

The Fundamental Sampling Principle (FSP) for PAT

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DOI: 10.62178/sst.004.005

ABSTRACT

The critical success factor in Process Analytical Technology solutions, whether this is in the form of analysis of an extracted process sample brought to the laboratory, or in the form of a calibrated sensor analytical prediction characterising an in-situ stream segment, is the performance of the process sampling interface. The role of the interface is closely related to the Fundamental Sampling Principle (Theory of Sampling, TOS) regarding both stationary as well as moving lots. This article argues that the functionality of the process sampling interface determines whether Process Analytical Technology solutions can be implemented to furnish analytical fit-for-purpose representativity, or not. Non-compliance with a simple geometrical requirement results in biased analytical determination with unavoidable reduction in representativity. This criterium determines the fate of Process Analytical Technology solutions and their engineering implementations for most vibrational spectroscopic modalities. Thus, a single TOS-informed inspection of a process sampling interface is able to render a principal qualifying/disqualifying assessment regarding representativity – but there are important exceptions in the radio wave and gamma ray parts of the electromagnetic spectrum. This is all about the inherent heterogeneity of the material subjected to PAT sensor technology. This article presents TOS' Fundamental Sampling Principle for the Process Analytical Technology realm. There is still a way to go for further process sampling interface development.

1. Introduction

The Theory of Sampling (TOS) distinguishes between two types of lots, stationary vs. moving lots; sampling from the latter is also known as process sampling. Process sampling is a core element in Process Analytical Technologies (PAT): samples are either extracted and brought to the laboratory for analysis, or – the ultimate PAT goal – an analytical sensor facilitates 'spectral characterisation' of a material process sample without bringing anything to the laboratory.

This article presents the apparent duality between a physical sampling process and a PAT spectral sampling-and-analysis equivalent 'spectral sampling', Fig. 1, intended to help appreciating the key role of the process sampling interface (PSI) to be more fully explained. The key understanding is that both the 'dual' sampling approaches (physical vs. spectral) are subject to – and can be characterised by the same TOS sampling errors.

2. Physical sampling

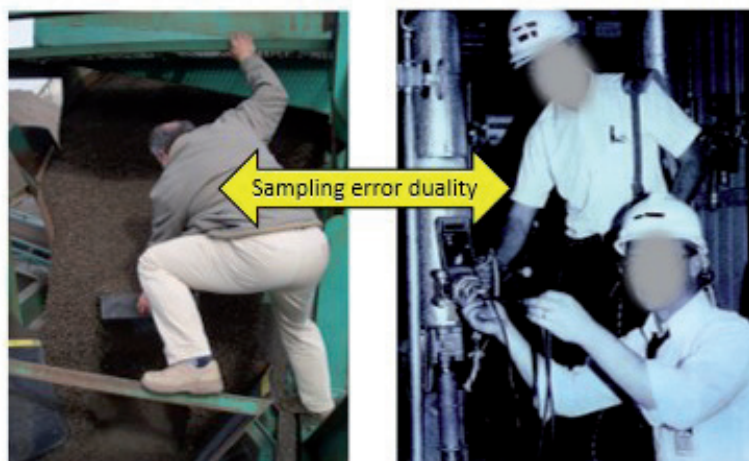
In the TOS realm, process sampling is traditionally thought of as how to extract a physical sample from a moving stream of matter (a process lot), aimed at subsequently to be characterised (analysed) in the laboratory [1–4]. For the present purpose there is no need to focus on the subsequent sub-sampling steps/operations involved in getting to the final analytical aliquot as these steps are governed by the exact same TOS principles as the primary sampling step, only scaled down, size-wise [5,6].

3. Fundamental Sampling Principle (FSP) for stationary lots

The FSP stipulates that all potential increments of any lot shall have an equal probability for being physically extracted and aggregated to form a composite sample under the condition that the extracted Q increments must cover the entire lot volume with a uniform density.

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A fundamental sampling duality: Physical increment/
sample extraction vs. sensor signal acquisition (PAT)



TOS: Identical sampling errors with, as without sensor technologies (PAT)

Figure 1: The apparent duality of physical sampling from –, and spectral characterisation of a process stream. With TOS' discriminating point-of-view, 'sampling' may be correct and representative or it may be imperfect, biased and therefore not representative. In Fig. 1 both illustrated sampling operations are non-representative (complementary representative sampling modes are shown in Fig. 3). *Caveat: examples are meant for illustration of principles only; no identification of company, personnel or equipment brand is intended).*

It is not only the number of increments that define the quality of the composite sample, but equally their mandated geometrical coverage. Both these attributes need to be optimised in order for the resulting composite sample to be representative of the whole lot.

Note: The representativity status of an individual sample cannot be ascertained if removed from the context of its sampling-and-analysis pathway. It is not possible to discern the representativity status of any sample in isolation. The attribute 'representative' can only be accorded to a sampling process if/when in compliance with all demands specified by TOS.

Fig. 2 shows a generic stationary lot (a schematic upper half-sphere is a stand-in for a general stockpile), showing the number of increments (Q) to be extracted to form a composite sample; for details on how to determine the optimal Q , see [2,3,5]. The sample to be extracted from an original lot is called the primary sample, which can be either a grab sample (a 'specimen' in TOS' language) or a composite sample (always to be preferred). TOS describes how grab sampling cannot be representative under any condition, for which reason only composite sampling is allowed [7,8].

Fig. 2 is a graphical rendition of the Fundamental Sampling Principle (FSP) for stationary lots, which is compared with its process lot equivalent below.

4. PAT sampling / Sensor analysis

If the primary sampling step were to be effectuated in the PAT realm, process sampling would be in the form of acquisition of a spectral characterisation of a segment of the moving stream of matter. The support for this spectral characterisation could be an extracted physical increment (a segment extracted from the moving stream) or it could be an in-situ segment of the moving flux (in-situ process increment). In the latter case, the desired PAT situation, the role of a process sampling interface comes to the fore.

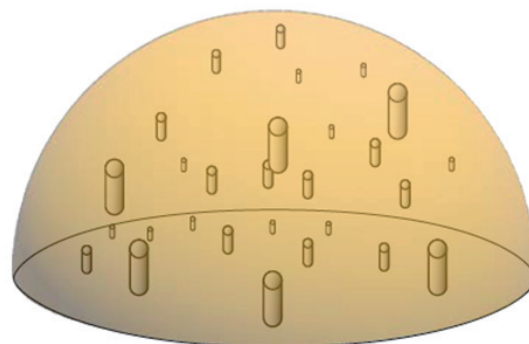


Figure 2: Graphical rendition of the Fundamental Sampling Principle (FSP) for a stationary lot. The Q increments to be extracted must cover the full lot volume with a uniform spatial density.

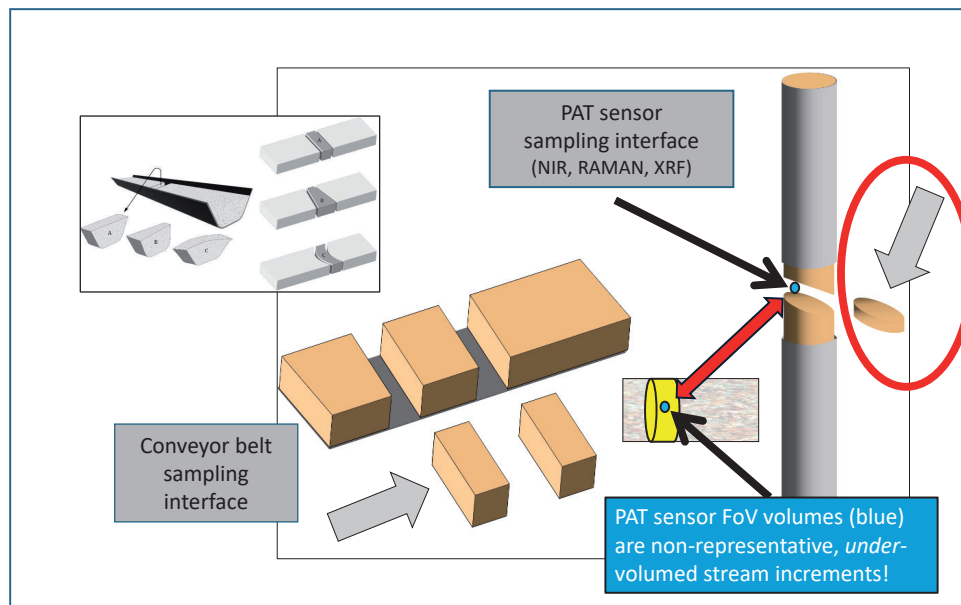


Figure 3: Graphical rendition of the Fundamental Sampling Principle (FSP) in the PAT realm, governing the role of the process sampling interface as either delineating i) transverse conveyor belt increments, or ii) facilitating equivalent cross-section increment cuts from ducted flow through a pipeline, the geometry of which is colloquially termed an ‘ice-hockey puck’.

Below is demonstrated the critical importance of proper stream segment delineation for 1-D moving lots, either of the conveyor belt – or the pipeline type, Fig. 3.

The primary role of the process sampling interface is to delineate either a transverse conveyor belt increment, or to facilitate delineation of the equivalent cross-section cut from ducted flow f.ex., through a pipeline; this latter volume is colloquially known as an ice-hockey puck. It is convenient to imagine this puck volume moving along with the ducted stream. Note how the ideal orthogonal transverse increment traces (the ‘stopped belt increment configuration’) across the stream become oblique because the increment cutting is taking place when the process stream is moving. This has no effect on the quality of cross-stream cuts; fully realised oblique cuts are equally good representatives of a complete slice of a flowing stream.

The TOS literature is abundant with serious warnings that the practical way many cross-belt samplers are designed and implemented are in fact biased and cannot deliver representative increments [2,3,5]. Fig. 4 is an anonymised illustration of a so-called hammer sampler – unfortunately popular in many practical installations in the mining and minerals processing industry, likely because of aggressively marketed low costs. But cost is not a driver for representativity!

The hammer sampler is an example of a Process Sampling Interface (PSI) for material streams conducted on conveyor belts, or on gravity driven or vibrating slides a.o. Fig. 4 serves to illustrate the important point that although the concept of a correct process increment may appear simple (like in the left part of Fig. 3), practical designs and implementations are not necessarily successful without OEMs being fully competent with respect to TOS. The underlying demand is of being able to extract a cut in the form of a full slice of the streaming matter (explained in full detail below). The issue here is about due diligence regarding the non-negotiable need to eliminate the two Incorrect Sampling Errors IDE and IEE during increment cutting – which is not the case for cross-belt samplers, while fully complied with for cross-stream samplers. For the present purpose it suffices to note that the physical realisation of increments can be lacking regarding representativity even for the apparently simple case of 1-D lots moved by conveyer belts: unmitigated Incorrect Sampling Errors may easily generate a biased sampling procedure, assuredly non-representative, see [2,3,5,7,8] for full introduction to TOS’ arguments.

The similar situation regarding a material lot experiencing ducted flow, e.g., through a pipeline can be used to present the increment geometry needed to comply with the full cross-section demand, materialising a full slice.



Figure 4: Anonymised illustration of a particularly popular type of cross-belt sampler, the hammer sampler. For very many designs, brands and implementation this type of equipment cannot deliver a representative cross-belt cut, as extensively described, documented and warned against in the TOS literature [2,3,5]. *Caveat: this example is meant for illustration of principles only; no identification of company, personnel or equipment brand is intended.*

For a PAT solution designed to extract a representative physical sample from a pipeline flow, the full slice increment demand translates into the form of a warped ice-hockey puck, Fig. 3 (righthand side). At present there are no OEM PAT solutions in compliance with this demand; there does not exist a physical equivalent to the archetype cross-stream cutter able to cut and extract a correct warped puck slice from a pipeline flow! But contending alternatives have been put forward trying to obtain a closely similar solution, e.g., by using a bypass loop. Alas ...

However, the vast majority of PAT solutions being offered today are designed around using an analytical sensor, a probe, either to be inserted into a pipeline ducting the 1-D lot, Fig. 1., or this solution is realised by way of a Process Sampling Interface (PSI), Fig. 5.

One of the much-lauded advantages of the 'PAT revolution' is that application of sensor technology eliminates the need for sampling, i.e. eliminates the need for extraction of a laboratory sample. While the latter is true, the first is very much not [9,10-12] – to be explained below.



Figure 5: Examples of process sampling interfaces (PSI) designed to be installed as part of ducted flow. Note how flanges allow flush implementation in pipelines, while offering openings and fixtures allowing to project sensor radiation orthogonally across the material flow a.o. *Caveat: these examples are meant for illustration of principles only; no identification of company or equipment brand is intended.*

5. The PAT realm

In the PAT realm, the role of the process sampling interface (PSI) is dual:

1. Correct delineation of representative process segments to be analysed
2. Facilitating analytical interaction of a beam of sensor radiation with the material support volume realised by the sensor FoV

The potential mismatch between delineated vs. realized analytical volume is the key topic of this article.

Here is the crucial issue:

Is the PAT sensor radiation beam able to interact analytically with the full support volume (puck volume) delineated by a specific PSI? If yes, the PAT system is unbiased (sampling wise) – if no, the PAT system is biased (to an unknown degree), because being fraught with unmitigated IDE/IEE deficiencies; full background argumentation in [9,10–12].

5.1 Terminology overview

In order to avoid unnecessary confusion, a distinction must be made between no less than three types of sampling:

1. Physical sampling, which could be called $\text{sampling}_{\text{TOS}}$
2. PAT sensor sampling, which shall be called $\text{sampling}_{\text{PAT}}$
3. Statistical sampling, which could be called $\text{sampling}_{\text{STAT}}$

The many different usages and meanings of the term ‘sampling’ is a historical result of independent development in diverse scientific disciplines; the reader is referred to [13] for in-dept discussion. Here we only need to focus on the relationship between the first two variants: $\text{sampling}_{\text{TOS}}$ vs. $\text{sampling}_{\text{PAT}}$.

5.1.1 The many meanings of the term ‘sample’

TOS stipulates that the term ‘sample’ shall only to be used in the meaning of a representative sample. This ties in exactly with TOS’ other liberating imperative, that only a sampling process can be assigned the attribute representative – Ergo: a representative sample cannot be defined by any inherent attribute but is to be defined solely as the product of representative sampling processes. This goes for both stationary and moving, dynamic process lots – and in the laboratory as well, where samples are usually affixed with the prefix “sub” (sub-sample).

All types of extracted material portions that cannot be shown to be the result of a representative sampling process shall, in the name of clarity, henceforth be termed ‘specimens’. Sub-samples derived by a non-representative mass-reduction process in the laboratory may well also have to be termed sub-specimens ...

For the present purpose, there is one last specification of importance in order to appreciate the current topic: “There are sample cells – and there are sampling cells” (the latter in the form of a sampling interface (PSI)). To highlight this crucial distinction, please compare Figures 5 and 6.



Figure 6: Illustrations of a number of sample cells; compare with Fig. 5. Caveat: these examples are meant for illustration of principles only; no identification of company or equipment brand is intended.

There is empowering clarification in acknowledging the distinction between a sample cell, into which is placed an already sampled aliquot, and a sampling cell (a sampling interface) the task of which is *both* to delineate the increment to be analysed and to facilitate sensor beam interaction with precisely this material volume flowing through the interface [7,8].

Sensor radiation travelling through the PSI, as well as absorbed and reflected signal impulses, define an 'analytical pathway' through the geometrically delineated increment volume. For the present purpose it is useful to imagine this pathway in the form of a (roughly cylindrical) radiation beam penetrating from one side to the other of the increment boundaries, extending across a full cross-section distance. Contrarily, the penetration depth of reflection spectroscopic modalities (diffusion reflection, specular reflection) will only extend along a fraction of this distance, effectively interacting with only a reduced volume element in front of the sensor head, see Fig. 3 (blue circles).

As exemplification, the following argumentation focuses on NIR spectroscopy: The vagaries of NIR penetration depth(s) were described powerfully in the 'Handbook of NIR Analysis' (4.ed) [12], from where a famous quote will help to make explain the situation (p. 434-435). Concerning analysis of a powder mixture:

"The NIR beam penetrates perhaps as much as 5 mm within the powder mixture. But the radiation that returns to the NIR spectrometer is mostly from the top 2 mm of a typical sample cell. The material in the sample cell may have to be analysed by a reference method (a HPLC method for example or other), which typically has the entire aliquot (extracted increment) volume as its support. If not carefully choreographed, a systematic support volume mismatch error will be committed because the support volumes analysed with different methods (PAT vs. lab reference) are not identical. It also needs to be considered that as the radiation interacts with the top layers, less radiation will be available to interact with the bottom layers of material. The amount of material analyzed may be less in the lower layers of material. In TOS' parlance this is a classic IDE/IEE, here termed a support volume mismatch error in a new disguise in the PAT realm, which did not exist when the classic sampling errors were defined and named in TOS".

The advent of this type of volume mismatch error will open up for clarification re. the TOS-PAT interrelationships, which are the main present topic.

"The mass analysed by the radiation may be estimated in some cases, ibid., but is generally not known in detail. Most analytical chemists know exactly the material that is analysed. In NIR spectroscopy, the situation is rather the opposite. Indeed, NIR spectroscopists are spectacularly the most successful analysts that do not know the exact sample mass being analysed!"

Now, what is the case for NIR spectroscopy can also occur for any other PAT spectroscopic modality for which penetration depth is a function of a.o. material density, composition, physical make-up (grain size distribution), top-bottom self-shielding a.o.

The only exception would be by penetrating radio waves, which is much used for volume moisture determination – and, at the other end of the electromagnetic spectrum, very energetic gamma ray Neutron Activation Analysis (NAA) for example, see the article by Kurth in this issue.

5.2 TOS as a contributor to PAT

The Theory of Sampling (TOS) is the comprehensive, necessary and sufficient framework stipulating the principles, unit operations and error management rules necessary to be able to extract a representative physical sample from any stationary lot [1,2,3,5]; the exact same framework guides sampling and sub-sampling in the analytical laboratory as well [6-8]. TOS is comprised of six Governing Principles (GP), five Sampling Unit Operations (SUO) and a set of Sampling Error Management rules (SEM) [5,10,11]. For the purpose of illustrating the interrelationship between sampling TOS and sensor sampling PAT it suffices to introduce the GP#1 and SUO#2, the Fundamental Sampling Principle (FSP) and the sampling process termed composite sampling, respectively. Both these elements were illustrated in Fig. 2. A quick overview of the entire TOS framework is given in [8].

Because there is a physical limit for the possibility of sampling 3-D lots (stockpiles) according to the FSP as lot size goes up, it is instructive to note how TOS goes about facilitating how to extract the 'internal' Q increments in practice – TOS's principle 'Lot Dimensionality Transformation' to the fore: The 'impossible-to-sample' 3-D lot is instead placed in a 1-D transportation modus, e.g. placed on a conveyor belt, whence all Q internal increments will eventually be available for sampling when passing muster in front of a suitable process sampling facility (not a cross-belt sampler, but a representative cross-stream sampler – or a fully-fledged PAT solution).

In this fashion Lot Dimensionality Transformation will make all internal increments available for either physical extraction, $\text{sampling}_{\text{TOS}}$ – or will present these as stream segments readily available for $\text{sampling}_{\text{PAT}}$. This operation is also what opens up for variographic process characterisation – the most powerful part of process sampling [2,3,5,9–12]; see the article by Romanach in this issue on ‘how pharmaceutical discovered variographic process characterisation’.

A highly beneficial advantage with TOS is that the basic how-to-sample framework for stationary lots can be directly carried over to the realm of process sampling as well [5,9,10], described more fully in [10–12]. A broad-scoped literature illustrating TOS’ role when applied in PAT can be found in [11,12,14–18].

But in the PAT realm, does the PSI design allow the sensor beam to interact with the entire ice-hockey puck volume? This is the (critical) question ...

5.3 Preamble to the key discriminating argument for assessing PAT solutions

All stream increments must be cut in the form of a full slice of the moving, or ducted, material (visualised in the form of an ice-hockey puck) because the material stream is heterogenous: There is no guarantee that a material stream ipse facto has a homogenous cross-section. If/when a sensor is only able to analyse a part of the necessary puck volume, Fig. 3, this is a lack of analytical due diligence. Systematic parts of the series of pucks passing in front of a PAT sensor head, i.e. those parts not intersected by the analysing beam volume, will never be able to contribute to the sensor signal. This means that the sensor signal cannot be representing the full series of cross-sections of the flowing 1-D lot – which is tantamount to saying that the whole 1-D lot is structurally not being represented. This type of beam-limited $\text{sampling}_{\text{PAT}}$ configuration is not representative. An attempt to illustrate current beam vs. cross-section geometries for many PAT solutions offered (and incorrectly championed) on the marketplace has been compiled in Fig. 7 below.

It is fair to point out that in the PAT community there is considerable debate as to how debilitating the heterogeneity argument above is in practice. For example, it is often stated that in ‘many industrial situations’ the unit operation ‘mixing’ has been invoked thereby reducing the heterogeneity of the streaming matter: “sensor results may still give a good indication of the current state of the system, which is not possible with end-of-process testing”. While such arguments may be of merit in specific cases (above all typically in the pharmaceutical realm), this is not a justification for liberal generalisations, as there are indeed an almost unlimited number of types of powders This is rather a matter for practical empirical justification, enter the Replication Experiment (RE).

5.4 The discriminating PAT argument

The degree to which an implemented PSI creates a sensor beam pathway across the increment cross-section in such a way the analysing volume fails volumetrically to correspond to the full ice-hockey puck geometry, thereby leaving parts of the increment volume without the possibility to interact with the analysing radiation, is a manifestation of a classic bias-generating IDE/IEE. The PAT sensor advantage runs a high risk of being forfeited on the grounds of a volume mismatch alone – unless the specific sensor solution has been thoroughly vetted by a dedicated Replication Experiment (RE). The key argument is pivoting around the volume mismatch between the sensor analysing beam volume (the location and implementation of which is an integral part of the geometrical design of the PSI) and the stream increment delineated simultaneously by the PSI.

The case where a sensor’s active analysing volume does not penetrate fully across the cross-section, shown in Fig. 3 as the blue volumes immediately in front of the sensor heads, is likely the largest potential volume mismatch error imaginable. Clearly what the sensor ‘sees’ in such cases is only a very small part of the fully delineated increment volume. There is manifestly no way the spectroscopic sensor signal from such a PAT solution can claim to be representative of the complete puck volume.

The above analysis of the PSI geometry necessary to guarantee representative sensor signals pertaining to the full cross-sections of moving heterogeneous 1-D flows leads to a definition of what shall be termed the Fundamental Sampling Principle (FSP) for the Process Analytical Technology realm (PAT).

5.5 The Fundamental Sampling Principle (FSP) for PAT

The 'identical volumes' demand constitutes the PAT realm equivalent to the Fundamental Sampling Principle (FSP) for stationary lots. IF/WHEN the analysing sensor volume (radiation footprint x effective penetration dept = ~ radiation beam volume) is not identical to the volume of the full delineated increment geometry (box, ice-hockey puck, orthogonal or warped), there are unavoidably significant fractions of each increment (the sampled flow segment) which is structurally unable to contribute to the sensor signal – which makes the PAT sensor signal biased. Despite many hopeful, but ill-informed claims that powerful chemometric data modelling (specific data pre-processing) can correct for a spectral sampling bias, the TOS explains with scientific logic and force that no sampling bias can ever be corrected for a postiori by any means; the interested reader can find a comprehensive exposé and full argumentation in a recent 'Perspective' paper [7].

The reason behind the 'equal volumes' imperative follows from the fact that all materials met with in science, technology and industry are heterogeneous – it is only a matter of to which degree, and at what scale [1–5]. Heterogeneity constitutes one of two main hurdles for representative sampling (the other is grab sampling, which can never be representative and which is therefore never an acceptable sampling procedure).

5.6 Heterogeneity – the adversary that easily may destroy PAT solutions

There is never a guarantee that a contemporary cross section of a moving flux of matter is homogenous. Material heterogeneity is a 3-D characteristic (at all scales). But when the width-depth heterogeneity of a streaming or ducted material is 'covered' completely by a correct geometrical form/volume extraction of the sampling increments, this is successful process sampling without IDE/IEE. This leaves only the remaining 1-D heterogeneity along the transportation direction to be dealt with – which is exactly the objective of process TOS.

Any vibrational spectroscopy modality being channeled by way of a PAT sensor is subject to the FSP for PAT. In Figure 3, note that a sensor can have a limited penetration depth, oftentimes resulting in what can only be described as sensor grab sampling (blue volumes in front of sensors). It is regrettably fair to say this insight is not widespread within the PAT community, nor in the relevant OEM industry.

To bring home this sweeping statement, Fig. 7 shows many examples of PSI configurations in which the radiation beam pathways are manifestly not identical to the contemporary increment volumes (all examples are culled from [20], but brought here in anonymised form).

5.7 Is all lost? – What can be done?

There are many PSI designs in use as part of a plethora of PAT solutions offered on the market, but many are regrettably afflicted with the IDE/IEE flaws pointed out in this article. Is there any chance some of them can still be used without sampling biases ruining the(ir) complete business? There is both good news (YES) and bad news (NO)!

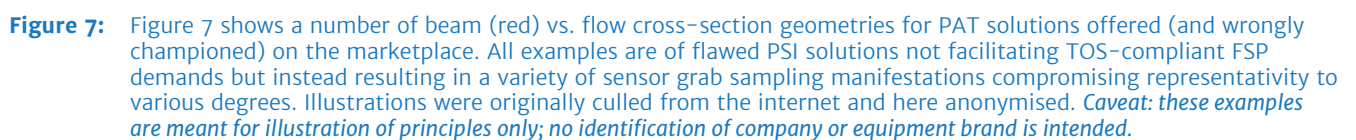
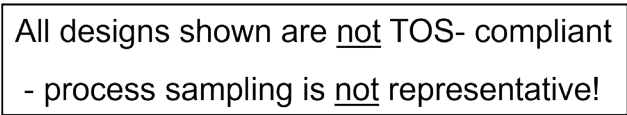
The capital question: "Is the performance of *this* specific PAT solution [your company / equipment / brand name here] acceptable, or not, can be answered very easily by applying the Replication Experiment facility. This will render an authoritative verdict w.r.t. fit-for-purpose representativity: pass or fail.

5.7.1 Replication Experiment

The Replication Experiment (RE) is described in a number of TOS publications at all levels, e.g. [2,5,7,8,12], of which [5] is likely the most relevant in the present context: DS3077, 2024, (p. 55–57). The simple RE delivers a %-age quality index for comparison with an a priori fixed representativity threshold, below which the particular performance can be declared fit-for-purpose, while a higher index value (higher %-age value) signifies that this quality attribute has been forfeited, i.e. the sampling method tested is not representative. Not testing existing PAT solutions with the simple RE facility is tantamount to not performing analytical due diligence!

5.8 Heterogeneity – good or bad?

The unresolved situations described above are caused by cross-section material heterogeneity which reduces the penetration depth performance of PAT sensors. But, on the other hand, on-line PAT solutions are highly valuable in enabling efficient process/product monitoring allowing inherent heterogeneity along the process transportation direction to be controlled to the benefit of many technological and commercial objectives; these advantages are described in more detail in [9,11,12]. So is heterogeneity a friend, or an enemy?



All materials, process intermediates, products of interest in technology and industry are characterised by a significant (:= not neglectable) heterogeneity, which may differ in nature and magnitude across the infinitely many materials met with in science, technology, industry, commerce, trading, society, but which must never be willingly ignored. For all these the Fundamental Sampling Principle for PAT cannot be ignored, lest a sampling bias be created, which will also characterise the final analytical results. In all these situations, there is no rescue: If-and-when the Replication Experiment does not return the verdict fit-for-purpose, the tested PAT solution does not live up to its representativity obligation. In all such cases there will be practical and indeed painful economic consequences to be faced!

6. Some relief – after all

However, there are redeeming issues that may bring relief.

As heterogeneity goes down, PAT systems merit go up. Indeed, many current PAT solutions and types of equipment were originally designed for expressly manifest low heterogeneity (liquid, two-phase systems, slurries) cases only.

Many current PAT solutions owe their success to the fact that these are only addressing materials with ‘practically neglectable’ heterogeneity. There is an enormous range and contrast concerning inherent heterogeneity across the almost infinite number of materials for which analytical determination within the PAT scope is of interest (or will potentially come into interest, as technologies develop). Heterogeneity ranges from extreme, high, intermediate, significant, low – to ‘practically neglectable’. Baring the last, this article specifically addressed the realm of significant heterogeneity (because this is where the biggest scientific and technological challenges lie) and illuminated the dire consequences if/when sampling is based on procedures and equipment not in compliance with TOS.

Fig. 7 show that a large proportion of current PSI geometries suffer from significant volume mismatch IDE/IEEs. This is an inconvenient truth which is better faced directly than attempted to be sweet-talked away: “My materials are only of (very) small heterogeneity ...”; “My materials are (always) very well mixed ...”; “In Pharma we are only processing and sampling already well-mixed, low heterogeneity powders ...”

While such Hail Marys may be true (in specific cases), they could just as well just represent a tradition for ignoring the hard problems illuminated in this article. Without being subjected to a stringent RE, many current PAT solutions are of inconclusive merit.

Although gas mixtures are often considered to be of very low heterogeneity, gas systems also have special challenges [20]. Sampling and analysis of materials in the gas phase is not covered in general sampling standards and guides, due to the often complex sampling conditions experienced. Most gas-phase materials exist in the region from ambient temperatures (~300 K) to combustion temperatures typically around ~1200 K. Common to both temperature margins, though predominantly for hot gases, or smokes, is the fact that continuous reactions often take place in material moving at high speeds, as well as when samples are cooling down to ambient temperatures, e.g. due to condensation at different dew point temperatures, *ibid*.

7. Going forward

PAT is not a finished, fully developed enterprise, on the contrary. The interesting scientific, technological and commercial challenges mainly lie where forward-looking agents are searching to transgress today’s boundaries for PAT application – necessarily often with respect to innovative technological developments trying to deal with increasing material heterogeneity, as more and more new product categories come into view under industry 4.0

But developments are also closely related to continuing analytical developments, which have been left out completely in this article. There is great inspiration to be found in a recent complementary review covering the last 20 years’ development as concerns the specific analytical aspects of PAT [21].

FURTHER READING

An article complementary to the current “PAT” theme: “Sampling for Glaciological “erratic rock” Provenance: the brilliance of Danish Geologist Arne Noe Nygaard” was published in *Sampling Science & Technology*, April 2025(3), 26–33. Despite its apparently very different subject matter, here can be found a surprising PAT analogue (section 5). The process sampling interface is diachronic, with a time frame between delineation and analysis spanning ~800 years – yet constituting a bona fide PAT scenario!

<https://doi.org/10.62178/sst.003.003>

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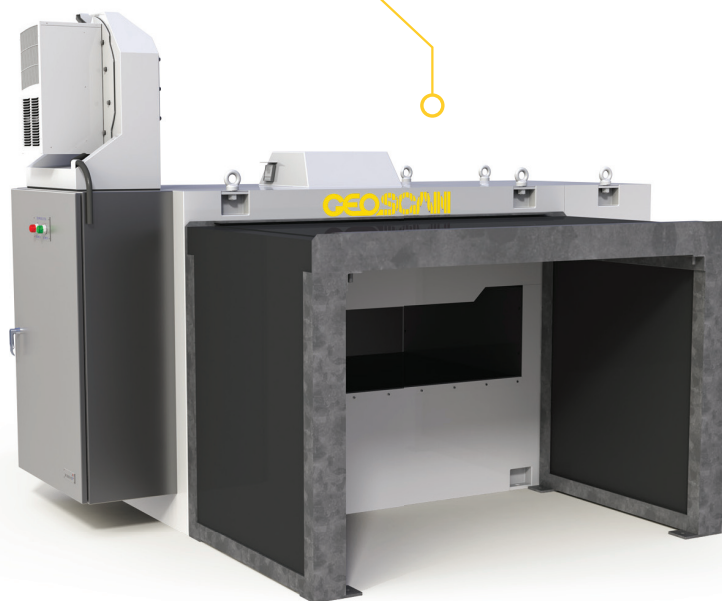


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