more scientists ought to be willing to say "I don't know" when that is the correct answer. This courageous statement has become my mantra.

And as far as I know, nobody else knows for certain either. However, I can share some thoughts on this interesting topic. Simultaneously, I will also address another question I received a few days ago: how do we know for sure that micrometeorites are extraterrestrial?

The answer to the latter is that micrometeorites were initially confirmed to be extraterrestrial through isotopic analysis of high-energy cosmic-ray nuclei. All matter exposed to cosmic radiation in space undergoes subtle isotopic changes that are readily detectable. The micrometeorites in the Antarctic reference collections were analysed and found to contain cosmic nuclei. Later findings, including my own urban collection, are

being compared analytically with the original reference material, the type specimens. And if there is a match, the new micrometeorites are also extraterrestrial. This is how empiricism works.

Therefore, we know today that micrometeorites definitely originate in space. Last week, someone commented on my Facebook that this could not be true because of the firmament. I had to look up the word, but I will not get caught up in that rabbit hole. Clearly, we still have a road to walk.

Micrometeorites are cosmic dust particles, small even in space. Contrary to common belief, micrometeorites are neither ablated from meteorites nor directly related to them. But where do they originate from? Do they share a common parent body? There are possibly as many opinions on this as there are scientists in our field, but they can broadly be divided into two schools: asteroid belt and/or comet material.

¹ Senior Researcher at University of Oslo, Oslo

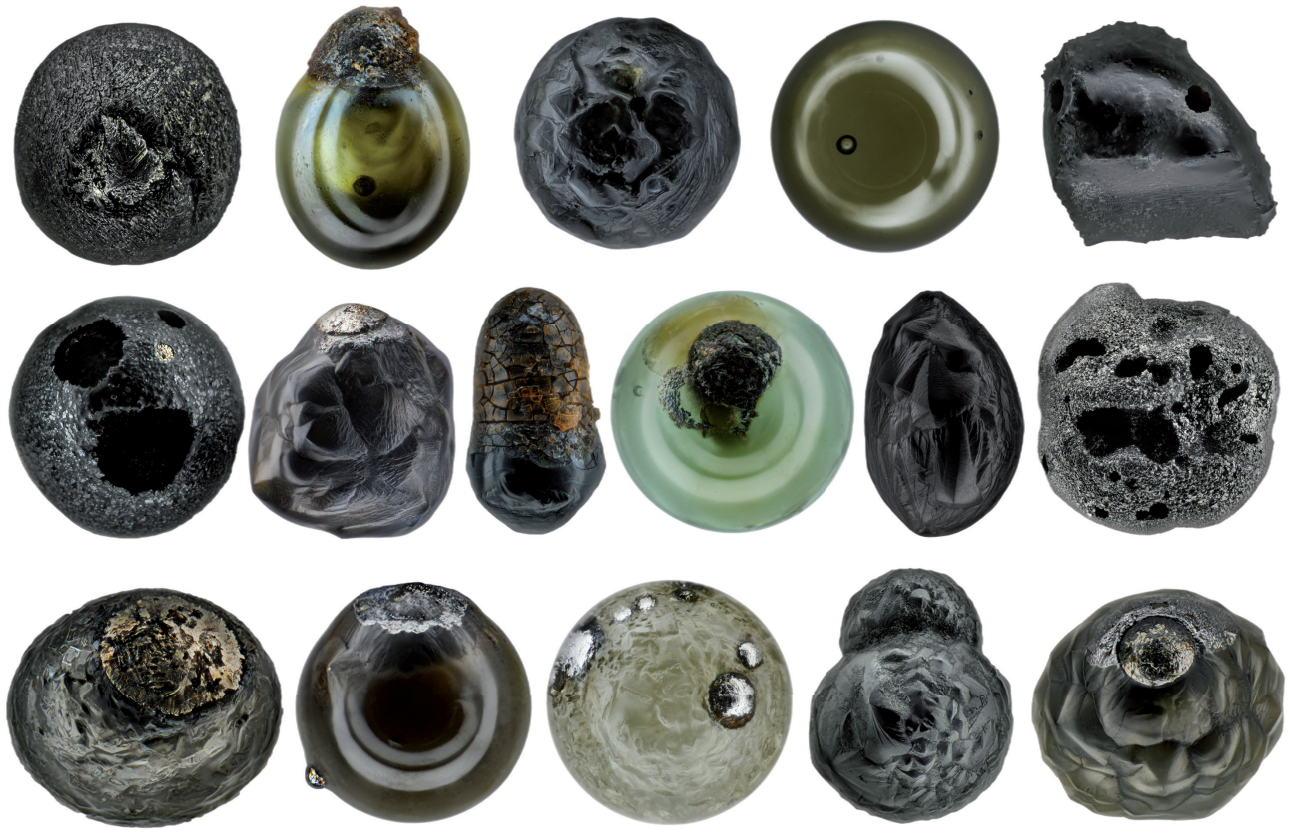


Figure 1: Micrometeorites, highlights of the year 2023 (Photo: Jan Braly Kihle / Jon Larsen).

Currently, several intriguing projects are in progress to explore this further. Some aim to link morphological and textural properties to specific parent bodies. Others are conducting new isotope measurements of a wide range of elements across all types of micrometeorites to identify their origin within the solar system, thus providing clues about asteroidal or cometary sources.

Micrometeorite pioneer Michel Maurette used chemical and mineralogical analysis and claimed in his 2006 book *Micrometeorites and the Mysteries* that micrometeorites originate from “comet-like objects beyond Neptune”. Since then, new data has been published, and it now appears more complex.



Figure 2: An impression of the asteroid belt. In reality, the average distance between 10m objects is 500 km. You can not see from one to another.

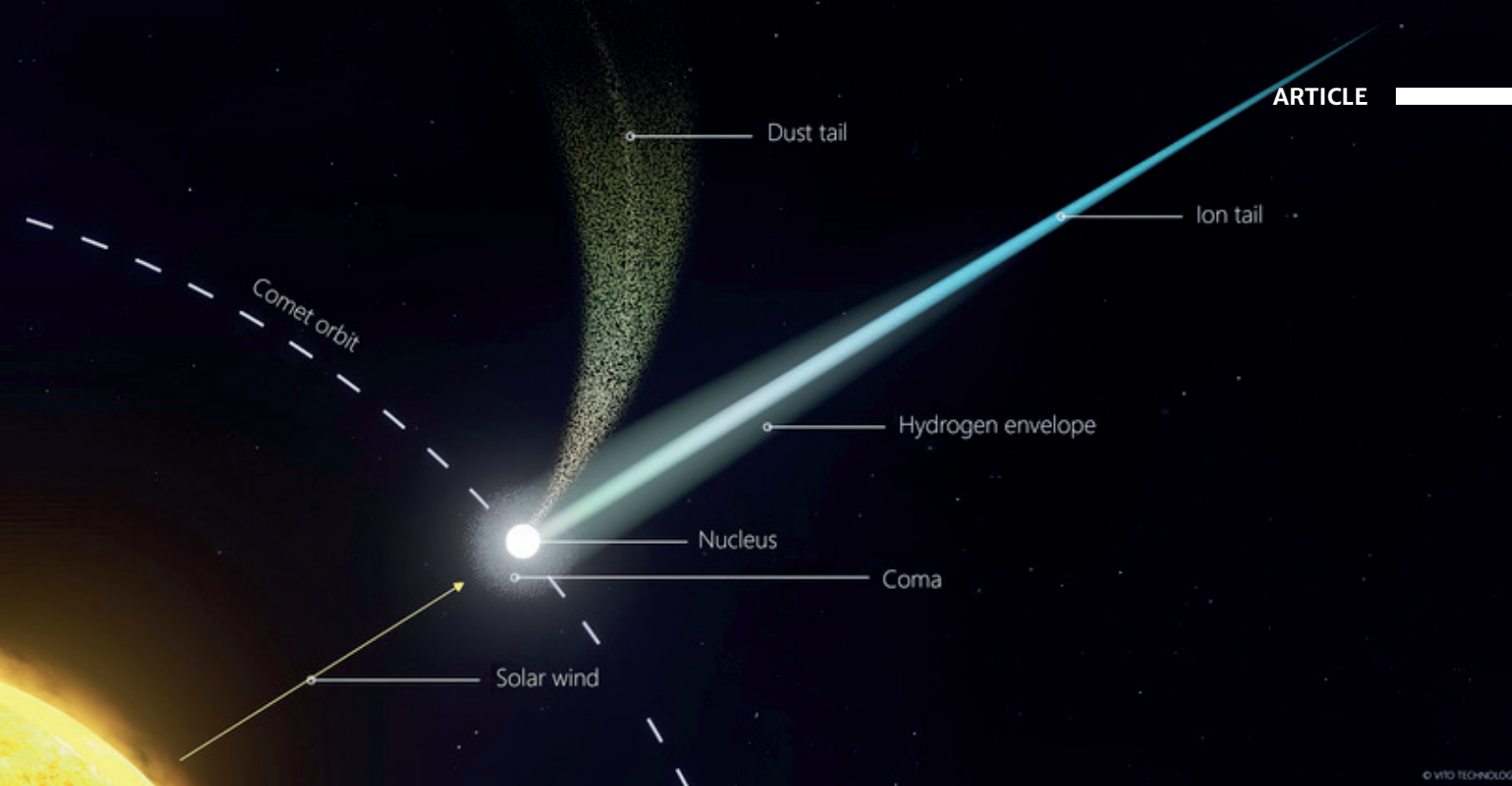


Figure 3: Anatomy of a comet. In our context, the dust tail is of special interest.

One day, hopefully, we will be able to identify the exact parent body of any given micrometeorite.

While we are gradually advancing in our quest to determine the exact origins, it may be useful to remind ourselves of the six possible sources of micrometeorites:

1. The Asteroid Belt between Mars and Jupiter. The asteroid belt contains a variety of ordinary chondrites, carbonaceous chondrites, burned-out comet cores, and other types. Matthew Genge and others point out the Koronis belt as the primary source of micrometeorites.
2. Short-period comets originating from the Kuiper Belt, and long-period comets from the Oort Cloud. These mysterious objects from the outskirts of our Solar system are often described as dirty snowballs—water ice with mineral particles and volatiles. David Nesvorný and others claim that as much as 85% of the cosmic dust, including the interplanetary dust particles, originate from comet's dust tails.
3. Planetary ejecta. We have identified achondritic meteorites from the Moon, Mars, Vesta, and other differentiated bodies. Matthieu Gounelle was the first to discover a micrometeorite of this origin. Data from the spacecraft Juno have led some researchers to believe that dust kicked up by Martian dust storms may be a significant source of the cosmic dust.
4. Particles from geysers and volcanoes on Enceladus, Europa, Io, and other moons.

5. Presolar and interstellar grains. It is estimated that ~1% of the cosmic dust entering Earth consists of presolar grains, which equals 100 kilograms per day. The platinum group nuggets which frequently appears on micrometeorites, originate from supernovae.
6. Dust from interstellar comets. Three of these have been observed entering our Solar System during the past decade alone. At least two of them, Comet 2I/Borisov and Comet 3I/ATLAS, with dust tails. Some of these extremely old particles may fall to Earth and be retrieved as interstellar micrometeorites.

Cosmos is a dusty realm. In the Solar System, regardless of the source, cosmic dust particles, as they journey towards the Sun, accumulate in the Zodiacal Cloud. The timeline of this process is the subject of Queen guitarist Brian May's thesis.

The lens-shaped dust cloud in the ecliptic plane is estimated to contain 10 billion tonnes of small particles. This is roughly equivalent to 285,000 years of Earth's cosmic influx. Over geological time scales, this is very short, especially considering how small Earth's accretion is compared with that of the Sun. There is, in other words, a large-scale renewal and continuous replenishment of cosmic dust in the Zodiacal Cloud, and an eternal exchange of dust particles among all celestial bodies: stars, planets, asteroids, comets, and moons. Meteorites are from the asteroid belt. Micrometeorites are from everywhere.

FACTBOX - Origin of Micrometeorites

For readers steeped in planetary geology and who have an interest in the cosmologic origin-of-things, here is an excerpt from a recent Ph.D. from Vrije Universiteit, Amsterdam – a Micrometeorite academic gem:

Jonker, G. (2026). “To catch a falling star: Micrometeorites as proxies for the chemical diversity and evolution of the Solar System”. [PhD-Thesis - Research and graduation internal, Vrije Universiteit Amsterdam]. <https://doi.org/10.5463/thesis.1585>

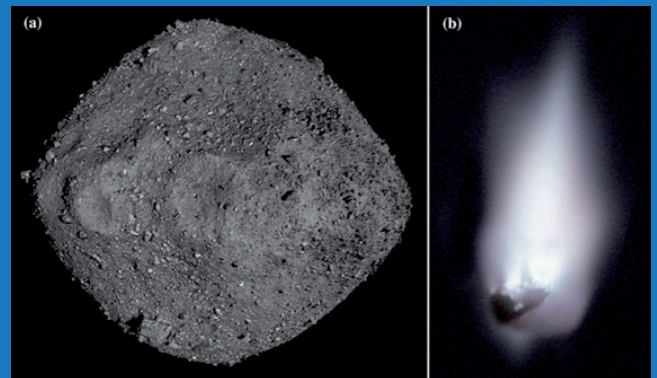
What makes micrometeorites important to study?

Although easier to analyze, larger meteorites do not provide a full representation of the Solar System's composition and only offer us a limited range of materials to study. Compared to these meteorites, micrometeorites sample a much larger diversity of precursor materials and parent bodies. In addition, their continuous and globally distributed flux allows us to observe potential flux changes through time. This enables us to obtain a clearer and more complete view of the full diversity of parent bodies and materials present in the Solar System, and its dynamical evolution through time.

Asteroids versus comets

The question of whether micrometeorites primarily originate from asteroids or comets is deceptively simple, but the discussion has been ongoing since the discovery of the first micrometeorites. Other planetary bodies are generally considered to have a low to negligible contribution to the cosmic dust flux to Earth, e.g., only a single micrometeorite has so far been proposed to have a lunar origin (Fernandes & Rudraswami, 2025). The dust production mechanism of comets is dominated by sublimation and occasionally by fragmentation of the nucleus, producing vast amounts of small particles. On the contrary, asteroids and possibly other planetary bodies produce debris mainly through impacts and collisions with other bodies, which are generally rare (Figure 1.2; Brownlee, 1985). As stated before, the number of particles with ordinary chondrite affinities increases with particle size, and thus, the cosmic dust flux $>500\ \mu\text{m}$ is likely dominated by asteroid-derived particles. However, for smaller micrometeorites, typically with carbonaceous chondrite affinities, both an asteroidal and cometary source is possible.

A cometary origin may be supported by the scarcity of chondrules in unmelted micrometeorites, which are abundant in asteroids but may be subordinate in comets (Engrand & Maurette, 1998; Genge et al., 2005; Taylor, Matrajt, et al., 2011).



Possible origins of cosmic dust: (a) Bennu, a carbonaceous chondritic rubble pile asteroid, as imaged by the OSIRIS-REx spacecraft during the sample return mission (NASA). (b) Halley, a short-period comet consisting of a conglomerate of ice and dust, as imaged by the Giotto spacecraft. The comet's nucleus is shrouded in a dense cloud of gas and dust formed through ablation as the comet neared the Sun in 1986 (ESA). Figure 1.2 in Jonker, G. Ph.D. thesis (2026).

Furthermore, numerical models of particle dynamics within the Solar System suggest that the bulk of the zodiacal cloud in the $\sim 10\text{--}1000\ \mu\text{m}$ size range consists of comet-derived particles, particularly from Jupiter-family comets (JFCs), but also Kuiper Belt and Oort Cloud comets at larger heliocentric distances. Micrometeoroids relating to confirmed comet-derived meteor showers typically have high atmospheric entry speeds well over $20\ \text{km s}^{-1}$ (Brownlee, 1997; Love and Brownlee, 1991). However, cometary dust from the zodiacal cloud could have relatively low mean atmospheric entry speeds of $14.5\ \text{km s}^{-1}$, which, coupled with comparatively lower densities, should allow such cometary particles to survive atmospheric deceleration (Genge et al., 2020; Poppe, 2016; Nesvorný et al., 2010; Yang & Ishiguro, 2018).

This suggests that the contribution of comets relative to asteroids in the production of micrometeorites smaller than $\sim 300\ \mu\text{m}$ could be more substantial than previously assumed. On the contrary, the hydrated and fine-grained nature of most micrometeorite precursor particles is difficult to reconcile with the bulk chemistry and petrology of directly collected cometary materials from the comet 81P/Wild 2 sample return mission, which are mostly anhydrous (Genge, Suttle, et al., 2017, 2020; Taylor, Matrajt, et al., 2011).

Numerical models and petrochemical observations are thus difficult to reconcile. The spatial origin of individual micrometeorites can also be deduced using cosmogenic nuclides. Their abundances may be used to determine the duration of irradiation, i.e., the cosmic-ray exposure (CRE) age, which documents the time of release from the parent body and accretion onto another body (Trappitsch & Leya, 2013). Using Poynting–Robertson dynamics, heliocentric distances at which micrometeoroids were released from their parent body can be calculated.

According to Feige et al. (2024), CRE ages deduced for micrometeorites and cosmic spherules are mostly ~10–1–102 Ma, corresponding to heliocentric distances of ~1–40 AU, mostly consistent with a likely asteroidal origin in the inner Solar System (near-Earth objects or Asteroid Belt; $n = 4$), or a cometary origin in the outer Solar System (JFCs or Kuiper Belt; $n = 7$). Noble gas measurements on a few Antarctic micrometeorites provide equally few absolute constraints on either asteroidal or cometary sources (Baecker et al., 2022). CRE ages determined for two relatively small IDPs are >900 Ma, corresponding to heliocentric distances of >150 AU, pointing to a cometary origin somewhere between the Kuiper Belt and Oort Cloud (Feige et al., 2024; Trappitsch & Leya, 2013). This would be in accordance with the consensus that most IDPs originate from comets (Genge et al., 2020). However, CRE ages may include a substantial period of irradiation prior to release from the parent body. Long periods of pre-irradiation would result in pronounced overestimations of the heliocentric distances, and may thus lead to misidentification of cometary versus asteroidal origins. Finally, coarse-grained UnMMs are linked to asteroidal ordinary chondritic sources (Genge, 2008). Rare ultracarbonaceous Antarctic UnMMs have been found to be highly enriched in deuterium, with excesses 10–30 times terrestrial values, and contain anomalously high concentrations of N-rich organic matter (50–90%), significantly higher than typical micrometeorites and IDPs. These rare particles, along with chondritic porous IDP-like micrometeorites, are believed to be the building blocks of comets formed within the cold outer reaches of the protoplanetary disc beyond the N snowline (Dartois et al., 2017; Duprat et al., 2010; Noguchi et al., 2015). They are among the only confirmed micrometeorites of cometary origin.

The discrepancy between numerical models and petrochemical observations persists to this day, meaning our understanding of either asteroid and comet chemistry or dust production and evolution is severely deficient.

Interstellar origins

Dust from outside the Solar System, i.e., interstellar micrometeoroids, may contribute a significant portion to the zodiacal cloud and the cosmic dust flux to Earth, but their existence is highly disputed and severely lacking scientific evidence. Hawkes and Woodworth (1997) suggest that ~1% of ~10 μg meteoroids could be of interstellar origin. However, these particles are characterized by extreme velocities of ~21–78 km s^{-1} , much higher than typical Solar System dust particle velocities, and hyperbolic trajectories associated with low zenith entry angles. These conditions make their survival in Earth's atmosphere and subsequent accretion on the surface highly unlikely. On the other hand, Hawkes and Woodworth (1997) argue that the existence of interstellar IDPs is not improbable, as radiation pressure from the host star could effectively eject these particles, with the Sun's radiation pressure conversely decelerating the particles sufficiently to allow atmospheric survival. Alternatively, interstellar matter could be transported into the Solar System by larger bodies. Such interstellar visitors include asteroid 1I/'Oumuamua (2017), comet 2I/Borisov (2019), and the recently discovered comet 3I/ATLAS (2025). 2I/Borisov produced a tail ~11 times Earth's diameter with an estimated dust production rate of ~2 kg s^{-1} , a total coma mass of 1.3×10^7 kg, and an effective particle diameter of ~200 μm (Jewitt & Luu, 2019). Although this dust could intersect with the Earth's orbit, the relative contribution of this mass compared to the zodiacal cloud's estimated mass of 3.5×10^{16} kg is minimal. Various stellar sources contributed to the cloud of gas and dust from which our Solar System formed. Most of this information has been obscured by extensive reprocessing in the Sun's accretionary disc. Tiny (sub)micron pre-solar grains form the exception and are found in some primitive meteorites, micrometeorites, and IDPs. These grains consist of various silicates, oxides, carbides, and metals (Yada et al., 2008; Zinner, 2004). Although not truly interstellar *sensu stricto*, the identification of these pre-solar grains allows the study of the most primitive materials from which our Solar System formed.

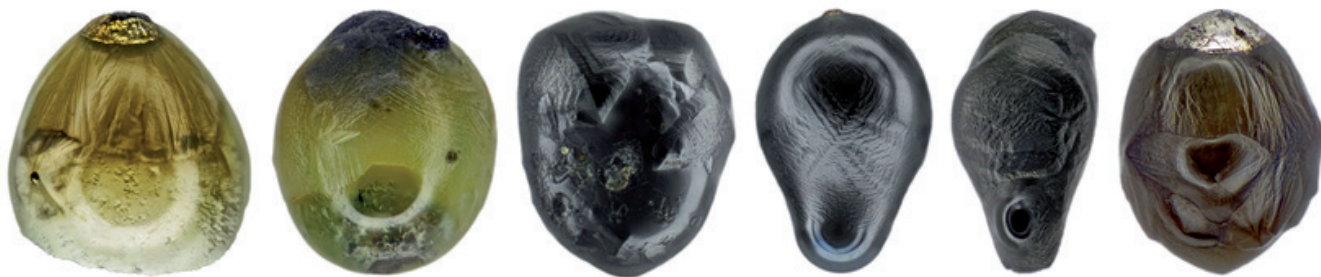


Figure 4: Micrometeorites in transitional stages between glass and crystalline (Photo: Jan Braly Kihle/Jon Larsen).

2. How To Find Micrometeorites

Great discoveries often originate from modest beginnings, and discovering your first micrometeorite is an unforgettable experience. To achieve this, we adhere to three principles: 1) magnetic extraction, 2) flotation, and 3) size fractionation.

In 27 steps, each with an illustration and a brief description, I outline a method for anyone to discover their own unique grain from space. This is just a basic introduction to get you started. I encourage you to enhance the process wherever possible.

1) Searching for micrometeorites can be done simply by placing a ladder against a rain gutter on a pitched roof. On a dry day, magnetic particles can be extracted in situ. Use a paintbrush to gather the dry particles and use the magnet directly in the rain gutter. When finished, you may jump straight to point six to continue the cleansing process.



Figure 5: Search in the school's rain gutter. The kids found 18 micrometeorites

If the rain gutter is filled with damp debris, I wear rubber gloves and collect everything in plastic bags. On the ground, it is placed in water-filled buckets to separate mineral particles from organic matter by flotation. Then you may continue from point fifteen.

But if you want to find a larger number of micrometeorites relatively easily, I recommend starting by searching for the right roof. A flat roof with a vinyl (PVC) cover is ideal, as it doesn't increase the number of particles on the roof. The larger and older, the better. I use Google Earth to locate large roofs. The lighter ones, like the one in the picture below, are usually covered with PVC.

When I identify a promising roof, I contact the owner with a brief explanation of my project and some references. Then I ask for permission to access the roof on a dry day and keep an eye on the weather forecast. When it's wet, the magnet doesn't work effectively, and we need to use a different method. In this post, we'll focus on how to extract magnetic micrometeorites from a dry roof. How to collect non-magnetic micrometeorites and work on a wet roof in a separate post.

The roof in the photo below is my local shopping centre. The first time I contacted them, a year ago, I found no fewer than twenty-one new micrometeorites here. Now, I want to see if any new spacerocks have fallen since then.

2) On the roof, there isn't much to see. It looks to be empty and has hardly any visible dust. Additionally, it has been raining, and water remains in the lowest parts of the roof, where the micrometeorites are situated. However, it is mostly dry, so let's give it a try.



Figure 6: On the roof, there isn't much to see.

3) I use my dust broom to gather loose debris and extract magnetic particles with a neodymium magnet. The instructions for holding the magnet and using plastic bags to collect the yield are shown in the photographs and explained further in the book *How To Find Stardust*.

Approximately eighty per cent of cosmic spherules are magnetic. The rest have experienced such high peak temperatures and rapid quenching during atmospheric entry that the nickel and iron have evaporated.

Today, we will extract the magnetic particles directly from the roof and collect them in a small plastic bag. This is the first of the three principles we use to find the needle in the haystack—one extraterrestrial particle among billions of terrestrial ones: Magnetism.

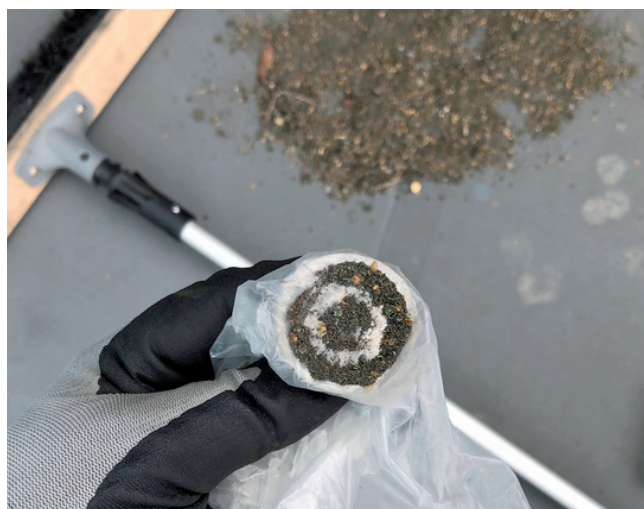


Figure 7: Magnetic particles attached to the hand-held magnet.

4) Micrometeorites are so small that they are carried by the wind. This is known as aeolian sediments in geology. On the ground or roof, rainwater washes them down to the lowest parts of the roof, usually near the drains. There, the micrometeorites may disappear. However, along the edges and in the corners, aeolian particles tend to gather, much like dust bunnies indoors.

In my area, the prevailing wind blows from the southwest, which means most of the wind-blown particles are in the northeast corner. The people on the ground are happily unaware of the cosmic drama unfolding right above their heads.

5) After three hours on the roof, I have collected a field sample of about 30 grams. Unfortunately, it rained the day before, so there is still water in the lowest areas of the roof, where dust particles (including micrometeorites) gather. I could have collected the entire slush in larger plastic bags and processed it later on the ground, but today it's mainly a quick check for really fresh stones from space.



Figure 8: The trophy bag in situ.

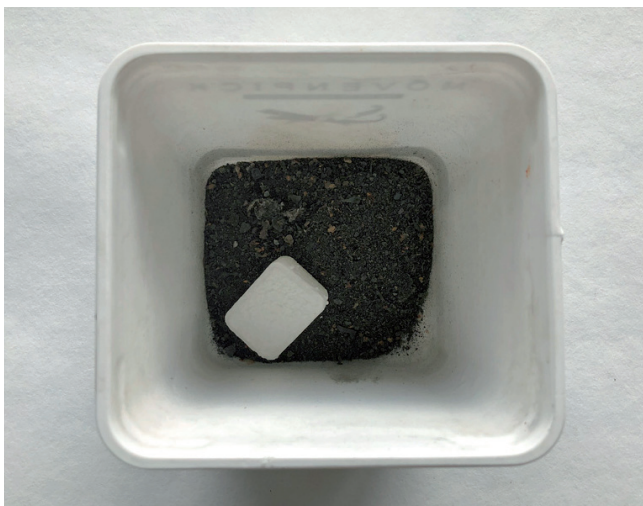
Before I leave the roof, I mark the sample with the find spot and date, as well as information about how the sample was collected (M for magnetic extraction) and the field search number. This is my field search number 986. Each field search takes a day or two, so I have spent years hunting for stardust, and I still love it!

It is crucial to properly label the field sample if you plan to collect multiple samples during the peak season and examine them later. In the book *How To Find Stardust*, there is a chapter about curating your collection. A handwritten journal with one entry per field search is recommended, as it will increase the scientific value of your collection.

6) This is the equipment we'll use for processing the field sample: a plastic box, a plastic spoon, some dishwasher detergent, and a flat plate. The methodology is still new, so it has great potential for improvement. Use my tips to get started, and then let your imagination take over to enhance it.



7) To begin the process, I place the sample from the roof into a bowl, in this case, an empty ice cream container. Along with the dust, I add some dishwasher detergent. This is not required. Alternatively, one may use a sonicator and/or distilled water. If the roof is inhabited by birds, I sometimes use alcohol first to kill bacteria from the droppings.



8) Fill up with water and use the plastic spoon to stir gently around. The aim is to clean the surface of each dust grain in the sample and rinse away the submicron dirt particles by flotation. This means that organic particles and submicron dirt float to the surface, while mineral particles, including micrometeorites, sink to the bottom.



9) After a while, we reach a crucial point in the process. Do nothing!

Let the sample rest for a moment without touching it. This is a moment of Zen. Allow gravity to do its work and let the dense particles sink to the bottom, while the smaller dirt particles float or swirl in the water. If you absolutely must do something, I suggest either observing the bubbles or closing your eyes and contemplating for a moment that you are reaching for the stars. And that somewhere in the dirt in front of you, right now, a stardust particle may be sinking to the bottom after a journey of billions of years through space and time. It's magical!

Then, gently pour off the dirty water. Ensure the heavier particles at the bottom stay in the bowl. A magnet placed beneath the bowl, or at the side where you pour out the water, can be helpful.





10) Refill with water (I use warm water), stir, and let the mineral particles settle at the bottom again. After a while, carefully pour off the dirty water.



11) Repeat, refill with clean water, stir, and allow the precipitate to settle at the bottom. Wait patiently; do not disturb the work of gravity. Patience is beneficial for us.

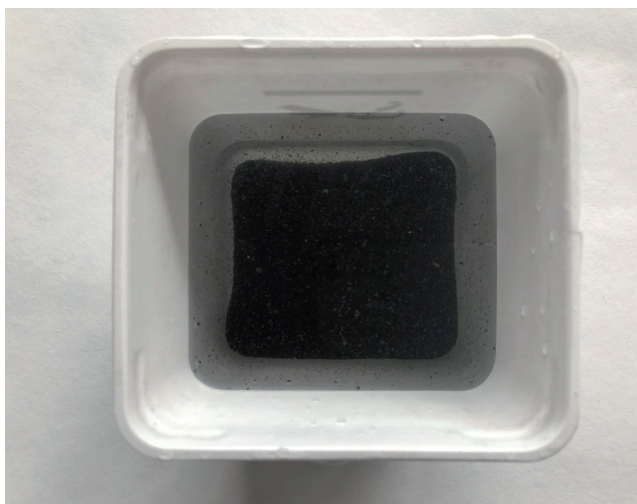
The young Buddha claimed he was only capable of two things: fasting and waiting. By searching for micrometeorites, you will not only expand humankind's knowledge about space but also develop your own patience.

12) Continue rinsing the sample, pour off the dirty water, and repeat the process. Gradually, the water becomes clear.

During this step, we apply the second of the three principles in the search for micrometeorites: flotation, which separates the dense mineral particles from the rest. Simultaneously, the micrometeorites are being cleaned, which is essential for accurately identifying both terrestrial and extraterrestrial particles under the microscope.



13) Continue until it looks clean.



14) Now the water stays clear, and it's time to move on to the next step.



15) Pour the wet dust particles onto a flat plate and tilt it slightly to remove most of the water.



15) Below is the clean sample. We have washed away approximately one-third of the initial mass, mainly consisting of dirt, organic material, and mineral particles with diameters of up to 50 microns.

Now, I place the plate to dry. On a sunny day, the quickest way is to put it outside in the sunlight. Alternatively, let it dry slowly indoors. Efficient warming lamps, drying cabinets, air fryers, and professional laboratory drying ovens are all available for those who can afford them.



Some scientists prefer to proceed directly to microscopy from here and complete the final part in wet conditions. I suppose this is a matter of personal preference. After a day on the roof and rinsing the sample, I usually take a shower and have a siesta while it dries.

16) Either way, after some time, the sample dries and we can proceed.



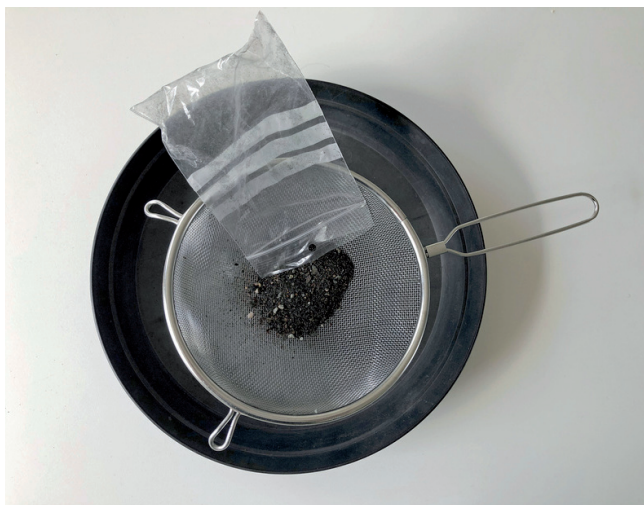
The sample now includes dry particles of all sizes, from roughly 50 microns and larger. It is quite remarkable how large particles the wind can transport, and the birds even bring bigger pebbles.

In this specific case, most of the sample consists of rust—small flakes from various mechanical installations on the roof, such as solar panels, air conditioners, antennas, tubes, drains, signs, and doors. Because of its monotony, examining this much rust under the microscope can be quite tedious, but the good news is that it is easily distinguishable from potential micrometeorites.



18) Begin by pouring the sample through a sieve with a 1.5 millimetre (~0.06 inches) mesh to remove particles that are too large. Most cosmic spherules are between 150 and 400 microns. We then apply the third principle to narrow down the sample for finding micrometeorites: size fractionation.

The purpose of fractionating the particles is to make it more efficient to examine particles of the same size under the microscope. At high magnifications, the depth of field is shallow. Zooming in and out on particles of different sizes is inefficient and eye-straining.



19) The particles remaining in the sieve are larger than 1.5 millimetres. These can be quickly examined under a microscope at a relatively low magnification or discarded.

From Antarctic collections, we know that a few super-giant micrometeorites exceed 1.5 millimetres, but such specimens are rare. The largest of the 5,600 micrometeorites I have found measures 1 millimetre.



20) The particles passing through the 1.5 millimetre mesh are then filtered through a finer mesh of 0.4 millimetres (0.015 inches, or 400 µm).

The largest particles (400 to 1500 µm) are now examined under the microscope at a relatively low magnification of around 25x. This process is quick, taking only a few minutes for this size range and magnification,

because the dark aerodynamic, complete stones from space are very different from the angular terrestrial mineral grains and rust. The key is knowing what to look for and what to ignore.

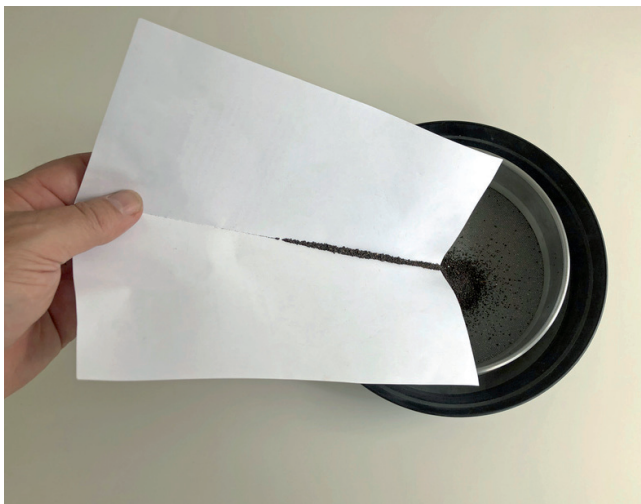
Recently, I obtained a sieve with a 0.5 mm (500 µm) mesh, which adds an extra step in the fractionation process. However, it also facilitates the identification of the not-unusual micrometeorites in the 400–500 µm range. This time, I found no large micrometeorites in the 400- to 1500-µm fraction, so I moved on to the next step: the particles that passed through the 400-µm mesh.



21) The <400µm particles are now passed through a third sieve, this time with a mesh of 200µm. What remains in the sieve are particles between 200 and 400 µm, where, according to Michel Maurette, most of the cosmic spherules are.



22) Below. I use folded paper as a funnel to collect the particles moving between the plates and sieves.



23) What passes through the sieve with the 200 μ m mesh are particles smaller than 200 μ m (0.2 millimetres). These can be further divided into even smaller sizes, where many micrometeorites might be present, but this requires specialised equipment, a powerful microscope, and keen eyesight. Micrometeorite expert Susan Taylor recommended ignoring particles smaller than 50 μ m.

Today, however, I will focus on the most important fraction—the sweet spot. This refers to what's remaining in the 400 μ m sieve—particles between 200 and 400 μ m in size. Most of the cosmic spherules are found in this range. Or, according to others, more specifically in the 123 to 300 μ m size range.



24) The sample in the 200 to 400 μ m fraction now weighs 7.1 grams, roughly 20% of the initial sample collected from the roof. Most of these particles are magnetic, but not all. All will, however, be examined under the microscope at approximately 63x magnification.



25) Now it's time to move on to the final part: microscopy. The photo below shows my equipment, which I have been using for years. It includes a Zeiss binocular microscope, water, two pointed wooden sticks, and a small plastic box with an air-tight lid to store potential micrometeorite candidates.

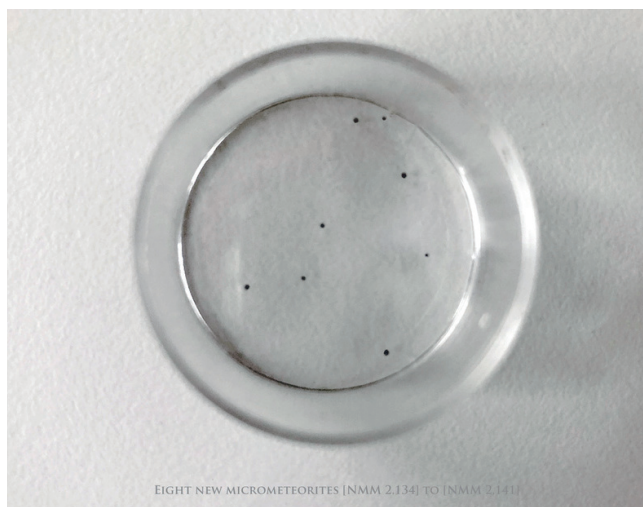


26) This is the proverbial search for the needle in a haystack, and it is important to know what to look for (the micrometeorites and their characteristic textures) and what to disregard. The various particles are described in the book *How To Find Stardust*.



With experience, as you become familiar with micrometeorite textures, it becomes possible to listen to a podcast or your favourite music during microscopy. Today, I played a double album of 70s prog rock and enjoyed both the music and the microscopy. By the time side four was over, so was the microscopy.

27) Here is the result: no fewer than eight ultra-fresh micrometeorites! Three barred olivine (BO) types, two scoriaceous (ScMM), one porphyritic olivine (PO), and one glass (V-type) with a metal bead.



The entire process — from contacting the shopping mall, sampling in situ, processing, and microscopy — has taken about eight hours. This is certainly acceptable, but not an ideal outcome. On two similar roofs, which I sampled for the first time this year, I found over 100 micrometeorites on each. However, today was a quick check, and the roof was somewhat wet.

In any case, one micrometeorite per hour, or roughly one micrometeorite per gram of sample (within the correct fraction), is not too bad either. When I started with this in 2009, it was considered utopian. Pure science fiction.

3. What to ignore

The micrometeorite community is expanding, and this month alone, hundreds of new hunters are reaching for the stars more or less from scratch. With a fresh sample from a rain gutter, a car park or a flat roof, it's time to enjoy the magical microcosmos under the microscope. Perhaps the first thing you'll see is something like this:



Figure 9: Particles in the 0.2 to 0.4 mm size range in ~30x magnification.

If so, I suggest using higher magnification to clearly see the surface structure of each particle. Among the sand grains, you'll notice several rounded objects, or spherules. But are they micrometeorites or just terrestrial contaminants? At first, it can be overwhelming—so many unusual shapes. Every experienced micrometeorite collector has faced this, examining countless spherules one by one. Over time, though, you start recognising the common types and can set them aside while hunting for the real micrometeorites.



Figure 9: The same particles in ~60x magnification.

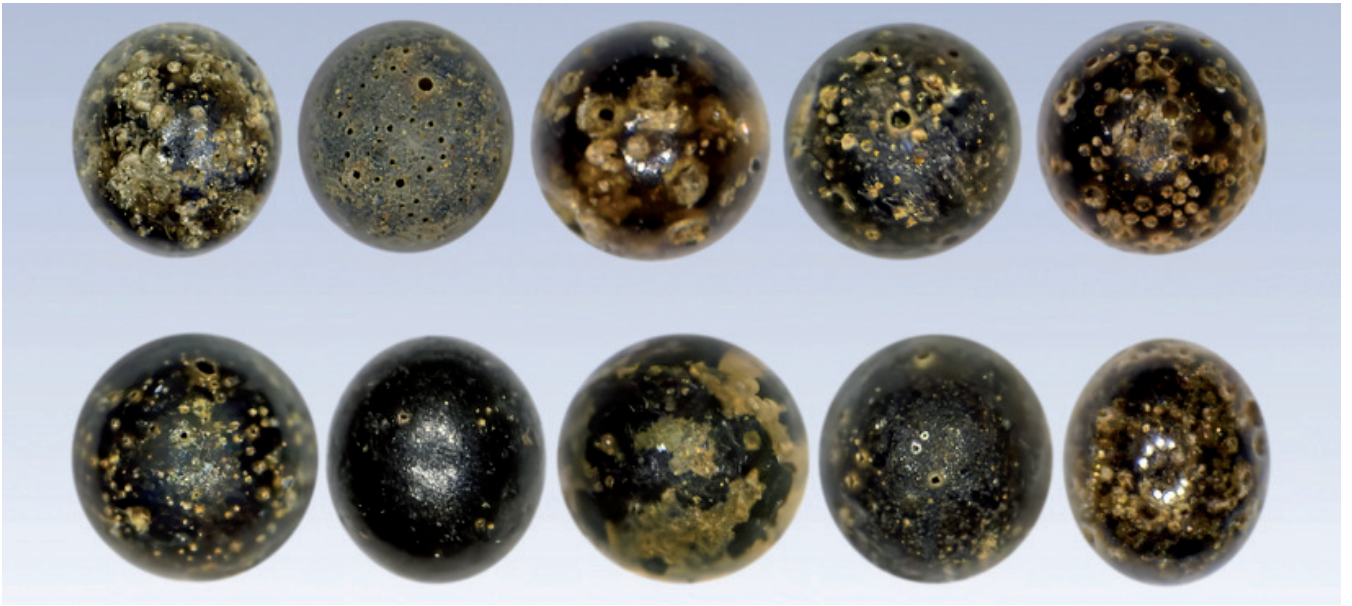


Figure 10: Achneliths, from a volcano (Photo: Jan Braly Kihle / Jon Larsen).

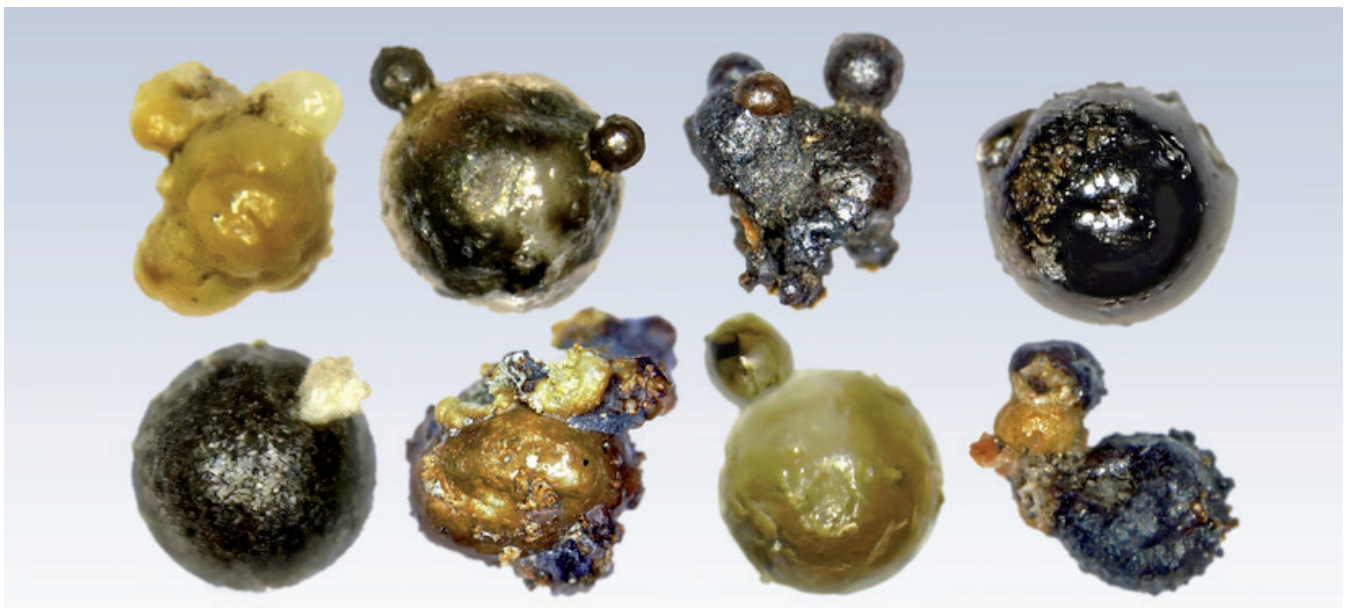


Figure 11: Fulgurites, from lightning (Photo: Jan Braly Kihle / Jon Larsen).

A fast way to learn about the terrestrial spherules is the textbook *In Search of Stardust*. It took me seven years to figure everything out, but you'll get it in a couple of hours. The book contains more than 1,500 photos of identified and classified spherules. When you've read the book, you'll be able to identify them all.

The key to scanning a dust sample under the microscope and spotting that needle in the haystack—a genuine micrometeorite—is knowing the most common terrestrial contaminants.

With practice, the process becomes quick, and you can even enjoy some music or a podcast while working at the microscope.

Remember, there are only nine types of micrometeorites, but a zillion different types of terrestrial spherules.

Happy hunting!

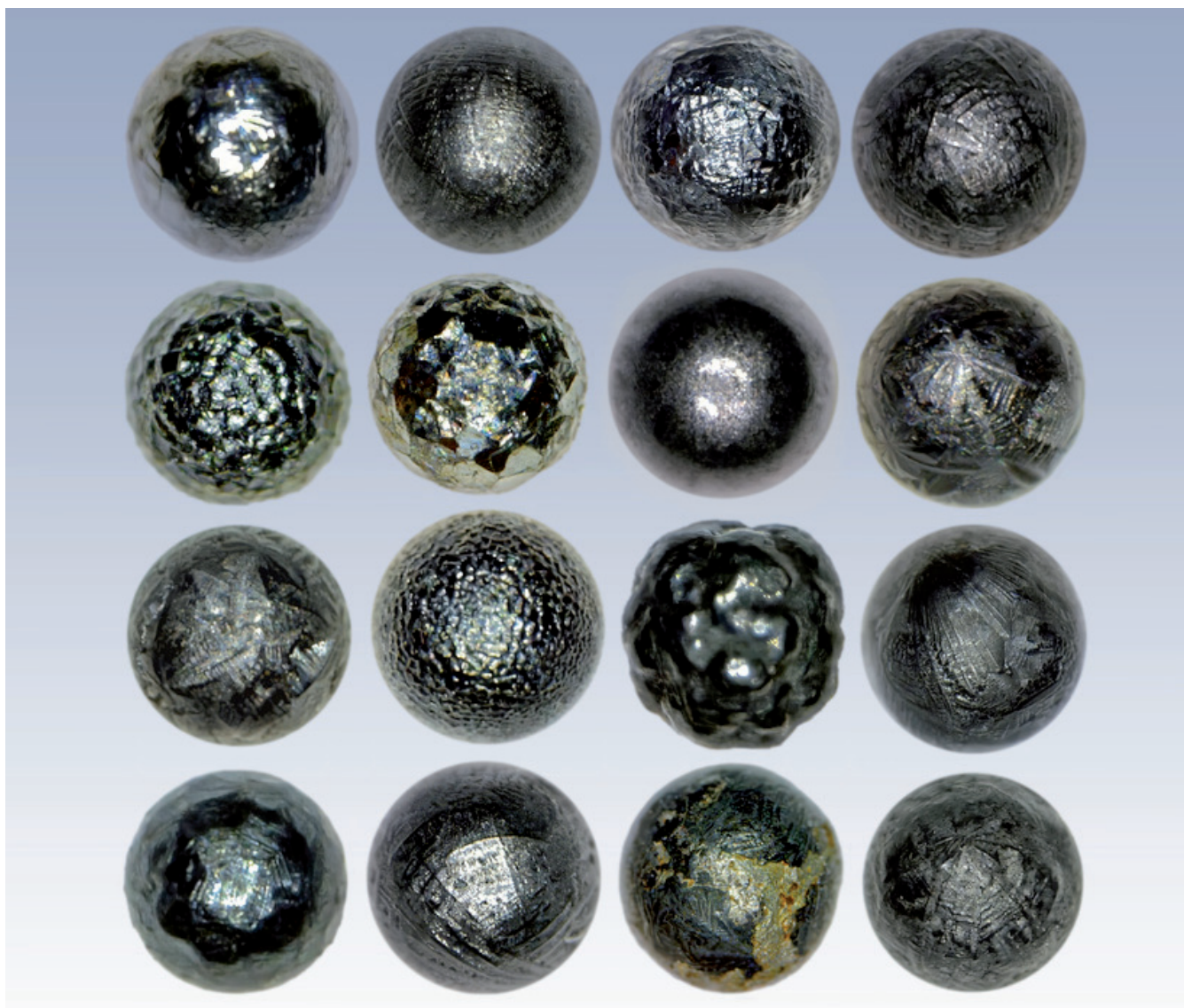
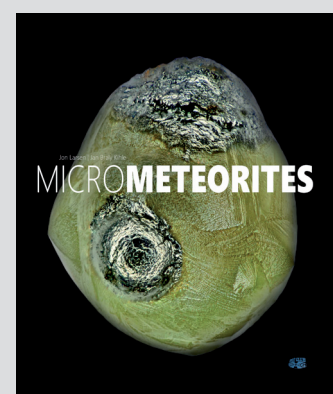


Figure 12: Industrial iron oxides from power tools (Photo: Jan Braly Kihle / Jon Larsen).

ATLAS OF MICROMETEORITES AND MORE ON PATREON

Legendary coffee table book with the World's most beautiful micrometeorites in large hi-res colour photos by Kihle/Larsen. Each photo has a short explanatory text, peer reviewed by Martin D. Suttle. Prefaces by Michael Zolensky (NASA), Matthew Genge (Imperial College, London), and the author, Jon Larsen.

You can find a lot more on Patreon, just sign up at patreon.com/ProjectStardust826/



FACTBOX - The Ten-Point Checklist for Micrometeorites

The ten-point checklist is used to determine whether a stone is a micrometeorite or not. Based upon what you can observe, or not, under the microscope, the identity of a candidate can be verified in seconds. Once you are familiar with these ten simple yes-or-no questions, the checklist will, in most cases, guide you through the maze.

The first six questions are confirmatory criteria, where the answers should be yes. The last four are exclusionary, and the answers are no. Karl Popper (1902–1994) claims in his *Empirical Falsification* that confirmatory criteria cannot be trusted because it is always possible to find supporting evidence, even for an incorrect hypothesis. A falsification, on the other hand, is more reliable (Photos: Jan Braly Kihle / Jon Larsen).

Confirmatory Criteria

1. Is the rock aerodynamic? Does it show signs of melting and hypervelocity?



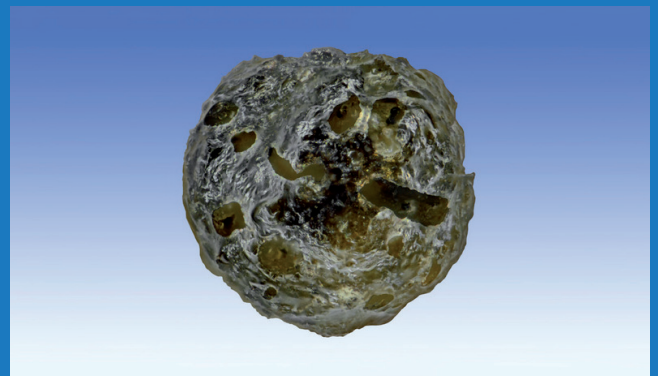
A micrometeoroid entering Earth's atmosphere at hypervelocity melts due to frictional heating. This causes an elemental differentiation in the particle, where dense elements (nickel and iron) gather as a core, surrounded by silicates, whereas the volatile elements evaporate and escape. Almost like a planet formation in miniature. Because of its small mass, the subsequent increase in atmospheric pressure leads to an abrupt deceleration where the metal core migrates to the front due to inertia.

The drop in temperature is followed by solidification and recrystallisation. This formation process, which is over in the blink of an eye, is different from all other types of rock formations on Earth. And it is the typical signs from this unique experience we are looking for when we identify micrometeorites by their visual appearance. This was sci-fi only ten years ago.

In most cases, cosmic spherules obtain visible flight characteristics, like slight elongation, a symmetric length axis, and characteristic elemental distribution:

Heavy metal (beads) in the front, followed by silicates, and escaping volatiles (vesicles) at the rear end. In the photo above, note also the pale area next to the metal bead, apparently drained of iron.

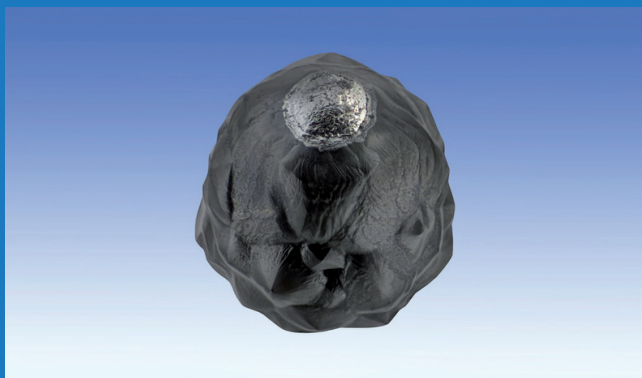
2. Are the colours, lustre, and translucence (if present) like those of most micrometeorites?



Unlike terrestrial rocks, which have extreme variations in mineralogy and chemical content, rocks from Space are surprisingly homogeneous. They are chondritic, which is the chemical signature of our Solar system at large. This means a limited range of colours, characteristic lustre, and translucence. The dominant mineral in stoney micrometeorites is olivine, in the magnesium variety forsterite. These crystals are often colourless, but for unknown reasons, most micrometeorites are black. Porphyritic olivine (PO) types are at times completely colourless and translucent olivine crystals glued together by a dark glass matrix. More frequently, due to minor traces of iron, they display hues of green (Fe²⁺) or brown (Fe³⁺).

Confirmatory Criteria

3. If there are metal beads on the surface, are they located in places that are consistent with aerodynamics, rapid deceleration from hyperspeed, and/or spin?



Ninety-nine per cent of all micrometeorites are stoney, only one percent is metallic iron oxide. They do, however, often contain metal beads, and where they are situated on a spherule, and what they look like can help us identify its origin.

In most cases, micrometeorites are oriented stones with one single nickel-iron metal bead in the front. The dense metal may have triggered crystallisation in the rock, in a way that is different from terrestrial spherules. An additional secondary bead, often enriched in nickel, may be situated at the rear end of the micrometeorite, due to spin perpendicular to the direction of flight.

If the stone has short terrestrial age and is fresh from Space, the metal bead may be surrounded by a thin, shiny sulfide rim. At times, you can see several beads caused by a more chaotic spin.

With experience, these unique features get quite easy to recognise. On the other hand, terrestrial spherules have not gone through the strong forces like the cosmic spherule formation, and their surface metal beads are placed more randomly. Here is a typical cosmic spherule, a cryptocrystalline turtleback variety, with a metal bead in the front surrounded by a thin sulfide rim. The bead has triggered crystallisation backwards, which is down in this photo. Note the exquisite symmetry along the length axis.

In the case of a V-type (vitreous, glass) micrometeorite, the metal bead is most often surrounded by a thin, shiny sulfide rim, and/or crystallisation in the glass. Characteristically, a glass micrometeorite may have a metal bead in the front, which has triggered a conical crystalline area, standing out from the spherical glass body. At times, we can also observe the characteristic Soap Bubble Effect, umbrella-like pyramidal crystal domains growing independently in the glass. On the opposite side of the glass micrometeorite, in the back, we can often observe an additional indication: A large open vesicle from degassing.

4. Is it a single rock without twin formations or aggregates? Is it complete all the way around?



Micrometeorites are lonely wanderers through Space and fall to the ground as solitary, aerodynamic, and complete stones. Contrary to angular, fractured, broken, and/or worn terrestrial mineral grains. To my knowledge, fused micrometeorites do not exist. Twin formations, triplets, spherule aggregates, and similar structures are common in terrestrial spherules, especially those created by industrial power tools.

When a micrometeorite lands on a rooftop with little activity compared with the turbulence down on the ground, it remains pristine, complete all around. A smooth, dark, undamaged spherule with recognisable textures (see point five). This is surprisingly rare in the urban dust.

Confirmatory Criteria

5. Does the rock exhibit any of the characteristic micrometeorite textures?



Three out of four cosmic spherules (melted micrometeorites) are classified as one of the three most typical textures: Barred olivine (BO), cryptocrystalline (CC), or porphyritic olivine (PO). And of these, the majority is barred olivine. If you learn to recognise what these three types look like, you may easily pick them out in a dust sample. They stick out.

In addition to these three types, around twenty per cent of the micrometeorites are glassy V-types. Here is a post about separating nonmagnetic glass (V-type) micrometeorites from anthropogenic glass spherules: ET or T glass spherules?

6. Is it the right size?



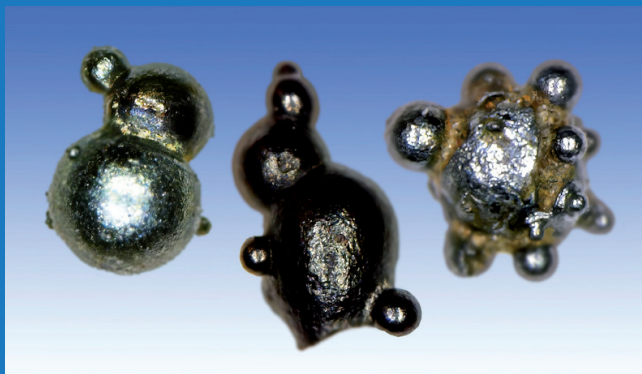
Most micrometeorites are between 0.1 and 0.3 millimetres in diameter. Objects smaller than 0.05 and larger than 1.0 millimetres in diameter are suspect.

Yes, there are micrometeorites smaller than 0.05 mm (50µm), but that is the lower limit recommended by Susan Taylor, who discovered the MMs in the South Pole Water Well. And there are other problems. First of all, smaller than that, the MMs get increasingly difficult to identify in an ordinary microscope; you need an electron microscope. Secondly, smaller sizes tend to be too small to melt during atmospheric entry, and unmelted micrometeorites are difficult to identify at all in a light microscope. Besides, in these small sizes, we enter the realm of the enigmatic and fluffy aerosol particles, floating in the atmosphere. They have so small a mass that they hardly fall to the ground at all. More about these interplanetary dust particles, later.

There are also micrometeorites larger than 0.3 mm, according to Maurette one in 250 may reach 0.5 mm. Larger than that, we call them giants, and if they get near 1.0 mm we call them supergiants. I have only found a handful (1/1000) of those. From the blue ice in Greenland and Antarctica, Maurette has reported about extremely rare MMs up to 3.0 mm, and Susan Taylor about “one strange object”, a spherule of stunning 0.5 mm. Larger than that, they will most likely burn up in the atmosphere. So the peak in the mass distribution of micrometeorites is somewhere between 0.1 and 0.3/0.4 millimetre. I recommend laboratory sives to find the sweet spot.

Exclusionary Criteria

7. Does the candidate have twin formations or complex forms (aggregates)?



This is common for industrial spherules but does not exist in micrometeorites. See also point four.

8. Are there any crash, splash, or roller marks?



This is frequently observed on industrial spherules, where the spherule may have hit the ground in a semi-liquid state.

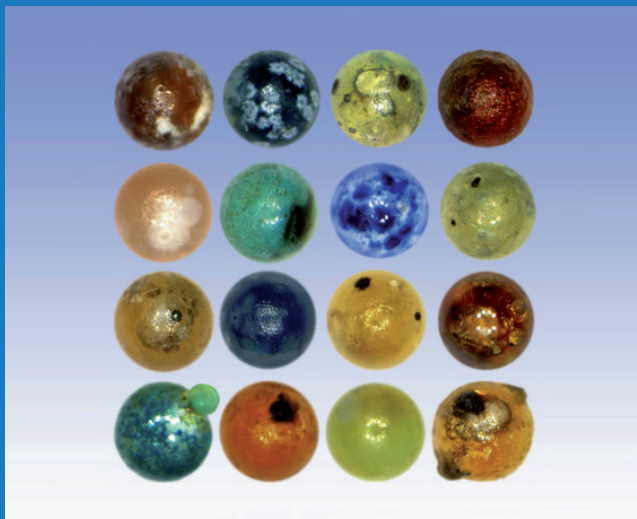
Micrometeorites, on the other hand, solidify in the upper atmosphere. Their kinetic energy is transformed into heat, and the small Space rocks fall to Earth cold, and at “terminal velocity”, only pulled by Earth’s gravity. Again, see point four.

9. Does the object possess one or more tails?



This is common on man-made spherules, but rare in micrometeorites.

10. Is the object rusty or does it have vibrant colours?



Olivine and magnetite in micrometeorites do not rust. Vibrant colours are common in fireworks and other anthropogenic spherules, but rare in micrometeorites. See point two.

If the conclusion remains unclear after going through the checklist, a chemical analysis is recommended. If a particle is chondritic and has the right textures, it is a micrometeorite.

EDITOR'S INTRODUCTION: PRIMARY SAMPLING AND PARALLEL ALIQUOT SPLITTING ERRORS AND UNCERTAINTIES

SST is a.o. conceived to furnish a platform for scientific and technological debate. In this issue, the editor is delighted to host a discussion regarding the validity of Photon Assay (PA) for quantitative gold determination of significantly heterogeneous geological deposits and mineralisations, especially for coarse-grained ores. Spurred by two initiating submissions by (F-B&O), the Chrysos corporation here responds, also with two entries i) a formal rebuttal letter, and ii) a fundamental technical review of real-world PA performance on heterogeneous gold ores. Reading these four contributions needs no further introduction – but the editor wishes to emphasize a potential elephant in the room.

While the debate over alleged worrisome issues pertaining to key PA analysis technicalities is comprehensive, there is an underpinning aspect which is not explored to the same degree of detail, i.e., primary sampling and certain sub-sampling of the original gold-bearing targets. What happens between a specific coarse-grained gold-bearing ore type/deposits is sampled in the field and 0.5 kg aliquot material (crushed to either coarse-grained or to powder status) is deposited in regular PA jars? With the authoritative overview of the Theory of Sampling (TOS) in mind, there is always the matter of primary sampling error uncertainty to be reckoned with, especially if different stakeholders do not employ the exact same sampling approach – as well as splitting uncertainties generated at a subsequent sub-sampling stage in the lot-to-aliquot pathway. The latter must be at identical stages for 'comparisons' to be valid, lest unrecognised sub-sampling error effects can compromise otherwise apparently fully valid protocols. This issue constitutes the most often encountered unresolved question of 'comparison' of the performance of competing analytical methods across different target materials. This is also of importance when comparing different variants of a specific analytical method, for example with respect to different spatial positioning of activated and emitting gold particles – and when comparing analytical performance in Round Robin experiments. N.B. Round Robin comparisons can only validate analytical accuracy and precision, but the additional, and potentially larger, sampling/sub-sampling accuracy and precision contributions are all too often unrecognised. For full discussion of 'sampling and sub-sampling uncertainties with hidden consequences'.^{1,2}

Enjoy this illuminating scientific debate!

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- 1 Esbensen, K.H. & Vogel, D.A. (2023) The Elephant in the Room: Unsubstantiated Complacency Regarding the 'Assay Exchange' Paradigm – Sampling Uncertainties with Hidden Economic Consequences. The *ALCHEMIST*, issue 110 (2023) <https://www.lbma.org.uk/alchemist/alchemist-110/the-elephant-in-the-room>
 - 2 Esbensen, K.H. & Vogel, D.A. (2024) The "assay exchange" paradigm – sampling uncertainties with hidden economic consequences. pp. 121-148 in Proceedings WCSB11. 11th World Conference of Sampling and Blending. Misty Hills Conference Centre, Johannesburg, May 2024. The Southern African Institute of Mining and Metallurgy. <https://www.saimm.co.za/Conferences/files/wcsb11-2024/WCSB11%20Proceedings%20Book.pdf>

Photon Assay: A New, Revolutionary Technique Everybody Wants to See Succeed – An Independent Evaluation Part 1: Experimental Bias Detection and Synthetic Sample Simulations

By Dominique François-Bongarçon¹ and Robert Oliver

DOI: 10.62178/sst.005.004

ABSTRACT

Photon Assay (CPA), a gamma-ray excitation technique marketed by Chrysos for rapid, non-destructive gold determination on ~450 g samples, has attracted strong interest in the mining industry for its speed and grade-control potential. Early, anonymous reports and comparative tests at nine anonymous gold deposits suggested systematic biases: crushed-material CPA readings were frequently lower than paired pulverized readings and differed from fire assays to extinction by 4–8%, though experimental designs were not always optimal.

To isolate effects attributable to sample preparation, controlled synthetic samples were prepared by spiking barren rock with ≥99.99% pure gold fragments of known mass and size. Four combinations of coarse/fine gold and coarse/fine barren matrix were tested under the standard PAAU02 service, with ten replicate analyses per jar. Student's t-tests (95% confidence) revealed statistically significant negative biases in three of the four cases, except for fine gold in a finely pulverized matrix. Coarse-gold samples also showed unexpectedly higher measurement variance, consistent with positional redistribution within the jar.

These findings confirm the importance of full pulverization prior to CPA and demonstrate the need for rigorous, site-specific validation before adoption. Further mechanistic studies are recommended.

1. Introduction and Marketing Overview

In the times of the gold rushes, the classical preparation for gold assays was as follows: jaw crushing; splitting of 500g; pulverizing; assaying 30g by fire assaying. The reason for the (small) 500g split after crushing was that the ring and puck pulverizers existing on the market would not pulverize more than 500g. A poor reason, but that was a time the economics of gold deposits were a lot less marginal than today and gold operations could commit gross errors and still make money. This protocol (which is still part of the South-African standards) lasted until maybe 40 years ago, when people finally realized that today's gold mines cannot afford such lousy splits. In parallel, similar economics for coarse gold mines was calling for larger assay charges. These classically went from 30g to 50g, then 100g. Multiple fire assays became routine, as well as more massive assaying techniques such as bottle roll leaching and screen fire assays.

The calls clearly were for both larger pulverization masses and for larger assaying charges. Larger pulverizers were constructed that were able to accommodate 1.5kg then 3.5kg samples, then continuous ringmills appear that did not have a mass limit. The continuous ringmill had its detractors on the basis of possible sample to sample contamination and alleged difficulty of cleaning (which was largely exaggerated). A first abuse was witnessed when the large pulverizers of the LM5 type, able to pulverize 3.5kg were seen by not-knowledgeable decision-makers as a license to reduce the collected field sample size from 10kg or more down to 3.5kg at the rig. It was easy, but devastating in terms of sampling variances, most of the time.

That was the point at which the massive assaying techniques also appeared.

¹ Agoratek International Consultants Inc., Canada.

Starting with bottle roll leaching, that could easily accommodate several kilograms of pulverized sample but had a large footprint in the laboratory and was time consuming. Next to appear was the PAL (pulverize and leach) system that had a reduced footprint and was faster. The sample (500g or 1kg) was leached in a rotating steel container with Leachwell catalyst, and was pulverized and smashed by small steel balls, not unlike a mini-ballmill. A new abuse appeared. The sales pitch for the PAL was that you did not need to spend money pulverizing before assaying as the sample was pulverized anyway under the effect of the steel balls during the agitated leaching in the container. As a result, samples as small as 500g were (again in history!) split directly from the crushed material under the bad judgment of not-knowledgeable decision makers, going back in history, with the same potentially devastating effect, since not all gold deposits are forgiving. In the meantime, screen fire assays (SFAs) were also used at times on samples of up to 1kg, to handle coarse gold situations. This was often done without realizing that not all coarse gold situations equate high sampling variances, and that SFAs came with their own realms of practical problems and were in no ways close to a panacea.

Then most recently a new technique marketed by Chryso, the Photon Assay (CPA), has appeared. It subjects a ~450g sample jar to high energy gamma ray excitation and detects gold's only natural isotope by the decay of its resulting metastable nuclear isomer. The method is non-destructive, so that samples can be recovered and re-assayed any other way desired, and the assay turn around time offered is at a record low, making it extremely desirable for grade control samples.

Allegedly, the penetration is total and the material assayed can be rock, crushed ore or pulverized ore, with no difference, for total contained gold determination. Of course this suggests a same marketing danger is present, in which non-knowledgeable decision-makers may see an (unjustified and dangerous) opportunity to skip the pulverizing step before final sampling of the jar contents. But this not the sole issue.

2. CPA Bias Issues

Indeed, from the onset of the CPA method, there were undocumented rumors on the streets that CPA readings on crushed material could differ from the reading of the pulps. A number of large mining groups and laboratories that were considering adopting the CPA for their assaying therefore engaged in some assaying tests.

One of the authors was asked to review the results of these tests statistically (mostly without being involved in the experimental design except in one case) at 9 anonymous fine and coarse gold deposits around the world, in Africa (5), Canada (1), South-America (1) and Australia (2). In each case but one, the data available consisted of crushed and pulverized CPA readings on the very same material, and of fire assaying of the samples to extinction. For some deposits the samples were from RC rigs while the other were from crushed core. Comparisons between paired data were made in a classical manner using simple t-tests applied using a 95% confidence level.

Results were concerning at best. In general, large biases between crushed and pulverized readings were present in all crushed cases, with statistical significance, and relative amplitudes of 7%–10% for hard rock and 1%–2.3% for RC samples, pulp readings being always higher in all cases but one. For the crushed RC (almost pulverized already by the drill bit), the differences to pulp readings were of course quite small (1%–2%) but significant in most cases. Differences between CPA pulp readings and FA to extinction were often of the 4%–8% order, FA being higher whenever significance was reached. In one RC case, however, the reverse was true with a relative bias of 2.6% and in 3 cases, no significance was attached to the observed differences.

At this point it is clearly paramount to fully test the method first before adopting it in any particular situation. In addition to the sampling considerations expressed above, it seems very unsafe to use CPA on material that has not been pulverized first. The experimental design is important so that if biases are indeed detected they cannot be unduly blamed on imperfections of the experiments. It should be noted also the CPA method demand special characteristics for the samples, as they must fill the sample jar completely well packed and tamped. Results are not adequate if the jar is not full. It is important to realize this certainly is a huge limitation about the routine use of the method.

3. Bias Testing

3.1 Denial Considerations and Issues

Several points are worth noting:

1. The marketers of CPA have been keen to deny there were any issues with biases in cases they had studied themselves.
2. When confronted with different test outcomes that differed from their, experimental design was usually blamed.
3. It is true most of the experiments above were not necessarily optimally designed. The only one for which design was fully controlled from the onset showed a statistically significant bias between crushed and pulverized reading on RC samples, of around 1% in relative terms (crushed reading higher). But it showed no significance for the difference of the same amplitude that was found between pulverized readings and FA to extinction. A slight doubt remained that needed to be verified.

3.2 T-test and Unequal Variances

The test to try and demonstrate statistical significance in this case is Student's t-test for the means of paired data. It is a very robust, hypothesis statistical test which applies well and usefully even if the two variables have different variances, provided the ratio of variances is less than 4 (a ratio which is far from being reached in all these cases). When run at a 95% confidence level to a calculated difference between pairs in a data set, if it shows statistical significance, it means there is a probability of at least 95% the experimental difference observed is due to an operational bias. In the contrary case, the test is simply inconclusive and it never means there is no bias.

Modifications of the test by Cochran, Cox and/or Welch exist to be applied when the variances are appreciably unequal. These modified tests are less stringent and will tend to be inconclusive more easily. As a matter of scientific logic, it is clear an inconclusive test cannot be used to deny the significance previously demonstrated by another test, even though this flawed logic was indeed used by the marketers when needed.

3.3 Experimental Take-away

More tests needed to be run, with fully controlled experimental designs, to assess the reliability of the CPA method as it stands today. But there was ample preliminary evidence the CPA method may present some accuracy problems, at least under certain circumstances. As a result, it was decided to run tests on synthetic samples, to confirm these observations and try to explain the bias mechanisms.

3.4 Synthetic Samples

To make a controlled, empirical measurement of biases arising directly from the physical form of the sample, an experimental procedure was carried out on synthetic samples of barren rock spiked with $\geq 99.99\%$ gold fragments. The gold content of the barren rock material was established as below the detection limit of the instrument by ten repeat CPA measurements. Synthetic materials were created with both fine and coarse barren rock, as well as fine and coarse gold fragments and are summarized in Table 1.

Table 1: Summary of synthetic materials created from barren rock and $\geq 99.99\%$ gold fragments.

Sample	Au P100 (μm)	Barren P ₈₀ (μm)	Au Grade (g/t calculated)
Coarse-Coarse	<850	2000	255.5
Fine-Coarse	<45	2000	287.2
Coarse-Fine	<850	75	2.655
Fine-Fine	<45	75	2.801

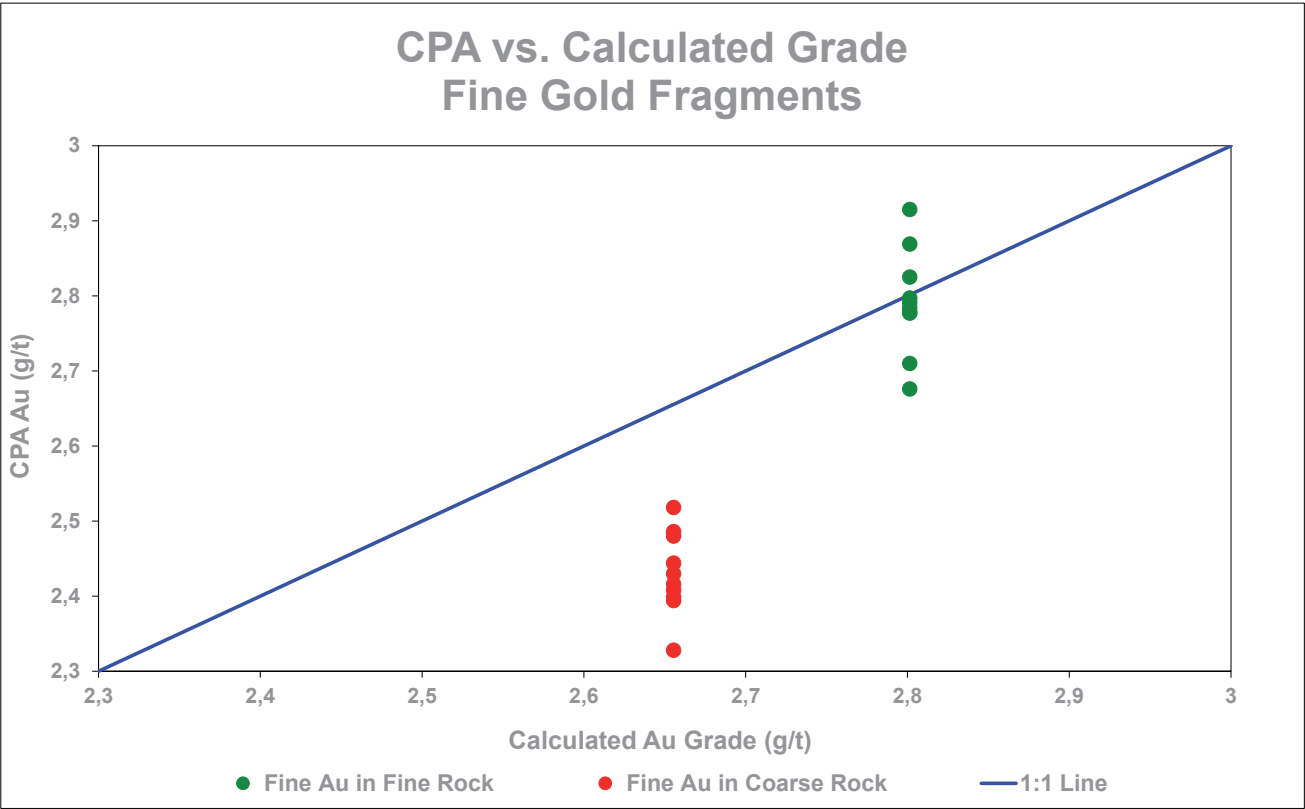


Figure 1: Measured CPA Au grades vs the grades calculated from the known mass of fine Au fragments and barren rock used to produce the material.

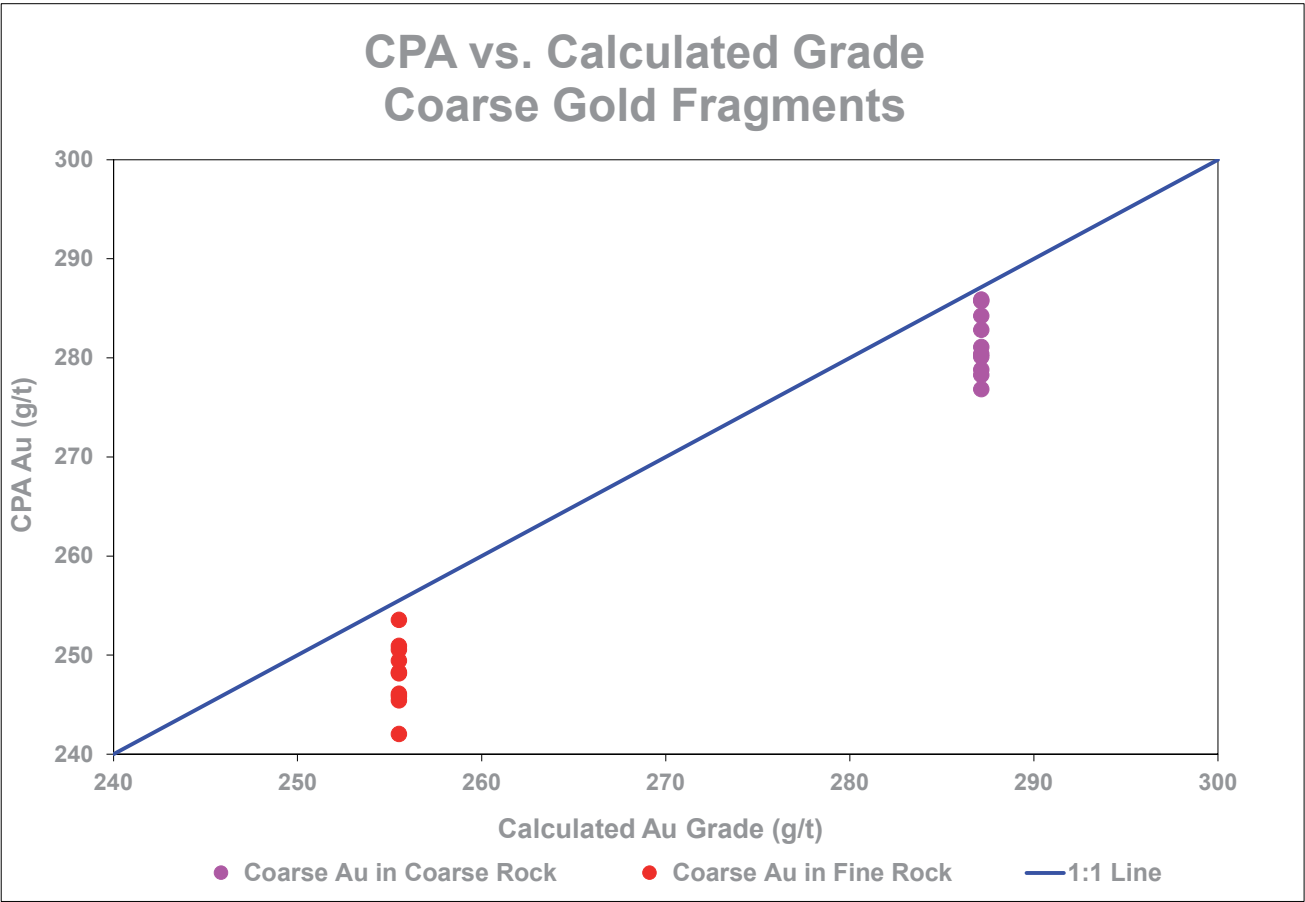


Figure 2: Measured CPA Au grades vs the grades calculated from the known mass of coarse Au fragments and barren rock used to produce the material.

Table 2: Summary of synthetic material gold grades as measured by PhotonAssay and the associated t-statistics.

Sample	Calculated Au Grade (g/t)	Avg PA Au Grade (g/t)	PA Au Grade Variance	Difference	t-statistic
Coarse-Coarse	255.5	248.024	4.41%	-2.93%	7.159
Fine-Coarse	287.2	281.406	3.51%	-2.00%	5.784
Coarse-Fine	2.655	2.430	0.12%	-8.48%	13.021
Fine-Fine	2.801	2.792	0.17%	-0.33%	0.424

The synthetic materials were placed into CPA jars and ran under the PAAU02 service (standard 2-cycle gold only service) and 10 replicate analyses were conducted on each jar (Figure 1 & Figure 2). Each jar was briefly shaken by the operator between measurements to induce reorganization of the fragments.

Student's t-test was carried out on the results to test the null hypothesis that there was no statistically significant difference between the average measured gold grade and the known true gold grade (Table 2).

The bias for CPA results of all material types was negative and met the threshold for statistical significance in all cases except for fine gold fragments in finely pulverized barren rock matrix. The larger variance associated with the coarse gold fragments was somewhat unexpected as the technique is expected to deliver tighter repeat precision with increasing grade.

This may be the result of changes in the fragments' positional distribution through the jar between measurements. The effect of positional distribution changes would be expected to be more pronounced for coarser particles, as was observed. The impact of this effect deserves further investigation.

4. Concluding Remarks

The authors invite the reader to discover the inner mechanism of the biases in the second part in this two part series of articles. They are sincerely hoping their work will help Chrysos turn this innovative technique into a new standard in the industry by addressing and resolving the issues described in this series.

Photon Assay: A New, Revolutionary Technique Everybody Wants to See Succeed – An Independent Evaluation Part 2: The Effect of Positional Heterogeneity on Gold Determinations Using PhotonAssay

By Robert Oliver¹ and Dominique François-Bongarçon

DOI: 10.62178/sst.005.005

ABSTRACT

PhotonAssay™ employs gamma activation analysis to provide rapid, non-destructive determination of gold in large (typically 400–650 g) samples. While the larger sample sizes are presumed to offer significant advantages for heterogeneous, coarse-gold bearing materials compared with traditional fire assay, the reported gold grades may be influenced by uneven spatial distribution of gold particles within the jar. This study investigates the effect of positional heterogeneity i.e. the uneven weighting of different regions within the PhotonAssay jar, on gold determinations.

Low- and medium-resolution maps of instrument response were generated by placing single, accurately weighed gold fragments at precisely controlled locations within filled jars and performing multiple replicate assays. Results reveal differences in weighting: the geometric center of the jar receives the highest response, while regions near the sides and, to a lesser extent, the top and bottom are under-weighted. These findings are consistent with non-uniform irradiation as the dominant source of the observed biases, with gamma-ray attenuation and detection geometry appearing less influential.

The positional weighting introduces a previously under-appreciated source of grouping and segregation error, even after the final assay charge has been prepared. This has important implications for assaying coarse-gold ores, where dense gold particles can segregate during handling and jar filling. The results suggest that PhotonAssay protocols may be vulnerable to biases in certain coarse-gold systems.

1. Background

PhotonAssay is a proprietary process owned by Chrysos Corporation for the determination of gold, silver and copper content in a diverse range of materials. This work focuses on PhotonAssay gold determinations using the standard gold service PAAU02, which are carried out by gamma activation analysis (GAA). A sample of the material to be analyzed is placed into a specialized, roughly cylindrical, high-density polyethylene jar. The jar is capped and weighed. The proportion of the jar's volume occupied by the sample is estimated by fill-o-meter, and the jar is handed off to a robotic system.

The jar is paired with a metal disc containing a reference element, and a linear accelerator (linac) generated 8.5 MeV photon beam is directed at the jar while it is rotated around its axis of circular symmetry.

Gold found naturally in the earth's crust is mono-isotopic, consisting exclusively of ^{197}Au . When irradiated with sufficiently energetic photons, ^{197}Au may become excited and enter a local energy minimum known as a metastable nuclear isomer (equation 1).



¹ Director of Laboratory & Technical Operations at ElementUSA

After irradiation, the jar is moved to a measurement chamber with two high-purity germanium detectors arranged above and below the sample. The metastable nuclear isomer ^{197m}Au has a half-life of 7.76 s and undergoes radioactive decay back to the ground state with the emission of a 279 KeV gamma ray [1] (equation 2).



The count of gamma emissions detected by the HPGe detectors at 279 KeV will be proportional to the amount of gold present in the sample. For the standard gold service PAAU02, this process is repeated twice for each jar, with 15 seconds of irradiation time and 15 seconds of measurement time per cycle [2]. Chrysos Corporation states that the process provides true bulk analysis of 400 – 650 g samples [3]. An assay charge of this size is more representative of the bulk material than a conventional fire assay charge (typically up to 50 g). This has distinct advantages when assaying ores containing coarse gold particles [4].

The exact process through which the 279 keV signal is used to determine the gold grade is a trade secret, however relevant factors include: time elapsed since irradiation, mass of sample, occupied jar volume, linac power, reference signals, interfering signals, and, critically for this work, spatial distribution of gold within the jar relative to the excitation beam and detectors, among others. Previous work by Dominy, et al [5] investigated the effect of reorganizing the position of gold-containing fragments within a PhotonAssay jar on the instrument's reported gold grade. Samples of coarse-gold-bearing ore were placed in PhotonAssay jars, assayed, then subsequently shaken for 30 seconds and re-assayed. This procedure was found to induce an insignificant negative bias and negligible increase in total measurement error.

The authors dubbed the uneven distribution of gold throughout a sample positional heterogeneity (similar to distribution heterogeneity as described by Gy).

The process of shaking a jar containing a coarse-gold ore may have two outcomes. Firstly, it may induce segregation of gold fragments within the jar, leading to a tendency for shaken jars to have a greater concentration of gold fragments in particular regions of the jar. On the other hand, shaking the jar may induce no meaningful gold fragment segregation, and simply randomly rearrange their locations.

While in the case investigated by Dominy, et al., only insignificant bias was noted, the presence of an increase in total measurement error, even a negligible one, indicates unequal weighting of different jar regions in grade determination. The absence of significant bias after shaking tends to indicate that the shaking procedure does not induce net segregation of gold fragments between regions of high and low weighting. No detail was given on the mode of shaking, limiting the ability to draw inferences on expected segregation tendencies.

The location of a gold fragment within a jar may impact both its irradiation by the excitation beam, and the detection of decay emissions. The rotation of the jar during irradiation should limit preferential activation of gold fragments on any side or along any diameters (Figure 1).

A beam centered on the jar with a width less than the jar could lead to preferential activation of gold fragments near the center of the rotational axis. The same could be true for a beam with non-uniform intensity across its width. As the beam centering, width and consistency are not known, this simply represents one possible example of how unequal weighting of jar regions can occur.

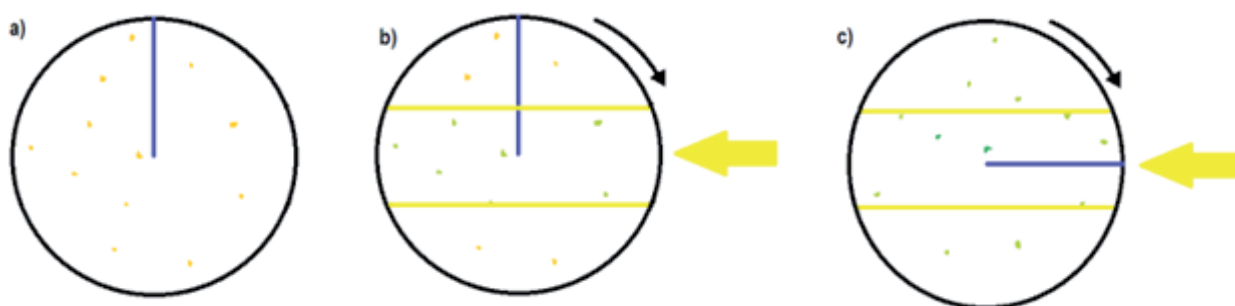


Figure 1: Top down view of PhotonAssay jar; a) depicts jar prior to irradiation with unactivated gold fragments in orange and with blue reference line indicating rotation; b) depicts jar at beginning of irradiation, excitation beam direction and edges in yellow, with activated gold fragments in light green and black arrow indicating direction of rotation; c) depicts jar once all gold fragments have been activated, fragments with longer periods within the beam path in dark green.

Similarly, the detection of gamma emissions originating in some jar regions may be more likely than those from others. The amount of gamma attenuating mass in the emission's path, as well as proportion of possible paths that intersect a detector may affect its weighting in the gold grade determination.

The aim of the present work is to determine the relative weighting of the regions of the jar.

2. Experimental

Two sets of experiments were conducted to produce low-resolution, medium-resolution maps of the detector response to gold particles throughout the jar's volume. While the medium-resolution map is more detailed and the locations more precisely defined, the technique used to construct the low-resolution map enabled particles to be placed at more extreme points in the jar, far from the geometric center.

2.1 Low-resolution Jar Map

A lot of approximately 1000 kg of nominal ¼ inch fragment size rock was obtained from Rail City Garden Center in Reno, Nevada. Riffle splits were taken for preparation and 30 g fire assay to verify gold content was less than 0.005 mg/kg. Approximately 1 kg of material was split from the lot and crushed to 100% passing a 2 mm screen. The crushed material was repeatedly riffle split to completely fill a PhotonAssay jar. Gold powder of purity $\geq 99.99\%$ and fragment size $< 850 \mu\text{m}$ was obtained from Sigma Aldrich and a fragment was separated and accurately weighed.

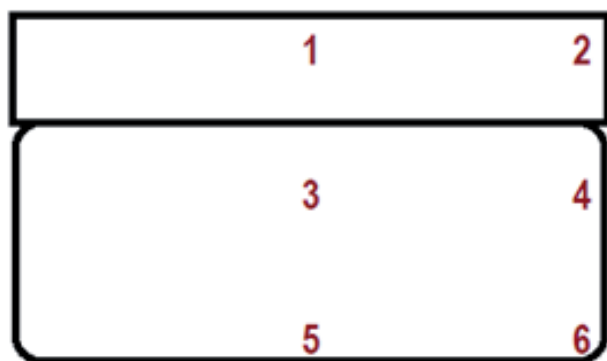


Figure 2: Cross-section of a PhotonAssay jar with the gold fragment locations indicated.

The fragment was immobilized on a piece of scotch tape and affixed to a specific location within the filled jar. With the fragment in that location, the jar was submitted to the PhotonAssay process ten times. The fragment was then moved to another location for ten assays.

This was repeated for six different locations within the jar (Figure 2).

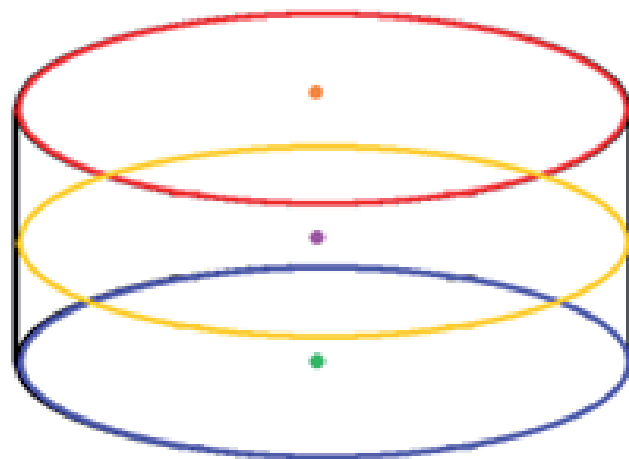


Figure 3: 3D wire-frame projection of jar with location 1 indicated by an orange point, 3 by a purple point, 5 by a green point, 2 by a red circle, 4 by a yellow circle and 6 by a blue circle.

Locations 1, 3 & 5 are points at the center top, center middle, and center bottom of the jar respectively. Due to the random rotational orientation of the jar when irradiation begins, a fragment at location 2, 4 or 6 may start at any point along a circle in a plane perpendicular to the jar's axis of circular symmetry. As a result, locations 2, 4 and 6 are not points but circles at top, middle and bottom respectively (Figure 3).

The material rejected in the splitting operation was pulverized to 85% passing a 75 μm screen. The pulverized material was repeatedly riffle split to completely fill a second PhotonAssay jar. This jar was then likewise subject to PhotonAssay ten times for each gold fragment location using a separately weighed gold fragment.

2.2 Medium-resolution Jar Map

2.2.1 Gold Fragment Positioning Rig

A PhotonAssay jar was taken and filled with epoxy resin which was allowed to solidify. The jar was mounted in a precision lathe and adjusted to a runout of <1 mm. A 12.7 mm hole was drilled into the center of the epoxy resin and end-milled to a flat bottom stopped just as contact was made with the HDPE jar.

The jar was then removed from the lathe and mounted in the compound table of a drill press. Additional 12.7 mm holes were drilled and end-milled to a flat bottom of the same depth as the center hole at 14 mm, 28 mm and 32 mm from the center.

2.2.2 Gold Fragment Positioning Rod

Separately, nylon bar stock was turned down to approximately 12 mm on the lathe, then cut to 42 mm length and mounted in the compound table for five 7 mm holes to be drilled perpendicular to the length through the rod at 8 mm from one end, then at 8 mm intervals through the length.

2.2.3 Gold Fragment Positioning Cup

A length of 8 mm nylon bar stock was turned down to 5.5 mm and a 4 mm hole drilled into its length to give a short tube.

The stock was parted after the end of the hole creating a short cup. From the same stock a small friction fitting cap for the cup was fabricated. The height of the cup with the lid attached was 5 mm.

2.2.4 Single Particle Instrument Response

A single fragment of $\geq 99.99\%$ Au was immobilized on a small square of tape and inserted into the cup, which was capped and inserted into one of the holes in the positioning rod. The rod was then inserted into one of the holes in the positioning rig and the jar was capped and submitted to the PhotonAssay instrument for the PAAU02 service. The service was repeated 10 times and then the location of the particle was changed to determine the instrument response throughout the jar. The various locations are indicated in Table 1 and shown visually in Figure 4.

Table 1: Positions in the gold fragment positioning rig where PAAU02 tests were performed on a single fragment of gold.

Location	Distance from axis of rotation (mm)	Distance from jar bottom (mm)	Repeat analyses
1	0	7	5
2	0	21	5
3	0	35	5
4	14	7	5
5	14	21	5
6	14	35	5
7	28	7	5
8	28	21	5
9	28	35	5
10	32	7	5
11	32	21	5
12	32	35	5

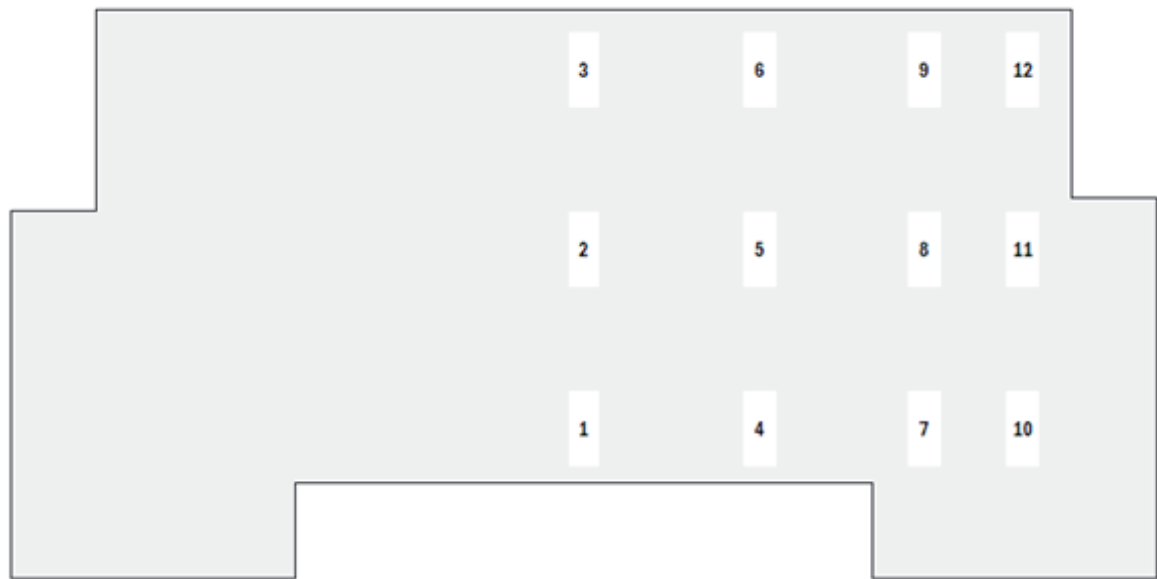


Figure 4: Schematic of the gold fragment positioning test rig in cross-section indicating the positions where a single fragment of gold was positioned and subjected to the PAAU02 service.

3. Results

3.1 Low-resolution Jar Map

The PhotonAssay-determined gold grades in the crushed rock jar (Table 2) show significant differences in the weighting of locations depending on both their distance from the axis of rotation and depth. The highest weighting is found in the geometric center of the jar (location 3). The repeat precision for locations along the axis of rotation (locations 1, 3 & 5) is consistent with precision at gold grades >1 ppm given by Chryso Corporation [2]. However, repeat precision for gold fragment locations at the maximum distance from the axis of rotation (locations 2, 4 & 6) was significantly higher.

Results for the pulverized rock jar had a similar pattern of weighting, low repeat precision among repeat assays on the axis of rotation, and high precision among repeat assays far away from the axis of rotation (Table 3).

From the different weightings for the six locations, heat maps were constructed showing hotspots where fragments are strongly weighted, and cold spots where fragments receive weaker weighting (Figure 5).

Table 2: PhotonAssay results of the jar containing 100% passing 2 mm rock with a 1.011 mg gold fragment placed at locations 1 – 6 for 10 assays each. From the PhotonAssay-determined gold grade, the detected mass of gold, error against the weighed mass of gold, and the bias were calculated.

Location	n	Mean PA Au (ppm)	%RSD	Mean PA Au (mg)	Au Mass (mg)	Error (mg)	Bias
1	10	3.196	1.7%	1.236	1.011	0.225	+22%
2	10	1.959	4.5%	0.758	1.011	-0.253	-25%
3	10	4.673	1.4%	1.798	1.011	0.787	+78%
4	10	2.349	6.5%	0.908	1.011	-0.103	-10%
5	10	3.101	2.0%	1.199	1.011	0.188	+19%
6	10	1.417	2.7%	0.547	1.011	-0.464	-46%

Table 3: PhotonAssay results of the jar containing 85% passing 75 μm rock with a 1.051 mg gold fragment placed at locations 1 – 6 for 10 assays each. From the PhotonAssay-determined gold grade, the detected mass of gold, error against the weighed mass of gold, and the bias were calculated.

Location	n	Mean PA Au (ppm)	%RSD	Mean PA Au (mg)	Au Mass (mg)	Error (mg)	Bias
1	10	3.780	1.9%	1.147	1.051	0.096	+9%
2	10	2.292	5.2%	0.696	1.051	-0.355	-34%
3	10	5.962	1.8%	1.798	1.051	0.747	+71%
4	10	2.936	4.2%	0.889	1.051	-0.162	-15%
5	10	4.193	1.4%	1.268	1.051	0.217	+21%
6	10	1.954	2.7%	0.59	1.051	-0.461	-44%

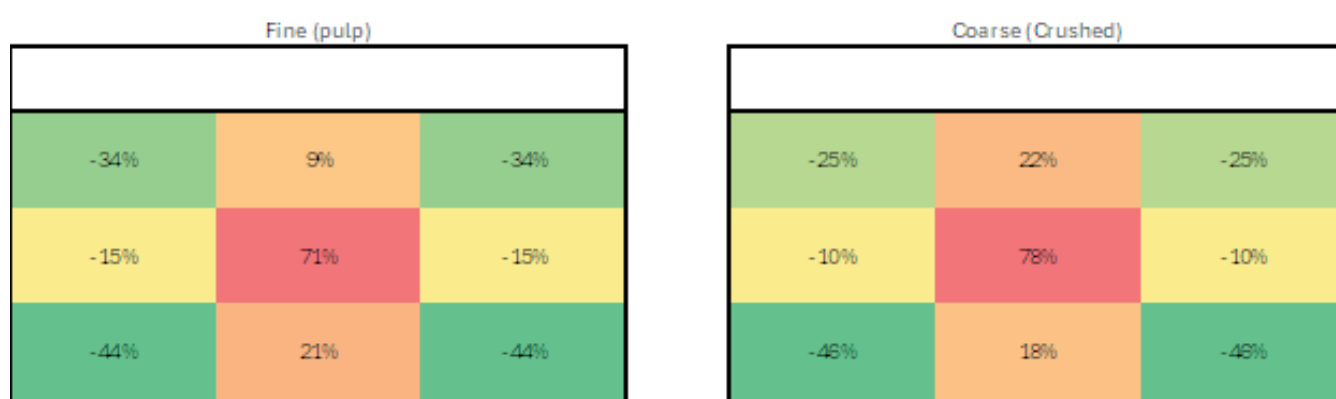


Figure 5: Cross-sectional heat map depicting the relative weight given to regions of the jar in determining their gold grades by PhotonAssay. Due to the random rotational orientation of the jar during analysis, there is no differentiation between the sides of the heat map, and the diagram is symmetrical.

While both jars were completely filled with sample material, the instrument's fill-o-meter gave readings as low as 84.8% for the crushed material, and 94.0% for the pulverized material.

In every case, the average fill-o-meter reading across the 10 repeats was >96% for crushed material and >98% for pulverized material.

3.2 Medium-resolution Jar Map

The PhotonAssay-determined gold grades in the gold fragment positioning test (Table 4) show significant differences in the weighting of locations depending on both their distance from the axis of rotation and depth. As with previous tests, the highest weighting is found in the geometric center of the jar (location 2).

From the different weightings for the six locations, a heat map was constructed showing hotspots where fragments are strongly weighted, and cold spots where fragments receive weaker weighting (Figure 6).

Table 4: PhotonAssay results of the gold fragment positioning rig with a 0.504 mg gold fragment placed at locations 1 – 12 for 5 service runs each. From the PhotonAssay-determined gold grade, the detected mass of gold, error against the weighed mass of gold, and the bias were calculated.

Location	n	Mean PA Au (ppm)	%RSD	Mean PA Au (mg)	Au Mass (mg)	Error (mg)	Bias
1	5	2.364	0.83	0.702	0.504	0.198	+39%
2	5	2.706	1.47	0.804	0.504	0.300	+59%
3	5	1.745	2.40	0.518	0.504	0.014	+3%
4	5	2.258	5.23	0.671	0.504	0.167	+33%
5	5	2.6185	2.10	0.777	0.504	0.273	+54%
6	5	1.697	3.68	0.504	0.504	0.000	0%
7	5	1.690	2.89	0.502	0.504	-0.002	0%
8	5	2.179	4.24	0.647	0.504	0.143	+28%
9	5	1.494	0.70	0.444	0.504	-0.060	-12%
10	5	1.432	1.23	0.425	0.504	-0.079	-16%
11	5	1.668	2.38	0.495	0.504	-0.009	-2%
12	5	1.083	5.07	0.322	0.504	-0.072	-36%



Figure 6: Cross-sectional heat map depicting the relative weight given to specific locations of the jar in determining their gold grades by PhotonAssay. Due to the random rotational orientation of the jar about its axis of rotation during analysis, there is no differentiation between the sides of the heat map, and the diagram is symmetrical.

4. Discussion

Differences in the relative weighting of jar regions may originate during irradiation, measurement, a combination of both, or other factors not considered in this work.

4.1 Irradiation

For an excitation beam centered on the jar and narrower than the jar width, it is expected that gold fragments closer to the geometric center are more strongly activated, leading to higher weighting for that region, as was observed. Fragments far away from the axis of rotation are activated more strongly as they pass directly through the beam path, and less strongly at other times.

A fragment far from the axis of rotation will experience intermittent periods of excitation, the frequency of which is proportional to the rate of rotation. For rates of rotation where the period between excitation is large with respect to the half-life of ^{197}mAu , differences in weighting may emerge. Fragments that end the irradiation cycle immediately before starting a period of excitation will have relatively low activity compared to those that end during or immediately after strong activation. This may be an explanation for the high repeat precision when far away from the axis of rotation observed in the low-resolution map experiments. Parameters of the process which to the knowledge of the authors are undisclosed would be required to evaluate further. It should be noted that in the medium-resolution map experiments, the higher RSDs at points further from the geometric center were not observed. The activation of fragments at locations at the extreme top and bottom of the jar in the low-resolution experiments indicate that the beam width is at least equal to the height of the jar. The difference in weightings between low-resolution experiment locations 1 & 3 and locations 3 & 5 tends to suggest that the beam intensity across its width is higher at the center than the fringes. The difference in weighting between low-resolution experiment locations 1 & 5 tends to suggest that the beam intensity is higher at the bottom of the jar than the top. This was further indicated by the results of the medium-resolution experiments.

4.2 Measurement

The excitation beam's 8.5 MeV photons will be only minimally attenuated by the jar, the reference disc or the sample material. On the other hand, the 279 KeV gamma emissions from decaying ^{197}mAu will experience significant attenuation for some paths ending at a detector. Additionally, some emission paths will not intersect a detector at all.

The degree of attenuation and the proportion of paths not intersecting a detector will be influenced by the activated fragment's position within the jar.

The most significant potential gamma attenuators are the reference disc and sample material itself. If gamma attenuation by the reference disc was the cause of differences in weighting for the jar regions, low-resolution experiment location 5 would be expected to have significantly less weighting than location 1. This is not observed, with positions 1 and 5 having similar weighting in the crushed rock jar, and position 5 having greater weighting in the pulverized rock jar. Similarly, we'd expect the medium-resolution map to show higher weighting for locations near the jar's boundaries, whereas the opposite was observed.

Gamma attenuation by the sample material would be highest for locations in the geometric center of the jar and lowest for locations at the top and bottom of the jar. In fact, the locations expected to experience greatest attenuation (low-resolution experiment location 3, and medium-resolution experiment location 2) had the highest weighting, making this unlikely to be the primary driver for the biases found.

Positions far from the axis of rotation would be expected to have a greater proportion of emission paths that do not intersect the detectors. This would result in lower weightings for low-resolution experiment locations 2, 4 & 6, which was observed. However, while locations 2 & 6 would experience this effect to similar degrees, location 4 would experience the greatest effect, giving even lower weighting. This is not observed, with location 4 having higher weighting than locations 2 & 6 for both jars.

Taken together, the results tend to indicate non-uniform irradiation during excitation as the more likely primary source of weighting differences observed between jar regions. If effects from gamma attenuation are present, they appear second-order, and obscured by the non-uniform irradiation.

4.3 Implications for Analysis

Understanding the different weighting assigned to regions within PhotonAssay jars has important implications for designing analytical protocols and interpretation of results.

A distinct advantage of true bulk analysis of 400 – 650 g samples is for the assaying of materials containing coarse gold fragments.

Coarse gold materials are challenging to sample due to high constitution heterogeneity arising from metallic gold's "nuggety" nature, and high distribution heterogeneity due to the tendency of dense gold particles to segregate [6]. Previous work by Minnitt, et al., using x-ray tomography to investigate behavior of gold fragments within simulated pulverized gold ore illustrated the tendency towards segregation in response to horizontal shaking [7].

PhotonAssay has demonstrated advantages over fire assay in accounting for higher levels of constitution heterogeneity when distribution heterogeneity is low [5]. However, unequal weighting of the jar's regions makes it vulnerable to grouping and segregation error, even after the final assay charge has been split from the lot. The PhotonAssay instrument's robotics transport jars, in part, by pushing them horizontally across surfaces. This motion may induce the type of segregation observed by Minnitt, et al. [7].

In as-of-yet-undisclosed results from a PhotonAssay user with which the authors are familiar, a large program of samples from an ore containing coarse gold were found to give a significant low bias for PA on <2mm crushed material vs fire assay. Understanding the low weighting assigned to fragments in the bottom and sides of the jar allows us to hypothesize that this bias originates from the segregation of coarse gold fragments.

5. Conclusions & Further Investigations

This work presents only low-to-medium resolution mapping of the weightings of jar regions. More comprehensive testing to include many increments of depth and between the center and edge of the jar would produce a fuller picture. A great deal more evaluation could be carried out with knowledge of parameters like the beam shape, width and consistency, as well as the rotation rate, precise geometry of the irradiation and measuring chambers, and the calculation of gold content from the HPGe signals. Further still, ability to control parameters such as rotation rate and rotational orientation would allow for better experimental design. Investigations of real-world coarse gold ore samples would further understanding of the interaction between comminution, segregation and PhotonAssay determinations. This could include size fraction analysis of ores known to display biases between PhotonAssay and fire assay, and possibly x-ray tomography of coarse gold ores within jars. Such work could ultimately be aimed at elucidating sample preparation and treatment protocols that account for and reduce the biases found in the present work.

ACKNOWLEDGEMENTS

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Rebuttal to François-Bongarçon & Oliver

By James Tickner¹

DOI: 10.62178/sst.005.006

Dear Editor,

We read with considerable interest the recent paper by François-Bongarçon and Oliver (F-B&O) concerning the PhotonAssay™ method for gold analysis (SST, this issue). As developers of the technology, we welcome rigorous technical discussion of PhotonAssay performance and sampling behaviour. Such scrutiny is important for any analytical method achieving widespread industrial application.

However, we are concerned that readers unfamiliar with PhotonAssay™ may come away with a misleading impression regarding both the maturity of the technology, the extent of comparison testing that has been performed, and the practical significance of the positional sensitivity effects discussed by F-B&O. We therefore wish to provide some additional context and clarification.

Historical and operational background

First, PhotonAssay™ is not a newly introduced or lightly studied method. The underlying physics, instrument design, calibration methodology, and sampling behaviour were originally developed over fifteen years at the CSIRO, Australia's national applied research agency. PhotonAssay™ has subsequently been commercialised and further developed by Chrysos Corporation over the past nine years.

Approximately one hundred detailed studies have now been performed comparing PhotonAssay's performance on measuring gold in crushed and pulverised material with fire-assay, cumulatively including hundreds of thousands of samples across a very wide range of ore types, preparation protocols and operating environments. More than forty PhotonAssay units are now operating globally, collectively running more than one million samples per month, with their results supporting JORC and NI 43-101 compliant resource reporting and day-to-day mine planning and operations. Consistent with best practice, Chrysos' clients routinely run inter-laboratory round-robins and comparisons to existing methods.

Comparison of PhotonAssay™ on crushed/pulverised ore with fire-assay

The assertions of F-B&O that PhotonAssay™ measurements on coarse materials routinely underreport with respect to measurements on RC or pulverised ore, and that PhotonAssay™ generally underreports with respect to fire-assay are not consistent with our extensive experience, nor that of Chrysos' mining and laboratory clients.

In the absence of any information on the design of the studies mentioned by F-B&O (including the mining operations involved, material selection, preparation and sampling, or statistical procedures followed) we can only offer some general comments on the likely cause of the alleged effects.

Across the very large number of comparison studies performed to date, PhotonAssay™ measurements on crushed and pulverised materials are generally self-consistent and show strong agreement with conventional fire assay across a broad range of deposit types. Where statistically significant differences have been identified, they can typically be explained by ordinary sampling effects, contamination during pulverisation, recovery limitations and QC fails in comparison methods, or inappropriate statistical treatment of heterogeneous assay data.

This latter point is important. Comparison of gold assay methods is statistically non-trivial. Ore grade distributions are strongly skewed and dominated by sampling variance. The uncritical use of standard metrics such as comparison of mean values, t-scores, simple regression etc can produce misleading conclusions when applied without appropriate treatment of multiplicative errors and heteroscedasticity. Considerable work has already been published on this topic, including by our group.

The Chrysos technical team has performed or contributed to many comparison and validation studies since 2017 across a broad range of deposit types, ore characteristics and preparation workflows.

¹ Chrysos Corporation Ltd, Australia.

In our experience, where apparent discrepancies between analytical methods are observed, careful collaborative review of the sampling protocol, preparation methodology, statistical treatment, underlying ore characteristics and QC performance is usually sufficient to identify the dominant contributing factors.

We therefore actively encourage independent evaluation of PhotonAssay™ performance and are always willing to work constructively with laboratories, consultants and mining companies seeking to better understand the technique or investigate unexpected results. This includes detailed review of comparison datasets, experimental design and statistical interpretation.

In the present case, while several studies and observations are referenced by F-B&O, the underlying datasets and supporting details have not been made available to us for technical review. We would welcome the opportunity to examine such results collaboratively and in detail. Our experience has consistently been that open technical engagement and transparent data review provide the most effective path to resolving apparent discrepancies and improving collective understanding of assay behaviour.

Positional sensitivity

One of the central questions raised by F-B&O – namely positional sensitivity within the sample volume, effects of material presentation, and interactions between sampling heterogeneity and instrumental response – is not new. These effects are well understood, have been explicitly modelled during instrument development, and have been extensively explored experimentally. Indeed, samples determined to have a significantly heterogeneous gold distribution are automatically flagged ‘HET’ in a standard PhotonAssay™ report.

As with any bulk radiation-based measurement system, PhotonAssay™ does not exhibit perfectly uniform sensitivity throughout the sample volume. This is a straightforward consequence of radiation transport physics. The relevant question, however, is not whether positional variations exist in principle, but whether they materially affect assay accuracy and operational performance in practice. Our experience, supported by extensive experimental data, is that they do not.

The recent F-B&O paper places considerable emphasis on experiments involving highly artificial distributions of gold within sample containers.

While such experiments can illustrate underlying physics, they do not by themselves establish that analytical bias will occur in practice under normal operating conditions.

For example, in Section 2.4 of Part 1, F-B&O describe repeat measurements performed on individual weighed gold fragments placed within jars of barren material. The reported variations of approximately 3–4% RSD are broadly consistent with the expected instrumental precision combined with limited movement of the fragments between measurements. Importantly, these experiments primarily illustrate local spatial response variations under highly controlled conditions and do not, by themselves, demonstrate the existence of significant operational assay bias.

In real ore systems, the dominant contributor to uncertainty is almost always the Fundamental Sampling Error associated with the heterogeneous distribution of gold itself. Indeed, the principal advantage of PhotonAssay™ – namely the use of sample masses approximately an order of magnitude larger than conventional fire assay – is precisely that it substantially reduces these sampling effects.

A key point is that positional sensitivity contributes only a small increment to the overall uncertainty when considered alongside ordinary ore heterogeneity and sampling variance. In operational terms, the effect is modest. Our modelling and experimental work indicate that the contribution of positional sensitivity to the overall uncertainty is comparatively small, typically increasing the effective relative sampling error by only a few percent under realistic operating conditions. Moreover, unless gold particles become grossly and systematically segregated within the sample volume, then positional sensitivity does not result in a reporting bias. This results theoretically from the design of the PhotonAssay™ irradiation and measurement systems, and is evidenced empirically by an absence of bias seen in our experimental studies.

Concluding comments

To present our arguments in greater detail, we have prepared a technical paper addressing the physical basis of PhotonAssay™ response, appropriate comparison methodology for heterogeneous ores, large-scale empirical comparison studies, and quantitative evaluation of positional sensitivity effects within the broader uncertainty framework of gold sampling and assay. We refer the interested reader to this paper, which appears in this issue of SST.

Our intention here is not to dismiss continued investigation of PhotonAssay™ performance – indeed, we strongly encourage it – but rather to ensure that discussion remains appropriately balanced and grounded in both the theoretical and empirical body of work that already exists.

PhotonAssay™ represents a fundamentally different approach to gold analysis from traditional small-charge chemical assays. Like all analytical methods, it has limitations and operating constraints that must be properly understood.

However, after extensive testing and commercial deployment, the evidence overwhelmingly indicates that the method provides robust, accurate and operationally valuable measurements across a wide range of ore types, mining and metallurgy applications.

Yours sincerely,
James Tickner

Chief Scientist
Chrysos Corporation

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PhotonAssay™: A Review of Real-World Performance on Heterogeneous Gold Ores

By James Tickner¹, Joel Chuah¹, Andrew Weatherstone¹ and Tim Sennett¹

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ABSTRACT

PhotonAssay™ is a non-destructive gold assay method based on gamma activation analysis which has been applied extensively across a wide range of gold ore types. This paper reviews real-world performance on heterogeneous ores, with emphasis on method comparison, sampling behaviour, and the practical significance of positional heterogeneity. The underlying physics of PhotonAssay™ allows direct measurements on aliquot masses typically an order of magnitude larger than conventional fire assay. Results from certified reference materials, large-scale feasibility studies, and detailed case studies across multiple deposit styles are examined. Across these studies, PhotonAssay™ shows strong agreement with fire assay and measurements on coarse and pulverized materials are consistent, with mean grade ratios generally close to unity and high correlations observed across diverse geological settings. The findings indicate that larger assay masses can reduce total sampling variance relative to conventional small-charge fire assay, particularly in coarse or nuggety ores where sub-sampling error dominates. Although spatial sensitivity variations within the sample jar are physically real, theoretical analysis and empirical evidence show that their contribution to total uncertainty is modest in practical applications. Overall, PhotonAssay™ provides a technically robust and operationally advantageous alternative for gold analysis on heterogeneous ores.

1. Introduction

The accurate determination of gold grade in mineral ores remains one of the most technically challenging analytical problems in the mining industry. Gold is commonly present at concentrations of only a few parts-per-million or below, is frequently distributed extremely heterogeneously, and often occurs in forms that create substantial sampling variance during conventional analytical workflows. Traditional analytical approaches, notably fire assay [1], have consequently evolved around extensive particle-size reduction and careful sub-sampling protocols intended to minimise these sampling effects.

Gamma activation analysis (GAA) [2–5] has been explored as an alternative method for gold assay since the early 1960s. Rather than chemically extracting gold from a small, pulverised aliquot, the technique directly measures gold atoms within a comparatively large sample using high-energy X-rays and subsequent detection of characteristic gamma-ray emissions from activated nuclei.

Chrysos' PhotonAssay™ provides the first widely available implementation of GAA and has been in commercial use since 2018. The physical principles underpinning the method have been extensively described elsewhere [6]. Samples are activated using high-energy X-rays to excite the naturally occurring gold isotope Au-197 into a short-lived isomeric state which subsequently decays via emission of a characteristic 279 keV gamma-ray. The high penetration depths of both the incident X-rays and emitted gamma-rays permit bulk analysis of samples weighing several hundred grams. A key consequence of this physics is that the measurement process is fundamentally insensitive to the chemical form of the gold and substantially insensitive to the physical presentation of the sample. Unlike chemical extraction methods, the PhotonAssay™ process does not rely on dissolution, melting, liberation or exposure of gold particles at freshly fractured surfaces.

¹ Chrysos Corporation Ltd, Australia

Instead, the main factors affecting analytical performance are the statistical uncertainty associated with counting the characteristic gamma-rays, and the accuracy of the corrections applied for gamma-ray attenuation and detection efficiency.

When considering the performance of any assay method, it is important to distinguish between genuine analytical performance (precision, accuracy and bias) and important but distinct factors relating to sampling. In short: how well does a method perform on the material with which it is presented, versus is that material representative of the original bulk?

The performance of PhotonAssay™ can be approached both empirically and theoretically.

Published [7–10] and extensive unpublished empirical studies have now been conducted on PhotonAssay™ performance using certified reference materials, drill core, reverse circulation samples, coarse rejects, process pulps and highly nuggety ores from a wide range of deposit types and geological domains.

Collectively, these studies comprise several hundred thousand comparison analyses and have been used to explore whether:

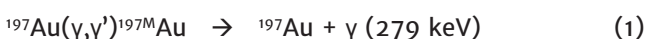
- any systematic normalisation (bias) differences are observed between crushed and pulverised samples, or between PhotonAssay™ and fire-assay measurements
- sampling behaviour follows well-established Theory of Sampling principles, namely decreasing with increasing sample mass and with reduced particle size
- the larger sample masses used in PhotonAssay™ reduce total sampling variance relative to conventional small-charge fire assay, even when performed without pulverisation
- observed positional or particle-size effects are important in practical operational contexts when appropriate preparation protocols are employed.

The present paper provides a technical evaluation of these issues, with particular emphasis on the comparison methodology, interpretation of sampling effects, and the practical significance of positional heterogeneity. Empirical findings are presented with supporting theoretical reasoning and modelling.

2. Physics of PhotonAssay™ Measurement

PhotonAssay™ is based on gamma activation analysis using high-energy X-rays generated by an electron linear accelerator. The accelerator is an electronic source that only produces X-rays when energised. For gold analysis it is operated to produce an X-ray beam with energies up to 8.5 MeV; for comparison, a method such as portable X-ray fluorescence (pXRF) uses a source operating at much lower energies of around 50 keV (0.05 MeV).

The reaction used for gold analysis is:



Gold comprises 100% of the only naturally occurring isotope Au-197. A gold nucleus absorbs a high-energy X-ray, converting it to a short-lived excited or meta-state. This state has a half-life of 7.73 seconds and decays to usually (70.9% probability) produce a gamma-ray with a distinctive energy of 279 keV [11].

A PhotonAssay™ measurement (Figure 1) consists of a 15 s period of sample irradiation during which the gold activity builds up, followed by a 15 s period of measurement during which the emitted 279 keV gamma-rays are detected and counted. Samples are automatically transferred between irradiation and measurement locations using a robotic shuttle. Each sample is typically measured for two irradiation/measurement cycles to improve sensitivity.

An important design goal is to optimise analytical performance by balancing three competing aims:

- maximise the sample volume (and hence sample mass) to reduce the Fundamental Sampling Error [12]
- maximise sensitivity for low gold grades by placing the X-ray source and gamma-ray detectors close to the sample
- minimise sensitivity to the location of gold within the sample volume to ensure a 'flat' system response.

The optimal design uses cylindrical sample jars approximately 100 mm in diameter and 50 mm high; these have a volume of 320 mL and typically hold 400–600 g of crushed ore or 300–500 g of pulverised ore. Samples are irradiated and measured with their axis oriented vertically (lid uppermost).

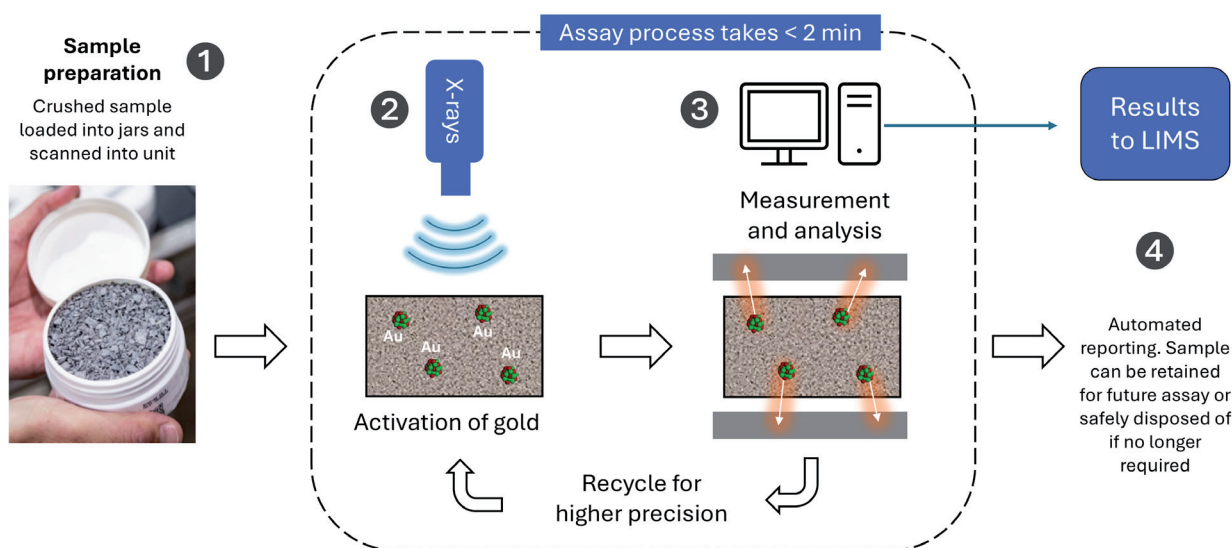


Figure 1: The PhotonAssay™ workflow: (1) samples are loaded into jars and registered (2) samples are irradiated using high-energy X-rays for 15 s to activate gold (3) samples are then transferred to a measurement station and gamma-rays counted using twin detectors; process repeated and results averaged (4) grades automatically calculated and reported.

Irradiation is performed through the side wall of the jar with the sample continuously rotating. Samples are measured between two cylindrical detectors (90 mm diameter) positioned immediately above their top and bottom surfaces.

This configuration allows analysis of a sample mass typically 10 times that of conventional fire-assay and affords a detection limit of 0.01 ppm. Variations in sensitivity of gold detection throughout the sample volume are discussed below.

A reference disc containing a bromide salt is placed in a pocket at the base of the sample jar and irradiated and measured alongside each sample. Bromine has a similar activation reaction to gold but produces a distinct and lower energy gamma-ray (207 keV). The bromine signal provides an automatic correction for any variations in the output of the X-ray source or detector efficiency. The penetration of X-rays and gamma-rays through solid material is described in terms of the mean-free path (MFP), which is the average distance travelled before interaction or absorption. The MFP depends on material density, but at the energies involved in PhotonAssay™ is only a very weak function of composition for typical rock matrices. For a common crushed-ore density of 1.6 gcm⁻³, the MFP exceeds 200 mm for the incident high-energy X-rays and is 50–60 mm for the 279 keV gold gamma-rays.

As these values are much larger than the top particle size in even coarse-crushed samples, the analysis is effectively insensitive to particle size. Of course, particle size affects the Fundamental Sampling Error, a point discussed in more detail later.

As the MFP values for the incident X-rays and emitted gamma-rays are comparable to the jar dimensions, determining the gold grade from the gold signal (measured 279 keV gamma-ray intensity) requires a correction for X-ray and gamma-ray attenuation inside the sample and a geometry correction for where the sample material is located with respect to the top and bottom detectors. These corrections are determined using the measured mass and sample fill levels that are recorded when the jar is scanned into a PhotonAssay™ system. A factory-set look-up table returns the appropriate correction factor from supplied mass and fill values.

Substantial experimental work has validated – in line with the theoretical arguments presented – that PhotonAssay™ is substantially insensitive to sample matrix and physical form across a wide range of ore types and process materials. A summary of this work is presented below, and more details are available in a range of Chrysos technical notes [10,13–14]. This behaviour contrasts fundamentally with conventional chemical assays, where liberation, dissolution kinetics, flux behaviour, reagent chemistry, and aliquot representativity all influence the final reported grade.

3. Method Comparison Framework

Comparison of different assay methods for gold ores is statistically non-trivial. Ore grade distributions are typically strongly skewed, heteroscedastic, and frequently dominated by sampling variance rather than instrumental precision. Naïve application of methods such as linear regression, ANOVA, correlation coefficients, or conventional Bland–Altman plots can produce misleading conclusions when applied to mineral assay data.

Meaningful comparison requires explicit consideration of sampling variance, grade distribution shape, multiplicative rather than additive error structures, aliquot independence, and the contribution of both preparation and analytical errors.

The framework adopted here follows the methodology developed in previous work [15] comparing PhotonAssay™ and fire assay results on large ore suites. We consider the following principles to be particularly important:

(a) All assay methods return an approximation to “truth”

In real ore materials, all methods measure aliquots drawn from larger heterogeneous masses. Consequently, disagreement between two assays does not necessarily imply analytical bias, and observed scatter frequently reflects sampling effects rather than instrumental failure.

For chemical methods, recoveries of the analyte from the ore matrix may be less than 100%, and all methods are subject to both random and systematic normalisation errors.

(b) Sampling effects dominate in coarse gold ores

For coarse gold ores, differences between two assays performed on different aliquots may substantially exceed instrumental uncertainties. Where coarse gold or nugget effects are present, larger assay masses generally improve representativity.

(c) Statistical equivalence is more important than pointwise agreement

For operational applications such as resource definition, grade control and reconciliation, the critical question is whether two methods produce statistically interchangeable grade populations. Measurement and sampling uncertainties make pointwise comparison less useful than population level metrics.

Following [15], our primary tool for assessing overall bias between different assays performed on the same sample suite is the logarithmic Tukey ratio plot. In such a plot (Figure 2, right) the pairwise ratio of grade measurements obtained using two different methods (y-axis, logarithmic scale) is plotted against the geometric mean grade (square-root of the product of the two grade measurements, x-axis, logarithmic scale).

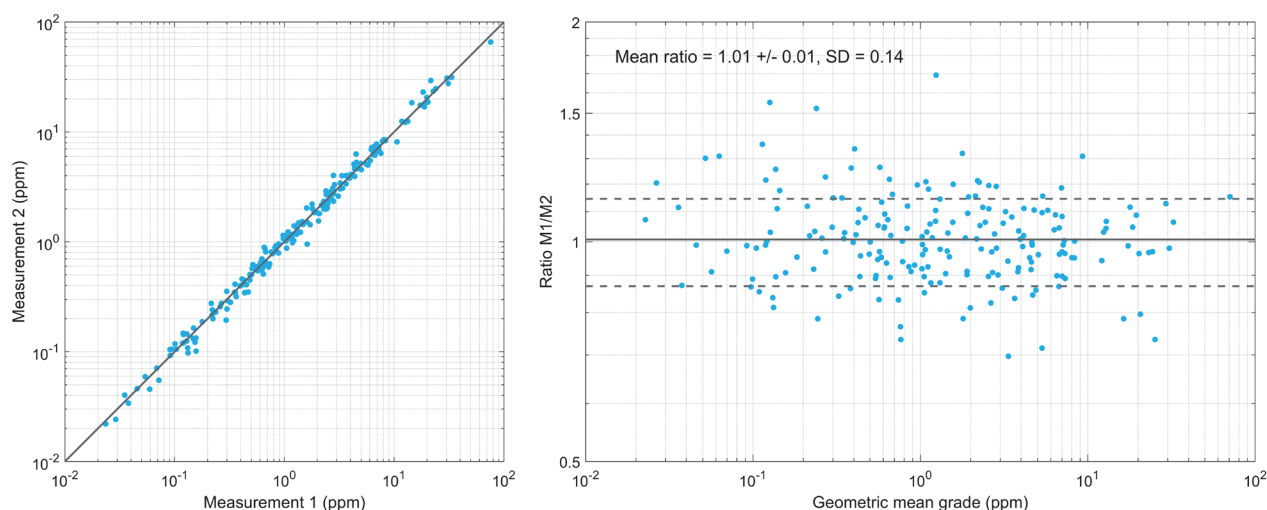


Figure 2: Traditional scatter plot on logarithmic axes (left) and Tukey ratio plot (right) for a synthetic data set comprising 200 samples with log-normal grade distribution. For each sample, grades are modelled assuming two independent, unbiased measurement methods each with a precision (relative SD) of 10%.

By focussing on the differences in the ratio of measured values from unity, the Tukey plot provides a much more sensitive illustration of small biases than a traditional scatter plot (Figure 2, left). Data cleaning – removal of obvious sample swaps, transcription errors, values below detection limit on one or both methods – is also facilitated. Finally, subtle trends in bias versus grade, often indicative of contamination during preparation, are also made readily apparent.

Any overall bias and its experimental uncertainty can be readily determined following the procedures detailed in [15]. The example illustrated in Figure 2 is based on a synthetic data set comprising 200 samples with a log-normal grade distribution. For each sample, grades are assumed to be measured by two independent, unbiased methods with a precision (relative SD) of 10%. The resulting mean ratio (1.01 ± 0.01) is statistically consistent with unity and the RSD on the pairwise ratio of measured grades (0.14) is consistent with the 10% contributions from each measurement, added in quadrature.

While the Tukey ratio plot is the preferred visual diagnostic for the reasons set out above, a range of statistical tests can also be used to characterise method agreement. A one-sample, two-tailed t-test on the log-transformed pairwise ratio is used to test the null hypothesis that the mean log ratio is zero, or equivalently that the two methods are unbiased relative to one another. The log transformation is appropriate given the multiplicative error structure and log-normal grade distributions typical of gold deposits and yields a test statistic whose assumptions – approximate normality and homoscedasticity – are better satisfied than for tests performed on the raw grade differences.

In parallel to the t-test, Cohen's d effect size is used as a standardised measure of effect size. The t-test addresses whether any difference observed between methods is distinguishable from zero with the given data. Conversely, Cohen's d effect size quantifies the magnitude of the difference and addresses the question of whether it is material. Conventional thresholds ($|d| < 0.2$ small, $0.2-0.5$ medium, > 0.5 large) provide guidance on the effect size and do not collapse with increasing sample size.

This is an important distinction, as statistical significance under hypothesis testing is not the same as practical significance. With a sufficiently large sample size, a t-test (or any hypothesis test) will reliably reject the null hypothesis of zero bias for arbitrarily small mean log ratios – differences that are immaterial for resource definition, grade control or reconciliation.

Conversely, a small study may fail to reject the null hypothesis for a bias that would matter operationally. Collectively reporting the Tukey mean ratio, t-test and Cohen's d effect size allows the user to separate out “detectable” difference from a “meaningful” difference.

4. Prior Experimental Studies

4.1 Certified Reference Materials

Initial validation of PhotonAssay™ was performed using suites of certified reference materials (CRMs) spanning multiple ore matrices, wide grade ranges, and provided by numerous manufacturers. The most comprehensive of these studies is reported in Chryso Technical Note TN-001 [13], which documents CRM test work conducted over the period 2019–2022 across multiple deployed PhotonAssay™ units in Western Australia.

Figure 3 presents results from the combined manufacturer study (suite S4 in TN-001), which included 94 CRMs sourced from CDN, OREAS, Rocklabs and Geo-stats and measured using PhotonAssay™. The CRM suite included a broad range of ore types, including sulphides, gold/copper ores, concentrates and oxides, and each CRM was measured using at least a 6×2 cycle analysis. The certified grades of these CRMs spanned several orders of magnitude (0.1–87 ppm). The reported R^2 between PhotonAssay™ and the certified values is 0.99994, as shown in Figure 3 (top). Figure 3 (bottom) shows the log-weighted comparison of PhotonAssay™ against the CRM values with a mean ratio of 1.01 ± 0.01 , indicating that PhotonAssay™ and fire assay can be used interchangeably on a diverse range of pulverised material types and matrices.

Of the 94 CRMs, five reported mean PhotonAssay™ grades that differed from certified values by more than 2 standard deviations, and only two (CDN-GS-13A at 13.2 ppm and G312-5 at 1.6 ppm) exceeded 3 standard deviations, a result consistent with normal statistical expectation for a dataset of this size and indicative of no systematic bias.

Overall, these results demonstrate excellent consistency between fire assay and PhotonAssay™ and indicate that the two techniques can be used interchangeably across a wide range of sample types.

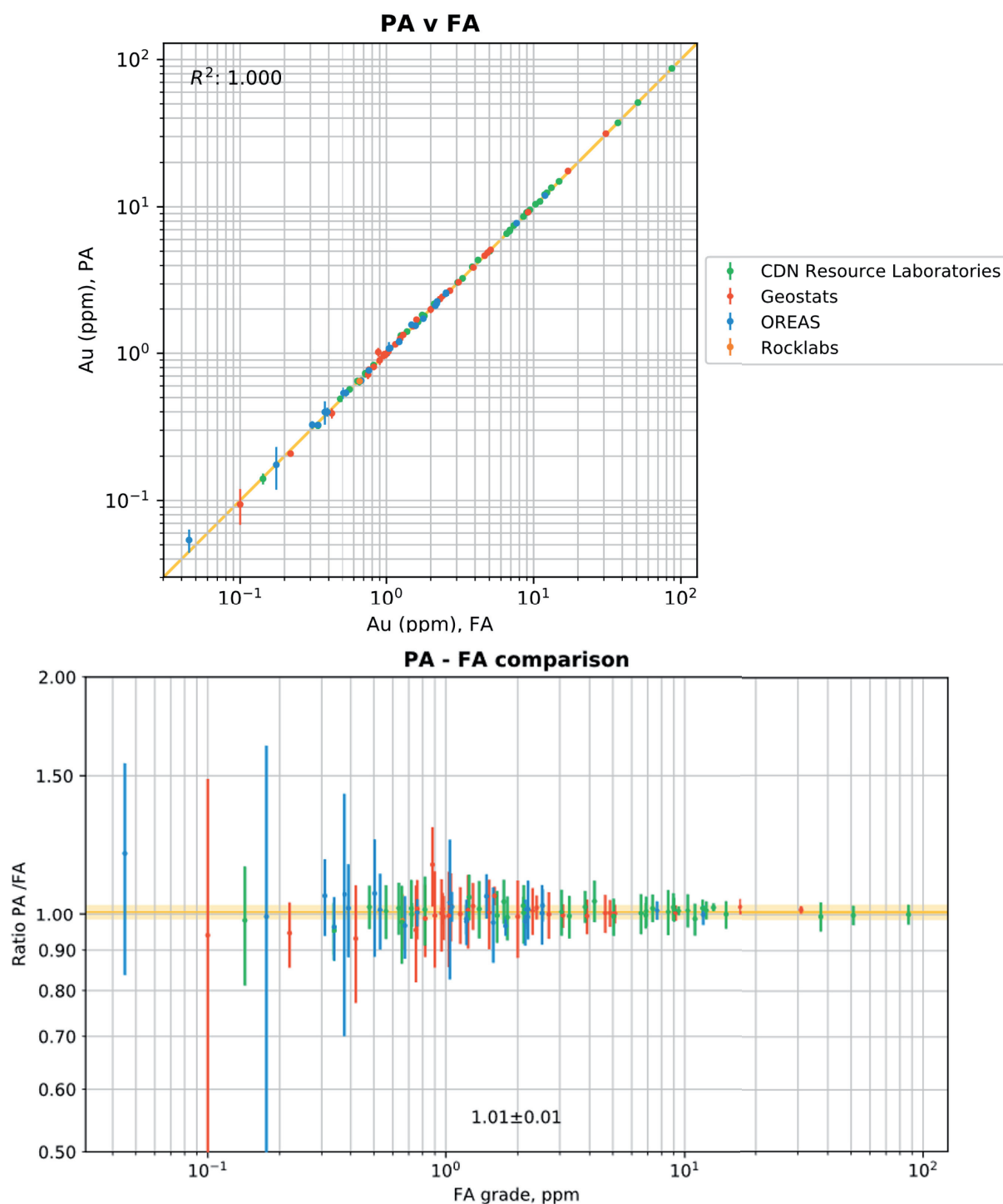


Figure 3: Top: Comparison of PhotonAssay™ gold grades (y-axis) and certified reference grade (x-axis) for 94 CRMs measured using the PhotonAssay™ system operating in Perth, Western Australia. Bottom: Tukey mean-ratio plot comparing the grades from PhotonAssay™ and fire-assay for the suite of CRMs. The ratio of the paired grades is plotted as a function of the mean sample grade, determined from the average of the two methods. The yellow band indicates the mean ratio and grade ratio variation (± 1 SD) averaged over all samples.

4.2 Large-Scale Ore Studies

Extensive feasibility studies have now been conducted comparing PhotonAssay™ and fire assay across a wide range of ore types and operational environments. Collectively, these studies comprise:

- More than 10,000 comparisons generated through over 100 Chrysos-led feasibility studies
- More than 200,000 comparison samples analysed across multiple independently-performed customer feasibility study programs
- Comparisons against multiple conventional analytical methods, including fire assay, screen fire assay, and pulverise-and-leach (PAL), as well as comparisons between crushed and pulverised PhotonAssay™ measurements.

These large-scale validation programs demonstrate broad industry evaluation and adoption of PhotonAssay™ performance across diverse operational and geological settings. Studies have evaluated a broad range of sample types from various operational settings, including diamond drill core, reverse circulation chips, blast hole samples and processing samples. Strong agreement between PhotonAssay™ and fire assay was consistently observed across diverse deposit styles.

Most users routinely analyse crushed ore and therefore commission studies comparing PhotonAssay™ performance on crushed product against fire assay. Here, we summarise results from a subset of 15 studies in which PhotonAssay™ analysis was performed on samples both after crushing and again after pulverisation, and fire assay was subsequently performed on the pulverised end product. For simplicity, we exclude studies that used alternative traditional assay techniques such as PAL, or those for which sufficiently detailed geological classification information was unavailable.

Table 1 presents a comparison of the different analytical methods with study results grouped across four major deposit types. With the constraints described above, this represents only a subset of the broader Chrysos feasibility study database.

Across the four deposit types, excellent agreement between crushed PhotonAssay™, pulverised PhotonAssay™, and fire assay gold results is seen. Mean ratio values are statistically consistent with 1.00, with narrow standard error bounds (± 0.02 1-SD), indicating no statistically significant bias between methods.

Table 1: Summary of feasibility study results across four geological domains. ‘Crushed’ and ‘Pulverised’ refer to PhotonAssay™ measurements performed on samples after different levels of particle size reduction. ‘Mean ratio’ refers to the average pairwise ratio of grades determined using different analysis methods following the process described in section 3; 1-SD uncertainties on the mean ratio are also reported.²

Deposit Type	N Studies	N Pairs	Comparison	Mean Ratio	Correl (R ²)
Orogenic	9	839	Crushed v Pulverised	1.00 $\pm$ 0.02	0.997
		841	Crushed v Fire Assay	1.00 $\pm$ 0.02	0.996
		833	Pulverised v Fire Assay	1.00 $\pm$ 0.02	0.998
Intrusion	3	772	Crushed v Pulverised	1.00 $\pm$ 0.02	0.995
		752	Crushed v Fire Assay	1.00 $\pm$ 0.02	0.995
		751	Pulverised v Fire Assay	0.98 $\pm$ 0.02	0.996
Epithermal	2	117	Crushed v Pulverised	1.00 $\pm$ 0.02	1.000
		114	Crushed v Fire Assay	0.97 $\pm$ 0.02	0.998
		113	Pulverised v Fire Assay	0.98 $\pm$ 0.02	0.998
Porphyry	1	100	Crushed v Pulverised	1.01 $\pm$ 0.02	0.997
		98	Crushed v Fire Assay	0.99 $\pm$ 0.02	0.994
		97	Pulverised v Fire Assay	0.97 $\pm$ 0.02	0.996

² Comparisons include only samples with reported grades above 0.01 ppm Au. Minor differences in the number of comparison pairs occur where one or more analytical methods fall below this reporting threshold for a given sample and are therefore excluded.

Table 2: Root-mean square relative standard deviations observed between measurements of aliquots taken from the same original sample; results combine both instrument precision and sampling errors.

Relative Standard Deviation by Sample Preparation and Deposit Type > 0.01ppm			
Deposit Type	PhotonAssay™ Crushed	PhotonAssay™ Pulverised	Fire Assay
Orogenic	18%	16%	36%
Intrusion	19%	13%	35%
Epithermal	10%	9%	7%
Porphyry	23%	18%	22%

Correlation between the different measurements is also highly consistent across all comparison pairs and geological domains, ranging from 0.994 and 1.00, indicating comparable dispersion irrespective of particle size.

Table 2 summarises the between aliquot grade variability for PhotonAssay™ measurements performed on crushed or pulverised material, or via fire-assay. Whilst reducing the particle top size is generally helpful, in many contexts PhotonAssay™ on crushed ore produces results with comparable precision at lower cost.

Overall, comparisons with fire assay demonstrate that PhotonAssay™ is robust across a range of geological settings, with no material difference evident among the three comparison combinations.

5. Detailed Case Studies

To expand the discussion, we report on two comparison studies in more detail.

5.1 Case Study A: Disseminated Gold Deposit

The first case study was conducted at an operating gold mine hosted in disseminated mineralisation within a West Africa greenstone belt. The deposit is characterised by fine-grained gold occurring predominately as microscopic inclusions within sulphide mineralisation, with grade distribution that is broadly homogeneous at the sample scale. Motivations for the client investigating PhotonAssay™ as an alternative to fire assay included the larger sample mass, reduction in sample preparation and faster turnaround time.

5.1.1 Study Design

The study comprised 250 samples from a disseminated gold deposit, each with a nominal mass of 1 kg. Each sample was crushed (~3 mm) and split into two jars, with PhotonAssay™ undertaken on each jar.

Samples were then recombined, pulverised (P80 ~75 µm), and split into three jars, with PhotonAssay™ performed on each jar. One jar was randomly selected for fire assay to extinction, with the remaining two jars set aside. This study design allowed direct comparison of PhotonAssay™ performed on crushed and pulverised materials with fire assay.

5.1.2 Results

Table 1 summarises the results from each comparison pair. PhotonAssay™ on crushed (~3 mm) material versus pulverised (~75 µm) material has a mean grade ratio of 0.99 ± 0.02 , indicating negligible systematic difference between the two particle sizes and confirming that PhotonAssay™ is insensitive to particle size preparation. Comparison of PhotonAssay™ on crushed material against fire assay has a mean grade ratio of 1.01 ± 0.02 , and PhotonAssay™ pulverised against fire assay has a mean grade ratio of 1.02 ± 0.02 . All three methods produce consistent results, with no meaningful normalization difference between any combination of method or particle size.

Figure 4 presents the Tukey ratio plots for all three comparisons. Pointwise grade ratios are centred around unity, with no obvious trend versus mean grade across approximately three orders of magnitude. Except at the very lowest grades (< 0.1 ppm) in the PhotonAssay™ crushed versus pulverised chart, where instrument errors start to become appreciable, the charts indicate strong homoscedasticity across the whole grade range; that is, the variance between measurements is independent of grade. This homoscedasticity reinforces that the agreement between methods is robust. Lower variance, indicated by the width of the yellow bands (which show a ± 1 SD range), is observed between the two PhotonAssay™ measurements than between either of the PhotonAssay™ results and fire assay, indicating better overall total precision—combined sampling and measurement error—for the PhotonAssay™ measurements performed on larger-mass samples.

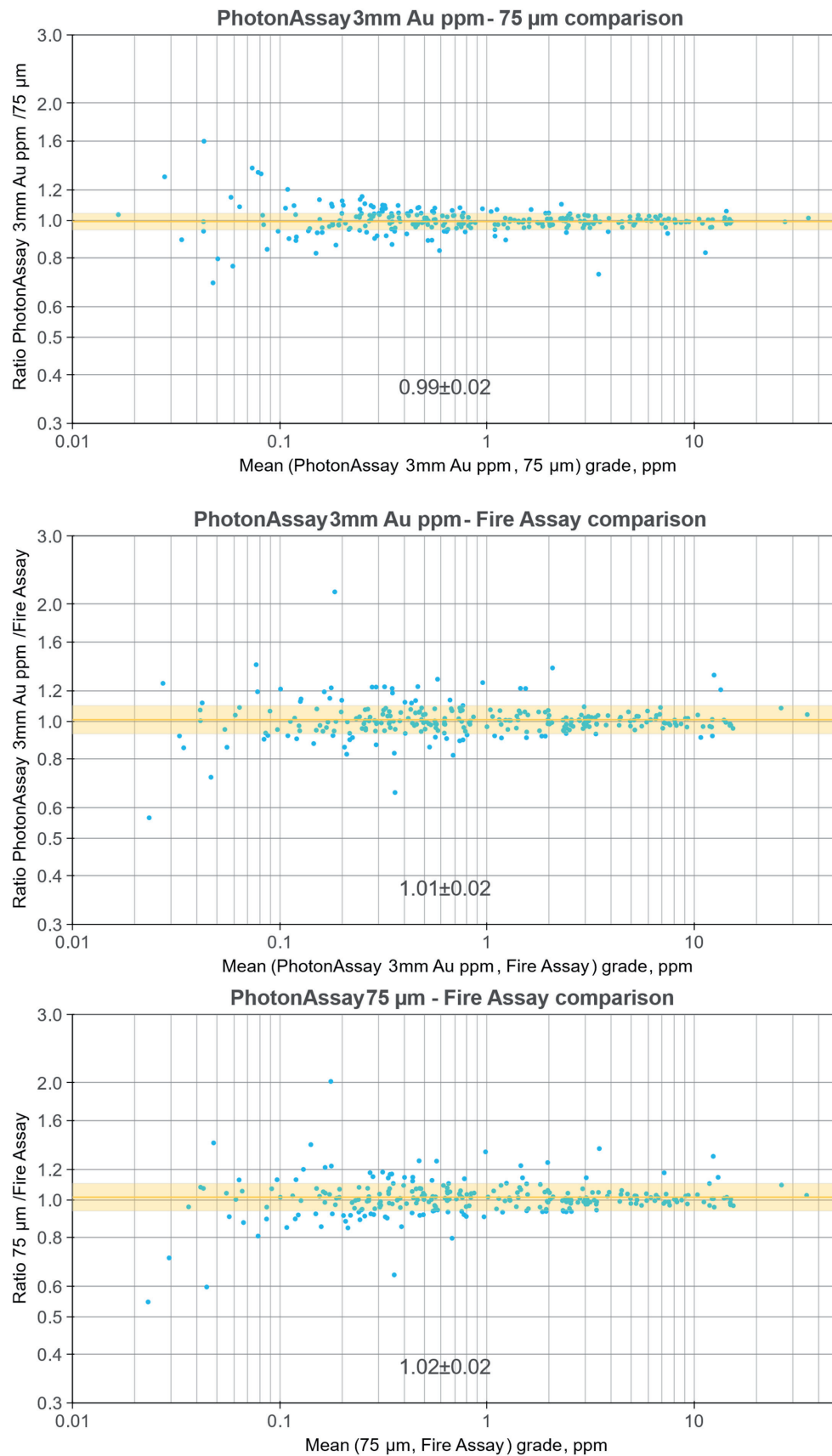


Figure 4: Tukey ratio plots for all PhotonAssay™ and Fire Assay comparisons for case study A. Blue points represent pairwise grade ratios for individual samples measured using different methods. The gold line shows the log-mean ratio and the yellow band the ± 1 SD width of the grade ratio distribution.

Table 3: Summary of results for case study A³

Comparison	N	Mean Ratio	Correlation (R ²)
PhotonAssay™ Crushed (–3 mm) vs PhotonAssay™ Pulverised (–75 µm)	264	0.99 ± 0.02	0.998
PhotonAssay™ Crushed (–3 mm) vs Fire Assay	265	1.01 ± 0.02	0.994
PhotonAssay™ Pulverised (–75 µm) vs Fire Assay	264	1.02 ± 0.02	0.996

5.1.3 Operational Implications

Findings from this study demonstrate that PhotonAssay™ delivers equivalent results on both crushed and pulverized materials, representing a significant opportunity to reduce sample preparation costs, streamline laboratory workflows, and reduce total assay turnaround time (TAT).

In any gold mine operation, pulverisation represents a substantial component of sample preparation expenditure, requiring dedicated equipment, consumables, maintenance, and labour. It also carries an increased risk of cross-contamination between samples due to the malleable nature of gold. In a conventional fire assay program, pulverisation is a prerequisite to obtaining a representative sub-aliquot from the larger sample mass. Where PhotonAssay™ is deployed, this step can be eliminated entirely without compromising data quality, as demonstrated by the particle size insensitivity observed across the full grade range in this study. The additional benefit of measuring a larger sample mass at the crushed stage further improves representativity compared to a conventional 50 g fire assay aliquot.

Collectively, these operational advantages demonstrate that PhotonAssay™ represents a technically equivalent and operationally superior alternative to conventional fire assay workflows in disseminated gold settings, delivering reduced preparation costs, improved sample representativity, and faster TAT without compromising data quality.

5.2 Case Study B: Coarse Gold Deposit

The second study was conducted at an operating gold mine characterised by coarse, nuggety gold mineralisation. The deposit is structurally controlled, with gold occurring predominantly along shear zones and associated quartz veining, resulting in an inherently hetero-

geneous gold distribution at the sample scale. This style of mineralisation presents well-documented challenges for representative sampling [17], as the uneven distribution of coarse gold particles introduces significant variability between sub-samples a characteristic that differentiates this setting from the disseminated case study to provide a contrasting framework within which to evaluate PhotonAssay™ performance.

5.2.1 Study Design

This case study included 150 samples (50 from exploration and 100 run-of-mine), with a nominal mass of 2 kg per sample. Each sample was initially split into two primary halves, with one half retained by the mine ("Original") for conventional fire assay analysis and the other ("Duplicate") submitted for PhotonAssay™ investigation. This primary split provided the first comparison point between the two methods.

The PhotonAssay™ Duplicate half was crushed (–3 mm) and split to extinction into typically four jars with PhotonAssay™ undertaken on each jar. Samples were then recombined, pulverised (P80 –75 µm), and jarred to extinction into typically six jars. Additional jars were required to accommodate the volume expansion of the pulverised material. PhotonAssay™ was undertaken on each pulp jar, providing a direct comparison between PhotonAssay™ on crushed and pulverised material. For exploration samples only, the site laboratory performed dual (2 × 50 g) fire assay analysis on the Original split and subsequently provided results to Chrysos for an initial comparison.

5.2.2 Initial Observation – Apparent Bias

Comparison of PhotonAssay™ results on the Duplicate split against the conventional fire assay on the Original split for exploration samples indicated a bias between the two methods.

³ Comparisons include only samples with reported grades above 0.01 ppm Au. Minor differences between comparison pairs occur where one or more analytical methods fall below this reporting threshold for a given sample and are therefore excluded.

The original fire assay results were biasing 6% higher for crushed material and 8% higher for pulverised material relative to PhotonAssay™ results, as shown in Figure 5. The scatter in the pairwise grade ratios is also significantly larger than what would be expected from analytical errors alone.

5.2.3 Fire Assay to Extinction

To investigate whether the bias could be attributed to the PhotonAssay™ measurements, follow-up fire assay to extinction was undertaken on every jar, including both the exploration and mining samples. This ensured that all gold present in the Duplicate sample half was captured, eliminating variability associated with sub-sampling error.

Table 4 presents results from several selected high-grade jars of the same sample where fire assay to extinction was performed for each jar, illustrating the degree of variability present between 50 g aliquots that is diagnostic of a persistent nugget effect that pulverisation has not resolved.

Figure 6 presents the mean ratio of PhotonAssay™ and fire assay to extinction results for the whole sample suite. The bias between the PhotonAssay™ and fire assay results is eliminated, and the variance is significantly reduced. Equivalent performance is observed for PhotonAssay™ performed on both crushed and pulverised material.

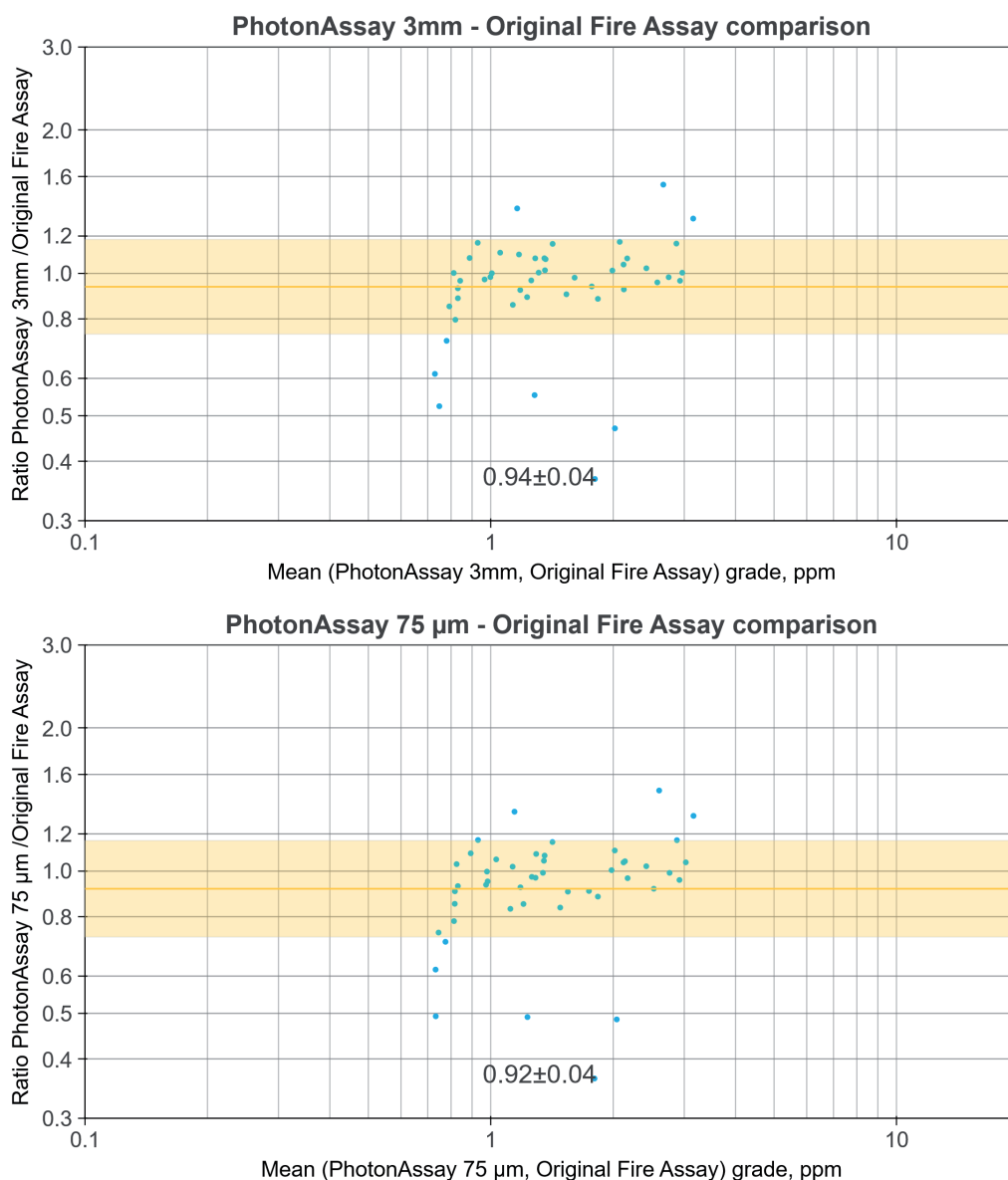


Figure 5: Tukey ratio plots of PhotonAssay™ measurements performed on the Duplicate sample split compared to fire assay measurements on the original split for the 50 exploration samples. See captions to Figure 4 for plot details.

Table 3: Gold grades (ppm) for individual fire assay aliquots performed on 6 PhotonAssay™ jars of pulverised material taken from the same original sample. Whilst individual fire-assay results are highly variable, their average is in excellent agreement with the PhotonAssay™ result measured on the entire jar.

Fire-assay results (gold, ppm)										PhotonAssay
Jar	Aliquot 1	Aliquot 2	Aliquot 3	Aliquot 4	Aliquot 5	Aliquot 6	Aliquot 7	Aliquot 8	Mean	Gold, ppm (Whole jar)
A	44.82	36.72	35.14	31.19	35.14	26.36	32.34		34.53	34.80
B	36.49	44.89	33.94	29.72	39.33	35.55	30.84	25.56	34.54	35.36
C	32.95	45.73	40.76	37.57	40.32	37.34	46.51		40.17	38.98
D	49.73	44.47	40.73	32.04	46.70	42.25	38.75		42.10	43.58
E	34.79	40.05	28.67	32.48	29.89	30.38	34.57		32.98	32.64
F	37.74	43.00	45.86	38.12	41.97	43.23	38.59	42.12	41.33	39.76

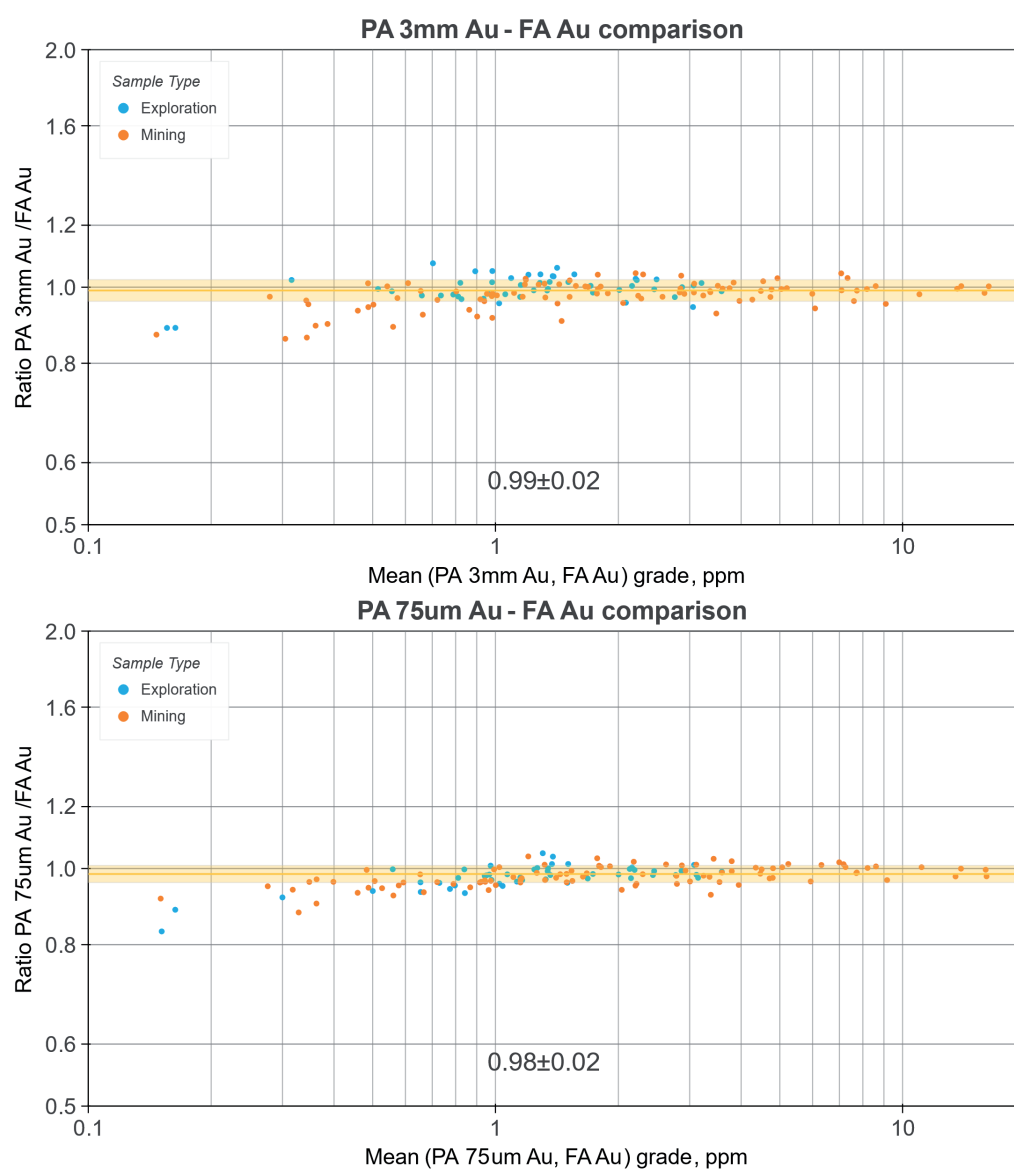


Figure 6: Tukey ratio plots comparing PhotonAssay™ and fire assay to extinction results on 50 exploration samples (red points) and mining samples (blue points).

This indicates that the originally observed bias for the exploration samples was associated with splitting the samples into Original and Duplicate halves, or with the subsequent pulverising, sub-sampling, and fire assay analysis undertaken on the Original splits.

This case study underlines the importance of follow-up analysis when unexpected results are obtained. In this case, an initial observation of “PhotonAssay™ biases low against fire-assay” was instead resolved as a problem with the original sample splitting or laboratory fire-assay analysis. Further, the fire-assay to extinction work showed the considerable variability between fire-assay aliquots that remained even after pulverization. The ability of PhotonAssay™ to measure an entire 500 g sample is particularly advantageous for such coarse gold deposits, strongly indicating the use of the method.

5.2.4 Operational Implications

The findings from this case study carry different but equally important operational implications compared to the disseminated deposit study. In a coarse gold system, the nugget effect cannot be resolved through pulverisation alone, as demonstrated by the persistent within-jar variability observed even after reducing material to a 75 µm top size. Conventional fire assay on a 50 g sub-aliquot is therefore an inherently unreliable estimator of true sample grade, regardless of preparation effort applied.

In a coarse gold setting, poor sub-sampling is unforgiving: errors introduced during splitting propagate directly into the assay result and cannot be corrected downstream. It is well recognised [17] that achieving consistent best practice in fire assay sample preparation is operationally difficult, requiring a high level of technical skill, rigorous procedural discipline, and reliable quality oversight at every stage of the preparation process. These demands are difficult to sustain consistently, particularly at mine sites in remote locations where attracting and retaining skilled laboratory personnel presents an ongoing operational challenge.

PhotonAssay™ offers a meaningful advantage in both respects. Technically, the measurement of the full jar mass reduces the influence of individual coarse gold particles on the result, significantly mitigating the sub-sampling limitation that undermines conventional fire assay in a coarse gold setting.

Operationally, the technique requires a comparatively lower level of operator skill to achieve consistent results, reducing dependence on reliable labour and making it more resilient to the workforce variability common in remote mining environments.

6. Positional Heterogeneity and Spatial Effects

A central criticism raised in the recent paper by François-Bongarçon and Oliver [16] concerns the positional variations in sensitivity within PhotonAssay™ sample containers, and potential effects on measurement bias. Specifically, they argue that non-uniform spatial distributions of gold, particle segregation, or sample presentation effects may significantly bias PhotonAssay™ measurements.

In this section of our paper, we describe the physics basis of the dependence of sensitivity on position and explore its potential impacts on both bias and measurement precision.

6.1 Physical Basis of Spatial Effects

The physics model underlying the operation of PhotonAssay™ was originally published in [6]. A simplified version is presented here.

The basic question to be addressed is straightforward: if a gold atom is located at a particular location inside a PhotonAssay™ jar, what is the probability that it will be activated and its gamma-ray emission subsequently detected?

The detection probability P is the product of three factors:

$$p = S \cdot D \cdot T \quad (2)$$

The source factor S relates to the intensity (or flux) of the incident X-rays; the higher the intensity, the more likely a gold atom is to be activated. The X-ray beam from the accelerator is not ‘laser-like’ but is emitted over a cone with an apex angle of about 20° (the off-axis flux drops to one half of the peak on-axis flux at a half-angle of about 10°). The flux decreases with distance from the source, so with the X-ray beam incident horizontally, it is greater on the side closest to the source.

The detector factor D captures the probability that the gamma-ray emitted by an activated gold atom will be successfully detected. Detection relies on three things occurring: the gamma-ray being emitted towards a detector (its initial direction is completely random); the gamma-ray escaping from the sample without interacting; and the gamma-ray depositing all its energy in the sensitivity volume of the detector. Practically, the closer a gold atom is positioned with respect to a detector, the higher the chance of its emission gamma-ray being recorded, as the detector subtends a larger solid angle at the decay position, and there is less intervening material to absorb the gamma-ray before it exits the sample.

Last and most straightforward is the time factor T . This captures the time-dependent aspects of the detection process, namely the increasing probability of a gold atom being activated the longer it is exposed to the X-ray beam, offset by the chance that it can randomly decay before reaching the detector system. Similarly, the longer the sample spends in the detector, the greater the chance that the atom decays can be detected. The time factor T does not depend on the position of gold atom within the sample, so does not need to be considered further in this discussion.

6.2 Mitigation of Spatial Effects through System Design

The variation in the source and detector factors with position can be mitigated through careful design of the activation and measurement systems.

Key mitigation factors include:

- Rotation of the sample during activation at a speed significantly faster than the gold activation half-life. The 60-rpm rotation speed (one revolution per second) substantially eliminates the 'hot-spot' on the side of the jar closest to the accelerator.
- Positioning two detectors above and below the sample and combining their results significantly equalises the detection response.
- Using large-diameter detectors that approximately match the diameter of the sample jars. The 100 mm diameter of the PhotonAssay™ sample jars was chosen with reference to a 90 mm detector diameter, the largest readily available commercially.
- Carefully selecting the disposition of the sample jar with respect to both the accelerator and detectors to compensate for remaining variations in S and D with position.

In arriving at a final design, positional effects must be balanced against sensitivity and sample size. For example, using a much smaller sample jar would reduce positional effects, but significantly decrease sensitivity and increase the Fundamental Sampling Error.

The total measurement variance σ_T can be written as:

$$\sigma_T^2 = \sigma_{\text{sampling}}^2 + \sigma_{\text{positional}}^2 + \sigma_{\text{measurement}}^2 \quad (3)$$

where the three terms on the right capture contributions from the Fundamental Sampling Error, positional sensitivity and measurement precision respectively. The variances due to sampling and measurement decrease proportional to sample mass, whereas the positional variance increases with jar size (and hence sample mass). The PhotonAssay™ jar size of 320 mL was chosen to optimise the total measurement variance.

Optimising the design of a PhotonAssay™ system to minimise the total measurement variance is a complex problem, as it depends in detail on the physics of X-ray emission, gamma-ray production, scattering and attenuation inside the sample, and detector operation. Computer Monte Carlo modelling methods [18] were extensively used to allow large numbers of design variations to be simulated and their performances compared. Careful experimental validation was then required to confirm the modelled designs.

6.3 Magnitude of Spatial Effects

François-Bongarçon and Oliver [16] present results of an experiment to measure the positional sensitivity variations of a PhotonAssay™ unit. They tabulate the average grade reported from 5 measurements of a gold particle positioned at different locations inside a sample jar. These results are in agreement with simulated results which were reported in Chrysos technical note TN-121 and are shown in Figure 7.

The coloured circles in Figure 7 indicate the grade that would be reported if all the gold in a sample were present at that location, divided by the grade that would be reported if the same amount of gold was uniformly distributed throughout the sample volume. The numbers on the left show the relative sensitivity of horizontal 'layers' of material inside the jar. Figure 7 illustrates a section passing through the centre of the jar.

The greatest variations in sensitivity are radial, with strongest gold detection occurring close to the jar axis and weakest detection near the jar outer walls.

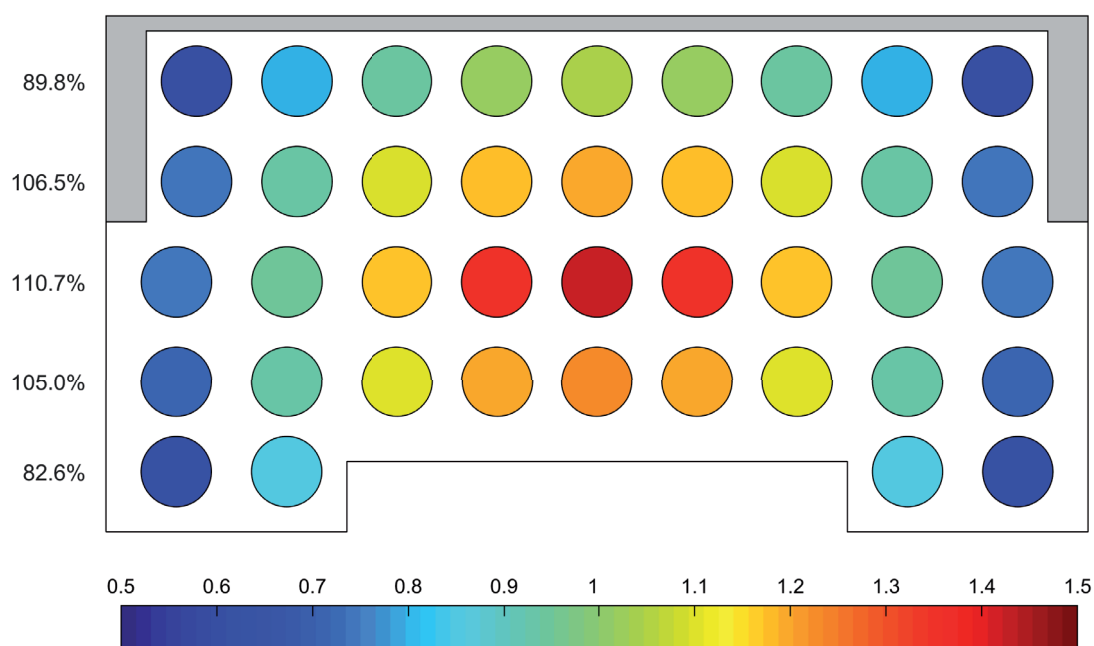


Figure 7: Sensitivity for a gold particle located at different locations throughout a section of a PhotonAssay™ sample jar. The values on the left are the weighted average sensitivities versus vertical position. See text for details.

The standard deviation in sensitivity for a randomly located gold particle is 32% – this indicates the relative standard deviation (RSD) of gold results that would be expected for repeat measurements of a jar containing a single gold particle where the particle is relocated at complete random between runs. The vertical sensitivity is significantly less, approximately ± 12 –17%.

6.4 Practical Significance

The practical significance of spatial effects on PhotonAssay™ performance can be explored with reference to both precision and bias.

Consider precision first. The total analytical variance (Figure 8) is the sum of the variances arising from the Fundamental Sampling Error, positional effects and measurement precision. This represents the variance that would be observed between measurements performed on different sample aliquots drawn from an original bulk lot. The sum of the positional and measurement variances represents the variance that would result from performing repeat measurements on the same sample, with sufficient mixing between runs to completely randomise the location of any gold nuggets. Last, the measurement variance alone corresponds to multiple repeat measurements of the same sample performed without any mixing or internal movement.

The Fundamental Sampling Error (σ_{SAMPLING}) is given simply by $1/\sqrt{N_{\text{EFF}}}$ where N is the number of gold particles or nuggets in the sample, $N_{\text{EFF}} = N/(1 + CV_{\text{NUG}}^2)$ is an effective number of nuggets which is smaller than N due to the breadth of the nugget mass distribution, and CV_{NUG} is the coefficient of variation (relative SD) of the nugget mass distribution. For the case of a sample where the expected number of contained gold nuggets is one, the FSE is 100%.

The positional sensitivity effect is approximately 32% (1-SD) for a single gold nugget measured for a single cycle, or 23% for a standard 2-cycle measurement⁴. For a sample whose gold content is divided between multiple nuggets, the positional effect is reduced, assuming that the positions of the different nuggets within the jar are uncorrelated. The positional error is then $k/\sqrt{N_{\text{EFF}}}$ where $k = 0.23$ – 0.32 depending on the degree of mixing that occurs between cycles.

Finally, the measurement error arises mainly from statistical fluctuations in the number of observed gold decay gamma-rays; this is well understood and reported sample-by-sample.

⁴ Assuming that the nugget location randomly changes between measurement cycles; this represents experimentally observed behaviour in samples that are not packed too tightly to prevent movement.

$$\sigma_T^2 = \sigma_{\text{sampling}}^2 + \sigma_{\text{positional}}^2 + \sigma_{\text{measurement}}^2$$

The diagram shows the equation $\sigma_T^2 = \sigma_{\text{sampling}}^2 + \sigma_{\text{positional}}^2 + \sigma_{\text{measurement}}^2$. Each term is enclosed in a colored box: $\sigma_{\text{sampling}}^2$ is in a purple box, $\sigma_{\text{positional}}^2$ is in a green box, and $\sigma_{\text{measurement}}^2$ is in a blue box. Arrows point from these boxes to descriptive text below: a purple arrow from $\sigma_{\text{sampling}}^2$ points to 'Different samples', a green arrow from $\sigma_{\text{positional}}^2$ points to 'Repeats with mixing', and a blue arrow from $\sigma_{\text{measurement}}^2$ points to 'Static repeats'.

Figure 8: Contributions to total analytical variance and physical interpretation.

The 1-SD precision varies from about 12% at 0.1 ppm, 6.5% at 0.3 ppm gold content, 4% at 1 ppm to 2.5 % at 3 ppm and to < 2% at gold grades above 10 ppm.

We can now investigate the impact of combining these different sources of uncertainty for some cases of interest.

Repeat measurements with mixing. For coarse gold samples with a grade of 1 ppm or over containing relatively few nuggets in a 500 g aliquot (say $N_{\text{EFF}} < 100$), repeat measurements will vary by more than the reported instrument precision. In very coarse materials (say $N_{\text{EFF}} < 10$), the RSD between repeats may be 10–30%, an order of magnitude greater than the underlying instrument precision. Samples that exhibit significantly different results in the top or bottom detectors, or between measurement cycles are automatically flagged ‘HET’ by the PhotonAssay™ reporting system.

Measurements on separate aliquots. The sum of the FSE and positional sensitivity contribution is given by

$$\sqrt{\sigma_{\text{sampling}}^2 + \sigma_{\text{positional}}^2} = \sqrt{(1 + k^2)/N_{\text{EFF}}}$$

In other words, the effect of positional sensitivity is to increase the FSE by a factor of $\sqrt{(1 + k^2)} = 1.025 - 1.05$. Equivalently, positional sensitivity reduces the effective sample mass by a factor of 2.5–5%, meaning that a 500 g sample is reduced to a 475–490 g mass from a perspective of total measurement uncertainty. This is a small effect.

Consequently, we arrive at the conclusion that whilst positional effects can produce large increases in measurement uncertainty for repeat tests performed on the same sample, their impact on overall measurement uncertainty (including the Fundamental Sampling Error) is marginal.

The samples where large positional effects are seen – those containing a small number of gold particles – are precisely those where sampling errors are largest.

Next, let us consider the impact of positional effects on bias. We use the term ‘bias’ to refer to a systematic under or over-reporting of grade, either for repeat measurements of an individual sample (with complete mixing between assays), or for a large suite of separate samples. Variations in reported grade for individual measurements are captured in the variance discussions above.

By construction, if locations of gold nuggets within the sample volume are truly uniform (meaning that all positions are equally likely to occur), then no bias is present. This is because the calibration of a PhotonAssay™ instrument is derived experimentally from measurements performed on uniform materials (generally certified reference materials or similar). If gold nuggets in a non-uniform material report randomly to any location, then on average their grade will correspond to the same grade that would be reported if the small mass of gold were uniformly distributed throughout the jar volume.

For a bias to arise, it is therefore necessary for gold particles to systematically report to certain locations more often than others. With reference to Figure 7, if gold particles preferentially report to the outer surface of the jar, for example, such samples would underread compared to samples containing the same amount of gold where particles report to the central axis of the jar.

We consider the most likely form of bias to be caused by vertical segregation, where owing to density, hardness or particle size effects, gold-bearing ore particles are preferentially sorted towards either the top or bottom of the sample.

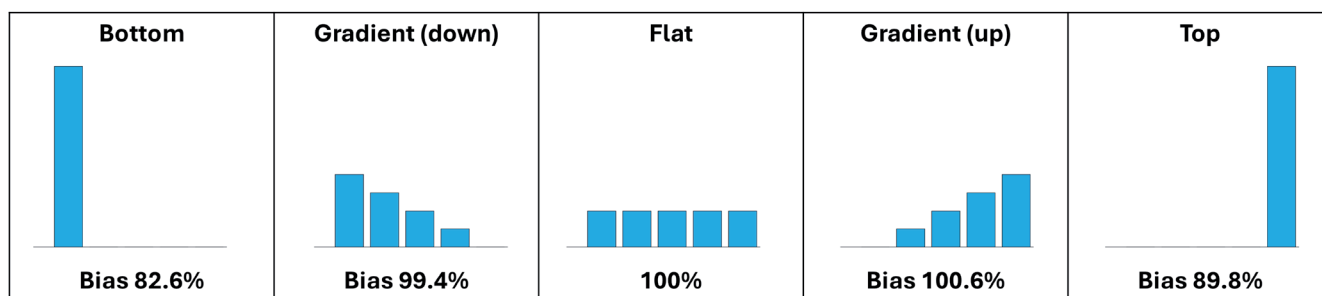


Figure 9: System responses for gold relative to uniform case ('Flat') for different distributions of gold particles within a full jar of ore. The bar charts indicate the relative proportions of gold present in 5×10 mm thick layers arranged from the bottom to the top of the jar.

We have modelled the system response for five simulated scenarios:

- 'Bottom' – all gold is present in the bottom 10 mm layer of material in the jar
- 'Gradient (down)' – the density of gold particles decreases linearly from a maximum at the bottom of the jar to zero at the top of the jar
- 'Flat' – gold particles are uniformly distributed throughout the jar
- 'Gradient (up)' – the reverse of 'Gradient (down)'
- 'Top' – all gold is present in the top 10 mm layer of material in the jar.

Results on the overall system response for these five scenarios are summarised in Figure 9. The response for the flat distribution is normalised to 100%.

For the two 'Gradient' cases, the variation in gold sensitivity is below 1%. This is because the variation in gold sensitivity versus height inside the jar is approximately symmetric about the jar centre. 'Missing' gold near the top of the jar is offset by additional gold near the bottom of the jar and vice versa, resulting in little change in overall sensitivity. Only in the extreme cases where all gold is present in the low sensitivity regions at the very top or bottom of the jar is there a significant drop-off in response, amounting to 10–17%.

In cases of significant segregation, the gold signals received by the detectors positioned above and below the sample during measurement will be discordant.

For example, in the 'Bottom' case the signal in the detector below the sample is approximately 5 times as large as the signal in the detector above the sample, with the converse result for the 'Top' case. Samples flagging such disagreement between the two detectors are automatically flagged 'HET' in the batch report. Manual review of the results from the two detectors can provide further indication of systematic gold segregation if required.

How common are these different scenarios in practice? The evidence presented in sections 4–5 suggest that the extreme 'top' and 'bottom' scenarios do not generally occur, as they would result in significant, systematic low biases in measured gold grades. Extreme top/bottom detector calculated gold grades are also not observed.

Repeat measurements on sample suites are commonly performed on PhotonAssay™ units located on different sites, typically as part of inter-lab round robins during early-stage feasibility studies, or as part of routine quality assurance by larger PhotonAssay™ users. Systematic shifts in grade, which would indicate potential material segregation during transport, are not observed.

Significant vertical segregation would also be indicative of severe issues with sample preparation and splitting. If the preparation of a PhotonAssay™ aliquot results in the majority of the gold reporting to either the top or bottom of the jar, this would suggest that gold is not evenly distributed during the splitting process; the splitting itself may then be introducing a bias.

7. Discussion and Conclusions

PhotonAssay™ is designed to provide robust analysis of gold in a wide range of materials. The well-understood physics of isomer activation, decay and measurement allow accurate models to be constructed to predict analysis performance, including instrument precision, detection limit, particle size and material composition effects, and sensitivity to sample heterogeneity.

Accumulated evidence from extensive testing on certified reference materials, inter-laboratory round-robins, large-scale validation and feasibility studies and operational experience running to tens of millions of samples has validated these models and demonstrated that PhotonAssay™ provides robust measurements of gold grade across a broad range of ore types.

The principal observations emerging from these studies are:

- PhotonAssay™ measurements on crushed and pulverised materials are self-consistent.
- PhotonAssay™ exhibits strong agreement with established analytical techniques across diverse deposit types
- Larger assay masses frequently reduce total sampling variance relative to small-charge fire assay, even on crushed material
- Observed discrepancies between methods are often dominated by ordinary sampling effects rather than instrumental bias
- Spatial heterogeneity effects exist but are modest in practical operational contexts
- Appropriate choice of comparison methodology is essential when evaluating assay method equivalence, particularly for highly heterogeneous ores.

Where statistically significant biases are seen, whether between PhotonAssay™ measurements performed on different material preparations (crushed versus pulverised, for example) or between PhotonAssay™ and traditional methods, a rigorous evaluation should be performed.

Our experience from more than 100 comparison studies indicates that differences can usually be attributed to one or more of the following factors:

- Inappropriate statistical treatment of the data, such as poor choice of bias estimator, handling of below detection limit (BDL) samples, sample swaps etc
- Contamination, particularly during the pulverisation step, leading to transfer of gold from high grade to low grade samples
- Poor splitting practices
- Unaccounted-for losses or normalisation uncertainty in the comparison method, for example incomplete gold recovery during fire assay or leach analysis
- Inaccurate measurement of fill levels of PhotonAssay™ jars, particularly for pulverised materials, where recommended fill procedures have not been followed.

Spatial response variations and positional heterogeneity effects are physically real phenomena and can be understood appropriately within the framework of radiation transport and sampling theory. However, a theoretical analysis and extensive experimental evidence indicates that these effects are generally small compared with the broader sources of variability inherent in gold ore sampling and assay workflows.

PhotonAssay™ represents a fundamentally different approach to gold analysis, based on direct non-destructive bulk measurement rather than chemical extraction from small aliquots. Notwithstanding its widespread use and industry acceptance, as with any assay method it is important to continue to compare its performance with existing techniques and understand any systematic differences.

The Chrysos team has extensive experience in conducting and evaluating comparison trials and are happy to provide advice or assistance.

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The ALOHA Sampler – An Alternative to Traditional Surface Water Sampling

By Charles Ramsey¹

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ABSTRACT

The Aloha sampler is an innovative new simple sampling tool to effectively collect and combine increments from dynamic liquid one-phase (and some two-phase) systems. It is extremely inexpensive and very cost-effective in use and delivers superior fit-for-purpose representative samples.

1. Introduction

Representative sampling of surface water is far from trivial. Distributional heterogeneity demands collecting multiple increments, integrating across and/or in depth the water target in question. In addition to traditional methods such as the isokinetic sampler, a new device, the Aloha Sampler, can more easily be employed in situations where suspended sediment is not a concern. Dip sampling (grab sampling) at the edge of surface water is the least representative method and should be avoided.

2. Background

The Theory of Sampling (TOS) provides a comprehensive approach to representative sampling. Sampling tools are an important component of designing reliable sampling protocols; optimal sample mass and the appropriate number of increments for a composite sample will not provide a representative sampling if the tools are incorrectly designed or utilised. It has been estimated that 75% of all sampling tools are incorrectly designed with the result that: “enormous research is mandatory in order to develop correct sampling systems for monitoring the environment [1].” Correct sampling tools must enable an equi-probabilistic selection of all particles (molecules) at the randomly chosen increment location. Another important role of correct sampling tools is the ability to “reach” into the material being sampled, thus making all the material “available.”

Full availability is a critical success factor to make inferences from the analytical result back to the material in question (in TOS called the lot, and called the “decision unit” in EnviroStat’s approach). This criterion has been formulated as the Fundamental Sampling Principle (FSP), see, for example, DS 3077 (2013)[2].

These two aspects, sampling tool correctness and FSP, are not the only design considerations. Some other important considerations for sampling tools are:

- durability
- easy to clean or decontaminate (if the tool is not disposable)
- easy to use (eliminate operator-induced errors)
- easy to maintain
- inert (does not interact with or contaminate the sampled media)
- maintain analyte integrity (eliminate adsorption, oxidation, leaching)
- efficient to collect and combine increments (to form composite samples)

The potential list of design criteria is too large to address here in full—it is always a function of the material sampled, environmental conditions and the analyte of interest.

¹ EnviroStat, Inc., USA.

3. Sampling of surface waters

There is a lack of sampling tools that meet the requirements of TOS for sampling of surface waters. Most surface water samplers are discrete point samplers (hand-held or weighted container samplers) and are typically some type of bottle that is opened and filled at one discrete point. These include dippers, lathes, using the sample container as the sampling device, and Van Dorn/ Kemmerer type (Figure 1). All of these types of samplers do not adequately address the inherent distributional heterogeneity of the decision unit.

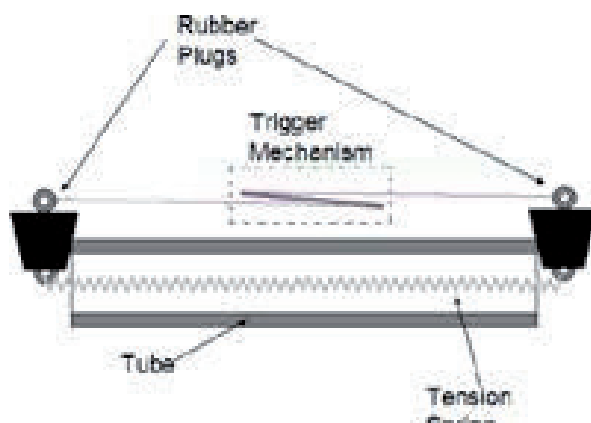


Figure 1: Generic design of Van Dorn/Kemmerer type sampler.

Sampling of surface water is always problematic due to its dynamic nature, especially since the composition changes with respect to both time and space. Examples of dynamic systems are industrial conduits, canals, lakes, rivers and oceans. The difficulty of sampling these systems is well recognised, alas very little has been done to develop tools and techniques to better represent such dynamic systems. The New Jersey Field Sampling Manual states: "Liquids, by their aqueous nature, are a relatively easy substance to collect. Obtaining representative samples, however, is more difficult. Density, solubility, temperature, currents and a wealth of other mechanisms cause changes in the composition of a liquid with respect to both time and space. Accurate sampling must be responsive to these dynamics and reflect their actions [3]".

In one surface water study[4], it was concluded that for individual samples drawn at 10-minute intervals (grab samples), the average variability (change in concentration between consecutive samples) was 60%—and as high as 700% for an individual result. This large variation on such a short time scale makes characterisation of surface waters virtually impossible if based on grab sampling.

In the same report it was also stated that the misclassification rate of water quality was: 33%, 64% and 71% for each of three study years, respectively (% estimates are relative sampling variability (RSV) measures, as described in DS 3077).

The Aloha Sampler (Liquid Sampler Patent 7571657) was developed to address these concerns by an operational mode that will allow more representative liquid sampling. The basic parts of the Aloha Sampler are an aperture cover (lid), and a receptacle for the liquid. The aperture cover has two holes, located along a diameter, that allow the liquid to flow into the receptacle when the sampler is submerged into liquid (Figures 2 and 3). The placement and size of holes allow for an approximate one minute fill rate if the holes are vertically aligned. If the Aloha Sampler is rotated slightly the fill rate increases to approximately two minutes. This gives the sampler flexibility to control the rate of liquid uptake.

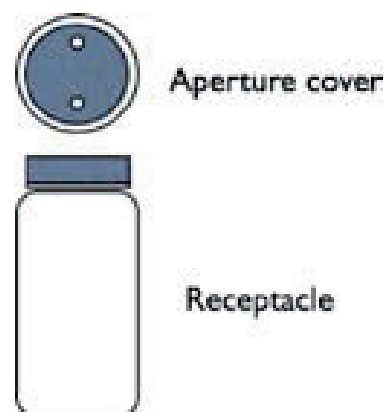


Figure 2: Aloha Sampler side and top view (Liquid Sampler Patent 7571657).

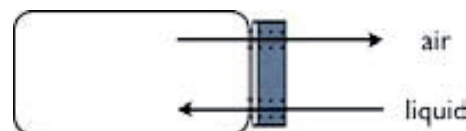


Figure 3: Basic operation of Aloha Sampler (Liquid Sampler Patent 7571657).



Figure 6: The Aloha Sampler in operation. Note air bubble leaving the upper hole in the aperture cover.

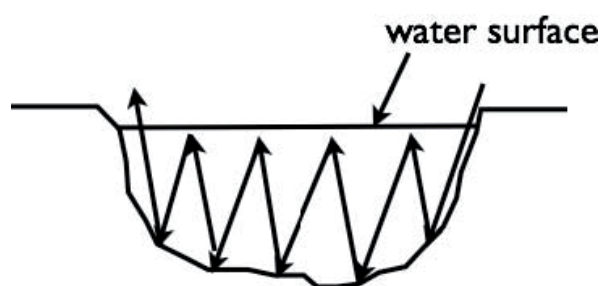


Figure 4: Continuous sampling path to represent a stream section without interrupting the sampling operation.

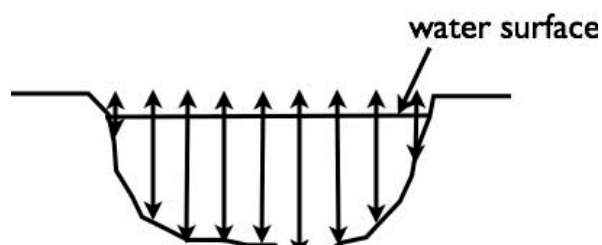


Figure 5: Collection of multiple vertical increments to form an integrated sample (composite sample).

The Aloha Sampler can be used in a continuous mode (sampler not removed from the liquid during sampling) (Figure 4), or non-continuous/intermittent mode (sampler removed from the liquid between increment sampling deployment locations) (Figure 5).

An example of a continuous operation would be sampling from a point on the shore of a river, out ten feet from the shore, from the surface to the bottom in one continuous motion, never breaking the surface of the water during collection. An example of a non-continuous operation would be sampling the length of a river where the Aloha Sampler is inserted in and removed from the river at each increment location (partially filling receptacle at each increment location). Both modes result in a reliable sample. The Aloha Sampler can be used to collect spatially and/or temporally integrated samples [5]. This allows great flexibility for either type of deployment. If the decision unit is small enough, a continuous sample can be easily collected. For larger decision units, a non-continuous sampling method may be desired due to the fixed filling time of the Aloha Sampler. Continuous sampling of liquids typically provides a more representative sample if the logistics allow integration of the entire decision unit.



Figure 7: Use of the Aloha Sampler with an extension pole.

To use the Aloha Sampler, simply submerge the device horizontally with the two holes aligned vertically (one above the other) to the desired depth of the liquid at a constant transit rate. The liquid will flow in the lower hole, and the air will escape through the upper hole (Figures 3 and 6). Once a vertically integrated increment is collected at a single location, move to the next location and take another increment etc. The transit rate, depth of liquid, fill rate and number of vertically integrated increments must be considered individually for each case, but it will always be possible to obtain a meaningful, optimised sample. Some pilot experimentation may be necessary to determine the ideal timing for specific cases—nothing could be easier.

The Aloha Sampler can also be attached to a pole to access hard to reach areas, Figure 7. Once the sample is collected, the Aloha Sampler aperture cover is removed and a solid cover is placed on the sample bottle. The sample is then prepared and stored in the same way as any other type of liquid sample. The Aloha Sampler can be sterilised for the collection of bacteria.

The Aloha Sampler has been used in Hawaii to collect data from construction activities to determine impact to nearby streams.

Multiple samples (replicate sampling) were collected for a specific project to determine the reproducibility of the Aloha sampling approach. RSV (%CV) is quite satisfactorily low for this type of sample collection (Table 1 and 2). These samples were collected using the Aloha Sampler on a pole (Figure 7).

Integrating a sample across the full width and depth of a stream is essential for collecting a representative sample. Cross-sectional variation in contaminant concentration is well documented — surface grab samples collected at a single point have been shown to underrepresent suspended sediment and sediment-associated constituents such as phosphorus, iron, and manganese by 20–60% compared to depth- and width-integrated samples [6,7].

One common workaround is to sample at a point sufficiently far downstream that the stream is assumed to be fully mixed. Various rules of thumb exist for estimating this distance. For high-gradient mountain streams with significant bed roughness and turbulence, complete lateral mixing occurs at approximately 25 stream widths downstream of a discharge point [8].

Table 1: Lihue Mill Bridge, Kauai, Hawaii, 5 November 2013. Owen Environmental, Kalaheo, HI.²

	Time	pH	Dissolved oxygen (%)	Total suspended solids (mg L ⁻¹)
Rep. 1	9:11	7.07	76.0	12
Rep. 2	9:14	6.96	75.5	13
Rep. 3	9:16	6.95	75.8	12
Mean		–	75.8	12.3
RSV (%CV)			0.3	4.7

Table 2: Lihue Mill Bridge, Kauai, Hawaii. 31 October 2013. Owen Environmental, Kalaheo, HI.²

	Time	pH	Dissolved oxygen (%)	Total suspended solids (mg L ⁻¹)
Rep. 1	11:11	7.07	73.9	13
Rep. 2	11:13	7.15	74.7	12
Rep. 3	11:19	7.08	72.9	14
Mean		–	73.8	13
RSV (%CV)			1.2	7.7

For slow-moving, lowland, or gently meandering streams — where turbulence is low and the transverse mixing coefficient is reduced — mixing distances of 50 to 100 or more stream widths are commonly required [9]. The United States Geological Service (USGS) characterizes this more broadly, noting that lateral mixing is generally complete within a few kilometers downstream [10].

There are, however, serious practical problems with relying on downstream mixing as a substitute for integrated sampling. First, a suitable and accessible sampling location may simply not exist at the required distance. Second, and more fundamentally, the mixing-zone assumption breaks down wherever the contamination is not a single, well-defined point source. In industrial areas, stormwater runoff zones, agricultural landscapes, multiple diffuse inputs enter the stream at different locations and different times.

Under these conditions there is no defined mixing zone, and complete lateral mixing cannot be assumed at any fixed downstream distance. Sampling at a single point under these circumstances does not represent the stream — it represents only one location in a heterogeneous cross-section. This is the bane of grab sampling of solids, only here in the liquid realm.

Therefore, it is preferable to collect a depth- and width-integrated sample at the actual point of concern, rather than assume against all odds the stream will become well mixed somewhere downstream.

4. Comparison to Other Stream Samplers

The Aloha Sampler is not designed to represent suspended particulate matter larger than 62 µm. Sampling particles above this size requires a more specialized device known generically as an isokinetic sampler. The underlying sampling concept is similar, but the isokinetic sampler includes a nozzle at its intake that is designed to match the velocity of the entering water to the ambient stream velocity.

² Total suspended solids by Method SM 2540 D, Dissolved oxygen and pH by YSI ProPlus Multi-parameter WQ Meter

Because the flow is not accelerated or decelerated at the nozzle entrance, the sample accurately represents suspended particulate matter of all sizes. The relationship between intake velocity and sediment concentration for isokinetic and non-isokinetic collection of water samples that contain particulates greater than 0.062 millimeters is described in [11].

When water accelerates as it enters a nozzle or open container, fine particles — which have less inertia — are pulled into the sampled flow more readily than larger particles, which are largely unaffected.

The result is an overrepresentation of fine particles relative to coarse ones. Conversely, when water decelerates as it enters the sampler, fine particles deflect away with the slowing flow while larger particles carrying too much inertia to change course in a similar manner, continue into the container and become overrepresented (Fig. 8). This principle applies to all sampling devices, including automated samplers using pumps.

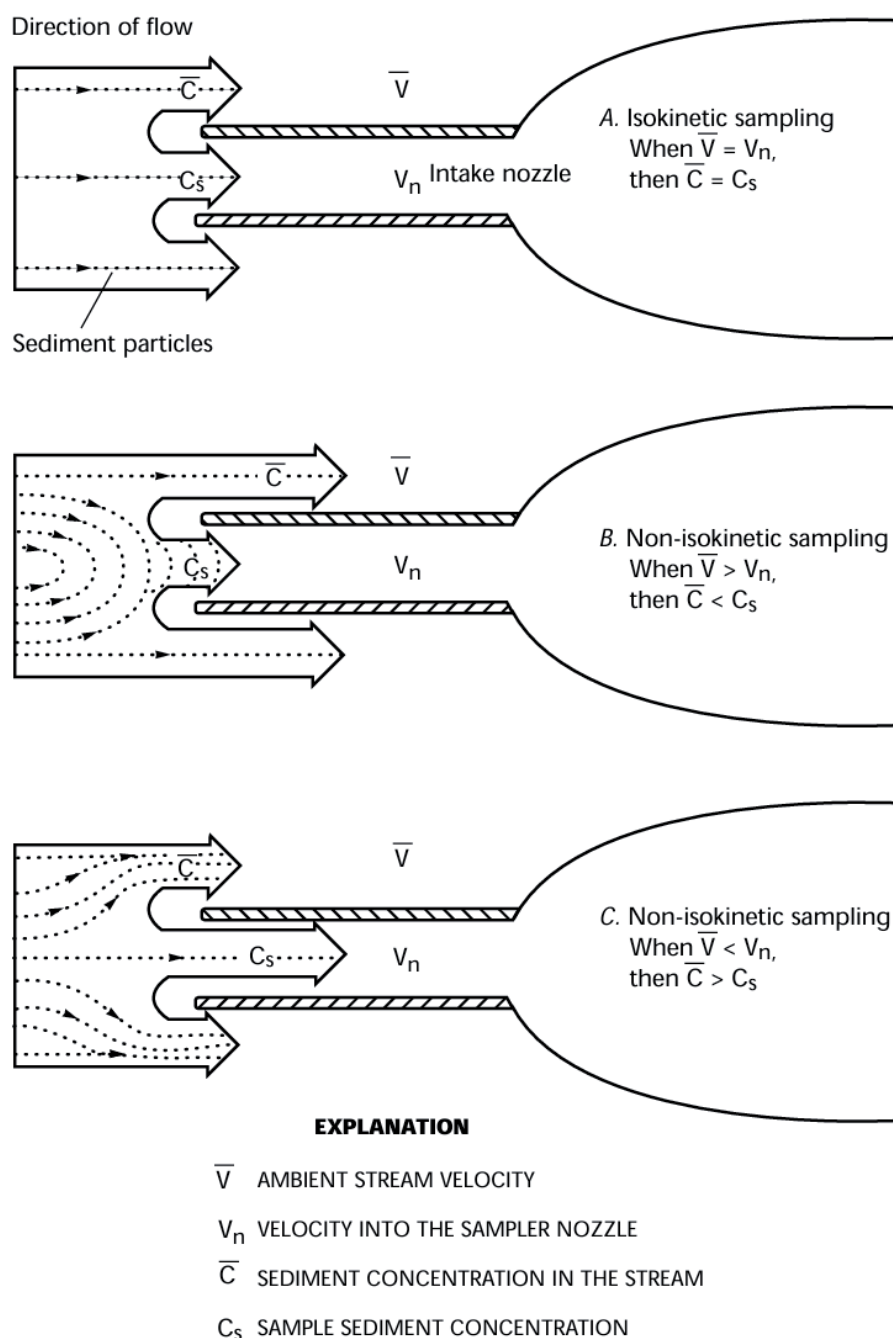


Figure 8: Illustration of non-isokinetic sampling copied from: Wilde, F.D., Radtke, D.B., Gibbs, J., and Iwatsubo, R.T. (eds.). National Field Manual for the Collection of Water-Quality Data, Chapter A4: Collection of Water Samples. U.S. Geological Survey Techniques of Water-Resources Investigations, Book 9, Chapter A4. Reston, VA: USGS, 1999 (revised). Figures 4-1, p. 27.

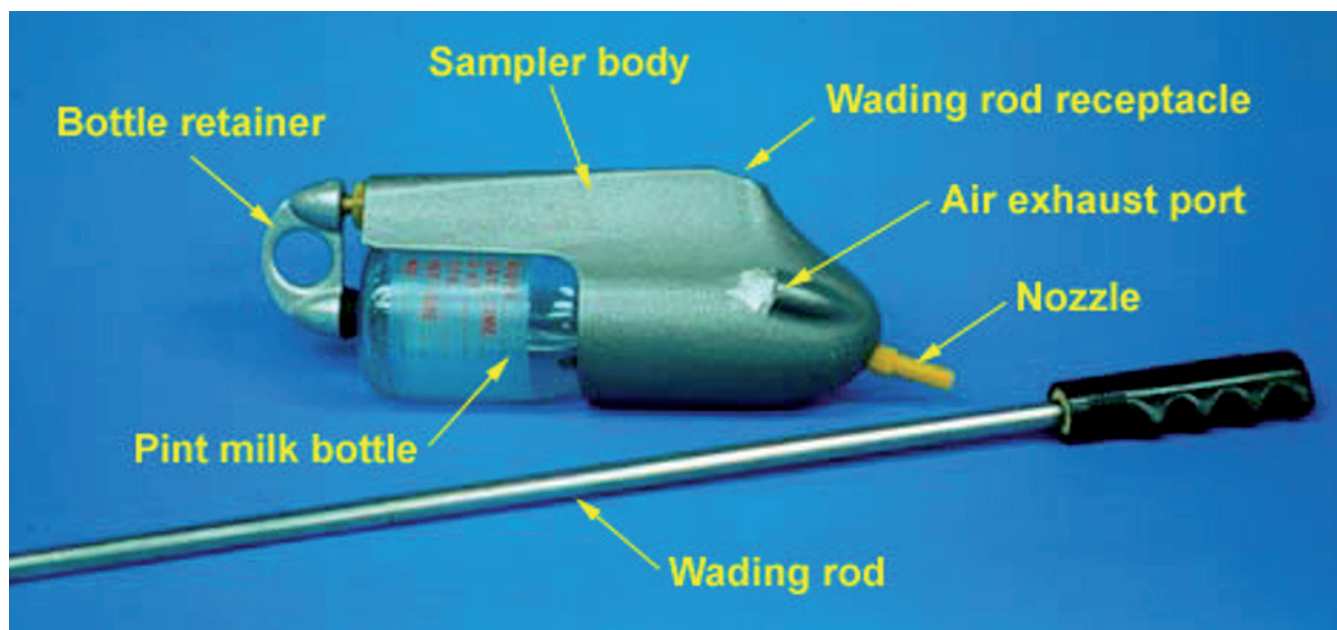


Figure 9: Example of isokinetic sampler. DH-48 Suspended Sediment Sampler. https://water.usgs.gov/fisp/docs/Instructions_US_DH-48_001010.pdf

A related issue arises once the sample container is full or nearly full. At that point the sampler must be removed from the water stream. Leaving it submerged after it has reached capacity introduces its own bias: fine particles, having little inertia, can be swept back out of the container and returned to the stream, while larger particles tend to settle and remain. The net effect is overrepresentation of coarse material relative to fines — the same directional bias as non-isokinetic sampling.

The isokinetic sampler functions correctly only in flowing water, where the nozzle can be oriented to face the current. In still or very slow-moving water — such as lakes, lagoons, and low-gradient ponds — ambient velocity is insufficient to establish isokinetic conditions, and the device behaves essentially like the Aloha Sampler, losing its size-representativeness advantage. While an isokinetic sampler can technically substitute for the Aloha Sampler in any setting, it is more complex to deploy and is generally unnecessary where only fine, or dissolved-phase constituents are of interest.

The USGS introduced the DH-48 isokinetic sampler (Figs. 8, 9) in 1948 [12], and this particular model remains in use today. In the decades since, the USGS Federal Interagency Sedimentation Project has developed numerous additional models suited to a wide range of specific stream depths, velocities, and sampling objectives [13].

5. Bottom Line Comparison

Full stream representation, including suspended material: The isokinetic sampler is the only appropriate choice. It is the only device capable of accurately representing suspended particulate matter of all sizes across the full stream cross-section, provided the stream has sufficient velocity to establish isokinetic conditions.

Stream representation, excluding suspended material (dissolved phase): Either the Aloha Sampler or an isokinetic sampler will work. Because any suspended material collected is filtered out prior to digestion and analysis, sampling bias with respect to particle size is irrelevant for dissolved-phase determinations. Depth- and width-integrated collection is always important for spatial representativeness.

Non-representative grab sampling: A dip sample (grab sample) collected at a single location only represents one point in time and space. It does not represent the stream cross-section and is inherently incapable of characterizing suspended material. Despite these significant limitations, it unfortunately remains the most common sampling approach in practice [14], despite ~70 years of the Theory of Sampling (TOS). Except for the isokinetic sampler, water sampling is not immune from inspiration and guidance from the Theory of Sampling (TOS), *ibid*.

6. Conclusion

The Aloha Sampler is a promising new tool to effectively collect and combine increments in a dynamic liquid system, producing highly flexible, problem dependent samples with very low sampling variability. It is extremely inexpensive in fixed capital outlay and very cost effective to implement and use.

The Aloha Sampler produces fit-for-purpose samples over a wide range of hitherto difficult-to-sample decision units. The Aloha Sampler is a significant improvement over commonly used sampling approaches and equipment targeting surface waters in a wide range of situations.

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Sampling under Duress – What Few Want to Say and Even Fewer Want to Hear

By Kim H. Esbensen¹

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ABSTRACT

Key topics addressed in the present contribution: i) use and misuse of the Assay Exchange paradigm; ii) manipulating mine, ore and metal processing sampling for increased profitability by ‘tuning’ sampling and assaying; iii) sampling for refining and metal accounting; iv) risk mitigation ‘games’. To paint the backdrop for the many ways to lose one’s righteous way, I first present a detailed analysis of the assay exchange formalism, the ‘scheme’, which is involved in most trading and commercial contractual transactions. Based on a thorough Theory of Sampling (TOS) analysis, it is revealed how no less than two hidden, very often un-recognised sampling and sub-sampling stages ‘before assaying’ play a crucial role in determining the reliability of the final analytical determinations, demolishing the notion that total Measurement Uncertainty is a matter of analysis/assaying only. There are many tempting opportunities for devious behaviour and lack of due diligence along the ‘lot-to-assaying-to settlement’ pathway, ranging from ill-informed negligence to deliberate fraud. Presented here are some of the more gregarious examples of sampling under duress – and what can be done about it. Indeed, what should be done about this is simplicity itself, exclusively and honestly relying on the Theory of Sampling (TOS) only, with voluntary full transparency.

1. Introduction

At a recent conference three gentlemen of science, technology, industry and commerce accidentally found one another in agreement on a not so gentleman-like three-pronged theme: “Use and Misuse of the Assay Exchange paradigm” – “Manipulating mine and process metal accounting” – “Increasing profitability by ‘tuning’ the sampling and assaying for exchange”. What do these topics have in common? On closer scrutiny, it turned out that all is not always right in the sampling realm!

Most individual experiences show that professionals and technical staff involved in sampling of ores, concentrates, refined metal products (f.ex., PGM), recyclates, spent catalysts and complex secondary mixtures all attempt to do the best job possible.

However, such best efforts are sometimes subverted by actions of the few that fully understand the mechanics of sampling and assaying and where to apply pressure to achieve ‘more beneficial results’ at particular stages in the logistics and processing chain from ore-to-refined and traded metal. This is unfortunately deliberate dishonest behaviour!

Below follows a sketchy trace of the origin and many manifestations of such misbehaviour, expounding their negative effects and impacts – but ending with showing the only, completely honest way forward.

¹ KHE Consulting, Copenhagen, Denmark

2. What caused this? – Part 1

The following conversation was conducted by the author in his erstwhile role as professor with an all-consuming interest in sampling. Knowing very well the necessary-and-sufficient principles behind representative sampling (having taught the discipline of the Theory of Sampling (TOS) for more than two decades), the question is: why are these principles not always followed where they demonstrably matter, for example where even very small deviations between true and estimated lot, batch, or consignment concentrations translate into highly significant economic gains or losses?

Think of industry sectors dealing with Gold, Silver, Platinum Group Metals (PGM), REE, critical minerals, large quantity commodities even? The following is a reflection by a very experienced agent at the front line where resource and commodity trading meets TIC companies (Testing, Inspection, Certification) offering services to this sector.

Upon direct questioning a relevant TIC-representative, the following statement resulted:

Evidence from the trenches

“Representatives from TIC companies feel that full application of TOS in the field can be challenging, at least when sampling commodities and minerals of high value. This relates to when stipulating sampling procedures to inspectors operating in remote locations around the world, on spot assignments with limited access to the whole consignment and with challenges in extracting a representative sample. The major challenge is to convince clients, a lot of them traders, to spend the necessary efforts – read **money** – to allow to open packaging for full access or pass the material through an automatic sampler to take a larger sample mass. I guess this applies to any industry. When global traders put their negotiation skills to use with us, the humble TIC service providers, they win. I mean, they win because we will compromise on the representativity of the sampling and play by their rules. But in the end, we all lose as the results from the labs will be biased. And then we will spend time investigating and dealing with a claim. Of course, we add the necessary remarks and caveats in our reports and certificates, but it is all a game. The game they play is to save face with their buyers by pretending their product is of high quality, but that the opponent’s ‘sampling’ and/or ‘assaying’ were done incorrectly. The other game they play is to use our knowledge of sampling to manipulate analytical results to their advantage. For example, finding out that natural segregation exists in high grade Cu concentrates, they try to manipulate the sampling technique into making a profit.

The more we educate such clients and share our knowledge, the more we are dragged into becoming puppets. In this context of dynamic and complicated mechanics of the global minerals trade, TOS is too often ignored, and the industrial practitioners are many times ignorant of the work the professional and theoretical samplers are putting into creating a TOS framework that will benefit the whole industry.

Experience with practical application of TOS in the field is a thing that may, or may not (often), also apply to commercial settlement aspects in the business realm. We are often asked to give training to operational teams in different trading houses w.r.t. to different topics of concern, mainly to explain the differences in weighing and sampling between two ends: pit vs. furnace – or loading port vs. discharge port.

I believe partnering with independent TOS experts would greatly contribute to the necessary education of the relevant industries.

[The veracity of this statement is beyond reproach. The rapporteur, known to the author, shall remain incognito. It is not who said this, it is what is revealed that is important]

3. What caused this? – Part 2

At approximately the same time a fascinating book was recommended to the author: *The Secret Club That Runs the World – Inside the Fraternity of Commodity Traders* by investigative reporter and author Kate Kelly.

Who is Kate Kelly?

"I look for ways to shine a light on the inner workings of policy and governance. If there are significant amounts of capital or lever-pulling shaping political, legislative or regulatory outcomes, I'm interested."

<https://www.nytimes.com/by/kate-kelly>

A few snippets from publisher blurbs about this book will set the scene:

"Nestled deep in the towers of banking and finance are the commodities traders who spend their days gambling with oil, gold, and corn a.o. contracts. They're highly educated world travellers with a penchant for risk, and they're here to bet big on the future of the raw materials that make our economies hum. They're very wealthy, barely regulated, and can be a force for tremendous good – or for ill!"

"Commodity players are a shrewd and indomitable lot. And the contracts they trade are still so loosely regulated that the correct combination of money and skill creates irresistible opportunity. That's why Kate Kelly is only half joking when she calls them the 'secret club that runs the world'. When most people think of the drama of global finance, they think of stocks and bonds, venture capital, high-tech IPOs, and complex mortgage-backed securities. But commodities? Crude oil and soybeans? Copper and wheat? What could be more boring? That's exactly what the elite commodity traders want you to think. They don't seek the media spotlight. Their astonishing wealth was created in near-total obscurity, because they dwelled either in closely held private companies or deep within large banks and corporations, where commodity profits and losses weren't broken out. But if the individual participants in the great commodities boom of the 2000s went unnoticed, their impact did not. Over several years the size of the market exploded, and so did prices for raw materials—raising serious questions about whether the big traders were intentionally jacking up costs ... What was really driving all those price spikes? Kate Kelly takes us inside this secretive inner circle that controls so many things we all

depend on. She gets closer than any previous reporter to understanding these whip-smart, aggressive, and often egomaniacal men (yes, they are nearly all men). They work hard, play hard, flaunt their wealth, and bet millions every day on a blend of facts, analysis, and pure gut instinct".

The present article is particularly interesting in these 'facts' and 'analytical/assay results', which are always considered fully reliable.

But are they?

4. Use and Misuse of the Assay Exchange paradigm

I admit that the above two information sources spurred more than a fleeting interest in these matters. But what really hit the head on the nail soon hereafter was being presented with a description of the well-known Assay Exchange 'mechanism'². The Assay Exchange description was of such superficiality and showed a debilitating lack of the necessary scientific underpinnings w.r.t. the principles behind proper representative sampling, the Theory of Sampling (TOS). The present author therefore decided to delve into the depths of issues not before visited, namely: What is the origin and rationale behind the Assay Exchange paradigm and, how it is used today?

Two months' detective work then quickly resulted in an expository paper, aptly titled – also for the preset purpose: "The Elephant in the Room: Unsubstantiated Complacency Regarding the 'Assay Exchange' Paradigm – Sampling Uncertainties with Hidden Economic Consequences" [1,2].

4.1 Key message

"The assay exchange paradigm is an integral element in many contractual agreements stipulating how business transactions rely on comparison of two independent assay results for commercial and trading settlement purposes. It turns out that the current Assay Exchange vs. splitting gap paradigm incurs no less than two un-recognised sampling uncertainties, which leads to hidden adverse economic consequences for at least one – and sometimes for both – contractual parties. The magnitude of this unnecessary uncertainty is never estimated, which leaves management and business stakeholders without information about potential economic losses – a clear breach of due diligence.

² This was parlayed by a much used 'expert' in another context, the specifics and details of which are of no relevance for the present exposé, but it revealed a seriously flawed understanding that called for more attention.

However, all that is needed to resolve this critical issue is stringent adherence to the Theory of Sampling (TOS) by mandatory contractual stipulations of only accepting representative sampling and sub-sampling principles, leading to a community call to action" [1,2].

4.2 Technical denouement

The elephant in the room is the tacit, unwarranted assumption that the contractual splitting gap is always centred on the true average lot concentration. Note for example in Figs. 2–5 below that an acceptable settlement assay is easily reached via the assay exchange scheme regardless of whichever analytical concentration level is bracketed by the interval defined by the cardinal three samples involved as analysed by seller, buyer, and umpire. But this assumption is challenged by the fact that the crucial primary sample (which is immediately divided in three sub-samples) is in fact the result of sampling a heterogeneous material. TOS-initiated readers will have smelled a scent already

4.3 Theory of Sampling (TOS)

All materials in the realm of technology, industry, processing, trading, commerce ... for which Testing, Inspection and Certification (TIC) is on the agenda, are heterogeneous – it is only a matter of degree. The Theory of Sampling (TOS) has for over 70 years demonstrated the severe danger involved in assuming that there is no sampling error involved extracting a primary sample. But this is not the place to detail TOS, as there is an ample source of excellent background literature available [3–8].

Without a modicum of TOS competence, the assay exchange scheme appears simple, easy-to-understand, and could not possibly lead astray ...

4.4 Assay Exchange paradigm – the grim reality

However, the technical reality behind the Assay Exchange paradigm is grim, as shown in Fig. 1, which emphasises that no less than two sampling operations are involved, each with its own sampling/sub-sampling errors and uncertainties – and all this indeed takes place before analysis. Surely this cannot avoid having an impact on the quality, and as it transpires, the quantity reported in the analytical results.

Following TOS, when sampling heterogeneous materials (e.g. broken ores, aggregate materials, concentrates, mixtures, recyclates – in general materials with significant grain-size and/or density contrasts), there is every reason to take notice – and especially to take appropriate operational precautions regarding the impact of the dominant primary lot sampling error (PSE) [3–8].

And there are equally good reasons also to mind the subsequent 'sample division' (aka sample splitting) producing the three tacitly 'assumed equal' samples for the seller, the buyer, and the umpire laboratory (if needed). This sub-sampling is generally associated with a secondary, non-vanishing sampling error (SSE), the magnitude of which can be both small, significant or large, depending on the operational competence (and the material heterogeneity). Indeed, SSE may often be smaller than PSE, but never neglectable, especially if suitable practical facilities to be used for appropriate comminution (crushing) and mixing are not mandated in contractual stipulations to be TOS-compliant, which is often not the case [3–8]; see also the reflections on the Round Robin test framework at the end of this article.

The degree to which it has been possible to reduce PSE will determine how close the analytically determined concentration in the primary sample will be relative to the 'true' lot concentration. Following TOS' understanding there are always also secondary sampling errors (associated with sample splitting), although never as large as those associated with primary sampling. The primary sampling stage errors typically dominate the total uncertainty budget, and it is therefore always necessary to take the most stringent science-backed precautions at this stage. This is practically never an element in typical Assay Exchange agreements and in relevant trading contracts.

Appropriate precautions first and foremost include TOS' ability to eliminate the so-called Incorrect Sampling Errors (ISE), which is the necessary condition for unbiased sampling [3–8]. But this is necessary for all sampling stages, because any non-zero level of residual heterogeneity within a sample/sub-sample opens up for non-vanishing uncertainty contributions related to splitting operations. These trivial TOS insights are unfortunately most often unrecognised in the assay exchange realm, with severe consequences to be laid bare below.

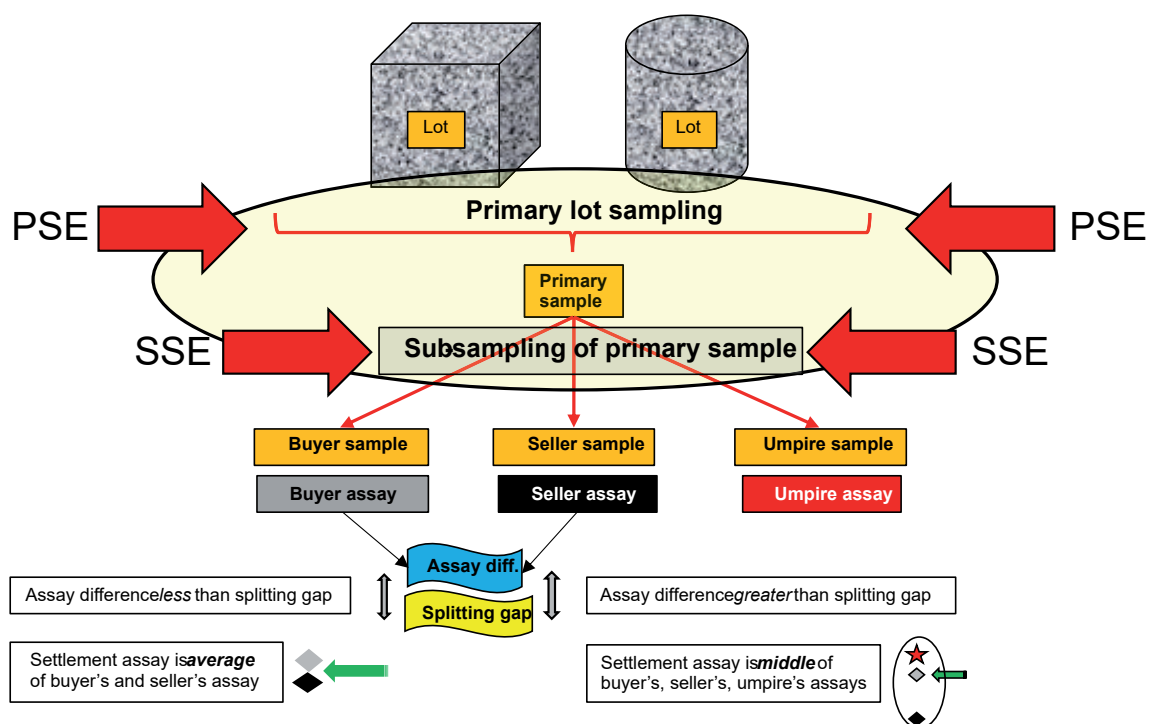


Figure 1: Assay Exchange reality – acknowledging two sampling stage uncertainty impacts PSE, SSE (red arrows). PSE := Primary Sampling Error; SSE := Secondary Sub-sampling Error. For full description of the Assay Exchange paradigm, see [1,2]. Illustration copyright: KHE Consulting teaching archive; used with permission.

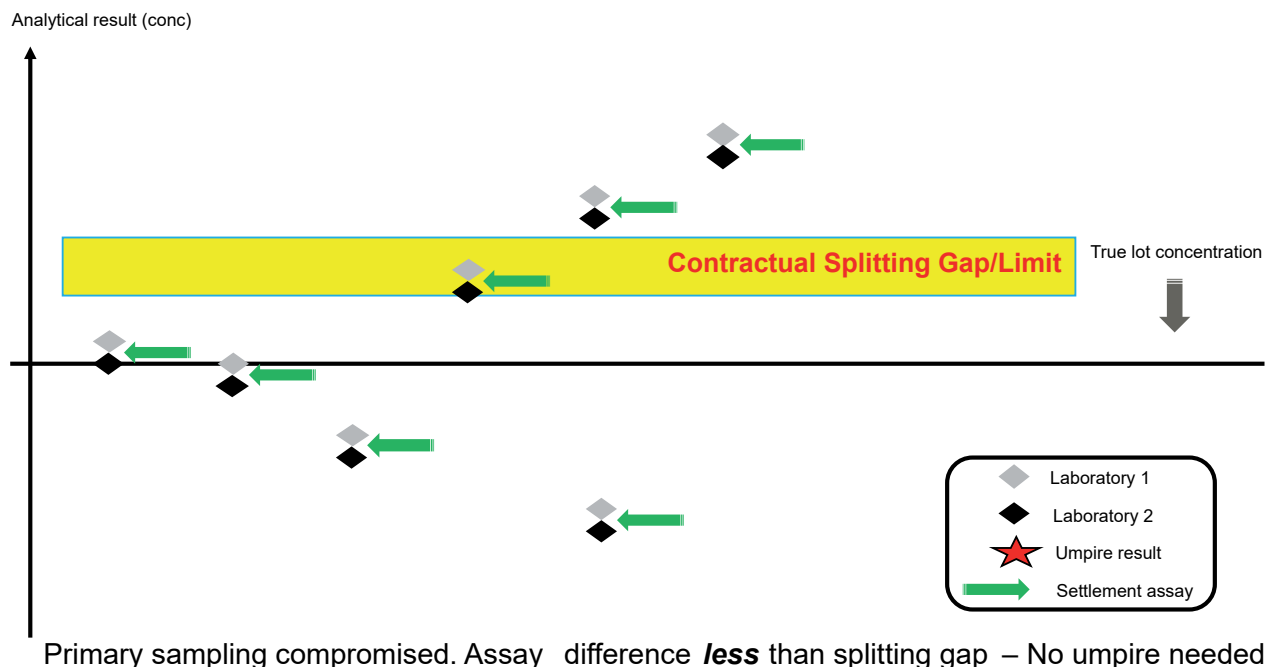


Figure 2: Illustration of a realistic splitting gap location (which is random as a function of the degree of incomplete sampling bias elimination and other potential ISE deficiencies at the primary sampling stage). The case illustrated here does not lead to 'go to umpire'; see [1,2] for full details. Illustration copyright: KHE Consulting teaching archive; used with permission.

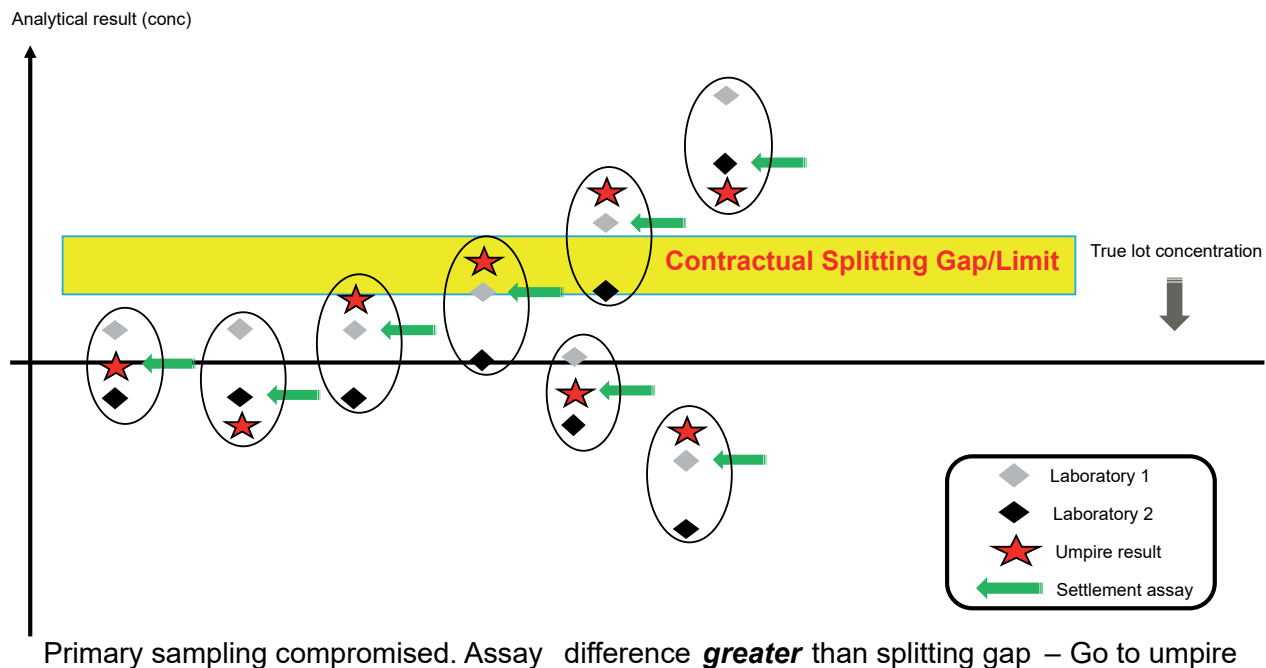


Figure 3: Illustration of a realistic splitting gap location (which is random as a function of the degree of incomplete sampling bias elimination and potential other ISE deficiencies at the primary sampling stage). The case illustrated leads to 'go to umpire'; see [1,2] for full details. Illustration copyright: KHE Consulting teaching archive; used with permission.

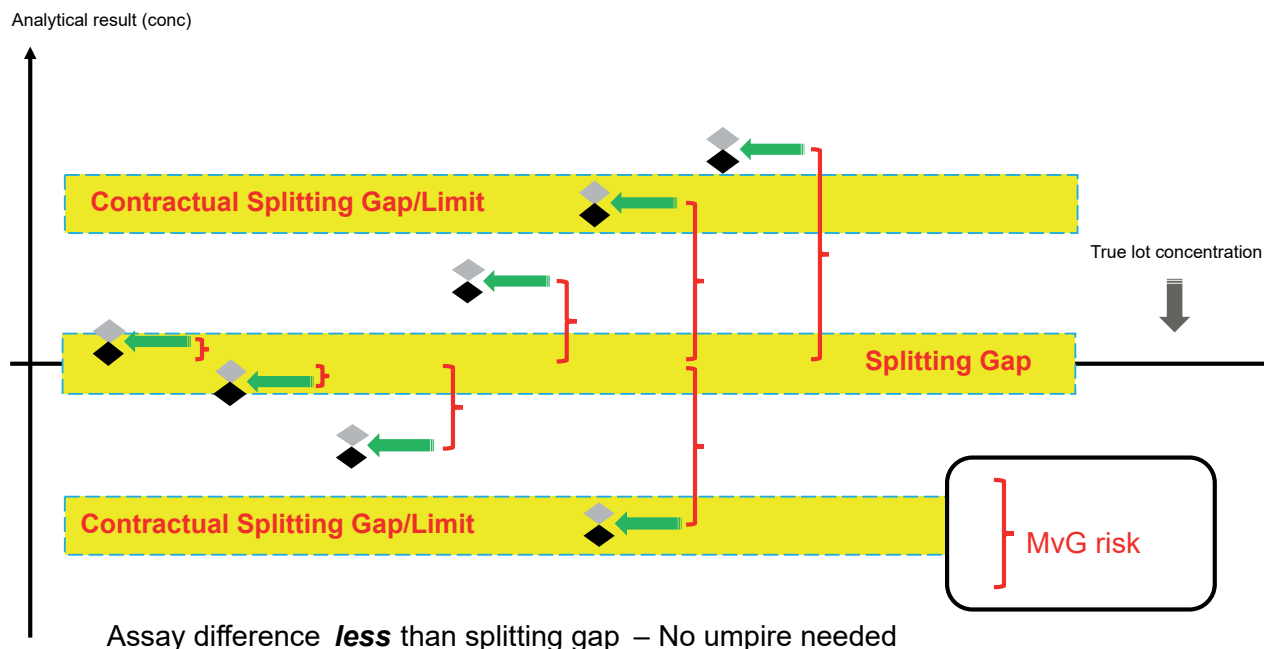


Figure 4: Illustrating the MvG risk; case of no umpire needed. The MvG error/risk is only (close to) zero in the case of vanishing primary sampling uncertainty; see [1,2] for full details. Illustration copyright: KHE Consulting teaching archive; used with permission.

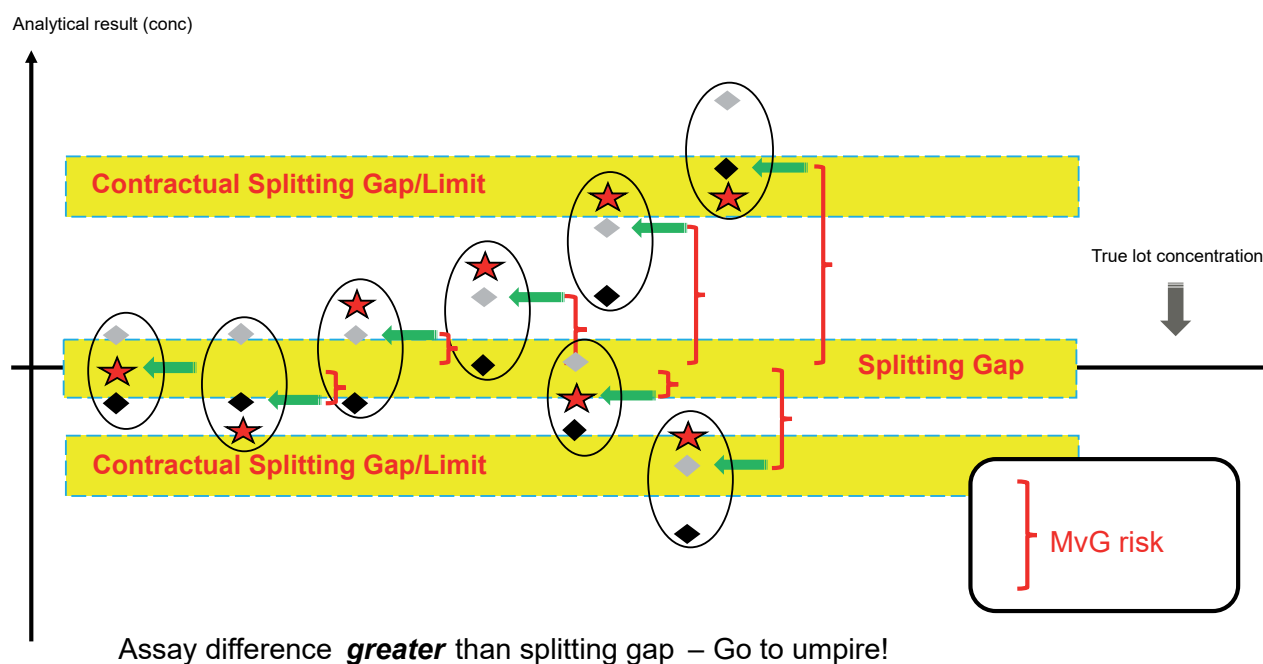


Figure 5: Illustrating the MvG risk; case of going to umpire. The MvG error/risk is only (close to) zero in the case of vanishing primary sampling uncertainty; see [1,2] for full details. Illustration copyright: KHE Consulting teaching archive; used with permission.

There are certain logical effects from the complementary PSE and SSE influences, as follows:

The degree of incomplete primary sampling bias elimination will impact the way the splitting gap is brought into action, manifested as a deviation from the assumed centering of the gap on the true lot concentration, as is shown in Fig. 2. This will be the situation regardless of whether the paradigm leads to ‘go to umpire or not, Figs. 3–5.

It is important to emphasise the distinction between this primary sampling effect and the splitting gap mechanism. If the primary sampling uncertainty is nil, i.e. were it possible to eliminate all (incorrect – as well as correct) sampling errors (full explanation in [3–8]), the assay exchange paradigm would be unassailable. Were it possible to counteract all adverse effects from both material heterogeneity and from adverse sampling procedures (grab sampling in essence) and hereby always ending up with a perfect representative primary sample for all materials with all kinds and degrees of heterogeneity, always employing optimal composite sampling – then, and only then, would there be no splitting gap deviations.

Alas, the entire history of the Theory of Sampling (TOS) shows that this ideal scenario is not achievable under any circumstance! There is always a minimum material heterogeneity, giving rise to a non-vanishing minimum sampling uncertainty even after everything embedded in “best practice” has been adhered to. This is why one cannot glibly assume that the splitting gap is always centered on the true lot concentration, but rather that there will always be an offset to some degree (small, intermediate, large), witnessed in Figs. 2–5.

4.5 Mismatch vs. Gap error (MvG)

Any deviation between the final settlement assay value and the “true lot” concentration is termed the ‘Mismatch vs. Gap’ error, MvG [1,2], Fig. 5. This uncertainty translates into an economic risk, the MvG risk, which needs to be managed. However, this is demonstrably not a provision envisaged in the conventional assay exchange paradigm, which does not even acknowledge a primary sampling error (PSE) influence!

Adding in the subsequent sample division error effects (which may include a potential sub-sampling bias), the relative deviations between the three analytical results from seller, buyer, umpire is now crucial.

The tripartite assay results from Lab A, Lab B, and the Umpire lab depend on to which degree the primary within-sample heterogeneity has been successfully reduced/eliminated by appropriate TOS action before the practical sample division (primarily by careful mixing) which also contributes.

The full MvG risk can be illustrated with graphic clarity as shown in Figs. 4,5. There is here a subtle issue that needs to be emphasised with force:

Within the conventional assay exchange paradigm, this MvG uncertainty is always assumed to be zero; therefore, it's risk management never appears as a task on the business RM agenda.

Figs. 4,5 show how the location in the Y-axis direction of the contractual splitting gap may be significantly displaced from the assumed closeness to the true lot concentration, mostly influenced by the degree of a primary sampling bias if/when this has not been successfully mitigated [3–8].

Note that the assay exchange scheme is typically followed regardless of this critical uncertainty, an uncertainty which is not acknowledged in the standard assay exchange paradigm! Is this but an innocent oversight (bad when it comes to settlement), or is this deliberately overlooked? Or, worse, is this deliberately ignored? In all these cases, what could be the motivation for doing so? This harks back to the anonymous conversation with a TIC-agent quoted in the beginning of this article.

There is a substantial risk in not knowing about, or not acknowledging, the MvG uncertainty! The critical issue is that current assay exchange practices do not include mandatory means to deal with sampling influences in the splitting gap settlement accounting scheme! There are few exceptions from this situation which are associated with highly knowledgeable companies and corporations, or with entities who are interested in using this lack of understanding for narrow, selfish interests) .

4.6 The point is ...

Thus, there will always be a real, non-vanishing risk of settling a business transaction based on the assay exchange paradigm at an assumed reliable assay level, which may in fact lie significantly distanced from the true lot metal content, as demonstrated in Figs. 4,5.

The gap displacement shown here is a direct rendition of what in reality becomes a significant settlement bias, which is not known at the time of analytical determinations, and which therefore cannot be counteracted by any rational means.

The gap deviation, the MvG error/risk, may be small (low heterogeneity materials; largely acceptable sampling performance) but it may just as well be large (significantly-to-excessively heterogeneous materials; non-representative sampling competence/procedures/equipment):

The point is that all this is unknown to the contractual parties, who believe that the assay exchange scheme will result in a fair settlement for both parties.

For many commodities the economic risk involved may perhaps not constitute reasons for much worry (bulk commodities with relatively low unit value), but as tonnages go up, the sum-total economic effect may still well accrue to appreciable, unacceptable amounts ("The secret commodity trading club that runs the world"). This fact is much more characteristic in the mining, minerals processing and metal refining industry sectors. Here matters are economically much more serious, for example for the precious metals refining industry concerning e.g., Gold, Silver, Platinum Group Metals (PGM), some REE and similar, where even minute amounts of misassigned, but certified, deviating concentration results between buyer-seller translate into highly significant economic consequences – absolutely worth a legal fight if/when discovered. As an example, a misappropriation of one oz of Gold represents a value of USD ~4,500; one oz. of Platinum USD ~1,750; readers can do their own math.

Thus, there are many possible adverse consequences of not being aware of the MvG risk! It is precisely the scope, width and severity of such consequences that caught the attention of the accidental trio of reflecting gentlemen indicated in the introduction. It is not possible that these issues are not also known to many more parties with functioning eyes and an educated, rational mind. Which begs the question: How widely is this hidden risk known throughout the minerals and commodities trading world and in specific related industry sectors for miners, smelters, and refiners?

5. Manipulating mine and process metal accounting

There is another way reaching the same potentially adverse results – only here resulting from quite deliberate actions. For example, insights into how process industry laboratories have been coopted by local operational management to produce analytical data that improves desired metal accounting totals, which the specific processing industry is trying to achieve, or, in other words, actions which are deliberately trying to keep senior corporate management and shareholders 'happy'. This operational pressure can take many forms, but the most frequent one is probably refusing to accept analytical data not corresponding to expected or desired levels – instead continuing to re-analyse until a more fitting result is obtained by sheer happenstance (sampling, sub-sampling and analysis of heterogeneous materials will always result in some spread of analytical results) and then taking exactly this datum as gospel, rejecting all other data points as somehow flawed. If ever there was a more blatant verification that a total sampling + analysis variability is always present! This modus operandi is certainly not confined to ore and minerals processing and refining metallurgy industry sector alone!

The laboratory process disruption this behaviour causes affects the basic KPI's a laboratory manager and staff are measured against, i.e., negatively impacting turnaround, sample throughput, often prompting "client complaints", which then show up as negatives in performance reviews and, worst of all, reducing monetary performance bonuses. The result of this kind of pressure and financial penalties is that laboratory managers and senior staff may 'adjust' data before release to reduce, or completely eliminate re-analysis demands, to ensure a more "smooth laboratory process" with continued 'good' operational reviews. This practice is certainly not confined to industrial and commercial analytical laboratories only! Whenever there is a potential substantial extra value on the horizon, temptations abound.

Potential fraudulent behaviour specifically in the analytical laboratory aside, the focus interest in this article is how sampling and sub-sampling plays an integral role at many stages along the full 'lot-to-aliquot-to-analysis' pathway: Lots of temptations for failing one's way! There is an interesting testimony of a dramatic awakening to these issues by laboratory personnel with operational responsibility following a basic introduction to the Theory of Sampling (TOS) [10]³.

Other issues are associated with the many sampling and sub-sampling stages before analysis in general: industrial technical staff may be under pressure to take samples at 'advantageous times', to adjust sample size, or to 'modify' sampling procedures (including sample preparation), or to 'look away' at critical work path junctures – all again to provide final analytical results that will better support certain objectives, be these commercial, payment optimisation, metal accounting, trading profit, or environmental monitoring. This author has personally experienced the latter related to alleged 'random sampling' of spillage water on an oil production platform, where this kind of pressure was revealed when subsequently data analysing quarterly compositional results. The guaranteed loser in all such dishonest executions of sampling, sub-sampling, sample preparation and analysis is – representativity. When representativity is lost, all bets are off. A major ploy is how a simple physical tests and quantification like moisture determination can easily be used to bias analytical result in a favoured direction ... by TIC inspection staff, by laboratory personnel, or by company or corporate management at different post-analysis levels.

Modified samples or process analytical samples/PAT sensor signals transformed into analytical data, will ultimately make it into data bases from which TIC companies and third-party laboratories will be tasked with providing independent analytical data to be used for final commercial settlements between i) buyer vs. seller; ii) seller's laboratory vs. buyer's ditto vs. the reference umpire laboratory – and so we're back to the assay exchange paradigm in many different (dis)guises, but with deliberately faulty, misleading, or downright fraudulent actions and data. What a world ...

3 <https://wcsb10.com/media/ogzbw012/wcsb10-economic-arguments-dec-2022-compressed.pdf> (p.36)

6. Increasing profitability by ‘tuning’ sampling and assaying for exchange

The net effect of the above bad practices (example selection in no way exhaustive) is voluntarily to bias the assay exchange database, which will therefore in effect disadvantage one or more of the parties in a final commercial transaction. So ...

1. There can be involuntary, unrecognized bias-generation in the form of assay exchanges influenced by the hidden sampling error impacts described above: This is negligence by lack of understanding the full framework of assay exchange, treating it as but an always true and fair ‘scheme’ to be followed in a spreadsheet. Or
2. iThere exist various forms of deliberate manipulations at one or more stages along the ‘lot-to-aliquot-to-analysis-to-risk management’ pathway. While the former is a clear lack of professional due diligence, the latter reflect a direct fraudulent, criminal intent – but they both lead to the same result, an untrustworthy settlement/ transaction database.

There also exist other potential ‘levers’ that can be activated within the regimen of analysis alone, e.g. application of ‘correction factors’ of many kinds based on data whose origin is lost in a historical fog or deliberately kept hidden. But the analytical realm *sensu stricto* is not a topic for the present focus.

A final topic is associated with the field of risk mitigation practices, which has its root in a combination of asymmetric factors inherent in the formalisms of ‘by the book’ assay exchange and the ensuing settlement mechanics. This is where e.g., metal refiners seek to manage exposure to Measurement Uncertainty (MU). But is this $MU := [MU_{analysis}]$ or $MU := [MU_{sampling} + MU_{analysis}]$? There is obviously a crucial difference! Industrial risk mitigation often involves anticipated, perceived, or misguided notions as to counterparty positioning. This is a complex mine field, driven by confidence in one’s own superior ability to shine a torch-light through the dense fog of potential economic gains vs. loss understandings of what goes on following the Assay Exchange mechanics. This could manifest itself as a deliberate over-, or sometimes under-reporting analytical concentration values in anticipation of counterparty actions (which may or may not actually be the case) and/or even trying to factor in general umpire performance as well. Obviously, this kind of economic gaming can rapidly develop into rather byzantine risk management practices – but such practices are not on the agenda here.

What is important is that for some involved parties, as well as for some neutral observers, this economic game can sometimes seem to be so widespread that it takes on what could almost be viewed as a legitimate industry ‘commercial practice’! But is it? The ultimate ‘number manipulating’ potential is so many-faceted that it needs its own comprehensive account (not touched upon here).

However, it is interesting how a key role is played out by sampling in this game: proper, representative sampling vs. sampling under duress.

So, what can be done? What should be done?

A preliminary step is to clear up the sometimes-confusing terminology used across different disciplines and applied technology fields: error vs. uncertainty vs. measurement uncertainty [11].

7. The way forward: Understand and eliminate sampling errors, uncertainties, risks

Status quo is that the standard assay exchange paradigm largely ignores the MvG risk.

The above analysis of misplaced, economically dangerous trust in the conventional Assay Exchange scheme without recognition of the two hidden sampling error uncertainty influences is tantamount to a significant unrecognized extra risk, almost never properly recognised. Embedding TOS errors (as TOS risks) in the general framework of Risk Management is treated in detail by Paoletti and Esbensen (2025) [12].

All the above complex technical relationships notwithstanding, there is a surprisingly simple way out of this under-brush of potentially nefarious behaviours:

It starts with the fundamental need for selection of a Decision Unit (DU); technical details can be found in [13]. The cardinal step in designing a representative sampling plan ‘from-lot-to-aliquot-to-analysis’ is a formal definition of an appropriate Decision Unit (DU), aligned with the transaction or settlement objective. The Decision Unit determines unequivocally the specific material target (in terms of location, timing, volume, mass) from which sample increments are extracted, as part of a composite sampling process [3–8].

The DU is the specific material to which the final analytical results apply and from which inference is to be drawn as to the characteristics of the whole lot. By insisting on an a priori DU definition, there can no longer be applied ‘encouragement’ or pressure to technical personnel, because there now exists a comprehensive, complete operational SOP (Standard Operation Procedure), which in the name of transparency of course is meant to be followed to the letter! Should ‘deviations’ later be discovered, the meticulously worked out DU definition, SOP and sampling plan will also serve to protect workers and personnel below supervising management levels in relation to criminal prosecution, lawsuits ...

8. Resolution

Here is the universal resolution – and it is an easy one. All that is needed to resolve the critical issues outlined above is 100%, stringent adherence to the principles of the Theory of Sampling (TOS) by mandatory contractual stipulations only to use (and only accept from counterparties) documentable TOS-representative sampling and sub-sampling practices; full details in [14,15]. As concerns the key sampling aspects, there is only need for the following two sentences that embodies the core of what shall be done:

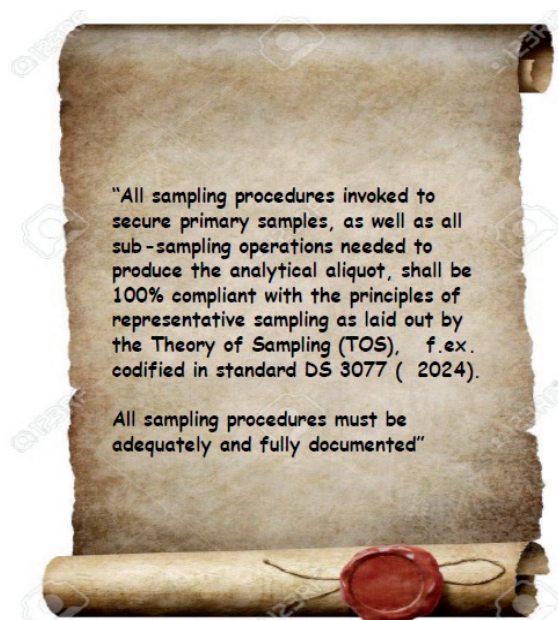


Figure 6: Contractual, settlement and agreement mandate – universal remedy against all sampling deficiencies. Illustration copyright: KHE Consulting teaching archive; brought here with permission.

Imagine the relief if/when the two sentences quoted in Fig. 6 were to be included in all trading and settlement contracts going forward. The entire array of debilitating issues regarding the assay exchange scheme – and all temptations to bad behaviour (re. sampling, analysis, risk management) could go away if/when this mandatory contractual stipulation is agreed upon by all parties!

Well, what is also needed is to instigate some directed business and cultural moral re-armament ...

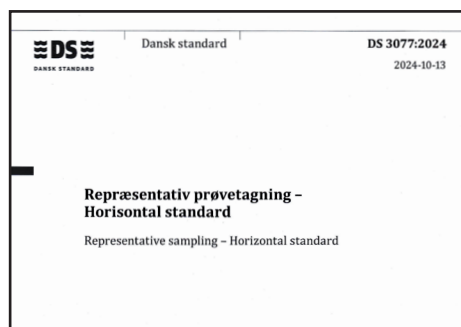
Then:

1. All sampling procedures would only be in the form of proper composite sampling (grab sampling is banned).
2. All bias-generating Incorrect Sampling Errors (ISE) would be eliminated from the primary sampling stage and from all sub-sequent sub-sampling stages as well, forcing $MU = [MU_{\text{sampling}} + MU_{\text{analysis}}]$ to be optimally reduced to $MU = [MU_{\text{analysis}}]$.
3. All industry sectors where sampling is a critical element will henceforward be honour-bound to follow the global standard DS 3077:2024 [14,15], Fig. 7.

9. Round Robin – no validation

Various suggestions are often given in defence of the assay exchange paradigm, for example: “Samples should regularly be sent for Round Robin (RR) assaying and comparison”. To which: The findings of RR comparisons, also called Proficiency Testing Programs, are highly sensitive to whether the sample division process producing assumed ‘identical replicate samples’ sent off to participating (and umpire laboratories) are indeed representative, or not – and are, as such, indeed scrupulously identical.

The Round Robin framework is based on the tacit premise that the distributed laboratory samples (which can be viewed as an augmented seller – buyer – umpire sample set), are indeed 100% identical. If/when not enough attention, or no attention at all, is directed at the critical dividing sub-sampling involved, the RR scheme is subject to the exact same critique as levelled above to the standard assay exchange mechanism. When no attention is directed to the sampling issues involved, the RR facility is only able to compare the analytical performances s.s. between laboratories (which is indeed the official objective of RR), but this leaves the sub-sampling variance out of consideration, effectively allowing a MvG risk/uncertainty to infiltrate the comparative analytical database.



3.43 theory of sampling TOS

framework of governing principles (GP) (3.16), sampling unit operations (SUO) 3.41 and sampling error management rules (SEM) together with normative practices needed to overcome adverse effects of material heterogeneity and incorrect sampling procedures

Note 1 to entry: TOS allows to design, implement, use, and maintain proper sampling processes and equipment ensuring sampling representativeness.

Note 2 to entry: TOS history: Body of theoretical developments initiated in 1950 by the French scientist Pierre Gy, who, over the period of the following 25 years, developed a complete theory of heterogeneity, necessary and sufficient principles and operations guaranteeing representative sampling, including appropriate sampling equipment requirements (design principles, specific operational and maintenance requirements), see the Bibliography [1, 3-7, 9, 12, 13, 15, 17 and 24].

3.44 total analytical error TAE

sum of all uncertainty effects due to a specific analytical measurement made on an analytical aliquot

Note 1 to entry: Aliquots can be extracted as physical sub-samples, or can be intact virtual samples, e.g., a volume of a flux of matter interacting with a spectroscopic analytical instrument, or similar (PAT). TAE reflects the uncertainty effects involved in analytical method validation *per se*. TAE is specifically singled out in TOS to avoid overlapping, or confusion with respect to TSE.

3.45 total sampling error TSE

combined uncertainty effects resulting from material extraction along the full sampling pathway from lot-to-aliquot TSE = ISE + CSE, see Figure 1.

This standard outlines a practical, iterative, self-controlling approach with minimal complexity, based on the Theory of Sampling (TOS). The generic sampling process described and all elements involved are sufficient and necessary for the stated objective, with the consequence that no exceptions can be allowed in order to be able to document the intended sampling representativity. It is necessary to consider the full pathway from primary sampling to analytical results in order to be able to guarantee a reliable and valid analytical outcome. This standard, including normative references, annexes (and further, optional references) constitute a complete and sufficient competence basis for this purpose. The present approach will ensure appropriate levels of accuracy and precision for both primary sampling as well as for all sub-sampling procedures and mass-reduction systems at the subsequent laboratory stages before analysis.

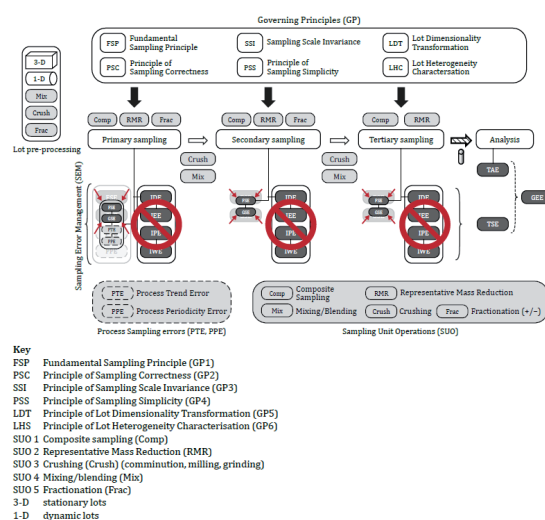


Figure 11 – TOS requirements for fit-for-purpose representativity (compare with Figure 1)

Figure 7: DS 3077:2024 “Representative Sampling: Horizontal standard”. Global standard stipulating the necessary-and-sufficient framework for defensible sampling in all of science, technology, industry, environmental monitoring, food, feed, pharmaceutical manufacturing/processing, regulatory authorities [14,15]. Illustration copyright: KHE Consulting teaching archive; brought here with permission.

Of course, conscientious RR organisers recognise that potential errors in subsampling may significantly influence the intended statistical comparison of laboratory analytical data, impacting on the validity of the conclusions on performance of the participating laboratories. Therefore, RR samples are often prepared to a much smaller particle size than what is common for commercial settlement samples and then subjected to (very) thorough mixing. One often stated reason is that a much-reduced particle size is helpful since it will increase mixing efficiency and will also help to reduce extraction errors e.g., from smearing gold left behind on the pulverising instrument, or by discarding oversize sample material that is too hard to crush. With RR this intensive sample preparation ‘does not matter’ as the aim is to compare analytical performances only. An RR dispatching facility will sometimes perform perfunctory homogeneity checks to verify that each divided sample generates the same analytical result when analysed with its own in-house laboratory. Only after such vigorous measures have satisfied the dispatching facility, will it send out the RR test samples to participating laboratories.

Notably however, such proficiency test samples no longer have a defensible representativity relationship with the donor material from which they originated; they have specifically been prepared to make the RR exercise, or Proficiency Testing Program, only, focusing on the relative analytical performances. It is as if sampling and especially sub-sampling effects in this case do not exist and need not be taken into consideration. But they most certainly do exist and will most definitely impact the comparison database; it is just that nobody cares about with which influences and magnitudes that have been left out of consideration. These sampling/sub-sampling effects will be incorporated in various in-between sample and in-between laboratory performance variances.

These ‘optimised sample set’ issues for RR purposes are in fact identical to the standard assay exchange setup in that the relationship to the original lot composition will never be known.

While this may be fully acceptable in the case in which one is well-knowingly, deliberately only interested in analytical performance comparison (which indeed is the *raison d'être* for RR), this also means that there is no saving grace w.r.t. the assay exchange paradigm even if samples are “regularly sent round for Round Robin (RR) assaying and comparison”. RR checks will never be able to detect and to quantify the associated sub-sampling errors and their resulting uncertainties. Therefore, to try to make RR testing more relevant, more realistic, efforts have been expended by some RR test organisers instead to employ real-world samples for the RR comparison of analytical performance, which are then subjected to Herculean mixing efforts a.o. before splitting. It is easy to understand the rationale for this based on the present exposé: Analytical laboratories are supposed to be able to analyse original lot material with optimal accuracy and precision (field samples, industrial samples, trading samples, environmental samples ... target materials are very different in nature). However, accuracy in the RR context is exclusively w.r.t. the analytical aliquot volume only. But this context is identical with the assay exchange context treated here. Thus, this more ‘realistic’ RR context will be subject to the exact same critique as was levelled at the standard assay exchange scheme above, although often with significantly reduced splitting uncertainties. Principally however, the result is that this version of the RR facility is equally unable to serve as validation the assay exchange paradigm.

Summing up: Agreement between analytical results from the same laboratory only attests to the consistency of analysis, while agreement between different laboratories does not guarantee representativity with respect to the original lot material. ‘True lot concentration’ cannot be measured – which is why the Theory and Practice of Sampling (TOS) was developed; see [8, Fig. 8] for an overview of the historical development of sampling practice and theory as solutions to societal needs and demands. Systematic effects will always arise when there are differences in i) sampling procedure, ii) preparation and iii) analytical techniques.

So, even the most analytically precise assay values are only the best possible estimates of the compositional characteristics of an original lot, subject to both random variability and potential systematic effects, reflecting the compound, complex, multistep sampling pathway from lot to aliquot – all of which takes place before analysis. And then there is risk mitigation, a game of its own, sadly not exclusively performed by former boy scouts ...

10. Conclusions

This contribution offers the dictum presented in Fig. 6 to all sectors in science, technology, industry, trading, commerce, regulating authorities, environmental monitoring and control, risk management (exemplification nor exhaustive) where sampling plays an integral role for reliable, representative analytical results upon which to be able make transparent, defensible decisions in society – together with a modicum of moral re-armament to fight temptations to economically selfish narrow-term interests!

ACKNOWLEDGEMENT

The author acknowledges revealing discussions leading to key insights into the murkier aspects of contractual settlement and commercial practices (overt, as well as covert) with key colleagues and industry representatives, who, for reasons not overly difficult to understand prefer to remain undisclosed. I thank them profusely for their valuable help to lay bare some of the behaviours described here – they know who they are. Two reviewers helped tremendously toning down and taking the edge of some of the remarks in the original manuscript – also greatly appreciated.

FURTHER READING

April 7th, 2026, the beginnings of a broader discussion of these issues could be found on LinkedIn under the heading “But let’s talk about what actually happens on the ground”. This discussion is a perfect complement to the present essay, greatly recommended

<https://www.linkedin.com/feed/update/urn:li:activity:7447296871074525185/>

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Two Gold Medal Laureates, One Breakthrough: Minnitt & Minkkinen on Liberation-Driven Sampling

DOI: 10.62178/sst.005.010

“For liberation-limited ores, the primary strategy is no longer to accommodate massive heterogeneity through impractically large sample masses, but to strategically apply comminution to unlock the ore’s inherent homogeneity. This paradigm change enables a move from costly, over-engineered sampling protocols to lean, precise, and economically optimized practices, fundamentally improving the efficiency and reliability of resource evaluation.”

This revolutionary news is cited from a recently published paper: “The Hidden Variable in Sampling Protocols: A Review of Liberation Evolution through Subsampling and Comminution” by Richard Minnitt and Pentti Minkkinen:

Minnitt, R., Minkkinen, P. The Hidden Variable in Sampling Protocols: A Review of Liberation Evolution through Subsampling and Comminution. *Math Geosci* (2026). <https://doi.org/10.1007/s11004-026-10292-y>

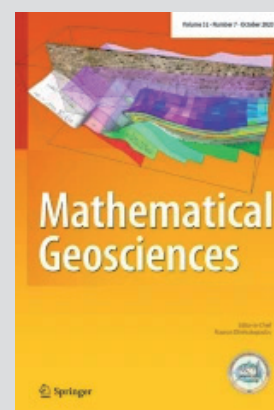
For readers of Sampling Science and Technology, this paper complements the discussion initiated in SST nr. 2 by Ana Carolina Chieregati, “A Brief Review of Heterogeneity Tests for Estimating the Variance of the Fundamental Sampling Error” (<https://doi.org/10.62178/sst.002.003>).

Enjoy reading this breakthrough achievement from two Pierre Gy Sampling Gold Medal awardees.

FURTHER READING

For decades, two powerful but disconnected theories have shaped how we estimate sampling error in mineral processing — with no bridge between them. Minnitt & Minkkinen now provide exactly that: a unified diagnostic framework that tells you whether your ore is truly heterogeneous or simply waiting to be unlocked through targeted comminution. The result is leaner, smarter sampling protocols.

<https://doi.org/10.1007/s11004-026-10292-y>



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- **Laboratory Assaying**
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- **Evaluation Services**
Sampling per Theory of Sampling (ToS / Pierre Gy) · bullion & sludge sampling
- **Smelting**
Au, Ag, Pt, Pd recovery from sweeps, slags, concentrates & anode slimes
- **Refinery**
Cast bars 9950-9999; 100 gm & 1000 gm; kilobars; granules; minted bars 2 g-100 g



RAND REFINERY

Review of Pitard & Pitard (2026): Theory of Sampling and Sampling Practice, 4th Edition (2026)

By Kim H. Esbensen¹

DOI: 10.62178/sst.005.011

A much-awaited renewal of Francis Pitard's monumental *Theory of Sampling and Sampling Practice*, 3rd edition (2019) was launched in February 2026. The fourth edition is the work of Francis and his son Maxime A. Pitard. This review compares the third and new fourth editions before assessing their scientific contents.

While the 3rd ed. totalled 693 pages (incl. References and Index), it is now achieved in 683 pages in the 4th. The core scientific text (38 chapters) has shrunk by 24 pages, but this is entirely due to a slightly smaller font and a denser layout and text deployment. While four references have been added in the 4th ed., the identical Index is still formidable and very useful (see why below). Two chapters are new, penned by the main author's son Maxime Pitard.

Unexpected surprise

The first 38 chapters of the 4th ed ... are identical to the 38 chapters in the 3rd ed! Both editions are massive, the List of Contents (LoC) alone comes to 20 pages! At first sight, this is overwhelming with a 4-tier organisation hierarchy: Part / Section / Subsection / Sub-Subsection. Indeed 20 pages is a bit exaggerated, since following the book's XIII Parts listing its 40 chapter titles gives a perfectly fine first overview with much less fuss. Still, for readers with a systematic mind, this level of detail may be welcome – and for any second (or third) reading, this meticulous detailing serves an important navigation purpose: any vaguely remembered topic can be found immediately.

The only organisational difference between the 3rd and the 4th edition (apart from adding the two new chapters) concerns minor, but important reorganisations within Part I “Introduction and a Management Strategy”, in which certain preface, introduction and historic summary sections have been stirred up a bit and served in a partly new order, which gives a better reading flow – as a much needed introduction to the

monumental task ahead of all readers. It is imperative to pay very close attention to this Part. For both editions, the last 2.5 pages of Part I becomes the vade mecum for the reader: “Subdivisions of the Text” is the booster rocket that propels the reader into getting off the ground right away. This is where an inspiring overview is to be found, a map for the reader's excursion into TOS: theory, practice and project management. The route through this vast terra incognita is unique to Francis Pitard.

For this reviewer it has always been a mystery why this highly circuitous route through all the core TOS presentations was devised this way. But this simply reflects the fact that there are many didactic roadmaps towards full comprehension of the Theory and Practice of Sampling. There exist other introductions to TOS' theory and practice on the sampling textbook market as well. Diversity is good for a discriminate readership with different abilities to follow the serious mathematical and statistical exposé in (the 3rd) the 4th edition.

Scientific scope

This is a scientific publication par excellence! It is a systematically worked through textbook, providing a complete introduction and very well-written development of the Theory of Sampling (TOS) and its application to a number of typical sampling objectives, e.g., sampling of precious metals and other analytes in trace concentrations, environment, moisture determination, particle size distribution metallurgical accounting, process control, blending monitoring a.o. with derived principles for ‘correct’ equipment design, implementation, usage, cleaning, maintenance and quality control. It is a pleasure for the reader to be treated to a com-

¹ KHE Consulting, Copenhagen, Denmark

prehensive historical view of the development of TOS through the lens of Francis Pitard's close collaboration with the founder of TOS, Pierre Gy through many decades, and to be invited in on the main author's unique grasp of the logical way to tie this together with the works of I. Visman and C.O. Ingamells into a single comprehensive framework. Nobody else could have done this without Pitard's enormous insight and experience, which is second to none in the world sampling community.

The 4th ed. is notable because of the two new chapters, one of which widens coverage of process sampling significantly and presents the all-important variographic data analysis and modelling tool in a renewed educational way. The 4th ed concludes with a refreshing graphic view on bias testing.

Scientific content

After having read the entirety of this book, this reviewer tried to come up with a condensed assessment of the 631 core pages involved but failed – it was simply too much. So instead, why not listen to the Maestro – it cannot be more focused than when it comes from author himself. THIS is the inspiring overview that compels you to want to read this book – and read all of it!

Addendum

The two last chapters are written by Pitard's son Maxime Pitard. Chapter 39 is an offering to the many readers without specific geostatistical training and competence, deriving the essential variographic understanding of the many variability components in process data, showing how variographics opens up for detailed insights in i) optimal sampling, ii) process monitoring and iii) process quality control. This didactic introduction is truly helpful for all novices to the intricacies of process sampling. Chapter 40 present a new educational packaging for bias testing, also giving a wider perspective on how sequential bias testing allows new insights regarding this critical characteristic: Is a particular sampling procedure biased, or not – but over which process interval does this conclusion hold up? This concluding chapter is a refreshingly new presentation of an approach originally proposed by Pierre Gy himself. This modern re-telling plus a highly informative graphic software (illustrated with instructive interpretations) is very useful for the reader. Bravo to the addendum!

Part I: Introduction and a Management Strategy

Because the prevention of any misunderstanding is essential, Chapter 1 has been devoted entirely to the definition of basic terms and notations.

Chapter 2 suggests a more effective management strategy based on a clear definition of structural problems (i.e., causes of problems) and circumstantial problems (i.e., effects generated by structural problems). The confusion between these two kinds of problems is costing alarming financial losses for many corporations around the world.

Part II: The Necessary Statistical Methodology

Chapter 3 is a refreshing presentation of important statistical concepts for the mining engineer, geologist, metallurgist, chemist, manufacturer of sampling equipment, regulator, or scientist who had little exposure to statistics. A careful reading of this chapter is essential before entering the complex subject of sampling.

Chapter 4 is a logical introduction to the components of the Overall Estimation Error OEE.

Part III: Heterogeneity and Homogeneity

Chapter 5 is a logical introduction to the notion of heterogeneity because it is a primary structural property of all materials we want to sample.

Chapter 6 is devoted to the heterogeneity of a zero-dimensional lot where a good understanding of Constitution Heterogeneity *CH*, and Distribution Heterogeneity *DH* is essential.

Chapter 7 is devoted to the heterogeneity of a one-dimensional lot and the notion of variography is introduced that is a critically important tool used throughout the book.

Part IV: Sampling Errors Introduced by Various Forms of Heterogeneity

Chapter 8 is an in-depth study of one-dimensional lots and an introduction to the continuous model.

Chapter 9 is an in-depth study of zero-dimensional lots and an introduction to the discrete model.

Chapter 10 is devoted to the Fundamental Sampling Error *FSE*, which is the minimum error possible involved in a sampling process of particulate materials. If something goes wrong there, then the sampling process becomes useless and vastly misleading.

Chapter 11 shows how to minimize the variance of the Fundamental Sampling Error *FSE* in sampling protocols, and an introduction to sampling nomographs.

Chapter 12 is devoted to the sampling for particle size distribution analysis. This chapter has a strong connection to Chapters 10 and 11 in its critically important applications.

Chapter 13 is an introduction to the Grouping and Segregation Error *GSE* and an in-depth study of segregation and its negative effects in sampling protocols and in processing plants.

Part V: Integration of Visman and Ingamells' Works into the TOS

Chapter 14 is an introduction to Visman's work.

Chapter 15 is an introduction to Ingamells' work.

Chapter 16 is an in-depth demonstration that Visman and Ingamells' works can be easily linked to the Theory of Sampling and actually add to it in a beneficial way.

Part VI: The Special Case of the In-Situ Nugget Effect

Chapter 17 is an introduction to a difficult problem in geostatistics when a constituent of interest clusters in an excessive way to the point that it becomes a sampling problem as well, although it is not the sampling of particulate material but the sampling of isolated clusters in unbroken materials.

Part VII: The Capital Notion of Sampling Correctness

Chapter 18 is an in-depth introduction to the Increment Materialisation Error *IME*.

Chapter 19 is a discussion about the various sampling modes that can be selected to implement a sampling protocol.

Chapter 20 is an in-depth study of the Increment Delimitation Error *IDE* taking place during exploration, mining and also when sampling the environment.

Chapter 21 is a review of the Increment Delimitation Error *IDE* taking place within processes.

Chapter 22 is a review of the Increment Delimitation Error *IDE* taking place at the laboratory.

Chapter 23 is an in-depth study of the Increment Extraction Error *IEE* taking place during exploration and mining.

Chapter 24 is a review of the Increment Extraction Error *IEE* taking place within processes.

Chapter 25 is a review of the Increment Extraction Error *IEE* taking place at the laboratory.

Chapter 26 is devoted to the Increment Preparation Error *IPE* and the notion of sampling integrity and the many problems it creates for contamination, losses, alteration of physical and chemical properties, training of personnel and possible fraud during the sampling of valuable commodities.

Part VIII: The Increment Weighting and Weighing Errors

Chapter 27 is an in-depth study of the Increment Weighting Error *IWE*, as good sampling systems and protocols must be reasonably proportional. Proportional sampling is the future of good sampling systems.

Chapter 28 is a review of weighing systems the incorrectness of them is indirectly connected to sampling problems. They are often a major source of reconciliation as people may not know exactly how much tonnage they process.

Part IX: Review of Some Notorious Sampling Problems

Chapter 29 is a review of a problem with a bad reputation in commercial sampling, which is the sampling for the determination of the moisture content. Companies often have severe disputes and even litigation on this subject.

Chapter 30 addresses the many peculiarities about the sampling of precious metals and other very heavy minerals.

Chapter 31 is a review of sampling practice for liquid and solid wastes and sampling of the environment.

Chapter 32 is a discussion about solvable and unsolvable sampling problems.

Part X: Chronostatistics

Chapter 33 suggests a strategy to take better advantage of existing chronological data.

Chapter 34 is devoted to the use of the variogram to elaborate meaningful process control charts.

Chapter 35 shows case studies where variography was an effective tool to discover sources of problems.

Part XI: Homogenization

Chapter 36 is an introduction to homogenizing processes.

Chapter 37 is devoted to bed-blending techniques.

Part XII: Recommendations to Manufacturers of Sampling Equipment and to Engineering Firms

Chapter 38 is a list of recommendations based on the contents of this fourth edition and will provide a quick check list to users of the TOS.

Part XIII: Addendum

Chapter 39 is a deep dive into the derivation of the variographic equation used throughout this textbook.

Chapter 40 is an introduction to an approach developed by Pierre Gy to visualize and interpret the results of a bias test.

Highlight (for this reviewer)

After the full theoretical and technical treatment in this excellent, indeed perfect textbook, chapter 32 shows up with quite a different tenor: “Solvable and Unsolvable Sampling Problems”.

After a very long career of practicing and teaching sampling science theory and the technology needed for solving practical sampling problems, Francis Pitard here vents quite an impressive amount of accumulated frustration as to why an overwhelming proportion of the world’s practical samplers, technicians, engineers, Original Equipment Manufacturers (OEM), management of individual companies and corporations, economists, regulators – you name it – have not gotten it yet: the benefits and the value of the Theory and Practice of Sampling. The main author has been involved in countless consulting projects, audits, and educational outreach enterprises – he knows the practical field intimately better than any other colleague (or competitor in the business realm). By way of the candid writing in this chapter, the reader comes away ‘feeling the same pain’. Anybody who manages to read the book this far will immediately feel the need to sign up for membership in the International Pierre Gy Sampling Association (IPGSA).

Conclusion

This textbook is unique, the only fully up-to-date, complete introduction to TOS. It is the most advanced written treatise on all aspects of sampling, at the highest scientific level. But it also states its intention to be comprehensible for any-and-everybody having understood that proper sampling is needed, for example the industrial engineer, metallurgist, geologist, miner, chemist, environmental scientist, academics too (TOS is still only taught as part of university curricula in but a few places worldwide) – as well for management (company, corporation) and for regulators and other relevant authorities. This is a tall order! This goal will depend on the effort the reader is willing to put in. Be this as it may, this book’s content cannot be recommended enough. It is clear Francis Pitard writes for his legacy – and the result could not be a finer scientific gift to the world!

And for those who might balk at its 683 pages and its elevated math and stat – get it anyway: It belongs on everybody’s professional shelf or desktop; it is (also) the ultimate HANDBOOK of sampling.

A grumpy postscript

There can be observed a few misquoted year-dating springled around, and some literature survey summaries appear to stop abruptly at the year 2017 (the 3rd edition was published in 2019). This could have been avoided, updating in an age where use of AI for mundane editorial work is acceptable.

However, the publication of a global standard: *DS 3077:2024 Representative Sampling – Horizontal Standard*, a significant achievement for the sampling community, especially for those seeking a condensed introduction to proper sampling in practice (which is the objective of international standards). But this standard is totally overlooked in this textbook, which is all the more surprising given that Pitard is the first author of a call for community action²: “IPGSA sampling competence: Crucial added value to international standards”. This a major disappointment!

This textbook is massive! Can one truly comprehend this monolithic curriculum by reading (it) alone? Besides, what can you do? Winston Churchill once stated: “You want me to speak – for how long? I can give a one-hour speech tomorrow, but if you only want a 10-minute speech, I must prepare for a week”.

It is not only that the book is massive, so is its price. For those brave enough to join forces with this reviewer in this mild criticism, every September you’ll find the evergreen Pitard grand course at Colorado School of Mines (CSM): “Sampling Theory, Sampling Practices and Their Economic Impact”³, a 5-day didactic bonanza covering the very same topics as found in the book – in fact the book is the course curriculum, handed out to all active paid-up participants. This course is second to none – see you there?

² https://www.saimm.co.za/Conferences/files/wcsb11-2024/30_WCSB05-Pitard.pdf

³ <https://proed.mines.edu/courses/sampling-theory-sampling-practices-and-their-economic-impact-c75n>

Contributors



Esbensen, Kim H.

Dr Kim H. Esbensen has been research professor in Geoscience Data Analysis and Sampling at GEUS, the National Geological Surveys of Denmark and Greenland (2010–2015), chemometrics and sampling professor at Aalborg University, Denmark (2001–2015), professor (Process Analytical Technologies) at Telemark Institute of Technology, Norway (1990–2000 and 2010–2015). From 2015 he phased out a 35 year academic career for a new quest as consultant and independent researcher. But as he could not terminate his love for teaching, he is regularly active as an international visiting, guest and affiliate professor. A geologist/geochemist/metallurgist/data analyst of training, he has been working 20+ years in the forefront of chemometrics, but since 2000 has devoted most of his R&D to the theme of representative sampling of heterogeneous materials, processes and systems: Theory of Sampling (TOS), PAT (Process Analytical Technology) and chemometrics. He is a member of several scientific societies and has published over 250 peer-reviewed papers and is the author of a widely used textbook in Multivariate Data Analysis, which was published in its 6th edition in 2018. He was chairperson of the taskforce behind the world's first horizontal (matrix-independent) sampling standard DS3077 (2013), 3rd. ed. soon to be inducted as an ISO standard. In 2020 he published the foundational "Introduction to the Theory and Practice of Sampling". Since 2013, he was editor of TOS forum and Spectroscopy Europe/World "Sampling Column", from 2024 amalgamated and metamorphosed into "Sampling Science and Technology" (SST). Kim received the Pierre Gy Gold Medal in 2013 and received the IPGSAs first Distinguished Service Medal in 2024.

✉ khe.consult@gmail.com

id <https://orcid.org/0000-0001-6622-5024>



François-Bongarçon, Dominique

Dominique François-Bongarçon graduated as a Mining Engineer and holds a Doctorate in Mining Sciences and Techniques at the Geostatistics Center from the Paris School of Mines (Paris Tech). He has more than 40 years of experience in the mining industry and works as a consultant in earth sciences for his own company, Agoratek International Consultants Inc., based in Canada. In 1992 he embarked on a career-long research in Gy's theory of sampling, and he worked with Pierre Gy as a consultant and on training courses. He contributed to the onset of the WCSB cycle of conferences (2003). In 2009, he was the recipient of the Pierre Gy Sampling Gold Medal. In recent times, he has been continuing his research in Sampling Theory, in the techniques and spirit of the QA-QC discipline and on mine-mill reconciliations. He is also making new advances in the handling of extreme grades in Geostatistics.

✉ dfbgn2@gmail.com



Larsen, Jon

Jon Larsen has a crazily mixed background: jazz musician (guitar player, composer, record producer), painter (surrealism), mineralogist (micrometeorites). Since 2009 he has focused on project “STARDUST” in which, in 2015, he succeeded in developing a method for extracting micrometeorites and cosmic particles from urban dust, leading to the discovery of the first array of urban micrometeorites, an achievement that was rated among the 100 most important events in 2017 in Discovery Magazine. Today he studies micrometeorites as an associated senior researcher at the University of Oslo (UiO) from where he collaborates with a wide group of international experts in the field. He is a very popular lecturer, and a dynamo within the online international micrometeorite community, where he posts almost daily updates of new stardust photos and info on Facebook. The STARDUST project has been presented in The New York Times, The Economist, National Geographic, Washington Post, 1843 Magazine feature as well as hundreds of regional newspapers and magazines worldwide. His international recognition is based on close collaboration with mineralogist and eminent photographer Jan Kihle. The first paper on the discovery of the urban micrometeorites was published in Geology (<http://geology.gsapubs.org/content/early/2016/12/05/G38352.1.abstract>). He has since published four books about these exotic space rocks and *how* to find them. Each one deals with a different aspect of finding, identifying, and verifying micrometeorites as well as curating collections: “In Search of Stardust”, “Atlas of Micrometeorites”, “Star Hunter” (The story about the discovery of the urban micrometeorites) and “On The Trail of Stardust” (Illustrated field guide about tools, techniques, and methodology). Mr. Larsen has an asteroid named after him: 63788 Jonlarsen and a mineral: Jonlarsenite.

✉ jon@treasuresfromspace.com



Minnitt, Richard

Dick Minnitt completed a MSc in geology in the Murchison Range and a PhD in the Richtersveld regions of southern Namibia. He joined Anglo American and later JCI, after which he spent 14 years doing contract and consulting work. He completed a second MSc in mining, and joined the School of Mining Engineering at WITS in 1995, where he taught courses in Mineral Economics and Geostatistics. His interest in sampling of particulate materials arose from the numerous visiting lecturers he invited to Wits University including Dominique Francois Bongarçon, Francis Pitard, Geoff Lyman and Kim Esbensen. Dick retired from Wits in 2017, but continues to consult for international mining companies and research in his fields of interest. He now holds a position as a Visiting Emeritus professor where he continues to teach postgraduate classes and supervises masters and doctoral students.

✉ Richard.Minnitt@wits.ac.za

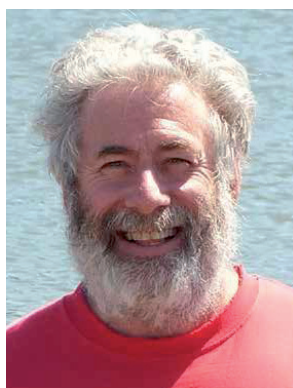
🆎 <https://orcid.org/0000-0002-0267-8152>



Oliver, Robert

Robert is Director of Laboratory & Technical Operations at ElementUSA. Coming from a background of industrial chemistry and extractive metallurgy, he has spent over 15 years working both in assay laboratories and in minerals processing plants in Australia, Southeast Asia and North America. Rob holds a BSc in Industrial Chemistry from QUT, a Graduate Diploma of Metallurgy from WASM and an MS in Nuclear Chemistry from Tennessee Technological University.

✉ ra.oliver@connect.qut.edu.au



Ramsey, Charles

Chuck Ramsey is the founder of the company EnviroStat, Inc. (www.envirostat.org). EnviroStat provides specialised training in the areas of field (bulk) sampling, laboratory subsampling, statistics and quality control. EnviroStat's approach integrates all facets of sample plan design, implementation and data interpretation. EnviroStat's methodology has been used by various state and federal government agencies as well as private industry for over 20 years to improve sample representativeness and defensible decisions.

✉ chuck@envirostat.org



Sennet, Tim

Tim Sennett is a mining technology specialist with more than 35 years of experience in the global resources sector, focused on analytical technologies for on-line measurement systems and laboratory analysis.

He currently serves as Technical Services Team Leader at Chrysos Corporation, where he supports the global deployment and optimisation of PhotonAssay™, Chrysos' award-winning technology that is transforming gold analysis through faster, safer and more environmentally sustainable methods.

Prior to joining Chrysos in 2019, Tim held senior technical and commercial roles with organisations including CSIRO, Thermo Fisher Scientific and Amdel, building deep expertise across mining and mineral processing operations, geostatistics, instrumentation and assay technologies. Based in Perth, Western Australia, he combines strong technical capability with commercial leadership, helping mining companies improve operational efficiency, data quality and decision-making.

Tim holds a Bachelor of Science in Physics and an MBA and is a regular presenter on innovation and analytical technology within the mining industry.

✉ tim.sennet@chrysoscorp.com



Tickner, James

Dr James Tickner is Chief Scientist and a co-founder of Chrysos Corporation. He heads the Science and Innovation team responsible for developing Chrysos' next-generation products. Previously, as Chief Technology Officer he was responsible for the development of Chrysos' flagship PhotonAssay technology.

Before Chrysos, he worked for 18 years at the Commonwealth Scientific and Industrial Research Organisation (CSIRO), leading a team of researchers and engineers developing radiation-based instruments for challenging measurement and image problems in the minerals and security industries. Technologies invented and commercialised by his group include on-stream X-ray analysis systems, on-belt neutron-gamma analysers, a novel fast-neutron Air Cargo Scanner and Chrysos' PhotonAssay.

Significant career awards include the Prime Minister's Prize for Innovation, the ATSE Clunies Ross Technology Innovation Award, the CSIRO Chair's Medal, the Eureka Prize for Science in Support of Defence or National Security, and the Australian Academy of Science Frederick White Prize. In 2024, he was elected as a Fellow of the Australian Academy of Technological Sciences and Engineering.

Dr Tickner has a degree in physics and a D.Phil in particle physics from Oxford University. He has authored more than 110 papers and articles in the fields of particle physics, nuclear instrumentation, data analysis and simulation and is a holder of numerous patents.

✉ james.tickner@chrysoscorp.com

How to contribute

Sampling Science and Technology (SST) serves as a collaborative platform fostering scientific and technological engagement within the global sampling community. Our primary objective is to have a significant educational impact, catering to various levels of interest.

SST embraces didactic studies, practical insights, illustrative case histories, and occasional theoretical articles tailored for the sampling community in both strict and broad senses. Your valuable contributions play a pivotal role in our mission to cultivate professional sampling competence across diverse societal sectors where sampling holds significance — spanning science, technology, industry, trade, food/feed, public health, and more.

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If you have scientific questions regarding a contribution, please contact the Editor-in-chief at khe.consult@gmail.com.

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Editorial Staff

Editor-in-Chief: Kim H. Esbensen, V.i.S.d.P (Person responsible according to the German Press Law)
E-mail: khe.consult@gmail.com

Editorial Asst.: ReConsider
E-mail: anne@reconsideredit.com

Contributors: Joel Chuah
Kim H. Esbensen
Dominique François-Bongarçon
Jon Larsen
Richard Minnitt
Robert Oliver
Chuck Ramsey
Tim Sennett
James Tickner
Andrew Weatherstone

Advertising Sales and Sponsorship Coordination:
Benedikt Dolzer and Kim H. Esbensen
E-mail: advertisment@sst-magazine.info

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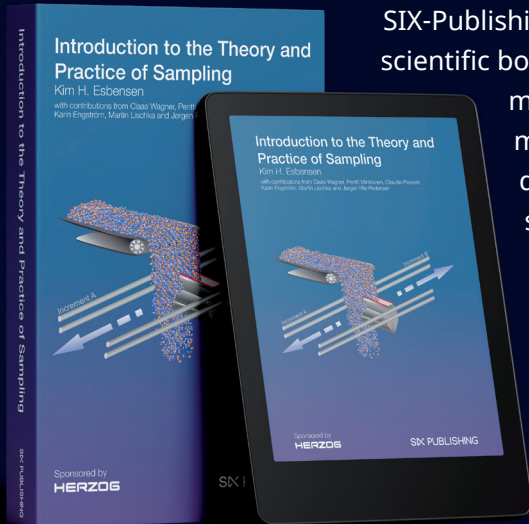
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