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Spectroscopy since 1975

Economic arguments for representative sampling in technology, industry, commerce, trade and society

This issue includes a Special Section on "Economic arguments for representative sampling", which starts on page 11.

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IMPOpen

EDITORIAL

This is an unusual issue, in that much of it is dedicated to a Special Section of the Sampling Column on "Economic arguments for representative sampling". We have been publishing the Sampling Column since 2014. It is edited by Kim Esbensen, initially with the help of Claas Wagner. The column started in a more tutorial style but has evolved over the years to tackle most areas of representative sampling.

Kim has said for many years and many times that there is no value in analysing something unless it is known to be representative of the larger mass of material it has come from. As you may expect from its title, this Special Section concentrates on the economic reasons for doing, or **not** doing, that. Mining features strongly since it has been the first major adopter of representative sampling, due to the mind-boggling sums involved in not doing so! Sending too much gold ore to waste is one thing, underestimating the concentration of toxic substances or genetic modified organisms is another. All have costs: often hidden, but no longer thanks to the Special Section which starts on page 11.

Kim has assembled a group of >20 leading sampling experts who have given a quite unique overview of the economic (and other) consequences of getting the sampling wrong.

Somewhat at random, here are just a few examples. Ralph Holmes (CSIRO) explains how a small sampling bias of 0.1% can cost an iron ore producer about **$23 million** a year! Claudia Paoletti (European Food Safety Authority) points out that sampling in the food and feed sector—ensuring safe food for the consumer—is not about just money, it is the very foundation of the trust we all have in a food product when we pick it off the supermarket shelf. Topically, Abel Arkenbout (ToxicoWatch Foundation) considers Campylobacteriosis from meat processed in slaughterhouses, and points out that this disease costs **€2.4 billion** per year in the EU alone! Further, campylobacteriosis is the most commonly reported zoonotic disease: one which can be transmitted from animal to human. Sound familiar? Getting the sampling right is kind-of important here! There is also plenty of advice on how to interact with and persuade senior management of the vital importance of representative sampling, from those who have been doing just that for years, some for decades.

The Special Section is organised into groups of contributions:

- Sampling in big scale operations
- Sampling in metals and minerals processing
- Sampling and the laboratory
- Sampling and management
- Sampling in society, environment, public health, pharma, trade

I am sure you will find much to learn from; some of which may even surprise you. In any case, there are plenty of ideas and thoughts that you can take into your own work.

From the Column Editor

The rationale behind this unique collection of articles is summed up in the first paragraph of my opening overview: "The Theory of Sampling (TOS) is all very fine, but it doesn't sell many tickets where it really counts, at CEO levels or higher (board of directors, investors, bankers). At this level decision-makers do not have the time, or cannot (or will not) make the effort to understand a **theory**. … sensing a marketing scoop, the Column Editor has asked almost more than 20 distinguished TOS illuminati to contribute to this definitive collection of 'business arguments for the TOS', writ large."

This collection took six months to put together, but it has been well worth it because of the unique opportunity to present (at least) three generations of samplers from all over science, technology, industry, commerce, trade and society. It has long been my wish to bring together the largest possible assembly of professional sampling proponents, united on a common theme. Together with invaluable help from Ian Michael and Martin Lischka (inspiring illustration wizard), we hope you will enjoy this. A tip: you can read the contributions in any order; if you, for example, are not in mining, start somewhere else—go and find what sounds most interesting to you first, to whet your appetite for the whole Special Section.

…and the rest

As to the rest of the issue, I am delighted that Tony Davies has returned with an interesting look at a Finding Aid (your own custom search engine on steroids) that has wide application for those working in spectroscopy. And it is free!

There are also our regular sections on News, Products (with a Product Focus on Raman Spectroscopy), Applications and the Diary of Future Events.

NEWS

NMR helps unravel why green tea is effective in treating cancer

An antioxidant found in green tea may increase levels of p53, a natural anti-cancer protein, known as the "guardian of the genome" for its ability to repair DNA damage or destroy cancerous cells. A study of the direct interaction between p53 and the green tea compound, epigallocatechin gallate (EGCG), points to a new target for cancer drug discovery.

"Both p53 and EGCG molecules are extremely interesting. Mutations in p53 are found in over 50% of human cancer, while EGCG is the major antioxidant in green tea, a popular beverage worldwide", said Chunyu Wang, corresponding author and a professor of biological sciences at Rensselaer Polytechnic Institute. "Now we find that there is a previously unknown, direct interaction between the two, which points to a new path for developing anti-cancer drugs. Our work helps to explain how EGCG is able to boost p53's anti-cancer activity, opening the door to developing drugs with EGCG-like compounds."

Wang, a member of the Rensselaer Center for Biotechnology and Interdisciplinary Studies, has used nuclear magnetic resonance (NMR) spectroscopy to study specific mechanisms in Alzheimer's disease and cancer, including p53, which he described as "arguably the most important protein in human cancer." NMR and other analytical techniques were used in the study of the binding of EGCG.

P53 has several well-known anti-cancer functions, including halting cell growth to allow for DNA repair, activating DNA repair and initiating programmed cell death (apoptosis) if DNA damage cannot be repaired. The N-terminal domain of the protein has a flexible shape and, therefore, can potentially serve several functions depending on its interaction with multiple molecules.

Wang's team found that the interaction between EGCG and p53 preserves the protein against degradation. Typically, after being produced within the body, p53 is quickly degraded when the N-terminal domain interacts with a protein called MDM2. This regular cycle of production and degradation holds p53 levels at a low constant. The work is reported in *Nature Communications* (doi.org/gk2pv4).

"Both EGCG and MDM2 bind at the same place on p53, the N-terminal domain, so EGCG competes with MDM2", said Wang. "When EGCG binds with p53, the protein is not being degraded through MDM2, so the level of p53 will increase with the direct interaction with EGCG, and that means there is more p53 for anti-cancer function. This is a very important interaction."

"By developing an understanding of the molecular-level mechanisms that control key biochemical interactions linked to devastating illnesses such as cancer and Alzheimer's disease, Chunyu's research is laying the groundwork for new and successful therapies," said Curt Breneman, dean of the Rensselaer School of Science.

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NEWS

Spectral imaging system to detect smoltification in fish farming

Smoltification is a complex series of physiological changes that allow young Atlantic salmon to adapt from living in fresh water to living in seawater. In salmon farming, this transition from "parr" to "smolt" is controlled using lights or functional feed to ensure a continuous and predictable supply of fish.

Scientists at SINTEF, one of Europe's largest independent research institutes located in Trondheim, Norway, have investigated hyperspectral imaging (HSI) to study the vital aspects in detecting smoltification, relying in part upon a BitFlow Camera Link frame grabber to grab high-speed video frames for analysis at more than 100 frames-per-second.

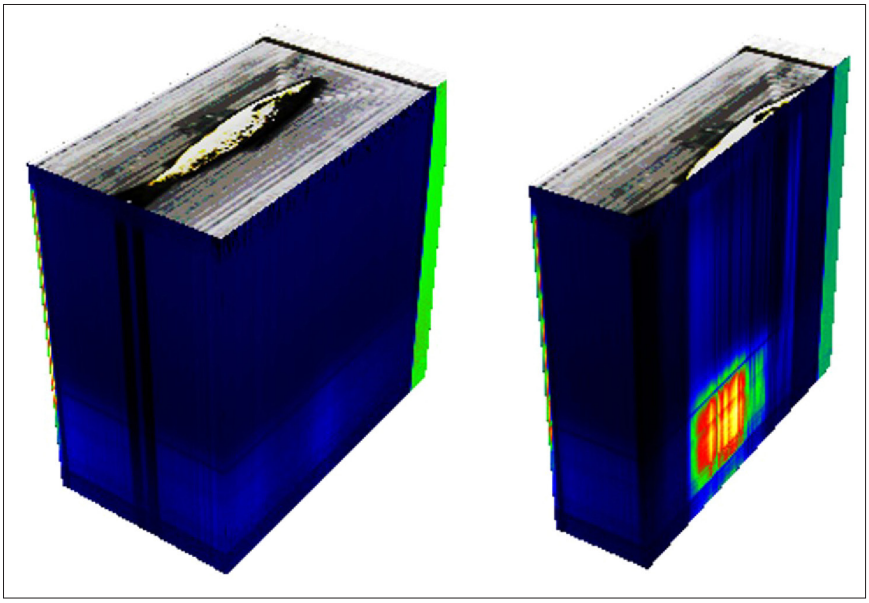


Illustration of the hyperspectral measurements as a 3D hypercube. The cube to the right shows a cross section through the fish lateral axis.

The ability to verify smoltification is critical since incomplete seawater adaptation may result in poor animal welfare and increased mortality. Animal welfare is of increasing importance in salmon farming, as the industry is under pressure to improve production and farming operations due to ethical concerns. Conventional smoltification assessments measure chloride content in blood samples after exposing fish to saline water, or by detecting the presence of ion-transporting enzymes through analysis of tissue samples from gills. These methods are time-consuming, so only a few salmon are typically tested from populations of several hundreds of thousands of fish.

To evaluate the robustness of its HSI approach, SINTEF placed emphasis on collecting diverse data with variations in fish colour, patterning, size and shape using three different salmon farming sites. Data were collected weekly in synchronisation with the sites' respective production and testing schedules. To make all data sets comparable, despite differences in ambient lighting conditions and exposure settings, all were normalised for comparison using white and dark reference images.

The raw data obtained from HSI were multidimensional images of individual fish, including their background. A stepwise procedure was used to process and analyse the data so the low-dimensional spectral characteristics could be observed, and classification of parr or smolt made possible. Wavelengths were optimised by factoring in water temperature, dissolved oxygen, water opacity and colour, as well as lighting and feeding regimes.

Upon conclusion of its study, SINTEF demonstrated a spectral imaging system where only three wavelengths are needed to identify the smoltification status of Atlantic salmon, and that this system could serve either as a supplementary or free-standing verification tool in fish production. In doing so, the researchers also laid a pathway to manufacturing low-cost spectral imaging instruments for use in production tanks or integrated in existing sorting and vaccination systems for faster, wider and more cost-effective population sampling of Atlantic salmon.

17th Confocal Raman Imaging Symposium

The 2021 Confocal Raman Imaging Symposium, held online, attracted 500 registrants to view and discuss 55 posters grouped under the topics: Advanced Materials Analysis; Environmental and Geo Science; and Life Sciences, Biomedical and Pharma Research. There were five featured talks and everyone was encouraged to offer ratings that were compiled to determine the winner of the 2021 Best Poster Award, and more than 80 researchers registered to take part in virtual equipment demonstration sessions.

During the one-week virtual Symposium, participants were invited to explore the conference platform and on-demand oral presentations. A good starting point was the thorough introduction to Raman spectroscopy and microscopy provided by Prof. Sebastian Schlücker (University of Duisburg-Essen, Essen, Germany). Prof. Barbara Cavalazzi (University of Bologna, Bologna, Italy) described how she uses 3D Raman imaging in her work on microbial paleontology, including the detection of the oldest fossilised methanogens ever found. Prof. Dominique Lunter (Eberhard Karls University, Tübingen, Germany) shared details of her investigations of skin penetration by pharmaceutical ingredients and the impact of penetration

enhancers. WITec's own Dr Ute Schmidt covered recent developments in studies of transition metal dichalcogenides and Prof. Laurene Tetard (University of Central Florida, Orlando, USA) presented 3D Raman analyses of thermal barrier coatings in jet engines.

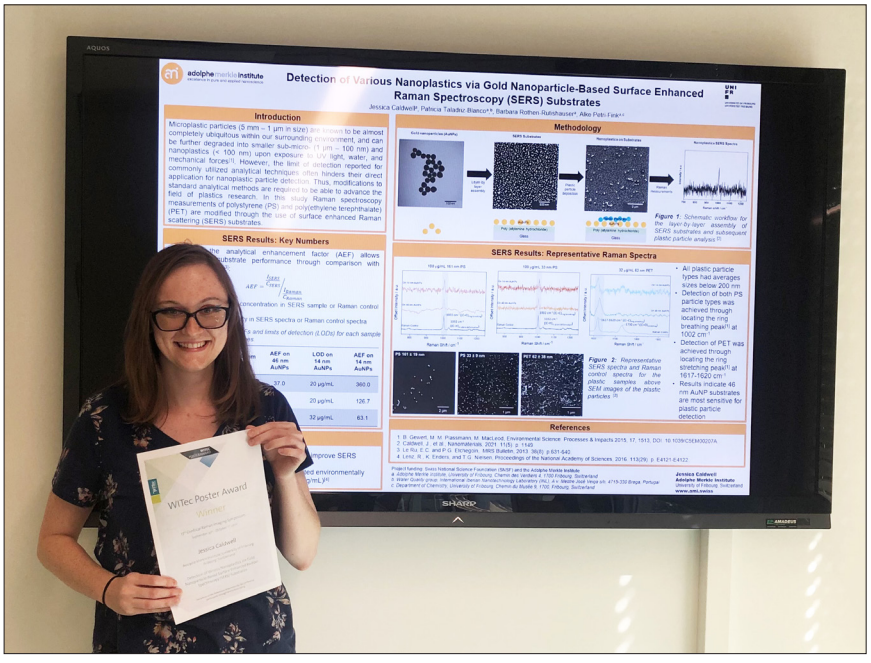
Along with the featured speakers, the 55 contributed posters provided a wealth of scientific content. In the end, one poster received the highest rating from fellow attendees and that honour belongs to Jessica Caldwell from the Adolphe Merkle Institute at the University of Fribourg, Switzerland. She won the Best Poster Award for her contribution: Detection of Various Nanoplastics via Gold Nanoparticle-Based Surface Enhanced Raman Spectroscopy (SERS) Substrates. Together with Patricia Taladriz-Blanco, Barbara Rothen-Rutishauser and Alke Petri-Fink, she explored one of the most resonant topics in contemporary science: the detection of micro- and nanoplastic particles.

Equipment demonstrations had previously been offered onsite in our laboratories on the final day of the Symposium. This year morning and afternoon sessions were hosted online every day of the conference to accommodate over 80 registrants. WITec application scientists showed the instruments in action with demos of confocal Raman imaging, Raman-AFM, topographic Raman imaging and Raman-based particle analysis coupled to a spectral database.

The 17th Confocal Raman Imaging Symposium flourished in its transition to a virtual event. Given recent disruptions, it was reassuring to see the spectroscopic imaging community persist in convening to share, discuss and celebrate new techniques and discoveries. We look forward to seeing everyone in person again when possible.

The 18th Confocal Raman Imaging Symposium will take place from 26 to 28 September 2022. Details including the list of invited speakers and reviews of previous symposia can be found on the Confocal Raman Imaging Symposium homepage: www.raman-symposium.com.

The book of abstracts from the 2021 conference is available: https://www.witec.de/assets/Download/News/WITec-AbstractBook-RamanSymposium2021-web.pdf



Best Poster Award Winner Jessica Caldwell presents the certificate in front of her poster about detecting nanoplastics using gold nanoparticle-based SERS substrates. © Jessica Caldwell, Adolphe Merkle Institute, University of Fribourg, Switzerland.

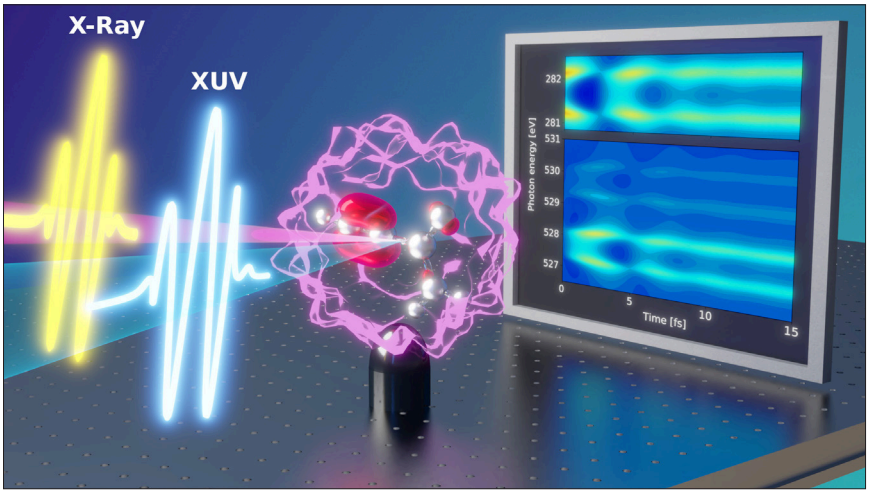
NEWS

Extending the power of attosecond spectroscopy

The last few decades have seen impressive progress in laser-based technologies, which have led to significant advancements in atomic and molecular physics. The development of ultrashort laser pulses now allows scientists to study extremely fast phenomena, like charge transport in molecules and elementary steps of chemical reactions. But beyond that, our ability to observe such processes on the attosecond scale means that it is also possible to steer and probe the dynamics of individual electrons on their natural timeframes.

One of the emerging ultrafast technologies is attosecond transient absorption spectroscopy (ATAS), which can track the movement of electrons at a specific site of a molecule. This is a particularly appealing feature of ATAS, because it permits tracing the evolution of the molecular system with spatial resolution at the atomic scale. Modern lasers can push chemistry into unexplored domains of light–matter interactions, where the role of theory in interpreting the results of ATAS measurements will be more important than ever before. But so far, the theory behind ATAS has been developed only for atoms or for molecules either in the absence of nuclear motion or in the absence of electronic coherence.

Now, a team of physicists from EPFL's Laboratory of Theoretical Physical Chemistry (LCPT) have extended ATAS theory to molecules, including a full account of the correlated electron-nuclear dynamics. The work was carried out in collaboration with Alexander Kuleff at Heidelberg University and published in *Physical Review Letters* (doi.org/gzqn).



Fingerprints of ultrafast electron-nuclear dynamics obtained with attosecond transient absorption spectroscopy. Credit: N. Golubev, EPFL.

"We present a simple quasi-analytical expression for the absorption cross-section of molecules, which accounts for the nuclear motion and non-adiabatic dynamics and is composed from physically intuitive terms", says Nikolay Golubev, a postdoc at LCPT.

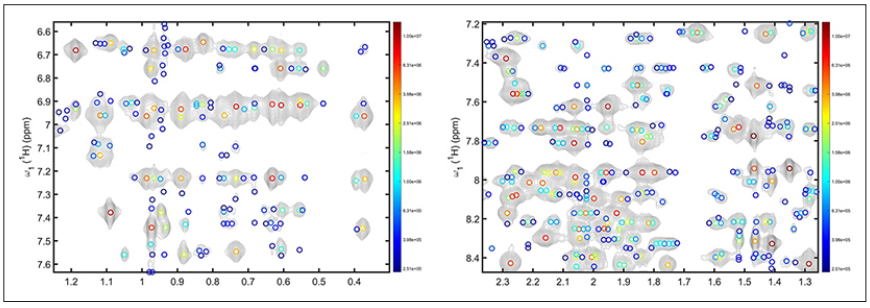
By extending ATAS theory, the scientists also show that this spectroscopy technique has sufficient resolution to "see" the follow-up decoherence of electron motion caused by the molecule's nuclear rearrangement.

Putting theory into practice, the team tested the polyatomic molecule propiolic acid as an example. "The simulation of X-ray ATAS of the propiolic acid was made possible by combining high-level *ab initio* electronic structure methods with efficient semiclassical nuclear dynamics", says Jiří Vaníček, head of the LCPT. By advancing our knowledge of the correlated motion of electrons and nuclei in molecules, the findings of the LCPT researchers could also help our understanding of various other "attochemistry" phenomena.

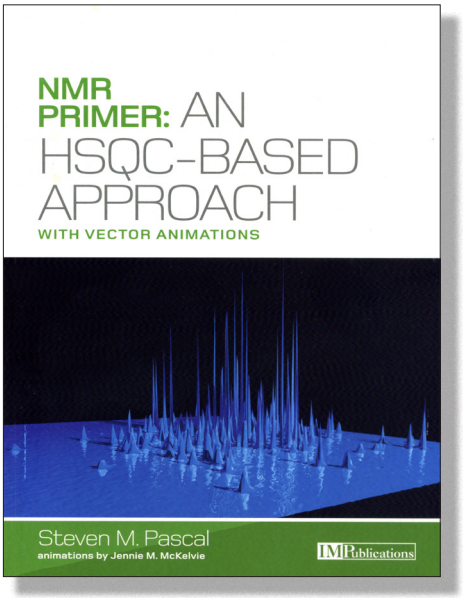
New machine learning method for faster and more accurate data analysis from NMR spectrometers

Scientists have developed a method using machine learning to better analyse data from nuclear magnetic resonance (NMR) spectrometers. NMR spectrometers allow scientists to characterise the structure of molecules, such as proteins, but it can take highly skilled human experts a significant amount of time to analyse that data. This new machine learning method can analyse the data much more quickly and just as accurately.

In a recent study, published in *Nature Communications* (doi.org/gzqm), the



Selected regions of 2D ^{1}H–^{1}H NOESY of Im7 with picked cross-peaks indicated as circles that are colour-coded according to their amplitude (logarithmic scale, see sidebar). DEEP Picker identifies strong and weak cross-peaks, including ones that severely overlap or show multiplet structures due to J-splittings, whose analysis is often challenging for traditional peak pickers. Reproduced from https://doi.org/10.1038/s41467-021-25496-5 under a CC BY licence.



NMR PRIMER: AN HSQC-BASED APPROACH

(with vector animations)

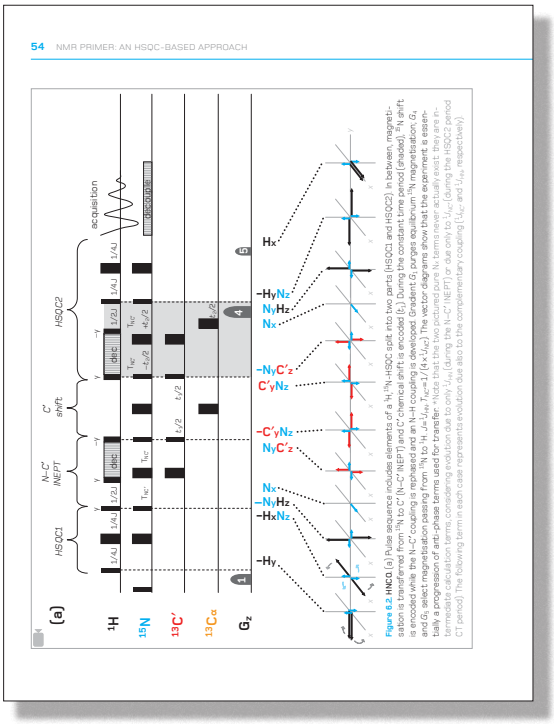
by Steven M. Pascal

This book has one aim: to explain the key two-dimensional protein NMR experiment, the $^{1}H,^{15}N$-HSQC, along with variants and extensions, in a generally accessible manner. Vector diagrams of one-, two- and three-dimensional pulse sequences are provided, along with accompanying animated versions. The animations allow the evolution of net magnetisation during the course of the experiments to be visualised and directly compared with the corresponding spin operator terms.

First, a brief introduction to spins, populations, the NMR experiment and relaxation is provided. Evolution due to J-coupling is next described and used to explain magnetisation transfer in the HSQC experiment and several variants. The extraction of structural, sequential and dynamic information is then illustrated via various extensions of the HSQC. Extensive footnotes and appendices introduce several more advanced concepts, such as sensitivity enhancement and the TROSY effect.

ANIMATIONS

The animations were originally created in Flash, which is no more. The animations have been converted to animated GIFs which enable them to be viewed easily with any browser. Control of these animations works best in Google Chrome using the GIF SCRUBBER extension: this allows pause/restart/reverse/speed control/etc.



BUY THE BOOK

NMR Primer: An HSQC-Based Approach costs just £24.95, plus postage & packing. This includes online access to the vector animations via an access code and password provided in each copy.

NMRPRIMER.IMPOPEN.COM

scientists described their process, which essentially teaches computers to untangle complex data about atomic-scale properties of proteins, parsing them into individual, readable images.

"To be able to use these data, we need to separate them into features from different parts of the molecule and quantify their specific properties", said Rafael Brüschweiler. "And before this, it was very difficult to use computers to identify these individual features when they overlapped."

The process, developed by Dawei Li and called DEEP picker, teaches computers to scan NMR spectra and deconstruct the spectra into readable peaks. The process involves creating an artificial deep neural network, and training it to analyse NMR spectra by feeding spectra that had already been analysed by a person into the computer and telling the computer the previously known correct result. The deep neural network was able to parse out the peaks in the highly complex sample with the same accuracy as a human expert, the researchers found. And more, the computer did it faster and highly reproducibly.

Rapiscan® Systems to distribute Metrohm Raman spectrometers to the security market

Rapiscan Systems and Metrohm USA have entered into a non-exclusive agreement for Rapiscan to distribute Metrohm handheld Raman spectrometer products globally to the security market through Rapiscan's Instruments Business Unit.

"We are excited to be teaming with Metrohm to broaden our product offerings for our customers using a technology that is complementary to those used in our trace detection systems", stated Dan Strellis, VP of Rapiscan's Instruments Business Unit. "These products are excellent at providing the user a tool to identify visible yet unknown materials that could be either a threat or benign in nature."

"Metrohm USA is thrilled to work alongside Rapiscan Systems to expand their portfolio of global security and forensic products. Metrohm handheld Raman instruments, working together with Rapiscan security products, will help improve safety for travellers and workers around the world," stated Edward Colihan, President and CEO of Metrohm USA.

BrightSpec has announced the start of operation of a broadband Molecular Rotational Resonance spectrometer at BASF's research centre in Ludwigshafen, Germany.

BASF will utilise MRR spectroscopy for the structure elucidation of organic compounds where isomerism is an underlying question. Major applications comprise stereochemical analysis, including chirality, defining the composition of mixtures without purification, and the facile structural analysis of gas-phase samples. Implementing MRR as a technology was driven by Senior Principal Scientists Wolf Stegmaier and Reinhard Doetzer of BASF's Competence Center Analytics.

"MRR is an excellent tool for elucidating structures in combination with the classical methods FT-IR, MS and NMR since it provides critical information orthogonal to them", stated Dr Doetzer. He continued: "We leverage MRR to increase the accuracy and speed of the structure elucidation process, boosting our analytical productivity. Not a day goes by when I don't think of a sample for which MRR would be the perfect method for solving a structure-related problem."

Dr Wolf Stegmaier added: "In gas analysis, MRR is providing quick answers for polar analytes without gas chromatographic separation or special detection systems. Its high selectivity is a great help in the direct analysis of complex gas samples; this is particularly so for the quantification of analytes in mixtures."

BrightSpec's Broadband MRR provides the ability to identify unknown molecules directly from a crude mixture. In conjunction with modern quantum-mechanical calculations, MRR allows the identification of the unequivocal three-dimensional structure of a molecule without reference standard or front-end separation. This combination increases sample throughput and reduces the cost for many applications across the pharmaceutical and chemical industries.

SAMPLING SPECIAL SECTION

Economic arguments for representative sampling

Special Section Editor: Kim H. Esbensen

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"A loss of a money is a certainty if the responsible entities have not made sure that *all* sampling and analysis performed to produce decision making information is representative. It is as simple as that…"

Sampling educator (2020)

A complaint has recently surfaced from the more business-oriented world that the sampling community mainly furthers "technological" arguments for engaging with proper sampling: "the Theory of Sampling (TOS) is all very fine, but it doesn't sell many tickets where it really counts, at CEO levels or higher (board of directors, investors, bankers). At this level decision-makers do not have the time, or cannot (or will not) make the effort to understand a **theory**." While seriously flawed and superficial, this opinion is nevertheless widespread, and especially so in those top-level decision-making circles where the sampling community would dearly like to make a greater impact! So, sensing a marketing scoop, the Column Editor has asked a distinguished group of TOS illuminati to address this economics issue head on. What follows below is the definitive collection of "business arguments for the TOS", writ large. So, read this column carefully—and forever hold your peace!

DOI: 10.1255/sew.2021.a30

The challenge

What is the best way to engage anyone who has never given much thought to **why** representative sampling is

SAMPLING SPECIAL SECTION

critically important for most endeavours in science, technology, industry, commerce, trade and society? This is in fact a standard topic within the sampling community itself: "What is the best way to promote the TOS—not only as a theory, but as a *practical tool* to help customers? Indeed, as a critical tool that will have a significant impact on the bottom line!"

The latter casts the issue into a rather direct format: "How to *sell* TOS-compliant equipment, system solutions, consulting and audit services to customers with only little, or **no**, familiarity with the need for proper sampling?"

Ever since the inception of the TOS (in 1950) there has been a healthy discussion about this issue, about which opinions are often sharply divided. There are traditionally two types of answers: the business argument "You stand to lose a lot of money **if you don't**…"; or the technical argument: "You need to understand these critical aspects of TOS, **or else**…".

Editor's introduction: Minimum TOS understanding: heterogeneity vs sampling procedures

Kim H. Esbensen
[a]Independent researcher, consultant, owner, KHE Consulting, Copenhagen

In order to be *reliable*, business decisions must be based on *reliable* analytical results, which in turn must be based on *representative* samples from the materials, lots and process streams. Thus, in one sense everything starts with being able to conduct appropriate sampling of *all* types of materials and lots in academe, technology, industry, trade, commerce and society. "Appropriate sampling" means "representative sampling". Otherwise, "What is the meaning of analysing a sample that cannot be documented to be representative? None, there is no meaning—it is only a waste of money." As it turns out, representative sampling is only dependent on two critical success factors: i) *how to* counteract the debilitating influence on sampling from material *heterogeneity* and ii) only using *composite sampling*—**never** grab sampling. **It is as simple as that**…

In a few more words:

Sampling procedures and equipment must be able to *counteract* the vastly different degrees of *heterogeneity* encountered in all materials and lots (stationary or moving) in need of reliable compositional characterisation. **Business leaders must acknowledge, and understand, heterogeneity**.

Sampling procedures must be *representative*, i.e. *bias-free*. Of the two most common sampling approaches used today, one is demonstrably **not** so—*grab sampling*. Only *composite sampling* can be made fit-for-purpose representative for **all** materials, at **all** scales and under **all** sampling conditions. **Business leaders must understand this and decree only to use composite sampling.**

This is really all there is to it…

By investing the miniscule effort needed to understand the above, management will actually have fulfilled its role; the rest *can* be left to the technical operative levels, but it is of course unsatisfactory to lead if not reasonably well informed about *what*, *when* and *how* the raw materials and the processes involved bring about the final product.

Here follows the minimum TOS knowledge needed at all levels—it isn't much. The first issue is often highly surprising, but it opens up for the singular critical insight needed:

*Sampling of materials, processes a.o. targets for which reliable analytical results are needed is a process that is **not** quantitively reproducible, i.e. repeated sampling (two, three or more "control samplings for example" will give rise to different analytical results. There is **always** a larger or smaller* sampling variability *(call it* sampling spread *if this is clearer for the reader). Why is that?*

*Because **all** materials and processes in technology, industry and society are* heterogeneous.

Because grab sampling is fundamentally unable to counteract the intrinsic heterogeneity met with in all materials, lots and processes for which business decisions have to be made, the results will be an undesirably broad *spread* of analytical results. The unacceptable consequences of a too-broad sampling + analysis spread is laid out in full below.

One would always wish for low material heterogeneity, but it is seldom possible to alter this for original lots easily without significant, and almost always prohibitive, economic costs. Is there another way? Yes, composite sampling.

Thus, both an ill-informed sampling approach (grab sampling) and/or sampling significantly heterogeneous materials, lots and processes without proper amelioration (grab sampling) will always result in a seriously *inflated* sampling + analysis spread.

Enter the TOS, the world's only fully comprehensive framework for

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Figure A. Heterogeneous materials, lots, processes are legion and come in a plethora of forms, containers, vessels etc. Because of heterogeneity, there will always be a significant sampling variability (sampling spread). Representativity w.r.t. the whole lot demands aggregating an appropriate number of increments covering the entire lot volume. It is clear why singular grab samples will always result in different analytical results, since they are extracted from different spatial locations. Repeated grab sampling will produce a larger or smaller sampling + analysis spread. Composite samples must contain a material-dependent necessary-and-sufficient number of increments in order to secure a "fit-for-purpose" representativity status. Composite sampling will also lead to a non-vanishing sampling + analysis spread, but with a much reduced magnitude, see Figure D. The TOS is the world's only necessary-and-sufficient framework for counteracting heterogeneity in the most effective way, always leading to a minimised effective sampling spread.

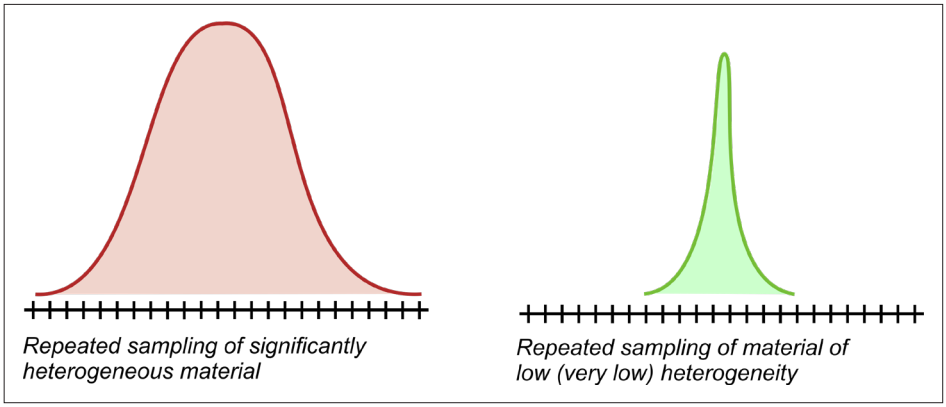


Figure B. Grab sampling of materials with widely differing heterogeneity will result in a characteristic sampling + analysis spread, the width of which is a direct reflection of the magnitude of the heterogeneity. The unacceptable business consequences of a too-broad sampling + analysis spread is laid out in full below.

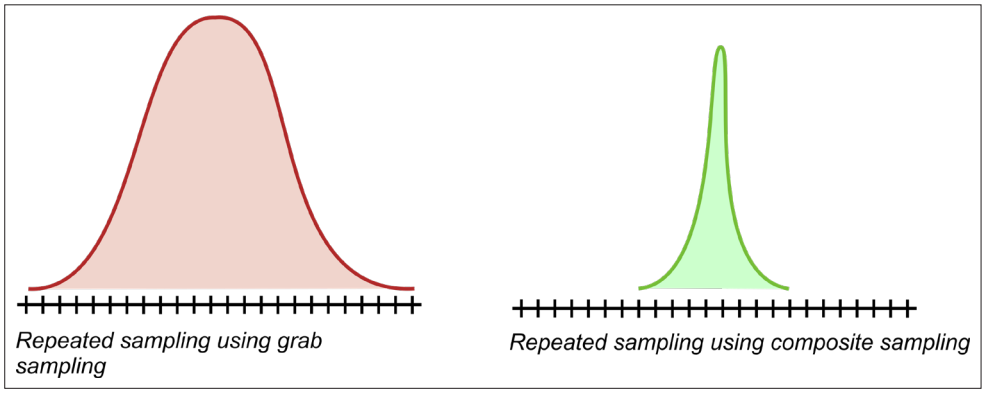


Figure C. Sampling spread as a function of using a non-representative procedure (grab sampling) compared to the world's only fully representative approach, composite sampling. The unacceptable business consequences of a too-broad sampling + analysis spread is laid out in full below.

representative sampling. The TOS stipulates **why** and **how to** use *composite sampling* for **all** materials regardless of their level of heterogeneity, Figures A and B. The TOS also outlines how to *calibrate* composite sampling (determination of the necessary-and-sufficient number of increments to aggregate) to be able to counteract heterogeneity at whatever level encountered (low, intermediate, high). The TOS is the world's only directive for how to implement representative sampling solutions that eliminate the negative effects from the two key critical success factors: heterogeneity and choice of sampling procedure.

Business decision consequences of not involving the TOS

For the reasons laid out above there is always an inherent, non-zero **risk** of making decisions based on inferior or downright wrong information, in this case numerical information (analytical results) which are fraught with unnecessary sampling + analysis uncertainty. **Risk management** is a due diligence requirement at the business level. With the few fundamentals laid bare above, risk management must include a minimum topical understanding of the risks stemming from sampling vs heterogeneity issues which all take place *before* analysis.

Making sure of optimal analytical performance is **not** enough—because the quality of analytical results depends much more on the *preceding* quality of the sampling procedures employed. Sampling uncertainties are typically 5–10–25 times *larger* than the optimised analytical laboratory performance—in direct proportionality to how well the sampling procedure has succeeded in mitigating the detrimental influence from heterogeneity—or **not**.

Inside or outside the analytical laboratory—that is the question!

Scores of examples exist of futile expansion of analytical departments with next to no additional gain in the form of improved business decision making. While knowledge and experiences with the entities behind such examples are obviously highly confidential, what can be revealed is that behind every known example there are equally many records of successful make-over operations—which all involved introduction of proper TOS knowledge to the corporation, company or organisation involved. It is difficult to put exact numbers on the economic gains (or thwarted losses) in these examples, but a start would be: What are the costs for a new analytical lab? For a significantly upgraded laboratory? For hiring one or more scientists or technicians? Compare this to now knowing for a fact that the root cause for particular bottom-line issues lies **outside** the laboratory! Enter the TOS, with which to clear up any-and-all sampling deficits—these alternative costs will in most cases have difficulty reaching even a fraction of what would have been waster on the "laboratory expansion" avenue.

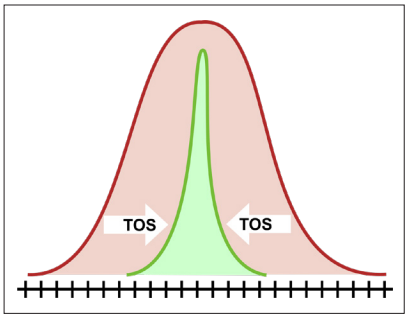
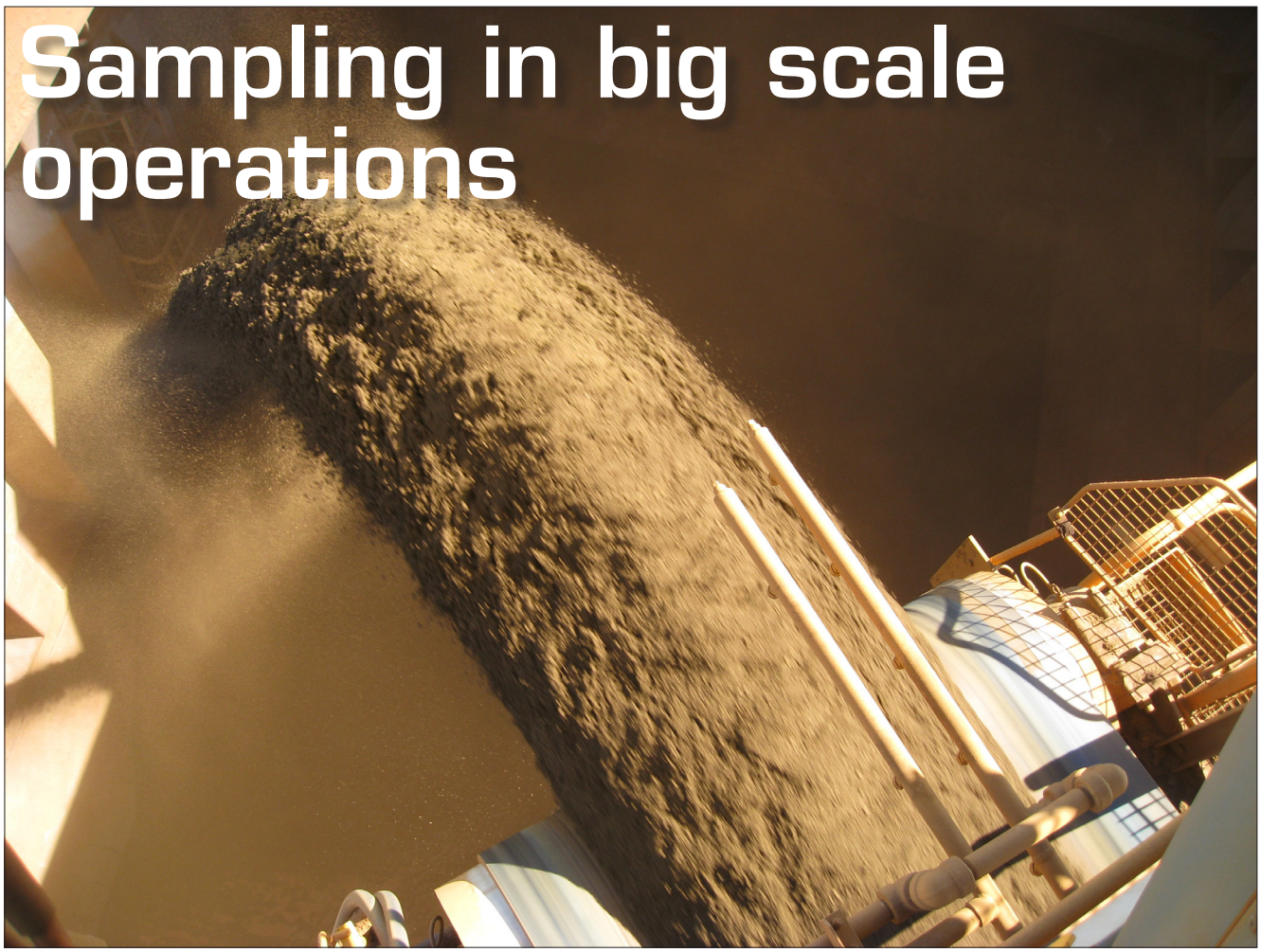


Figure D. The The solution guaranteeing representative sampling of significantly heterogeneous materials is always using appropriate sampling procedures (composite sampling)—the TOS.

Resolving such issues lies at the heart of successful risk management at the top management level. The alternative, being ignorant of the consequences of not caring about the mere "technicality" of *sampling*, is an assured inferior bottom line result without anyone in the organisation being able to point to viable remediation avenues... the TOS to the fore!

To **motivate** readers to include a smattering of the TOS in the risk management setup of their operation is the very thrust of this Sampling Column. Below we present a bonanza of economic arguments for involving the TOS at all levels.

SAMPLING SPECIAL SECTION



Sampling in big scale operations

Section contents

SAMPLING SPECIAL SECTION

The classic publication on sampling and analysis costs in full-scale mining—Editor's summary

Pedro Carrasco, Pablo Carrasco and Eduardo Jara

Incorrect sampling operations cause huge economic losses to the mining industry, here illustrated by three industrial cases, which also show that when the Theory of Sampling (TOS) is applied correctly (ensuring unbiased sampling and analysis), considerable amounts of money can be saved.

Case 1

Sampling density influences the estimated value of mining plan alternatives

Before decisions regarding a US$640 M investment for a heap leaching facility in northern Chile, alternative spatial sampling grid densities for open pit mining of a low-grade oxide zone porphyry copper deposit (grids from $100 \times 100\ m^2$ down to $10 \times 5\ m^2$) result in markedly different Net Present Value (*NPV*) estimates spanning US$345–450 M as a function of the drilling pattern sizes. A difference between US$345 M and US$450 M, i.e. a **30% increase** in estimated resource value, is solely due to increased diligence regarding the most appropriate sampling plan, which would not have been revealed without the TOS (and geostatistics). Carrasco *et al.* a.o. conclude that "improper drilling patterns result in misleading economic decisions, e.g. wrongly dismissing good business opportunities, faulty designs of milling capacity and overestimation of waste dump capacity.

The *hidden* value loss in Case 1 is **US$105 M**.

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Case 2

Consequences of installing a TOS-compliant sampler at a tailings discharge location

A US$0.5 M TOS-compliant sampling station was installed to monitor a tailings stream in a large copper operation in central Chile. The tailings were to be sold off to another reclaiming company, so both parties have a vested interest in introducing reliable grade estimation procedures. Before installation, traditional tailing copper grade had been *assumed* to be 0.15% based on conventional metallurgical balance calculations in the preceding minerals processing pathway. The newly installed unbiased sampling station proved the earlier assumptions wrong—the actual grade turned out to be 0.20% copper. While this may seem only a relatively small deviation (an underestimation of 0.05% copper), the tailings flow rate is 96,000 tons per day, so large tonnages are involved here. But what could be worse, this underestimation had been taking place for 87 years! This difference, over this period of time, represents an accumulated loss of copper not accounted for in the company's accounts which had been assumed correct over this long period of mining business. To be fair and to count on improved technology gains a.o., it was decided to calculate the value of this loss for the last 20 years only. Based on contemporary copper prices and production costs, some 175,207 tons per year were unknowingly lost, which when calculated on an *NPV* basis amounts to a staggering **US$2207 M**.

Conclusion

Correct representative sampling practice and equipment discovered a hidden loss of a magnitude of more than **US$2 billion**. It does not take an economics degree to compare this with an investment of US$0.5 M.

Case 3

Economic consequences of a biased grade control system based on blast hole sampling

Blast hole sampling is inexpensive, efficient and often performed manually in many mining industries handling very large tonnages. This is recognised as being a major risk in the industry, but is nevertheless still often preferred from a narrow economics and logistics perspective. In Case 3 this was the established procedure in which a quickly acquired "sample" of 250 g was supposed to represent a lot of 2 tons. Amongst other things, this approach generates a huge Fundamental Sampling Error (FSE). This is a highly significant bias of unknown and inconstant magnitude amounting to ~70% of the total observable grade variability. In other words, 2/3 of the analytical information with which mining planners are supposed to work, was in reality just… *noise*. An alternative procedure (diamond drilling) is more expensive but also more accurate and precise, so deciding on introducing this would obviously depend on a reliable estimate of the accumulated losses from the blast hole approach. The mining work procedures a.o. involved classifying ores vs waste, based on a so-called "cut-off grade" of 0.40% (technical details are not relevant here, see the original publication[1]). Complicated geostatistical procedures were used to present relevant information. In terms of *PV* (present value): $PV = B^+ - B^-$ [B^+ *NPV* of wrongly sending ores to the waste dump; B^- *NPV* of, equally wrongly, sending waste to the processing mill]. Based on reliable yearly average costs and performance data, the economic calculations ultimately presented to management were as follows:

Total loss of revenue by misclassification due to blast hole sampling: $B^+ - B^- =$ **US$156 M**

Total loss of misclassification due to the alternative diamond drilling sampling: $B^{+}-B^{-}$=**US$22M**

Again, no kudos for being able to reach a conclusion in a manner appreciated by upper management.

General conclusions

General conclusions from Carrasco *et al.*[1] include:

1) Improper (non-representative) sampling practices can produce monumental value losses.
2) For a single big mining company, amounts up to US$2billion were lost over 20 years.
3) Incorrect sampling (including non-optimised analysis) not only leads to unnecessary economic inefficiency and contributes towards unsustainable exploitation of Earth's resources.
4) In the present context, focus must be on the TOS' ability to help reveal hidden value and economic losses otherwise not known to management—all realised by making sure that "…all sampling and analysis performed to produce decision making information is representative".
5) The most efficient way to discover hidden losses is to foster skill and the ability to understand the different sources of variability—and to understand that estimation is not identical to reality; there are always error effects and uncertainties. The only framework for guaranteed reduction (in optimal situations, elimination) of such adverse effects is by introducing and supporting TOS knowledge.

Read the original paper here

1. P. Carrasco, P. Carrasco and E. Jara, "The economic impact of correct sampling and analysis practices in the copper mining industry", in *Proceedings: First World Conference on Sampling and Blending (WCSB1)*, Ed by K.H. Esbensen and P. Minkkinen, *Chemometr. Intel. Lab. Syst.* **74(1),** 209–213 (2004). https://doi.org/10.1016/j.chemolab.2004.04.013

SAMPLING SPECIAL SECTION

Incorrect sampling practices always have significant economic consequences—and never more so than where tonnages are large…

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Case 1. Even a small sampling bias can have a BIG negative economic consequence

Poor sampling procedures for iron ore can lead to preferential exclusion of coarser high grade particles from shipment samples for analysis due to cutter apertures that are too small or cutter speeds that are too high. This leads to a negative bias on Fe content—the result is that shipments are also carrying away substantial lost revenues!

Where the money comes in

Assume a small negative bias of only 0.1% Fe on an iron ore shipment of 250,000 dry tonnes at 62% Fe and an iron ore price of US$150 per tonne of contained iron.

$$\text{Financial loss} = 250{,}000 \times 0.62 \times 150 \times 0.001 = \text{US\$23,250}$$

just for one shipment! If the company loads 1000 ships in a year, i.e. exports 250 Mt/a (not unusual for a major iron ore producer), the loss then amounts to about US$23 million per annum.

The lesson: Take an even closer look at sample station design and sampling performance!

Case 2. Good risk management—but still…

Even when sampling bias has been successfully eliminated, there may still be issues due to poor sampling precision. Due to the uncertainty that persistent poor sampling precision creates in terms of shipped grades, a mining company may decide to target shipped iron ore grades at 0.25% Fe above contract grade to minimise the occurrence of off-specification shipments and associated penalties. This indeed appears to be good risk management. The company, therefore, needs to "high grade" production, but the inevitable consequence is that some low-grade blending ore, that could otherwise be sold as high-grade ore, ends up on the waste ore dump with no financial return even though the same amount of money has been spent mining this misclassified ore as for the higher-grade ore. High grading production also reduces mine life.

Where the money comes in

Assume the contract grade is 62% Fe, so the target grade has to be 62.25% Fe to minimise penalties, and the grade of the low-grade blending ore is 55% Fe. The percentage of low-grade ore (LG%) lost can be calculated from the following equation:

$$100 \times 62 = 62.25\,(100 - \text{LG\%}) + 55 \times \text{LG\%}$$

thus

$$7.25\,\text{LG\%} = 6225 - 6200 = 25$$

hence, LG% = 25/7.25 = 3.45%.

For a shipment of 250,000 tonnes of ore at 62.25% Fe, the bottom line is that

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8625 tonnes of low-grade blending ore that could have been sold as high-grade ore at 62% Fe ends up as waste. The financial loss is about US$150 × 8625 × 0.62 = US$0.8 million. With better sampling precision, the target grade can be brought closer to contract specification, thereby improving the utilisation of low-grade blending ore.

The lesson

Two examples for everybody to learn from, including higher management levels. The quest for sampling optimisation (bias elimination in Case 1 and the need to improve sampling precision in Case 2) is never over and getting it right pays welcome dividends! Understanding sampling fully is the only remedy against hidden losses, unnecessary extra operational costs, and contract and trade contract disagreements. Theory of Sampling (TOS) to the fore!

SAMPLING SPECIAL SECTION

Critical sampling in the cement industry: economic drivers

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The total global cement production in 2020 was around 4.1 billion tons, making it the industrial processes sector responsible for the highest single contribution of emitted CO_2 worldwide, with no less than 27% of the directly industrial-released CO_2.[1] Modern rotary kilns in cement plants have a production capacity of 5000–10,000 t per day, and for each ton of clinker produced, ~910 kg CO_2 are emitted to the atmosphere.[2] These emissions stem from three main sources: i) decarbonisation of limestone, ii) fuel for the rotary kiln and iii) fuel for the electricity consumption of the cement plant. There is a vital sampling role hidden away in this big picture, illustrated here with five scenarios for a critical process control parameter termed "LSF" (Lime Saturation Factor), the economic impact of which is the main focus here.

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CO_2 budgets

In order to meet international agreements on climate change targets, and with introduction of "CO_2 certificate trading" in Europe in 2005, in addition to diligent process control, a new aspect for successful and economic cement plant operation arises. Due to CO_2 certificate trading, the importance of reliable sampling in cement production must be considered from the point of view of the lowest possible CO_2 production and the highest possible reliability of the data obtained.[3] Studies have shown[4] that a 5% variation in the single most important process monitoring parameter, LSF (see Technical Info Box), leads to an increase in CO_2 emissions of up to 16.4 kg CO_2/t clinker. Likewise, CO_2 emission from carbon-based fuels, by a similar 5% variation in LSF, increases by 17.2 kg CO_2/t clinker.

A sampling bias can very easily be introduced regarding the LSF, which can have severely amplified economic consequences.

The economics of it all

To illustrate the economic consequences of these technical relationships, one estimates the current financial impact based on a certificate price of €55 t^{-1} CO_2 (even

Technical Info Box

Compared to many traditional mining and minerals processing industries based on heterogeneous mineralisations and materials (e.g. base metals, gold ores), cement production is based on relatively homogeneous raw materials (clay, limestone), supplemented by a few aggregates to ensure consistent product quality. Traditionally, therefore, rather less attention has been paid to the strictness of the TOS within this industry. Sampling of the clinker is typically performed from the running process stream with a cycle of one sample per hour. After sampling, the clinker is coarsely crushed in a jaw crusher to a grain size of less than 5 mm. This allows representative sampling to reduce the sample quantity to approximately 100 g. In modern plants, samples are transported to the laboratory by pneumatic transportation. In the laboratory, sub-samples are finely ground (< 45 µm) and prepared for automated X-ray fluorescence (XRF) and X-ray diffraction (XRD) analysis. To be able to use automated analysers, only about 10–15 g of sample material is needed, which is pressed into a steel ring (Ø 51.5 mm). Since the penetration depth of the analyser's X-rays is only a few micrometres, in reality only a very small portion of these few grams is analysed. It is obvious that sampling plays a critical role in this measuring system context. The effective sampling rate (clinker-to-aliquot) is closely related to the clinker production rate (see Table 1) but can be estimated as ~1 : 50,000,000—which under all circumstances is daunting.

However, the subsequent sample preparation also has a considerable influence on the analytical result. A measurable parameter for the quality of sub-sampling and sample preparation is the *standard deviation*, used as a measure of spread between replicated sampling and analysis results.

In addition to the classical elemental breakdown of chemical analysis, three so-called *moduli* are used in the cement industry for chemical classification. The most important of these is the so-called Lime Saturation Factor (LSF) which is calculated as follows:[5]

$$LSF = 100 \times CaO / (2.8 \times SiO_2 + 0.65 \times Fe_2O_3 + 1.18 \times Al_2O_3)$$

The three critical moduli are used to monitor and control the production targets. During the cement manufacturing process, heterogeneity of the intermediate products decreases continuously from the raw mixture to the finished product (good process control). The composition of the raw material mix and of the secondary fuels used are of significant importance for the clinker burning process efficiency, and also have a decisive influence on the composition of the clinker. Process control must, therefore, be carried out in such a way that the chemical and physical properties of the clinker remain as constant as possible. For this sensitive target, the quality, representativity and reliability of process sampling operations ARE of key importance.

Table 1. Estimated additional CO_2 release for different production capacities caused by erroneously determined LSFs and the financial impact in terms of CO_2 certificate price trading. These certificate costs could be saved by running the cement plant with a well-controlled process close to product specifications and with optimised power consumption.

	Rel error (%) LSF factor	Production in t/day			
		1000	2000	5000	10,000
Additional release (kg CO_2 / day)					
Clinker	1	3280	6560	16,400	32,800
	2	6560	13,120	32,800	65,600
	3	9840	19,680	49,200	98,400
	4	13,120	26,240	65,600	131,200
	5	16,400	32,800	82,000	164,000
Fuel	1	3440	6880	17,200	34,400
	2	6880	13,760	34,400	68,800
	3	10,320	20,640	51,600	103,200
	4	13,760	27,520	68,800	137,600
	5	17,200	34,400	86,000	172,000
Estimated costs for CO_2 certificate (€)					
Day	1	370	739	1848	3696
	2	739	1478	3696	7392
	3	1109	2218	5544	11,088
	4	1478	2957	7392	14,784
	5	1848	3696	9240	18,480
Year (300 days)	1	110,880	221,760	554,400	1,108,800
	2	221,760	443,520	1,108,800	2,217,600
	3	332,640	665,280	1,663,200	3,326,400
	4	443,520	887,040	2,217,600	4,435,200
	5	554,400	1,108,800	2,772,000	5,544,000

though increasing prices can be expected for the next years). The economic consequences of non-optimal LSF estimation are **huge**, as shown in Table 1. Here a relative error for the LSF ranging from 1% to 5% is considered, correlated to the simulation data given by Cao *et al.*[4] for typical daily production rates.

Highly sensitive sampling

It is very easy to introduce a significant variability in process monitoring and control if proper attention is not brought to bear—making representative process sampling essential. This can be illustrated for the same LSF parameter, based on XRF measurements. Results are presented below from an analysis repeatability test (10 analytical results from the same sample). One re-analysis shows an "accidental" higher amount of Fe_2O_3 which, however, changes the average LSF magnitude significantly, from 105.44 to 102.15. This single sample preparation variation is consequently responsible for a relative error of ~4% for the LSF, Table 2. With the economic impact of even small LSF variations as shown in Table 1, all sampling, sub-sampling and sample preparation variability is decidedly unwanted. TOS to the fore!

Insight leads to greater climate responsibility

The above economic relationships define three main goals for continuing vigilance regarding optimised cement production control to be in optimal compliance with increasingly stringent climate policy efforts, which today should be included in sustainability reports from all forward-looking cement manufacturers:

- Process and product specifications, as close as possible to minimum climate impact demands
- Design of alternative, more climate-friendly cement products
- Low-energy operation and low-CO_2 cement plant emissions

Thus, today there are both environmental, technological, economical (plant scale, global climate scale) as well as somewhat "hidden" sampling drivers for a continuously evolving cement industry—no longer mainly driven by narrow economic incentives alone. The TOS has a role to play nearly everywhere, and the economic costs for even a minor lassitude can be substantial, as was shown above (Table 1), in which a LSF uncertainty of 4% (rel) results in estimated potential additional certificate cost of **€4.4 M per year**.

There are other, non-optimised sampling issues in cement production, first and foremost primary clinker sampling. Often scoop sampling is applied in this stage, a sampling method that critically needs to be reconsidered, because a complete cross-section of the process stream is traditionally considered "almost impossible" to achieve. Remarkably there are not many publicly available clinker sampling rate estimates, nor assessments of the associated sampling errors.

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2. P. Stemmermann, U. Schweike, K. Garbev and G. Beuchle, "Celitement – a sustainable prospect for the cement industry", *Cement Int.* **8(5),** 52–66 (2010). https://celitement.de/wp-content/uploads/2020/07/2010-10-26_Celitement_a_sustainable_prospect_for_the_cement_industry-1.pdf

Table 2. Routine XRF analytical results from a simple replication experiment (10 analytical aliquots prepared from the same sample) showing how easily the LSF can be impacted by non-representative sampling, preparation or analytical inconsistences. The primary clinker sampling variability must be added to this error, which is solely due to sample preparation and analysis.

Test	Al_2O_3	SiO_2	CaO	Fe_2O_3	LSF
1	4.39	20.17	67.27	2.84	**105.93**
2	4.38	20.19	67.21	2.81	**105.78**
3	4.42	20.33	67.40	2.79	**105.40**
4	4.41	20.33	67.41	2.80	**105.41**
5	4.42	20.33	67.43	2.83	**105.39**
6	4.43	20.24	67.33	2.79	**105.67**
7	4.42	20.34	67.33	2.81	**105.21**
8	4.44	20.39	66.63	4.48	**102.15**
9	4.48	20.46	67.54	2.77	**104.92**
10	4.46	20.38	67.51	2.81	**105.26**
Mean	4.42	20.32	67.31	2.97	
SD	0.03	0.08	0.25	0.50	
RSD	0.6%	0.4%	0.4%	16.9%	

3. C. Wagner and K.H. Esbensen, "A systematic approach to assessing measurement uncertainty for CO_2 Emissions from coal-fired power-plants—missing contributions from the Theory of Sampling (TOS)", *Chem. Eng. Res. Des.* **89(9),** 1572–1586 (2011). https://doi.org/10.1016/j.cherd.2011.02.028
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SAMPLING SPECIAL SECTION

Sampling of gold ores for commercial purposes

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Let us take the example of the sampling of a gold ore coming from a small high grade deposit where the ore is to be beneficiated at a third party concentrator. There are two reasons why the ore must be sampled in an accurate manner. First, there must be a good estimate made of the contained gold so that the mine pays royalties to the state correctly. Second, the contract with the concentrator needs to pay the miner fairly for the gold contained in the ore and apply penalties for deleterious elements also contained in the ore as determined from the assays of the incoming ore. In this example, we show the impact of sample precision on the possible cash flows for the concentrator or the miner. It is assumed that the sampling is "correct", this is, that it is unbiased. The matter of whether the sampling is "representative" hangs on whether the sampling is "fit for purpose" (which is the real meaning of representative sampling) and can be judged by whether or not the economic risks faced by the parties involved are acceptable.

This example is based on an actual mine/concentrator collaboration, except that the grades and ore characteristics have been altered somewhat for reasons of confidentiality.

The ore is taken to be a difficult one containing coarse gold at a mean grade of 30 g/t and showing individual small bulk sample grades up to 180 g/t and down to less that 2 g/t. The distribution of sample grades is heavily skewed and follows an approximate log–normal distribution of grade, as might be expected. The standard deviation of the grades is very close to the mean grade. Production from the mine will be in daily 400 tonne batches which will be sequestered at the mine prior to shipment. Each batch will be sampled and assayed in order to determine if it is high enough grade to be sent to the concentrator. The ore will also be sampled again as received at the concentrator.

The critical question is how precise the daily sampling must be in order to control the risk of under- or over-payment for the ore over a period of time. The uncertainties due to sampling, sample preparation and analysis attached to the assays upon which payments are based are statistically independent and can be positive or negative and may be normally distributed. The assays can be viewed as true metal contents with a random uncertainty added to each one. From the point of view of a single assay upon which payment is made, the uncertainty may be positive or negative leading to an over-payment or under-payment, the magnitude of which is directly related to the variance (or standard deviation) of the uncertainty.

However, taking a longer-term view, it will happen that a run of positive or negative uncertainties can occur which will leave the mine or concentrator with a temporary deficit. If the concentrator is on the losing end of this run, they will be genuinely out of pocket as they will have over-paid the mine. This will have a direct impact on their cash flow as the gold they have paid for will not arrive at the bullion room. If the miner is on the losing end, he will be none the wiser unless his exploration and mine plan is so good that he can detect the fact that fewer ounces of gold have been realised from the mined ore than predicted from the mine plan. Nonetheless, he will be less well-off than he should be and this will impact his cash flow.

It is quite possible to make some simple calculations which show the extent to which the positive or negative runs of assay uncertainties can add up. Figure 1 shows five realisations of how positive or negative uncertainties can occur and add up to a significant value after a series of payments on a monthly basis. The magnitude of the deficit or surplus is measured in standard deviations of the uncertainty. In four out of the five cases, the difference from the true value has reached ten standard deviations after 60 months or 5 years or less.

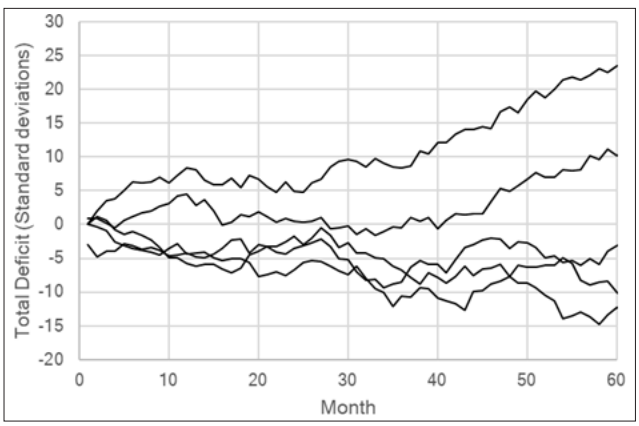

Figure 1. Random accumulation of surplus or deficit on payments in terms of assay standard deviations.

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If the little mine ships ore 5 days a week, we can count 20 days as the nominal payment period and the ore shipped will be nominally 8000 tonnes. At an average grade of 30 g/t this is 240,000 g or 7717 ounces. At a value of $1700/oz, this is $13.1 million. Now assume that the standard deviation of the uncertainty at the end of the payment period is 4%. Then one standard deviation corresponds to $0.524 million, five standard deviations to $2.62 million and ten standard deviations to $5.24 million.

While these figures are relatively small compared to the overall revenue from the mine, the value is significant and even a deficit of a few standard deviations is enough to cover the cost of a well-designed sampling system for the mine. With advance planning, a sampling system can be put together from second-hand equipment that will be capable of delivering results that might be able to improve on the uncertainty of 4% relative on the 20 day payment period.

Achieving accurate sampling of coarse gold ores

There has been much discussion of how to work out a satisfactory sampling protocol for ores containing coarse gold. There has also been debate on exactly what constitutes a "coarse" gold ore. And there has been debate on how to pulverise a gold ore containing "coarse" grains of gold without having the gold smear onto the surface of the grinding equipment with the loss of gold.

Then there is the problem of assaying a sample before or after pulverisation. There are now two methods of dealing with relatively large samples of gold ore that can be submitted for analysis without pulverisation to pass 150 µm or 106 µm.

The first is the **P**ulverise **a**nd **L**each (PAL) system that accepts a 1 kg sample of ore up to about 5 mm in size and puts it in an iron pot with grinding balls and an accelerated CN leach solution and tumbles the pot for about one hour. At the end of the tumbling, both the ground solids (now 75 µm or so) and the supernatant solution can be recovered. The solution can be analysed directly and the solids recovered, rinsed, dried, weighed and subjected to fire assay. Multiple 1 kg subsamples of the same ore can be used as determined by the analysis protocol. The advantage of the method is the large sample mass possible and the fact that there can be no loss of gold to smearing as such gold will be dissolved.

The second method is the new Photon Assay procedure brought to a commercial readiness by the CSIRO in Australia and now being rolled out in analytical labs and dedicated corporate facilities across the world. In simple terms, the method uses samples up to 500 g in mass contained in a jar and the jar is irradiated by 8–10 MeV x-rays which are highly penetrating of the ore and excite the gold nuclei which then decay with the emission of 279 keV gamma-rays, which are also highly penetrating. Multiple 500 g samples crushed only to <~2 mm can be used for an ore. The method is non-destructive. Current data show the method to be more accurate than any other methods for samples above about 1 g/t. The approximate standard deviation of an assay at 1 g/t is 2.5% relative and reduces as the sample grade increases, as indicated by available literature. The method has also been extended to Ag, Cu and moisture analysis.

Both methods are relatively cheap as sample preparation is minimised, but the PAL method does require fine assay of the residual solids to ensure that all the gold is captured.

The key to understanding the problems of gold analysis when the gold grains or gold grain clusters are coarse is to recognise that the size distribution of the gold grains/clusters controls the number of gold grains/clusters to be found in a sample of a given mass. The number of grains/clusters of a given size (or equivalent mass) in a sample follows a Poisson distribution and this fact permits calculation of the distribution of grades that will be observed over correctly sampled subsamples of the ore for the ore in the state of comminution at hand. It also permits a simple calculation of the sampling variance for the ore subsamples. It does not matter what the state of comminution the ore is in; it matters only that the size (mass) distribution of the grains be known or can be estimated with reasonable precision. Further, if it is legitimate to assume that the mass distribution of the grains/clusters can be assumed to follow the often-seen Rosin–Rammler (Weibull) distribution, the sampling variance can be written in terms of the 95% passing size of the grains/clusters, a grain/cluster shape factor and a parameter describing the breadth of the mass distribution.

In the author's development of statistical sampling theory.[1] the sampling variance due to the intrinsic (constitutional) heterogeneity can be written in terms of a sampling constant for the element of interest, K_S, as

$$\frac{\sigma_{IH}^2}{\bar{A}_L^2} = \left[\frac{1}{M_S} - \frac{1}{M_L}\right] K_S \qquad (1)$$

where the mean grade is A_L, and the sample mass is M_S, M_L is the mass of the lot from which the sample is taken and σ^2 is the sampling variance due to the element of interest. In a simple case where the gold grain mass distribution is unimodal, the sampling constant can be shown to be

$$K_S = \frac{\rho_{Au}}{A_L} f g d_{95\,Au}^3 \qquad (2)$$

where ρ_{Au} is the density of the gold, f is a shape factor, g is a size distribution factor having a value not too different from 0.25 and d_{95Au} is the 95% passing size (by mass) of the gold grains/clusters. The sampling constant has units of mass. The validity of this formulation of the sampling variance for a gold ore has been tested against the excellent (but very rare) data on gold sampling variance as a function of the top size to which the material was crushed.[1–3]

The fact that the number of gold grains in a set of gold mass fractions in an ore follow a Poisson distribution can be used to calculate the so-called characteristic function for the sampling distribution of the ore and this function can be inverted to provide the probability density function. This capability is a new tool in sampling theory that can be used to shed light on the impact of gold grain/cluster size on sampling variance

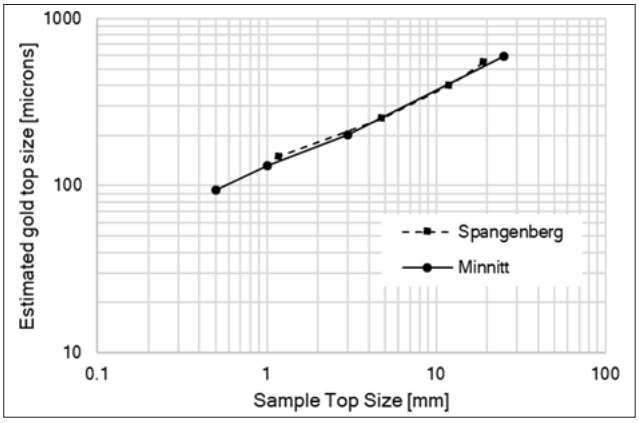


Figure 2. Gold grain/cluster top size estimated for data of Minnitt *et al.* and Spangenburg from observed sampling variance estimated from individual assays of 30 nominally identical subsamples assayed to extinction.

and particularly on the skewness of the sampling distribution.

Figure 2 shows the 95% passing size of gold grains/clusters calculated from the observed variance over 30 nominally identical subsamples at each top size for a ~12 g/t gold ore. It is likely that the gold at the larger top sizes is in the form of substantial clusters and not discrete compact grains.

The observed behaviour, virtually identical for two independent analyses of the same type for a single gold ore, shows a reasonable log–log decrease of estimated top size of the grains/clusters as a function of top size to which the ore was crushed. This permits the calculation of the sampling variance at any intermediate sizes and may permit some extrapolation to larger or smaller sizes. Clearly, what are probably clusters are being broken down with the crushing until at 0.5 mm top size the clusters have been broken into grains.

It is also interesting to compare the sampling probability density functions calculated for the data of Minnit. These are shown in Figure 3. The skewness of the distribution is clear at the 25 mm top size. Note also that the density functions calculated provided an excellent match to the actual distribution of the 30 results at each top size.

The ore characterisation provided by the method of creating set of nominally identical subsamples of the ore and analysing to extinction to permit calculation of the variance over the subsamples and *interpreting the results by the method presented here* is far more useful and sensible than attempting to interpret the data according to Gy's so-called K-α model which has caused difficulties and controversy for many years now.

To sample a gold ore and achieve a result with a controlled overall sampling variance, it is necessary to consider all sources of variance that impact the total sampling and analysis variance. The sampling of a run of mine ore is the most difficult task as the ore grade can vary substantially in the raw ore coming from one or more mining faces. The mine plan and the *in situ* grade estimation data upon which the mine plan is based is the only source of information at the early stage of mine development. It is better to over-estimate the variability than to be tempted to believe the ore is more homogeneous than it might be. Next it is mandatory to have an estimate of the ore heterogeneity as determine by the sampling constant for the ore at various top sizes to which it might be crushed. The variation of the heterogeneity (as quantified by the sampling constant) with the size to which the ore is crushed must be established by a test similar to the procedure described above. Only then can a sampling system be correctly designed in a way that will stand up to scrutiny under commercial sampling conditions.

Example

Let us take the case envisaged above and consider the design of a sampling system that will achieve very good results even when the average grade for a lot is lower than the overall average. Note that the sampling constant for the ore is

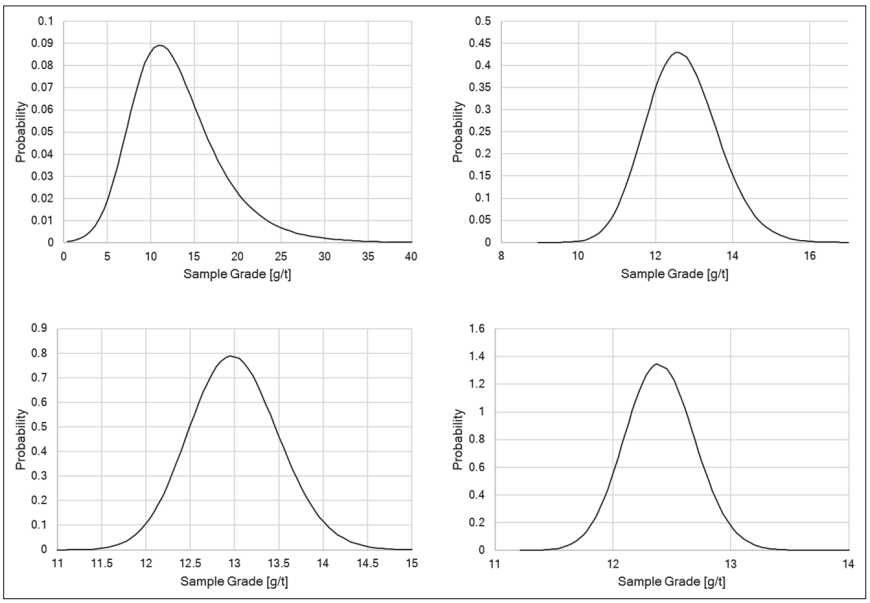


Figure 3. Sampling probability density functions for the ore at a series of top sizes to which the ore was crushed. 25.0, 3.0, 1.0, 0.5 mm, top to bottom, left to right. Sample mass is 273 g in all cases.

inversely proportional to the ore grade so that low grade or is more heterogeneous than high grade ore. With the objective of considering a somewhat worse case than average, this example will take the average grade to be 10 g/t with a standard deviation of feed to the sampling plant of 15 g/t. The lot mass for sampling is 400 t, which production from one day which is to be classified as ore or waste. The grade variation in the feed to the sampling plant will be taken to be random with the standard deviation of 15 g/t. The analysis will be assumed to be carried out by Photon Assay with a standard deviation of 1.5% relative (the grade is above 1 g/t). It will be assumed that the ore is fed to the sampling plant over a 2–3 hour period and design will be for 2 hours or primary feed. The 95% passing size of the feed is 75 mm.

The variance due to the time variation of the feed grade (distributional heterogeneity) is determined by the number of increments taken over the lot by the primary sampler.

$$\sigma^2_{DH} = \frac{\sigma^2_{feed}}{N_{inc}} \quad (3)$$

The mass of ore collected as primary increments is determined by the feed rate, number of increments, the aperture of the primary cross-stream cutter and the velocity of the cutter through the stream as

$$M_{pri} = N_{inc}\frac{Qw}{3.6v} \quad (4)$$

where Q is the feed rate in tph, w is the aperture in metres ($\geq 3d_{95feed}$) and v is the cutter velocity in m/s (max 0.6 m/s). The mass is given in kilograms. The primary increments are crushed to 3 mm and sampled by a secondary sampler and the collected mass of the secondary increments is determined by a similar formula.

To determine the variance due to the IH of the ore at the primary and secondary stage of sampling, Equation (1) is used with appropriate values of the sampling constant.

The optimisation of the sampling protocol is best done by setting up a spreadsheet using the formulae provided herein and then working with the number of primary increments collected and the mass divisions at each stage of sampling. It is never immediately apparent where the controlling variance will appear.

The heterogeneity of the ore is controlled by the grain/cluster sizes in the ore. In what follows it has been assumed that at effective sizes are 900, 220 and 50 µm at top sizes of 75, 3 and 0.106 mm. These are plotted in Figure 4. Also plotted are the sampling constants at the three top sizes.

The variance budget for the sampling system after optimisation is provided in Table 1.

The optimisation indicated that the most critical aspect of the system was due to primary sampling DH. It was necessary to sample at 30 second intervals to bring the variance down. This then dictated the secondary sampling, which involved feeding the primary increments collected in a bin over a 4-hour period. This change from 2 to 4 hours was dictated by the need to collect at least six secondary increments for each primary increment. The mass of primary increments collected was 7500 kg and the mass of secondary increments collected per lot was 30 kg with crushing of primary increments to 3 mm.

Table 1. Variance budget for the sampling system after optimisation.

Component	Relative variance	Relative standard deviation (%)
Primary sampling DH	9.37E-03	9.68
Primary sampling IH	2.5063E-05	0.50
Secondary sampling IH	0.000084	0.92
IH due to splitting of secondary increments	0.001186	3.44
Analysis variance by Photon Analysis	0.00005625	0.75
Total for 400 tonne lot	1.07E-02	10.36
Total for 20 lots per month		2.32

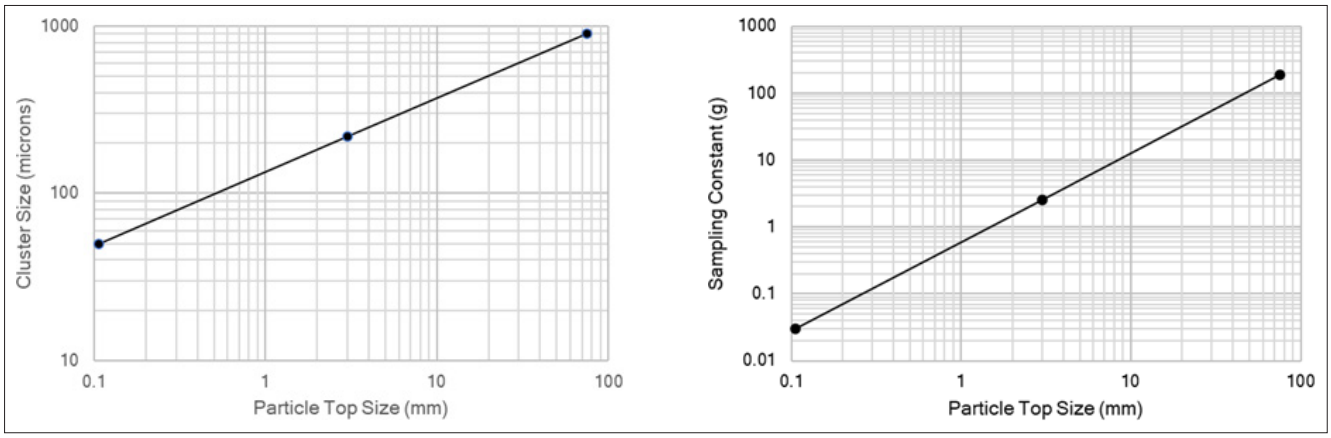


Figure 4. Assumed gold grain/cluster sizes and calculated sampling constants at 0.160, 3 and 75 mm.

Introduction to the Theory and Practice of Sampling

Kim H. Esbensen

with contributions from Claas Wagner, Pentti Minkkinen, Claudia Paoletti, Karin Engström, Martin Lischka and Jørgen Riis Pedersen

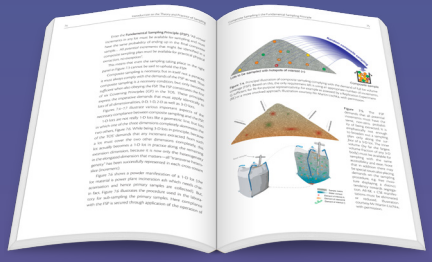
"Sampling is not gambling". Analytical results forming the basis for decision making in science, technology, industry and society must be relevant, valid and reliable. However, analytical results cannot be detached from the specific conditions under which they originated. Sampling comes to the fore as a critical success factor before analysis, which should only be made on documented representative samples. There is a complex and challenging pathway from heterogeneous materials in "lots" such as satchels, bags, drums, vessels, truck loads, railroad cars, shiploads, stockpiles (in the kg–ton range) to the miniscule laboratory aliquot (in the g–µg range), which is what is actually analysed.

This book presents the Theory and Practice of Sampling (TOS) starting from level zero in a novel didactic framework without excessive mathematics and statistics. The book covers sampling from stationary lots, from moving, dynamic lots (process sampling) and has a vital focus on sampling in the analytical laboratory.

"I recommend this book to all newcomers to TOS"

"This book may well end up being the standard introduction sourcebook for representative sampling."

"One of the book's major advantages is the lavish use of carefully designed didactic diagrams"



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The 30 kg of secondary increments was split to 2 kg at which point either four aliquots at 0.5 kg or two aliquots at 1.0 kg could be formed, the first for four replicate Photon Assays with a relative standard deviation of 1.5% per assay and the latter for duplicate 1 kg screen fire assays with pulverisation to 106 µm. The assay uncertainty for the screen fire assays was estimated to be larger than the Photon Assays, assuming a relative standard deviation for a single fire assay of 4%.

The results from this sampling example are very good for the monthly average relative standard deviation of 2.32%. It is clear that in this case, the critical issue is taking a sufficient number of primary increments from the highly variable feed. The IH of the ore manifests itself through the variance component due to splitting the ore at a size of 3 mm. Reduction of the ore past 3 mm is not necessary for Photon Assay and the Photon Assay method eliminates the sample preparation of the ore to nominally passing 106 µm with screen fire assay at 76 µm. The possible losses of gold in the preparation process are eliminated.

Conclusion

The material presented has explained the issues involved in the sampling for highly variance coarse gold ore based on heterogeneity assumptions that are in line with the heterogeneity found by Minnitt *et al*. for Witwatersrand ore. The calculations underline the fact that it is not generally possible to guess where the critical point in the sampling system design will occur and the value of having a reasonable estimate of the ore heterogeneity as a function of ore top size. The calculations highlight the value of modelling the sampling constant for the ore as a function of gold grain/cluster top size. Clusters of grains are clearly important to deal with.

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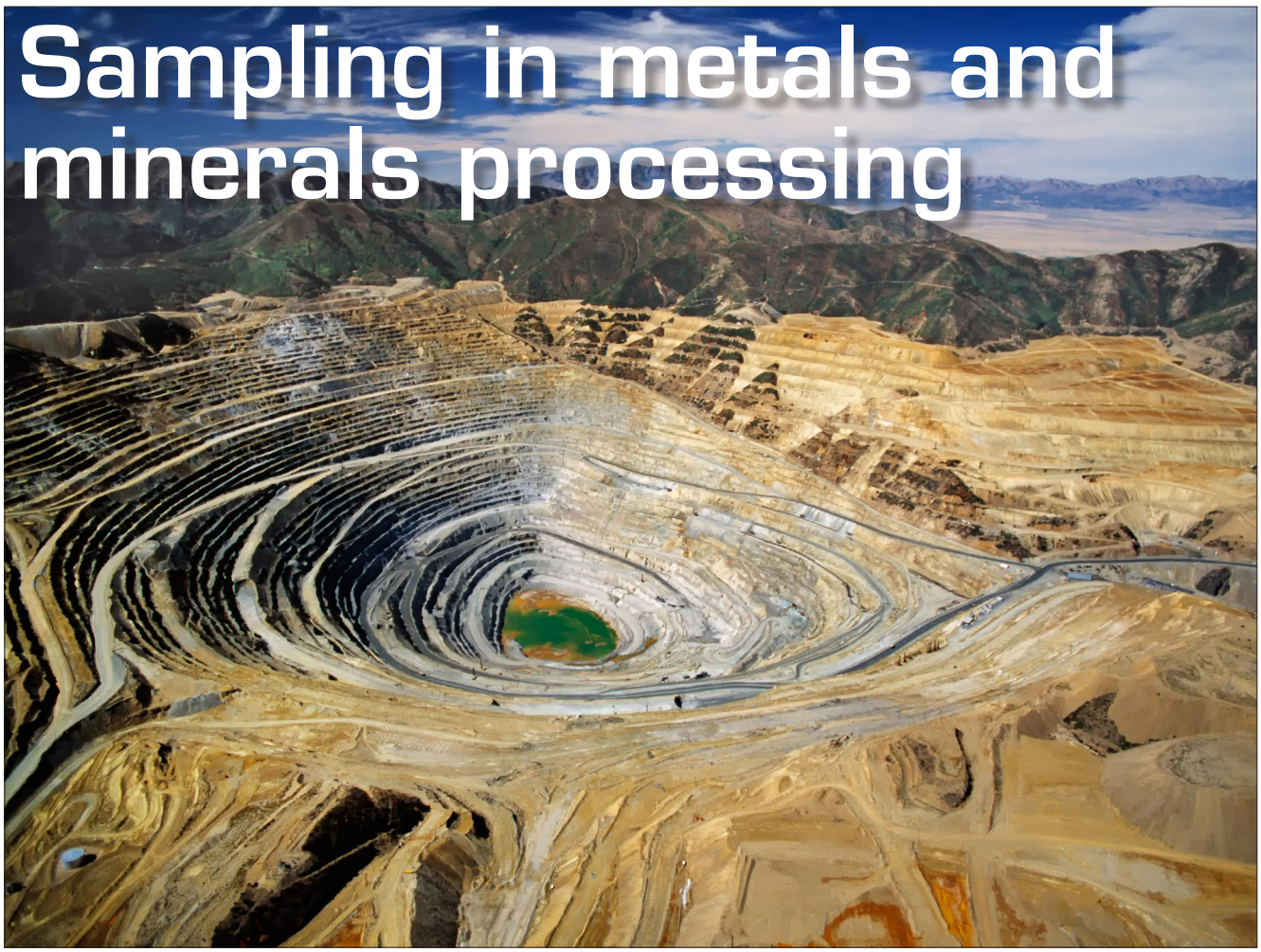
SAMPLING SPECIAL SECTION



Sampling in metals and minerals processing

Section contents

SAMPLING SPECIAL SECTION

Metal accounting: a direct link between sampling and financial management

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Editor's summary
As defined in the "Code of Practice for Metal Accounting",[1] Metal Accounting is part of Financial Accounting and helps in defining production costs and revenues, as well as stocks and WIP (Work In Progress) inventories. It is also the baseline for estimating the net value of the company. Metal Accounting is based on reconciled material balance which is itself based on critical measurements. Any uncertainty in measurement, due to the inevitable measurement error, in which the sampling error is generally the main component, results in an unwanted—and unnecessary—financial risk. Two examples are presented below together with associated economical risks and losses.

Example 1: Underestimating losses and overestimating metal in WIP

A custom copper smelter processes concentrates coming from numerous mines around the world. After blending, the concentrates are processed through a flash smelting furnace producing copper matte. The main copper losses at this stage are through slags and fumes. The latter are made up of fine particles containing copper, which are recovered and recycled to the furnace. But slags constitute a significant real loss of copper.

In this example, granulated slags were manually sampled on the conveyor belt discharge with one increment every two hours, collectively constituting a daily composite sample. To perform a quality control variogram analysis, a specific sampling campaign was performed by taking one increment every 15 min and analysing each increment. Though most increments had a copper content close to the usually observed daily average content for slags, several showed a significantly higher content corresponding to spots of matte *entrained* by slags. With the old sampling approach, such spots are *"hidden"*—hidden from view and hidden from metal accounting. For the baseline purpose it was then decided to install an automatic cross-stream sampler at the discharge end of the belt conveyor, taking one increment every 15 min.

For comparison, over one month, the old sampling method continued to be performed in parallel with the new, much more frequent approach. The average content for one month was 0.66% with the old method and 0.95% with the new automatic sampler, which is a significantly large difference when accumulating over time. It is clearly a bias as the day-by-day analysis indicated that the copper content was slightly lower for 5 days with the new sampler, but significantly higher for 13 days.

Considering a production of 1000 t/day of slag during 350 days in the year, and a price of US$9400 per ton of Cu, the value of the revealed copper loss can easily be calculated:

$$\text{Loss} = 350 \times 1000 \times (0.95\% - 0.66\%) \times 9400 =$$

US$9.541 million

This sampling issue has two financial impacts:

1) Significantly, one part of copper is reported with slags due to thermodynamic equilibrium between slag and matte phases. But another part is due to entrainment of matte with slags in the form of matte droplet. This is what occurs when observing "spots" of high copper content. This is due to poor control during the slag and matte discharge process. By observing this effect and the operating conditions when it appears, it is possible to improve the process control strategy, specifically for the quantity and quality of the furnace feed, provided the feed control, based on sampling, is sufficiently accurate to avoid such spots. The recovered monetary value will be able to pay for installing an accurate cross-stream automatic sampler, which will provide a much-improved regular analysis enhancing the possibilities for furnace control. It can also pay for a well-designed automatic sampler for feed control, or, much better, an online full-stream analyser that will drastically reduce total process sampling errors.
2) When establishing the material balance for metal accounting, such hidden losses run the risk of impacting also on the intermediate stocks (WIP) estimates. Indeed, some of these, such as matte skulls, dust or converter slags, are very difficult to measure in mass, but more seriously also for copper content. Consequently, typically no measurements are performed, or if any are carried out, they will unavoidably result in large unwanted measurement uncertainties. When running data reconciliation, the imbalance due to biased slag sampling is counterbalanced by the less accurate parameters associated with the relevant WIP, namely their Cu content. Month after month, the overestimate of Cu mass accumulates as an overestimate of the material mass and of its Cu content. At the extreme limit, Cu content can exceed 100% (physically absolutely impossible of

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course) or inventories may report large WIP masses, which *de facto* do not exist. When such discrepancies between accounted inventory and reality are revealed, an accounting adjustment will have to be made, which will decrease the value of the company and, ultimately, give it a bad reputation on the stock market—many negative cascade effects can arise from neglect of basic sampling quality requirements.

This example shows how a poor sampling procedure can hide a potential route of revenue improvement and can generate a financial risk at the level of **several millions of US$ per year**.

Example 2: Copper concentrate trading

A custom smelter buys copper concentrates following this procedure:

1) The copper concentrate delivery is accepted based on "provisional data" provided by the *seller*: the wet mass of the material, the average moisture content, the inferred dry mass and the average metal contents.
2) During the concentrate delivery unloading, the mass of the wet material is measured by the *buyer* and samples are taken for determination of moisture and metal contents, constituting the "smelter data".
3) Finally, after a few months, negotiations between seller and buyer ends with a set of mutually acceptable "final data" which are then used to calculate the objective *value* of the delivery for final invoicing. If too large discrepancies are observed between provisional data and smelter data, an umpire laboratory can be used to redo sample analysis and a conformity assessment organisation will be asked to control mass measurement systems as well.

Provisional data and smelter data come from "measurements" which are inherently uncertain for mass, moisture content and Cu content. A representative of the seller can be present during delivery unloading to *validate* the wet mass measurement and the moisture content determination. In that case, the final value for dry mass is defined during the delivery, and the negotiations are focused on metal content only.

The delivery unloading is carried out using a belt conveyor. A static belt weigher measures the mass per batch (batches are typically scaling at approximately 5 tons). The following cross-belt automatic sampler is taking one primary increment per this batch mass (5 t). 100 increments corresponding to a lot of 500 tons are combined for copper analysis.

This standard procedure gives a relatively good precision. Typical relative measurement errors are 0.21 % for the wet mass and 4.9 % for the moisture content, giving a 0.5 % error for the dry mass and 0.66 % for the Cu content. The last value corresponds to TOS-correct sampling, but it is well-known that cross-belt samplers (also named hammer samplers) **cannot** provide correct, bias-free sampling.

Considering, for example, a delivery of 17,000 tons with a provisional Cu content of 26.000 % and a smelter Cu content of 25.825 %, this analytical difference is acceptable by both parties, because it is of the same magnitude as the measurement error for Cu content. This difference corresponds approximately to a value of US$280,000 (estimated for copper alone). But **if** the smelter uses a poor-quality sampling system, its results will not be able to influence the negotiation so that the final value will be closer to the provisional value provided by the seller, which has assuredly slightly overestimated—this is not good for the smelter.

Conversely, a high-quality sampling system, associated with an efficient metal accounting system (data reconciliation reducing the uncertainty in the delivery quality estimate), will tip the scales in favour of the smelter. This positive economic difference can represent up to about **US$1 million per year** for such a wise smelter.

Conclusions

These two examples demonstrate with great economic clarity the advantage of adapting accurate (bias-free) sampling systems, based on the Theory of Sampling (TOS), as verified by *competent persons*,[1] to limit the financial risk from hidden evidentiary lacunae—and generate revenue instead. Only copper has been considered here, but other sources of revenue such as precious metals—or penalties associated with undesirable components—will also be impacted by the quality of the sampling system. This is why *any* investment in accurate and efficient measurement systems, including sampling systems, will very often be counter-balanced by the associated *revenue increase*. This will also be able to pay the costs of system maintenance, which is vital to maintain the stringent level of accuracy needed for *proper* metal accounting.

Reference

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SAMPLING SPECIAL SECTION

Loosen the TOS stipulations and face the economic consequences

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Grab sampling for material accounting

A small polymetallic mining operation intended to evaluate the potential for upgrading its mineral processing plant by adding a new metal recovery line at some strategic point in the circuit. The objective was to recover some of the companion metals as by-products of the main commodity. These potential by-products had so far been disregarded because of non-favourable market prices, relatively low grades and lack of ore-body knowledge. A geometallurgical assessment revealed that these metals were hosted in suitable mineral phases and could be easily recovered though further concentration. The circuit itself was relatively simple with very little recirculation, each stream of the circuit branching out from the main route being sent for stockpiling or disposal in waste piles. To evaluate at which location in the circuit upgrading would be optimal and which strategies to implement, a thorough *material balancing* was needed in order to assess the overall distribution of the metals in the different plant streams, and in particular in the so-called *residues*, in terms of metal grades and recoveries.

The data available for this case is a combination of on-line sensor data (flowmeters, belt weighers etc.) as well as analytical assays from samples collected at various locations in the circuit, or from some residue/wastes stockpiles; the data covers one month of operations.

A first attempt at reconciling the comprehensive data base showed huge variations between the initial and reconciliated data for the main commodity (±50%) and significant discrepancies between metal accounting and real production outputs, which were even larger for the lower grade by-product metals (deviations up to ±150%). This issue was not new and, as a consequence, an external audit was conducted in order to evaluate the sampling procedures in use.

Three main points of concerns were raised:

1) The coarsest residue streams were sampled by grab sampling "all around the perimeter" at the bottom of the stockpiles only.
2) Sampling of a hydrocyclone bank overflow. Indeed, the operator instead of collecting the *whole overflow stream* from the collecting tank, was systematically collecting the overflow of one hydrocyclone only (the most accessible one).
3) The primary pulp samples were stored in "big bags", which were not leakproof and which were in fact used to drain out the water "without losing the sample".

All of these sampling practices are in opposition to the TOS' basic principles, whereby a sample is considered representative only if all particles making up the lot have the same probability to end up in the final sample. The sampling practices revealed by the audit were clearly not in compliance with this cardinal rule and were identified as responsible for the metal accounting discrepancies observed.

The technical explanation as to *why*, and *how to* remediate these deficiencies follows.

1) Grab sampling is a very dangerous practice as it generates a range of sampling errors (GSE, IDE and IEE), most of which cannot be quantified, nor corrected for. Even though this has been known for a long time at the mine site, grab sampling was still thought to be "good enough" by the operator and by management. In the present case, the grab samples collected from the stockpiles typically weighed around 20–30 kg, too small to be considered representative! Indeed, getting a representative sample (i.e. TSE < 20%) from the corresponding stockpile, some of the coarsest streams would require at least a 20–30 ton sample. **Remedial action:** Sampling the same materials, but at the discharge point of the corresponding conveyor belt feeding the exact same stockpile, using composite sampling, would achieve a TSE of about 4% with only a 20 × 20 kg aggregated sample. This will result in a representativity which is 20/4 = 5 times improved, for one or two hundredth of the weight (i.e. *400 kg as opposed to 20–30 tons*). Not included yet in this balance is the huge time and efforts saved, which, of course, will also impact in the bottom line significantly.
2) By only extracting from the *most accessible* hydrocyclone overflow stream from a bank of six hydrocyclones, the operator was effectively only sampling one-sixth of the whole stream and, therefore, committing several serious sampling errors (GSE, IDE and IEE). Worst, these errors were *systematic* as the operator always sampled the same hydrocyclone. **Remedial action:** This is, of course, an issue that can easily be overcome by sampling the *whole* output stream—especially as the output hydrocyclone overflow collection tank is located only a few metres away from the position of the present calamity.
3) In metallurgical accounting, the moisture content and wet mass of the material being sampled is of equal importance as metal grades for determining the mass of contained metal

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in a given stream.[1,2] By allowing pulp samples to "dewater" from non-leak-proof big bags before measuring the moisture content, the operator introduced an enormous bias in moisture content estimation and, therefore, also in the estimated metal content after reconciliation. Also, this procedure resulted in a considerable loss of ultrafine particles (slimes), which "happen" to contain significant amounts of some of the desired by-product metals, but were lost with the uncontrollably leaking water. **Remedial action:** This issue was easily overcome by placing the pulp samples in *impervious sealed containers* for immediate delivery to the weighing and moisture determination station.

The TOS' universally optimised 1D sampling approach

Large heaps, stockpiles or similar storage facilities cannot be sampled *in situ* (grab sampling). They can only be sampled correctly (in theory and practice) through a lot of work, such as transfer or displacement of the whole lot, which is often not practical and always costly. Indeed, such (very) large multi-modal lots are frequently also extremely heterogenous. Such industrial 3D lots must be converted into a 1D lot (in which the two width–height dimensions are negligible compared to the third processing dimension). In practice, this often means transferring *the entire lot*, without material losses, on a conveyor belt and collecting the samples during this process. This is admittedly a costly, time-consuming process, but it does guarantee representativity. With (very) large lots, there is always a desire to find a cheaper and logistically less demanding solution—always subject to the universal representativity demands.

And there is such a solution in the present case. The whole sampling problem could simply have been eliminated before the stockpile had been completed. Instead of sampling the 3D stocks, it is much easier to sample the 1D streams **before they reach** the terminal end of the conveyor belts used to build up the stockpile. The most efficient sampling always takes place while the lot is a moving stream, and this can easily be performed so as to guarantee representativity by using correctly designed, usually automatic, sample cutters at the relevant discharge point, and by applying material-dependent composite sampling. A much simpler, much cheaper and guaranteed TOS-compliant solution!

Lessons learned

In the present case, if the decision had been made based on the initial *non-representative grab samples*, the upgraded processing circuit would have been implemented at the wrong process location and the corresponding designed flowsheet would have been sub-optimal, if not useless. The incorrect sampling issues have instead been resolved with very little investment—an external audit and three automated samplers—which served both the expansion project as well as the daily production control and reconciliation obligations well.

The incorrect grab sampling practices showcased above would have resulted in unacceptable financial consequences in the form of a net loss of >2M€. This figure corresponds to the Total Investment Costs (TIC) of the initial by-product recovery circuit designed for the wrong process stream and was calculated based on simulation results through process modeling and simulation software based upon the biased data. The final TIC values are extremely sensitive to the circuit feed rate which determines the size (or number) of processing units necessary. In the present case, the feed rate of the originally selected process location was *double* that of the plant stream selected after the audit. This means that the original by-product recovery circuit was severely over-sized. Worse, ⅔ of the TIC of the original circuit was accounted for by gravity recovery equipment, which, however, is inefficient in the size range of the process stream selected, as revealed by the audit.

In the mining, and many other industries, business decisions and project evaluations are heavily dependent on representative sample collection along the entire value chain from exploration to closure.[3,4] Sampling errors are invariably larger when samples are collected and, therefore, must be representative of *several* metals or properties *simultaneously*,[5–7] such as was the case here where several new by-product metals were targeted. Only implementation of strict, TOS-compliant, sampling procedures at the earliest stage of a mining project will allow proper management of technical and economic *risks* by preparing for best possible business decisions through access to documented reliable data to be used to optimise a mine plan over the full Life of Mine (LOM) horizon—ultimately also a prerequisite for maximising the Net Present Value (NPV).

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SAMPLING SPECIAL SECTION

Costs of inferior sampling related to calibration for optimal mineral sorting

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This example originates from the mining industry with some parallels to the previous exploration example.

Decision and routing of material into ore and waste streams is achieved using dedicated Particle Ore Sorting (POS). POS is a mineral processing method, where particles in a stream are identified individually by a sensor-based detection technology (e.g., X-ray transmission or near infrared spectrometry) and—based on binary classification into ore and waste—are separated using targeted pulses of compressed air (Figure 1).

POS is often physically located separately from other functional units of the process, such as milling and flotation. A POS process island as shown in Figure 2 usually comprises of crushing, screening, sorting and auxiliary equipment, such as the compressor station delivering the compressed air for the physical separation process.

The efficiency of POS depends on two fundamental factors. One is the detection efficiency, i.e. the reliability with which the equipment correctly classifies ore as ore and waste as waste. The other factor is the efficiency of the pneumatic physical separation process.

The *value* created by a sensor-based ore sorting process often lies in the rejection of *marginal waste*. The inherited value would not justify spending the costs of processing and is described by the so-called cut-off grade. The sharper the sorting island can operate to this cut-off grade of the separated waste, the more economic value is created. If the grade is lower, additional mass could have been rejected, saving processing costs and debottlenecking the plant for higher grade feed which results in additional revenue. If the waste grade is too high, value is lost to the waste fraction and the ore reserve is underutilised. In mineral processor terms, high grade ore must be recovered, achieving a high recovery of the pay element(s) in question, though the focus lies on controlling the waste grade. A recommended practice is here to install a suitable sampling system on the waste material stream from the ore sorting station. What makes a POS system special in the context of the TOS is that POS processes particles sized 10 mm and larger, necessitating higher sample masses than with smaller average particle sizes due to the Fundamental Sampling Error. As a consequence, it results in the necessity to apply suitable automated mechanical sampling systems.

So far, so good. But what is the decisive increment extraction rate and what should the sampling rate be to discover fluctuations in waste grade over time with a desired fidelity? What if for half of the day the waste grade is too low and for the other half it is too high? Daily sampling would then mask this fluctuation and indicate that the waste grade is exactly on target.

A benchmark case is POS separation with high ore-to-waste and waste-to-ore misplacement, reducing recovery and increasing mass flow towards the main plant. A sampling station collecting increments for a composite day sample averages out the fluctuations of waste grade,

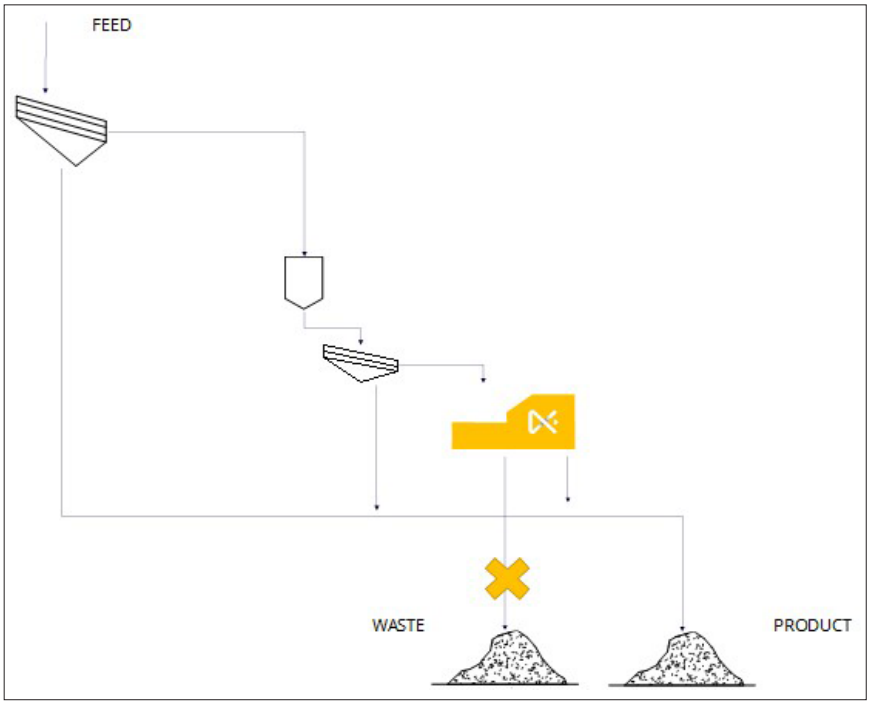

Figure 1. Simplified flow-sheet of a POS station. The undersize flows from the screens are too small for sorting and are bypassed and combined with the product fraction from the POS equipment. The cross marks the position of sampling the waste fraction.

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Figure 2. Sorting island installed at the Mittersill tungsten mine in Austria.[1]

even though a Sampling Error may be minimised according to the TOS.

An optimised case addresses optimisation of the sampling protocol. For example, by increasing the increment extraction and the accompanying assaying frequency to better monitor in-stream fluctuations over time. This is mainly an investment in the sampling, sample preparation and assaying operations. It is expected that this will be mainly a proportional increase in operating expenses. Better visibility into in-stream variation combined with a faster turnaround time of assay results makes it possible to optimise the operational parameters of the POS equipment to better follow the variation (i.e. distributional heterogeneity) over time.

This example illustrates the specific sampling challenges for POS technology due to large particle size but is in principle directly transferable to performance monitoring of all process equipment. Equipment control and optimisation must be data driven and process focused using fit-for-purpose sampling equipment and procedures to unlock value along the mineral process value chain.

NPV over identical mine life	
Base case	$712 million
Optimised case	$763 million

The increased *NPV* over the lifetime of a typical mine is $51 million: more than sufficient to pay for the efforts of designing and implementing the optimised sampling protocol and additional assay costs. This is a quite satisfactory investment on the table of any board of directors!

In mineral processing there is so much more to understand and to monitor better, with which to increase efficiency and thereby to increase both profitability as well as sustainability of the industry.

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SAMPLING SPECIAL SECTION

The hidden costs of poor sampling in the mineral industry

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There are costs and there are costs …

There are different types of cost in sampling: CAPEX, OPEX, paybacks and hidden costs; the last one being more complicated to evaluate. CAPEX (capital expenditure) of a sampling station is easy to determine: the customer (end user or engineering firm) contacts us and/or our competitors to obtain a cost estimate. This should always contain more information about maintenance, and a spare part list so as to estimate OPEX (operational expenditure). Many examples have already been given to demonstrate and calculate paybacks of a bias-free sampling station in the mining industry for trade sampling. The magnitude of such paybacks are from a few hundred thousand euros to a few million euros per year depending on the commodity being produced (iron, copper, manganese, bauxite, coal etc.), plant capacity and, of course, the type of bias. Many case studies are presented in this collective Sampling Column.

All international sampling experts can confirm similar experiences as those reported below, while performing on-site measurements in order to (a) control brand new sampling solutions, (b) control existing sampling solutions to estimate inherent biases and (c) design the best sampling plan and technical approach to obtain representative samples. Because of the large numbers involved, as well as due to a high level of material heterogeneity, *appropriate sampling* is a well-known issue in the mining industry. Nevertheless, all the information above is necessary to convince management (technical and financial) to invest in these vital, large sampling stations.

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A worst-case scenario

In a worst case, an iron ore producer ended up losing a long-term contract with his client (steel producer) because the producer was not able to guarantee the quality of the ore over several months. None of the sampling solutions installed at the producer's port ship loading facilities complied with ISO 3082; which is the International Sampling Standard for iron ore; and neither had they been designed according to the Theory of Sampling (TOS).

But not always

Nevertheless, this is not always clear. A subcontractor was bidding for a new iron ore beneficiation plant where a sampling station compliant with ISO 3082 was required. During our technical meeting, a complete sampling station (a primary sampler and two different stages of size reduction and mass division) was presented. The project manager was looking at the drawing of the complete station and asked: *"Where is the sampler?"*. He did not understand that a complete station is required for the project and smiled back to us: *"This is not what we need. We looked at the PID and it shows a single spoon called "Sampler". We included €50,000 in our quote for this spoon."* He did not agree with our explanations and all our calculations and finally said: *"No way"*. Six months later, after all the appropriate technical aspects had been clarified between the subcontractor and the engineering firm, the project manager came back to us, requesting a quote for the complete sampling station that had been presented earlier. The final cost was more than half a million euros.

In the mineral sector

In the mineral industry, numbers and costs are at lower levels, but sampling errors and/or biases can also have important financial consequences that are equally difficult to demonstrate and evaluate at the beginning of a project: these are the *hidden costs*. We have listed below some examples seen in our few decades experience as a manufacturer of sampling solutions.

Case 1

A few years ago, a mineral processing plant decided to control its production along the full process of crushing raw material and screening them into specific size fractions. A few cross-belts and screw samplers were installed at various locations in order to control chemical composition. It was understood by everyone that these types of samplers do not comply with the TOS, nor any existing sampling standard and that the material collected cannot be representative. Nevertheless, analytical results were always "on target". Was it because the chemical composition of the product was "almost homogeneous", or because the specific size fractions collected by these non-representative samplers were the only ones of interest in the contract specifications—nobody knows!

Two years later, the plant wanted to remove manual sampling elsewhere in the plant, and management decided to install the same existing technology (screw and cross-belts), now to control product quality at their truck loading stations. The critical aspect to be controlled was the size distribution. Samples were required both for the plant's own laboratory, as well as for their client's.

The analytical results of these analyses were all way *out-of-specs*! Both laboratories went crazy. Plant management

first decided to re-process some of the product already loaded in trucks (nightmare); then decided to stop the plant for few days in order to inspect all the crushers and screens to better understand the cause of this non-conformity. The plant finally had to pay penalties to its customer for non-compliance with the contractual specifications.

The explanation is easy for anyone who is familiar with the basics of the TOS: cross-belt samplers (also called hammer samplers) were not able to collect the fine material located close to the belt, and, therefore, this type of sampling technology under-represents the proportion of fines—and the screw samplers crushed down particles having a specific size fraction due to friction on particles in the gap between the rotating screw and its casing. This increased size fractions of the small particles, resulting in the reduction of the other size fractions of larger particles. This had nothing to do with the quality of material being loaded, but was due to the sampling technology that modifies the size of some particles. The client forced the plant to improve quality control in their process because they had lost confidence and the plant was finally forced to replace these non-representative samplers by appropriate representative ones. It is difficult to estimate the hidden costs of this entire issue, but the economic consequences for the plant are very clear.

Case 2

Another mineral processing plant was built at the beginning of the 2000s. There are several process stages before the furnace, which is fed by air-slide conveyors. The size distribution of the particles feeding the furnace is controlled; especially the proportion of fine particles; so as to optimise process efficiency. A "sample taker" was installed in one of the air-slide conveyors. This sampling system is composed of a single opening with a vertical pipe in the lower part of the air-slide where material is supposed to "fall" by gravity; two valves allow material to be discharged and collected.

To better comprehend the sampling issue, understanding of the working principle is necessary. An air-slide conveys material by the means of a fluidising bed. It is composed of two casings; one above each other; separated by a fluidising grid. Air is introduced in the lower part and passes through the fluidising grid so as to create the fluidising bed. The incline of the air-slide creates and guides the flow toward the discharge end of the conveyor. Due to the airflow, turbulence creates a high level of segregation, based on both density and size of particles in the product flow. The sampler in place creates an opening in the fluidising grid with a pipe going down that guide sampled material by gravity to a sample collection vessel; two gates prevent from any pressure difference in the process.

Due to this working principle, the device collects particles located close to the grid, which are always the larger and heavier ones, while the fine particles remain in the upper part of the enclosure and will consequently follow the main stream, resulting in an under-representation of these fines. Stabilising the process has always been an issue at the plant and it is understood that the existing "sampling" equipment is not able to give the process operators the necessary accurate information (content of fine particles) to optimise their process.

A decision was made to replace the existing non-representative sampler by a TOS-compliant correct sampler. Care was taken on the flow of air as well as on the limited place available to install a new sampler. This is why a new sampling solution has been especially designed to meet these special requirements. Hidden costs are also significant in this example, but complicated to estimate in details. The only solution is: representative sampling!

Case 3

Energy is critical in mineral processing plants for two main reasons: cost and CO_2 emissions. In the lime industry, the process is composed of a kiln (vertical or rotary) to calcine limestone ($CaCO_3$) in order to remove CO_2 and obtain CaO (lime). Sampling at kiln discharge in order to measure the remaining CO_2 content (unburnt content) gives the necessary information to optimise the kiln process in terms of product quality and to reduce energy consumption. Cross-belt solutions are popular in this industry and, as said previously in Case 2, fines are not collected (or at least most of them) which creates an important bias, because they are consequently under-represented in final sample. This results in biased measurements on the unburnt content (the smaller the particle is, the better the calcination has been).

In this plant, when a part of the production is considered as being out-of-spec, it goes to waste. This part has been evaluated and fluctuates from 5% to 12% of the production. In order to reduce this waste, operators increase the heating process resulting in a significant rising cost of energy. Are they going to waste because of real poor quality or only because of a poor non-representative sampler? The solution was to install a representative sampler at belt end discharge of the conveyor located directly after the kiln, in order to be as close as possible to the heating process and to reduce the lag time between sampling and analysis.

It is again difficult to estimate the hidden cost of energy when operators increase heating process, but the numbers may be significant. Nevertheless, it was easy to calculate the payback of the sampling station based on the portion of production that was wasted in this plant; payback of the TOS-compliant sampling station was within three to four months only!

Case 4

Another lime producer received claims from its customer because the remaining CO_2 was out-of-spec in some specific size fractions (not all of them); and this issue was not constant over the time. A solution was found: measure the remaining CO_2 at the discharge of a crusher located after the kiln, so as to control the quality of each size fraction of the lime sold to the customer. A sampling station was installed and increments screened into the different size fractions of the contractual specifications; each of these was prepared individually in order to obtain a final sample representing each of all the size fractions produced and sold.

The number of claims was reduced significantly, with an obvious commercial advantage for this plant.

Conclusions

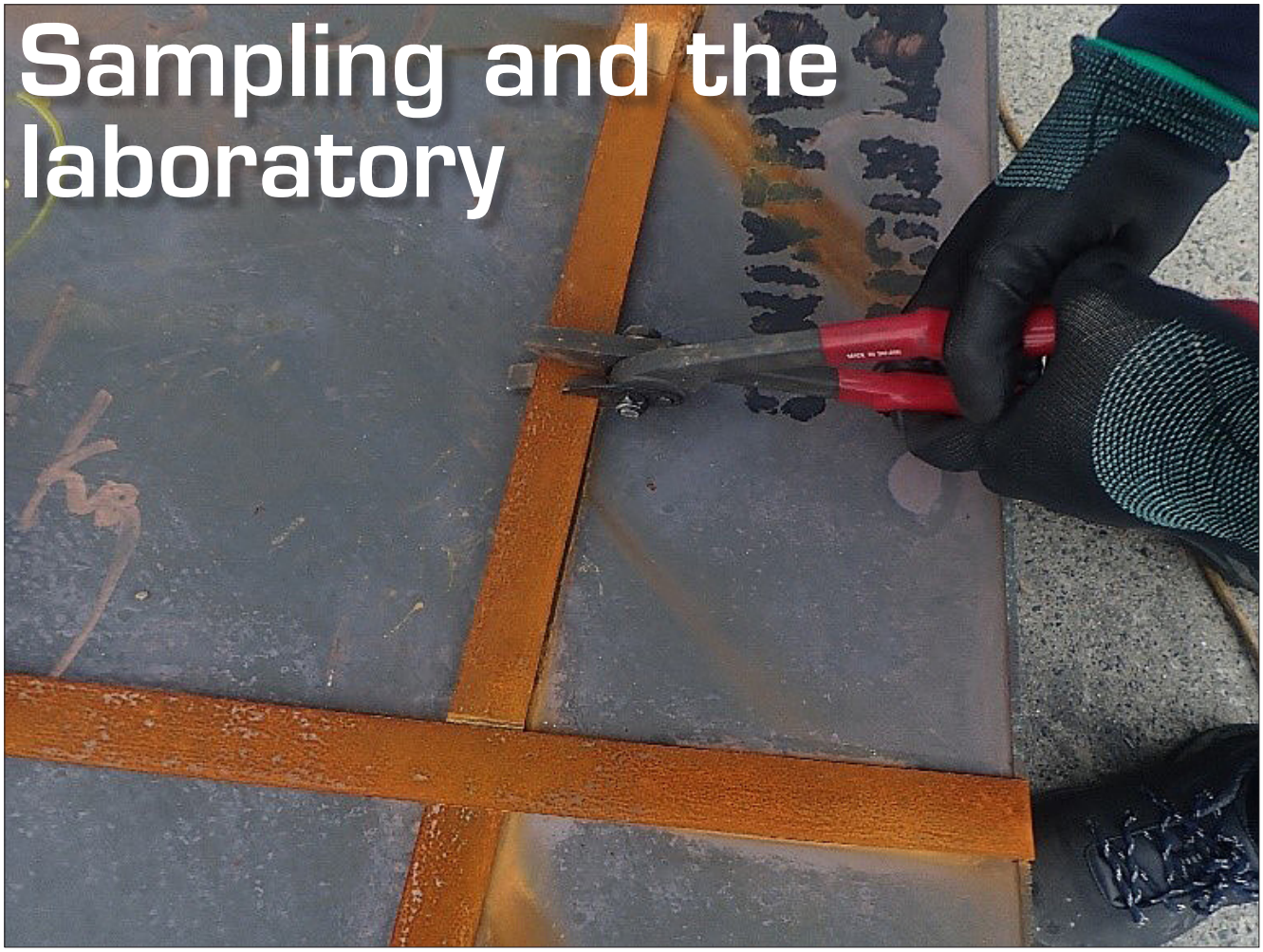
Such hidden costs due to poor sampling are common in the entire solid bulk industry. To avoid the famous "if only I had known this before!", knowledge of the good practices in sampling and in the TOS should be improved and increased at all different levels of management to give them all the tools to take the right technical and financial decisions. This does not necessarily mean to invest in solutions that are more expensive, but to better understand what is really necessary to meet their expectations and, thereby, stop losing money. Whatever the situation is—quality control, process control, metal accounting, trade—sampling is the first crucial step to reliable measurements and many decisions are taken based on these analytical results. It is worthwhile remembering a famous sentence of M. Pierre Gy: *"On primary sampling, bias can be up to 1000%, up to 50% on secondary sampling, whereas it never exceeds 0.1–1% in analysis"*. Reliable (accurate and precise) analysis requires representative samples.

The skies are clearing for the 10th World Conference on Sampling and Blending (WCSB10), 1–3 June 2022

Chairperson Elke Thisted and Head of the Scientific committee, Kim H. Esbensen flanking Proceedings Editorial Assistant Anne J. Cole

Register for WCSB10 at https://wcsb10.com

SAMPLING SPECIAL SECTION



Sampling and the laboratory

Section contents

SAMPLING SPECIAL SECTION

The TOS—a must in the analytical laboratory (industrial, commercial, academic)

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Understanding what sampling variation is, and how it is estimated, has been a "light-bulb" moment for our analysts after having been introduced to the TOS principles.[1] So often we have had a situation where analytical work and results can be verified, but our customer still insists it doesn't meet expectations. Short of driving the poor analyst crazy with re-work tasks, which usually only produces the same "incorrect result", I now have an avenue of action that allows us to guide the customer and analysts to the path on how to focus on only taking representative samples. This is decidedly more welcome than always having to hear: "Take the sample back to the lab—repeat the analysis".

Much time is spent determining the combined total uncertainty for specific analytical methods under validation, however, very little attention is given to the preceding sampling errors and the challenges heterogeneity poses to this issue. I now know that sampling errors dominate over their analytical cousins. Also, using variographic characterisation as a quality control tool for process and measurement system monitoring is a very powerful technique that could help process controllers explain the sources of real process variations that occur on their product lines instead of simply following through by blaming the analytical lab. I found that the international standard DS 3077 (2013) and in particular its use of illustrations and industrial examples captured the true complexity of the principal types of Sampling Errors and helped to conceptualise the TOS principles in a strikingly visual way, making it easier for a typical chemical analyst to relate to the scenarios involved before analysis. After all, we have to isolate the absolutely smallest aliquot for analysis—as demanded by highly sophisticated analytical instrumentation. It is, therefore, highly surprising that the one area of greatest error affecting analysts' results is the same topic largely ignored in Analytical Chemistry/Science Training programmes, again the sampling errors. This gives rise to "brilliant" analytical results, i.e. extremely precise results, but for non-representative samples for which accuracy with respect to the lot is not accounted for. In fact the accuracy of the analytical results with reference to the original lot is completely without control—and one cannot even estimate the magnitude of the sampling bias incurred (because it is inconstant, as is another insight provided by the TOS). This makes for a very unsure analytical laboratory. After this course I wonder how many questionable results have been released by laboratories all over the world over many, many decades—and the revelations brought about by the TOS are still not known!

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SAMPLING SPECIAL SECTION

It does not matter what is wrong when applying TOS: it is money out of the window every time

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Gold segregation in pulps

An underground narrow **gold** vein (1–2 m width) operation was known to contain coarse gold particles up to 1.2 mm in size, and rarely up to 4 mm. The vein had an average global reserve grade of 17 g/t Au. Monthly reconciliations were up to ±50 % on grade.

From drill core and underground face chip samples, a 2 kg sample was pulverised and a 30 g fire assay undertaken. There were no formal sampling protocols or laboratory QA/QC system. With new owners, **much needed** systems were introduced into the existing laboratory. It was identified that the pulp duplicates displayed poor precision (±66 %). In addition, the pulverisers were not cleaned between samples and there was evidence of gold contamination between some samples.

Several tests were undertaken on 2 kg pulp lots, where the pile was mixed, flattened and 40 consecutive 50 g sub-samples taken for fire assay. The variability was remarkably high, and in one instance the range between the minimum and maximum values was 500 g/t Au. These findings confirmed that the pulps were **highly** heterogeneous due to the poor comminution of gold particles during pulverisation. Different pulp subsampling techniques further augmented the level of **Grouping and Segregation Error (GSE) influences. Also, day and night shifts processed pulps by two different methods**: the laboratory day shift homogenised the pulp by "mat rolling", then simply scooped off 30 g from the top of the pile, **certainly** thereby missing gold that had segregated to the bottom of the pile. The night shift placed the pulp on the mat, shook it rigorously, flattened the pile and cut a series of sample lines through the pile with a greater chance of picking up segregated gold at the pile base, **a kind of "Japanese slab cake" approach**. In essence, the "mat roll" method ***understated***, whilst the "slab cake" technique ***overstated*** the gold grade. The emphasis of day versus night shift could change between an inconsistent mix of exploration, grade control (as discussed here) and plant samples. Therefore, the negative versus positive assay bias on the grade control samples was variable.

During a four month leave of absence by the "overstating" shift manager, the understating shift manager had taken control and changed the pulp splitting to **be the new approach**. The mine records were revisited for this period, and it was found that a number of stope blocks representing *c.* 8 % of annual production had been abandoned due to the apparently low grades achieved (below the breakeven cut-off). The matter also caused production delays, as ore **supposed to be** included in the mine plan was not available.

The stope-bounding drives and raises were subsequently re-sampled using saw-cut channels and assayed using a new protocol. They were found to be of ore grade and subsequently mined out recovering 7000 oz Au. At the time of operation, these recovered ounces represented c. **US$7 M** in mid-2005 (**US$12.8 M** in July 2021). This would have been lost if the pulp issue had not been identified in a timely manner. **In addition to this tangible result, delays in the mine plan caused financial loss and previous misclassification will have caused unquantifiable loss.**

Figure 1. Screen fire assay is always a good option in the presence, or suspected presence, of coarse gold. It provides a good spatial measure of the problem. It is important to ensure that a nylon screen is used that is fire assayed to extinction. This removes sample-to-sample contamination of the screen. Duplicate or triplicate fire assays should be applied on the undersize fraction to check the level of heterogeneity—some "fine" coarse gold can still pervade the fine fraction.

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The key issue was that coarse gold needs to be treated differently.[1] Pulps bearing liberated gold cannot be homogenised; GSE can be highly problematic; and proper protocols and procedures must be set up both in the mine and in the laboratory. A screen fire assay was introduced to account for coarse gold (Figure 1), along with improved laboratory procedures and better staff training. The 2 kg pulp was split using a TOS-compliant riffle splitter to 1 kg for screen fire assay. QA/QC protocols were introduced, particularly covering equipment cleaning and contamination monitoring. Barren flushes between samples were introduced and were assayed at a rate of 1 in 20. Where visible gold was observed or high grades expected, additional barren samples were introduced and automatically subjected to fire assay. **What made the change highly economical? Introduction of proper TOS-training and procedures and responsible Good Laboratory Practice.**

Grab sampling for grade control

A shear-zone hosted underground operation had consistent reconciliation problems. Mineralisation did bear some coarse gold, though this was not dominant. Most gold was sulphide-hosted and below 200 µm in size. There was a general under-call with respect to the drilled reserve grade (7 g/t Au) of around one third.

Audit—and study the problem!

A test study was undertaken based on 200 routine grab samples collected from a 765 t stockpile. For the total population, the mean grade was 12.8 g/t Au, the minimum grade 0.01 g/t Au and the maximum grade 79.7 g/t Au. There are several grade permutations possible if an exhaustive 20 set sample batches are drawn. Out of 200 samples, the lowest grade combination of 20 samples was 0.1 g/t Au, and the highest grade 49.1 g/t Au. The mean was 10.6 g/t Au. The test stockpile was fed to the plant which has an autosampler after secondary crushing, where a batch mean head grade of 4.2 g/t Au was determined. The mean of the first grab 20 samples taken was 8.2 g/t Au, which implies under normal circumstances that the lot would have been sent to the plant as ore. Eventual plant reconciliation with the plant gave a batch grade of 3.9 g/t Au. At the time, the breakeven mine cut-off grade was 4.7 g/t Au, **which would have meant it going to waste.**

The operation was clearly battling reconciliation problems and achieving a lower head grade. The reserve model was based on diamond drill data on a 20–30 m × 20–30 m pattern. Face chip sample data was ignored, as it was biased and only represented around 50 % of mine faces due to operational constraints. As a result, all material dumped on the surface stockpiles, which included mineralised waste, and marginal, medium and high grade ore, was grab sampled prior to being sent to the waste tip or plant. Given the biased nature of grab sampling, most of the mineralised waste and marginal ore was sent to the plant diluting the ore feed. Grab sampling was considered the key issue. The grade estimate was also considered to be sub-optimal.

Figure 2. Grab sampling of gold mine stockpiles—a monumental exercise in futility!

N.B. Decisions on whether to send material from the stockpile to the plant were based *solely* on stockpile grab sampling (Figure 2). Each stockpile represented approximately 500–750 t of supposed ore. Twenty to twenty-five 3–4 kg samples (total in the range 60–100 kg) were grabbed from over stockpile at a fragment size of generally <10 cm. Each sample was sent to the laboratory for a 500 g cyanide leach (LeachWELL) pulverise-and-leach (PAL) assay.

This study showed that the use of grab samples to assess grade was problematic **in the extreme**. Most stockpiles were sent to the mill as ore. This was, in part, related to a higher proportion of gold in the fine (<1 cm) fraction, thus biasing grab samples high. An important point to note is that each grab sample or group of 20 grab samples did not represent the stockpile. Grab sampling is prone to chronic sampling errors (e.g. FSE, GSE, IDE and IEE). **FSE calculations indicated that a 25 t sample would be required from each stockpile to achieve an acceptable FSE of ±20 %.**

Improved approach: Grade control subsequently re-focussed to use the

diamond drilling, which was closed to a 12 × 12 m spacing. LeachWELL (1–2 kg) was used for all samples and grab sampling was stopped. The resource model was also improved via the use of an optimised kriged block model. A managed low-grade stockpile was introduced. As a tangible result, reconciliation improved to be within ±10 % for grade and tonnes within six months.

Where the money went: It was hard to evaluate the **unnecessary** cost effect of the grab sampling, but best estimates were that between Aus$2–4 M was lost by processing misclassified waste, and Aus$5–7M in gold lost by misclassifying ore as waste for a benchmark 12-month period—making it likely that potentially between **Aus$7M and Aus$11 M were lost per year**.

The cost of grab sampling is very nearly always high, and never higher than in gold mining operations.[2] Professional auditing is cheap compared to the amount of money saved! Lessons for upper management: if ever the term "grab sampling" is observed in a report, fire the relevant supervisor, get a professional audit, train staff at all levels on proper TOS procedures and enjoy the reaped economic benefits.

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Between the devil and the deep blue sea

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Sampling for analysis is a multi-stage operation, from extracting a primary sample, via sub-sampling… towards the final analytical aliquot. At each stage, a sampling error will result if not properly identified, reduced or eliminated, collectively adding to the error budget. Nobody wants the total measurement error to be larger than absolutely necessary, lest important decisions based thereupon are seriously compromised. Many unknown hidden costs can be found between sampling and analysis: lost opportunities and a lot of bold, red figures below the bottom line. In a previous issue, one of the peers of the world sampling community Pentti Minkkinen presented an extensive feature on the economic consequences of not engaging in proper sampling in this critical interregnum.[1]

Reference

1. P. Minkkinen, "Sampling vs analytical error: where the money is … ", *Spectrosc. Europe* **33(5),** 46–50 (2021). https://doi.org/10.1255/sew.2021.a25

SAMPLING SPECIAL SECTION

Laboratory test sample representativity: an easily neglected aspect in consignment and its economic impact

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An unrepresentative sample is unable to reflect the true quality of materials and goods, and will eventually cause laboratory chemical analysis results that cannot substantiate trade settlements between buyers and sellers. In quality inspection of mineral products and metals, sampling errors account for ~80% of the total error, with sample preparation errors responsible for ~15% and analytical errors accounting for only 5%. If sampling is poorly represented, no matter how accurate the sample preparation and chemical analysis, quality grading can be severely compromised. Ignoring primary sampling, there are still significant representativity problems arising from sample preparation causing all parties difficulty when trying to find an answer to the crucial question: "where did the money go?". Thus, at the second and third stage sampling levels also, huge economic losses can occur for the buyer *or* the seller. Three cases from the international copper industry sector are presented.

Example 1: Significant trade settlement impact from sampling and grading of high purity copper cathode material

Copper cathode material is usually divided into three categories according to the content of impurities. Impurity element concentrations of Class A cathode copper shall not exceed 0.0065% in total, while lead (Pb) must not exceed 0.0005% and iron (Fe) 0.0010%. Reliable control of misrepresentation of samples used for laboratory testing has a great impact on quality grading and pricing of high pure cathode copper.

Africa is rich in non-ferrous mineral resources, especially copper mineral reserves.

Many Chinese companies have started operating in Africa, building mining plants, concentrating mills and smelters, and eventually smelting and producing copper cathode material and selling it globally. Copper cathode material is usually produced and traded directly in the original size format of 80 × 80 cm square plates with a thickness of about 1 cm, which weighs ~200 kg per piece. To ease transportation, copper cathode plates are usually strapped together using high strength steel bands into bundles suitable for loading weights of typically 1–2 tons each.

If the Class A copper cathode sampling process is contaminated by strap steel bands, as shown in Figure 1, it will lead to an excessive iron content, resulting in a grade reduction of the copper cathode products. Each quality grade class reduction results in a price reduction of ~$30 per ton. For a smelter with an annual output of 200,000 tons of copper cathode with, say, 10% of samples contaminated, the annual output value is reduced up to **$600,000**, calculated as follows:

Economic Loss = 30 × 200,000 × 10% = $600,000

Figure 1. Copper cathode plates contaminated by steel band straps. © The authors

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Product degradation will not only bring *pro rata* economic losses to the seller, but also affects its reputation as the performance stipulated in the contract turns out to be difficult or impossible to achieve, ultimately leading to a reduction in the seller's market share, with reduced corporate profits of the whole enterprise.

Example 2: Representative sampling of copper concentrates in ton bag packaging directly determines the procurement risk of the smelter

Due to poor resource endowment, low grade, difficulties in exploitation and process, Chinese copper concentrates are far from meeting the needs of domestic copper smelters. A large amount of copper concentrates are imported. Consignment copper concentrates are packaged either in bulk or in ton bags. The economic results for bulk copper concentrate consignments are relatively stable and less controversial because of the relatively easy operability of the sampling methods employed. However, due to very uneven quality fluctuation distribution *between* bags, copper concentrates packaged in *ton bags* often have large deviations (gaps) between the in-material quality (analytical results) when determined in loading and unloading ports, gaps which exceed the "reasonable" error range assumed in contracts etc.

A large smelting enterprise in China needs to import more than 500,000 tons of copper concentrates every year. Due to the type of inconsistent sampling approaches just described at loading and unloading, final copper grade difference of the two ports was up to 1.5%. In order to identify the *cause* of this apparent poor quality match, 20 tons was randomly selected from a shipment of 500 tons to serve as a basis for detailed investigations of the between-bag quality fluctuations. The resulting test results are shown in Table 1.

Between-bag copper variations (never zero) ranged up to a maximum gap of 11.16%. If the between-bag coefficient of variation (CV%) is not carefully controlled, this may easily propagate into a large compositional gap in the final results. The domestic smelter, as the buyer, takes account of large material quantities for which the compositional estimations must be determined with a very high accuracy and precision.

As an example, the smelter used copper concentrates transported by sea, with 20,000 tons per delivery; the relevant London Metal Exchange's copper price was about $9400 per ton. If the copper shipment unloading port's estimated copper concentration was 1.5% *higher* than the loading port, regardless of the impact of other valuation elements and processing fee deductions, a value of **$2.82 million** was due to the contested differently indicated amounts of copper alone.

Table 1. Copper content in randomly selected copper concentrate bags.

Bag No.	Cu (%)	Bag No.	Cu (%)
1	16.36	10	21.35
2	18.58	11	25.69
3	19.06	12	22.64
4	18.65	13	19.45
5	18.45	14	19.70
6	24.14	15	26.08
7	18.74	16	23.68
8	27.52	17	16.82
9	22.43	18	19.20
Mean	21.07		
Range	11.16		

Example 3: A detail from blister copper sampling and preparation

China has a huge need for copper raw materials. In addition to directly importing copper concentrates as raw materials for domestic production of copper cathodes, Chinese companies also construct copper smelting facilities overseas to obtain copper products such as copper blister, copper anode and copper cathode, which are also sold domestically.

The copper content in copper blister is usually around 99%. For trade purposes, copper blister is usually delivered in the form of ingots or anode plates. Generally, the content of copper, gold and silver is used as the characteristic pricing elements of the product—sometimes including other specific impurity components. The analysis is preceded by a sampling procedure which generally includes the following steps: randomly pick out a defined number of ingots from a consignment, further select a few points on each ingot for drilling out and collect all *cuttings* to become a *composite sample*, which is milled (ground) and

Figure 2. Copper blister. © The authors

from which a test sample is produced for analysis of the content of each element involved in the contractual specifications.

Both parties in the trade use analysis results as the basis for a fair trade settlement—which should always cause no issues *were* trading parties using only one analytical facility. But when using two, the road is open for possible *deviating analytical results*, which at first are sometimes difficult to understand as they manifestly represent the *same consignment*. But there is always a rational explanation, an example of which is shown below.

Blister copper sampling procedure

Occasionally when enterprises sell blister copper, the two parties agree on a proscribed sample preparation method in the trade contract as follows. Drill blister copper ingots, grind all the collected cuttings, followed by *screening* by a 40-mesh sieve, followed by further grinding of the left behind, over-sized sample part again, until the complete composite sample has passed through the screen.

Table 2. Copper content in different particle size categories.

Particle size bin	Mean copper %
>40 mesh	99.15
<40 mesh	98.85

However, the mandated method in Chinese domestic industry is to *separate* the material of the up-sieve and down-sieve size bins into identified sub-samples. According to the screened mass ratio, weighing is also carried out of the separated up-sieve and the down-sieve sub-samples, which are then analysed for copper content.

As an internal control, after a batch of samples are sieved, sub-samples of these particle size bins are tested separately to obtain their specific copper contents, as shown in Table 2. The reason for the resulting diverging results may be due to the different constituent particle sizes, or it may be a result of the repeated grinding operations, which causes the material to be *oxidised*, resulting in a lowered pure copper content for the small particle sizes.

A large copper smelter established overseas by China has an annual output of about 20 tons of copper blister. If the sample preparation method of all 40-mesh sieves is used in trade accounting, this alone may bring about a 0.3% reduction in copper content. The unit price of copper blister at the time of writing is US$9400 per ton, regardless of the influence of other pricing elements. Thus, for this smelter, this single detail of sample preparation procedures alone may represent a loss of up to **US$5.64 million** in trade **per year**. Every *detail* matters in global commodity trade ….

Conclusions

These consignment examples demonstrate the economic importance of even the smallest differences in laboratory preparation and analysis approaches. Sub-sampling, sample preparation, transportation and sample storage processes may all have significant effects on the quality and representativity of samples that eventually enter the analytical instruments. Only by careful and strict control of each operation can the test samples ultimately used for analysis be qualified as representing the full, comprehensive quality of commodities and the goods—equally in the interest of both buyers and sellers. The apparent *minute* issues treated here for a large-volume bulk commodity, may quickly lead to surprisingly large, added or lost, values which are far too large to overlook in consignment economics.

Between the laboratory and management

The reader is referred to two earlier Sampling Columns dealing with how to run a commercial analytical laboratory notably with, or without, the TOS on the agenda: Does management have the necessary foresight to accept the challenge of also caring for "the customers of the customer of the laboratory"? This is an exciting two-part story, both of which are just a click away.

K.H. Esbensen, "A tale of two laboratories I: the challenge", *Spectrosc. Europe* **30(5),** 23–28 (2018). https://doi.org/10.1255/sew.2018.a3
K.H. Esbensen, "A tale of two laboratories II: resolution", *Spectrosc. Europe* **30(6),** 26–28 (2018). https://doi.org/10.1255/sew.2018.a4

SAMPLING SPECIAL SECTION

Section contents

SAMPLING SPECIAL SECTION

The ultimate manager's argument for representative sampling

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From **management's** perspective the cost of sampling must be as low as possible: samples are "just" a necessity to enable the laboratory to do its tests. Once the lowest cost sampling method has been identified and implemented—either by the in-house quality department or through a Testing, Inspection, Certification (TIC) service provider—management is done with sampling… Well, except for the occasional slap on the wrist to the samplers when there is a complaint on quality, or a dispute: "Our client does not get the same control results as our own". This must clearly be the samplers' fault; they took the wrong sample!

Anyone with Theory of Sampling (TOS) knowledge will disagree with this scenario and will go through fire and water to try to explain that there is no such thing as a right (or wrong) sample. When there is no representative sampling process, there are only *specimens*… those pesky lumps of matter collected uncontrollably from a lot: specimens are **not** representative by TOS definition.

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Sampling experts always find themselves explaining the "risk of being wrong" and love to bring up the hidden cost of using a non-representative sampling process. These confident boffins happily

and relentlessly illustrate with numerical examples, or graphs with error margins, precision and accuracy … that a non-representative sampling process is very likely to significantly reduce, e.g., life-of-mine or result in a financial loss during a transaction (they have an endless array of horror stories from all over industry to tell).

Yet often the experts are met by a **yawning** manager, or by a manager having a trader mind set, who is feeling lucky that he or she may also benefit. The "risk of being wrong" may just as well flip into "the 50 % possibility of being favoured". Especially when we TOS illuminati throw in statistics, standard deviations, variances, use "±" signs and may top it all off with a normal distribution graph etc., **then** the managerial thinking still goes: "Even in the worst case, on balance I will be okay!"

WRONG, sadly!

The real world

The process of *representative sampling* depends on two critical success factors:

1) elimination of Incorrect Sampling Errors (ISE) and 2) reduction of the Correct Sampling Errors (CSE) to an acceptable level.

Here, in order to avoid the **yawn**, we will completely skip all further *explanations*, those dull "technical explanations", but leave the reader with sufficient references (should the interest develop) for proper sampling *access to* how to make sure every particle can and will be *included* in the sample, and how to decide on the necessary-and-sufficient number of increments to *select* (thereby also fixing the all-important question about the optimal sample mass); for references, just look at all other contributions above and below.

The technical truth

Thus, for now, we can refer to what is easily understood by managers—Murphy's Law, which states that that there **cannot** be an overall "on balance" when representative sampling is addressing significantly heterogeneous materials and lots, as when compromised by the desire to involve the least expensive sampling approach (grab sampling), which unfortunately is tantamount to allowing a significant *sampling bias*. This is a single-sided effect that is *always* a **cost** and *never* a **benefit**; again, just look at all other contributions above and below.

The magnitude of this cost?

The costly truth

Well, let Murphy's Law decide that for you, instead of us experts trying to make "reasonable" *assumptions* about inherent heterogeneity and shaky, but dead-cheap, sampling procedures (again grab sampling) in order to quantify a monetary amount or build the resource model

for the new mine for example, you know much better yourself!

But, by the way… now that you know this critical issue in these simple terms, imagine how your shareholders will react next time the results from a non-representative sampling process interfere with the bottom line of your annual reports!

What to do—how to go forward?

Simplified there are just three phases for representative sampling.

1) The planning phase, *prior* to sampling
2) The actual sampling
3) Making managerial, *inter alia decisions* based on the sample (results)

The TOS' focus is overwhelmingly on phase 1) and phase 2), e.g. to determine essential stuff like heterogeneity which is needed for better planning. Phase 3) is only for the user… e.g. the manager.

The economic impact

The economic impact of *representative* sampling is abundantly clear: it is essentially *neutral* and does not favour, nor prevent, a specific wishful thinking. Ironically representative sampling delivers **exactly what a manager expects** from a sample: something that can be considered as factual and true… as fully representative of the bulk from which it was taken from, and for which reason one can have complete faith in the corresponding analytical results.

How to tell it to management

So, no big Dollar or Euro amounts to be presented here, no complicated statistical results, no graphs, no error margins. Just you, your imagination and the knowledge that *representative* sampling is a process that can remove all your fears of a financial claim, or of upsetting your shareholders, or the fear of prosecuting regulators.

Ultimately the economic argument for *representative sampling* is just that, the most coveted position regarding all business risks: "peace of mind".

Just a warning though: If the adjective "representative" is removed from any sampling process—all the above goes away in a blink!

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SAMPLING SPECIAL SECTION

Never cry sampling? Denial, denial, denial—pay the price!

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Introduction

The objective of this contribution is not to add to an already large list of horror examples of hidden economic losses, but rather to raise a cry of alarm about what is experienced as a classical *denial* of cost-consequential sampling recommendations. A couple of real-world examples borrowed from the mining industry will almost tell the story by themselves.

Case 1. To dare to tell …

The first tale of denial concerns the author of this short piece, who failed for too many years to appreciate the full extent of similar situations.

A long time ago a colleague and I were asked to work concerning mine-mill reconciliations at a very large gold–copper operation in a far-away country. A cursory audit of earlier practices quickly revealed that sampling of blast holes for grade control was **not** performed to good standards. But to make things worse, the corresponding samples were not even prepared by the commercial laboratory on site; technicians simply scooped *some material* from the sample bag in lieu of the complete and tedious preparation they had been asked to implement. Demonstrations duly made to company management, the entire lab was immediately **fired** and put on a charter plane out of the country the next day. Upper management then requested that we provide an estimation of the damages incurred along the years.

We had never done this kind of a job before and we believe, until today, few professionals have really attempted it. So, we first tried with a few statistical tools, and were able to conclude that the main issue that was triggered consisted of approximately 2% of treatable ore instead ending up on the waste dump. But *denial—self-denial* in this case—crept in when it was found that actual costs to the mining company amounted to a mind-boggling **$7.5 million in yearly net profits**. In complete disbelief, we redid the evaluation using geostatistical tools instead (more powerful and more relevant than straight statistics), and purposely in a completely different way, but this only confirmed the exact same conclusion. And to be frank, it was not until several years later, when sharing courses on Sampling Theory with our late friend Pierre Gy, that our denial finally stopped for good. Pierre presented examples from his own career in which, in a very similar situation, he had reached the very same monetary conclusions.

That day, we learned our lesson about the hard necessity of *daring* to be *bold* at times, to *tell*. The sad fact is that grade control is one of those domains where the cost of bad sampling can reach unfathomable levels of losses—of *never-seen* money.

Case 2. It can get much worse …

However, in more recent times this example, which had profusely haunted our minds for decades, started to pale into insignificance in comparison to a new situation, this time concerning a large process plant. Indeed, this was in another domain where a lot of money was also at stake. This example is about a sub-optimal metallurgical processing plant. Another friend and I had audited

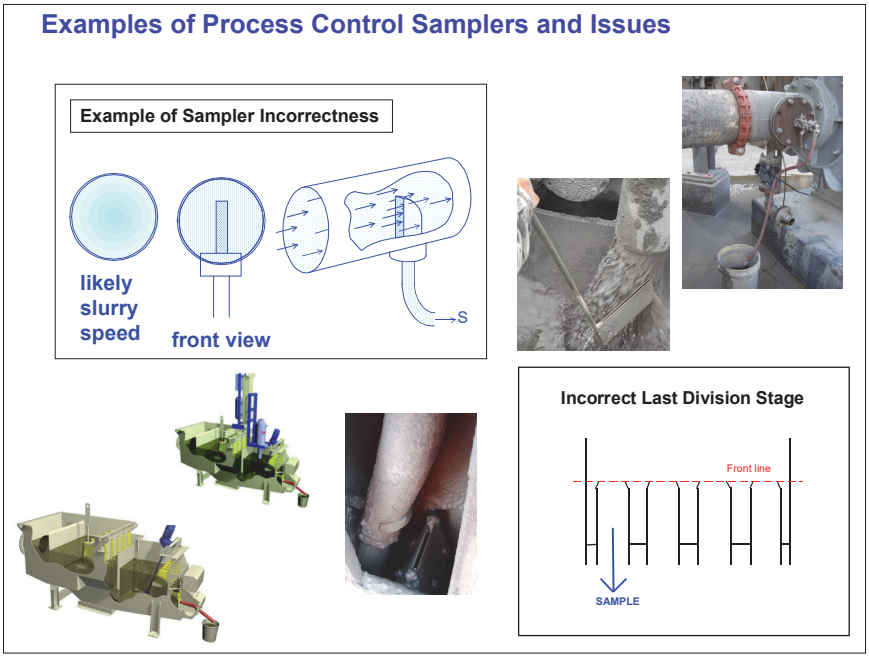

Figure 1. Examples of process samplers, all with "issues" that should always be called out!

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a copper plant in which, quite tragically, "less than perfect" process control samplers were used for metal balance. Immediately here below will be shown how "less than perfect" …

The ore deposit contained a mineralised rock type (RT#1) and higher-grade rock type (RT#2). The plant had initially been designed solely for sulfides ore RT#1, grading at around 1.5% maximum Cu content (assessed from test work). However, in an attempt to increase metal production, the mine was now sending a mixture of RT#1 and RT#2 to the mill, grading at 2% Cu on average. But the plant turned out not to be able to process this mix well with a good metal recovery (for good mineralogical and process design reasons, i.e. "bad reasons" actually). As a result, as detected by the study of mine–mill reconciliations, a large proportion of the metal received in excess of 1.5% Cu was unfortunately going through to the *tailings*, un-recovered (it turned out this was largely in the form of un-floatable, microscopic, native metal present in RT#2).

The feed **to**, and the tails **from** the plant were sampled using process-control samplers that were decidedly **not** designed for quantitative sampling. Both provided negatively biased sampling, both failing to detect this additional, denser, unrecoverable metal when it passed through. In Figure 2 these bracketing in/out "sampling" stations are symbolised by trash cans—"with good reason".

As a result, the plant metal balance matched the mine-predicted grade within reason when processing pure RT#1 (i.e. up to 1.5% Cu), but showed a large difference of ~0.35% Cu when the grade increased to 2% Cu by adding RT#2 ore. A significant part of this difference represented native Cu put in the tailings *without anybody ever knowing*, as it was undetected in both the feed and tail samples—but these sampling stations were indeed inexpensive.

Over the elapsed year at the time of the study, the mine had produced and sent to the plant, 50 Mt of ore at 2% Cu (RT#1 *plus* RT#2). In addition to the properly measured, normally unrecoverable metal (recovery is not 100%, even for RT#1), the native metal in the 50 Mt, accounting, say, for ~0.10% Cu, had gone through and was unduly lost to the tailings without anyone suspecting/measuring it. *[One may perhaps argue whether it was less than 0.10% Cu or much more, but this does not qualitatively change the mind-boggling conclusion below.]*

The additional metal loss would thus possibly represent 0.1% × 50 Mt = 50,000 t of metal Cu worth more than $7000/t on the market today. This is a staggering **$350 M for the one year in question!** Would this not be quite a nice budget with which to address process optimisation as well as the really serious plant sampling issues?

So, you may well ask: ***WHAT*** did the mining company do? It went into *denial*, finding it more comfortable internally to ignore the problem rather than facing it—the company was, after all, hugely profitable already. Hopefully, however, some day these tailings will undergo some secondary recovery process. ***WHO*** will dare to be bold and *tell*?

It is perhaps worth reflecting that, as pointed out to us by the editor, the very first job Pierre Gy was involved in was—you guessed it—re-evaluating a set of discarded tailings in a mine in the former Belgian Congo, see his own fascinating career story in Reference 1.

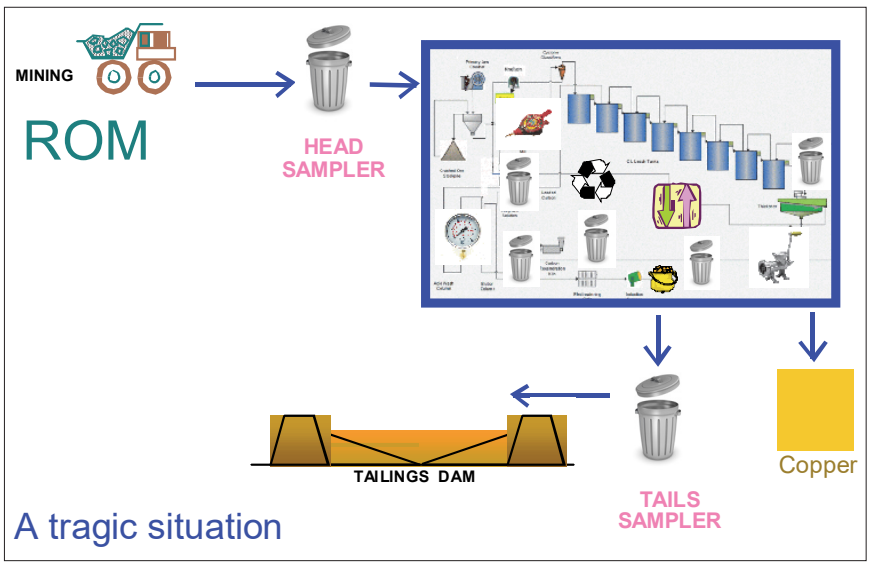

Figure 2. It is impossible to monitor and control a complicated process based only on seriously compromised sampling stations at input and output locations (here represented by the caricature of trash cans—perhaps a bit rude but this does allow the message to get through with clarity.

Conclusion

Monetary losses to bad sampling can be huge and sometimes far beyond what one may choose to believe. Denial can tragically hamper operations' optimisation and leave unseen economic opportunities by the roadside. One should indeed cry "Sampling problems" whenever encountered!

Reference

1. P. Gy, "Part IV: 50 years of sampling theory—a personal history", *Chemometr. Intell. Lab. Syst.* **74(1),** 49–60 (2004). https://doi.org/10.1016/j.chemolab.2004.05.014

SAMPLING SPECIAL SECTION

How to motivate for correct sampling projects based on costs and benefits of fit-for-purpose sampling solutions

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Editor's summary

Mining companies are generally reluctant to install high-cost sampling systems at operations that have been "functioning well" for many years. The principal objection to installing new equipment to extract correct and representative samples in process flows is the time and costs involved. The Theory of Sampling (TOS) provides a structured framework for identifying and quantifying the errors and bias associated with any sampling event, but this may often be insufficient to motivate for investment in new, correctly designed sampling equipment. Financial losses arising from substandard sampling installations are usually *disregarded* because value-added economic benefits from good quality sampling solutions are most often *invisible*, while the adverse cost from inappropriate systems are plainly obvious. Depending on the specific needs, a Fit for Purpose (FFP) sampling solution may be acceptable, provided the magnitude of sampling errors is understood and assay results are interpreted accordingly. Categorical levels of acceptable accuracy and precision can be established depending on the sampling position in the mining value chain and the nature of the decisions to be made. Objective benefits of proposed FFP sampling solutions must be presented to relevant decision makers in such a way that adverse subjective decisions based on only poorly resolved economic information are made difficult (impossible). Examples of benefits from motivating such implementation of FFP sampling solutions at sampling facilities around the world, are presented.

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Introduction

Humans rationalise differently based on individual cognitive processes or reasoning (culture, experience, educational background, management level). Decision-makers in mining financial departments may rationalise very differently about spending funds on corrective sampling compared to technical sampling experts, meaning that well-conceived corrective sampling projects could be rejected. Irrespective of the appropriateness of the technical design, or imperatives of the Theory of Sampling (TOS), approval for implementing a corrective sampling solution is declined unless value-added benefits can be defined and corroborated with numerical proof. The fact that the costs of poor sampling *never* show up as a line item in annual financial statements means managers do not see a figure that represents a *loss* to their earnings. Attitudes towards meaningful expenditure on correctly designed and installed sampling equipment, therefore, remain obstinate. The rationale for the implementation of improved sampling solutions must be presented as simply as possible leaving little room for subjective interpretation.

Estimating added value from implementing sound TOS-based sampling practices does not require a long or complicated report. A simple "back to basics" approach, pointing out the critical points and findings with a summary of the financial benefits provides a much better chance of getting your point across. The "sampling fraternity" should also acknowledge that implementation of the "close to perfect sampling solutions" are not always feasible. The need to make compromises, knowing that not all solutions are perfect, may still provide *some* added value by reducing sampling errors compared to current operations.

Here is a look at a back-to-basics approach for demonstrating the benefits of installing corrective sampling protocols and equipment to those approving budgets and to reluctant shareholders.

General concepts

Several observations have come to light as a result of presenting appeals to the boards of companies for funding to improve sampling facilities.

Distrust of large unsubstantiated numbers

The adage that "If something sounds too good to be true, then it probably is" is still applicable. Statements that say "… better sampling can produce an additional US$25,000,000 worth of on-grade ore *per annum*…" sound too good to be true and arouse a certain level of scepticism in the listeners. Numbers this large appear unrealistic and are probably not trustworthy unless they can be validated by realistic examples. It is better to begin by offering small numbers, for example "…correct sampling can deliver an additional US$7500 for a 100,000 t shipment of iron ore…" and allow the decision makers do the mental arithmetic themselves. Producers who, for example, deliver over 3400 shipments of this size per year can easily see the potential value of better sampling.

Disinterest in statistics without practical application

Technical statements with equations and figures could be lost on non-technical managers and executives. What they would prefer to hear is "…let me show you what improving your Sampling, Preparation and Measurement (SPM) can do for your profits."

Executive committees have neither the time nor the interest in detailed or complex calculations of precision that technical jargon alone will seldom motivate budget approval. The insight, interest and understanding of sampling technicalities is **not** common amongst such audiences, but simple statements such as "…every 0.01% improvement on the SPM precision could potentially increase the on-grade production by 0.01%..." are more likely to pique their interest long enough for budget approval.

Penalties for out-of-spec products

The cost of underestimating the target analyte content is not reported in financial statements as it is not quantifiable, and in many cases misunderstood. What should be seen on a company's financials are the costs incurred due to *penalties paid* for delivering off-spec grade ore and deleterious elements that exceed allowable limits. Quantifying the amount paid in penalties highlights a quantifiable "real cost" that could be reduced by implementing better sampling practices and systems.

Names mean more than numbers

The role and responsibility of financial managers may very likely not allow them the privilege of time to digest the theoretical aspects of the TOS. Collaboration and certification of designs by well-known reputable experts add greater confidence to improved sampling solutions than complex formulas. Recruiting specialists who are able to validate or verify decisions about proposed sampling installations is an effective method of convincing project owners and shareholders that improved sampling will be money well spent.

Few are impressed by jargon and equations

Correct sampling nomenclature and application of equations to estimate financial benefits is critical, but shareholders and financial managers are unimpressed with complex procedures and formulas. Shareholders are much more likely to approve projects provided one can demonstrate that the estimated added value through improved sampling has been validated by reputable persons or sources.

Fit for purpose sampling

Providing correct sampling solutions is a high-cost exercise. Inevitably the more stringent project owners are about installing correct sampling solutions, the higher the capital costs will be. This article does not dispute the fact that samples cannot be trusted if the principles of the TOS are not followed. The rational man strives for perfection, but knowing that things in life are rarely perfect, this article wants to demonstrate that "inferior sampling" may sometimes still offer value. Of course, the value depends on how the resulting analysis and associated confidence intervals will be used. This also assumes that benefits are not outweighed by the cost of taking, transporting, preparing and assaying the sample—a simple concept, but one that may in fact be overlooked by the sampling fraternity.

ISO standards vs the TOS

"ISO compliant" is a term often used when discussing upgrades to sampling facilities. ISO standards, although critical in establishing standard methods of sampling, preparation and analysis for various commodities and materials, are too often used out of context! There appears to be a widespread misunderstanding that compliance with a relevant ISO standard will *automatically* result in the best possible sampling results. ISO standards should be looked on as *recommendations* to be used to assist a facility in ascertaining a minimum precision and level of confidence in accordance with international standards. However, improving sampling equipment and methods above the minimum requirement recommended by ISO standards, can indeed add further value to a producer. As an example, if iron ore producers reduce the precision on a 270,000 tonne lot, below the β_{SPM}[a] of 0.34% Fe stipulated by ISO 3082, substantial improvements in on-grade ore production can be achieved.

Compliance is one thing, but before setting a limit on the resources assigned to sampling and analysis, it is critical to establish the monetary value of each sample using a minimum requirement, compared to what it could be worth if additional resources were spent on improving it. Rather than strict compliance with minimum requirements from relevant ISO standards, other aspects, especially efficiency for operational purposes, should be considered when specifying a sampling point. For example, taking a higher number of primary increments, and analysing more subsamples than required by ISO during the loading of an iron ore vessel can give a better indication of the grade during loading. This can then be used to blend the product mixture that goes into the vessel more efficiently.

Although some principles *may* be the same it is definitely unwise to apply guidelines from a single ISO standard to *different materials*. For example, the ISO 3082 for iron ores should **not** be used to estimate sampling compliance of phosphate fertilisers, because the material characteristics are in fact detrimentally different; in this case the proper material-specific standard must be applied. Where no specifications are available for a material, TOS practices such as heterogeneity tests and sampling calibration for establishing nomograms should be applied, although the work efforts (costs) are never small. Explaining the need for, and the workings of, a full-scale industrial heterogeneity test is no small feat in the board room.

Motivating a sampling project

The objective of a sampling study should be to demonstrate how improved sampling practices can improve profitability. Motivating a project to improve

[a]Overall precision for Sampling Preparation and Measurement $\beta_{SPM}=2\sigma_{SPM}$.

sampling equipment and protocols requires an understanding of the complete value chain so that expectations about the outcome of the sampling project are met. This may include defining the levels of reliability and precision to be achieved as a result of improvements to sample extraction, sample handling/transport, sample preparation and measurement. Motivating for added value and increased profit from improved sampling precision **must** be supported by realistic estimates of the capital cost and required investment. The capital investment needed for taking better samples using better sampling equipment, ensuring the correct sample size and sample frequency, must be calculated accurately. In addition, the costs of ensuring samples are correctly transported, prepared, analysed and reported, within an acceptable turn-around time that allows real-time changes to be made, must be established. The total investment required in terms of time, money and effort must be understood by managers and financial officers, if proposals to improve sampling processes are to have credibility and integrity. The skills of producing a convincing *business case* should be on everybody's agenda, sampling experts no exception.

Case studies and examples

Rapid turn-around vs high precision

A smelter aimed to get less than 5 ppm precious metal in slag which it sells as silica waste for US$3/tonne. Slag analyses over a six-month period indicated the precious metal content to be as high as 18 ppm. The operating costs to recycle slag through the furnace, after it has cooled, is approximately US$5700/tonne, so although the sampling error could be reduced by improved sampling methods, the cost-benefit would be minimal unless the samples can be collected and analysed *before* the slag is cast. On average around 10 tonnes of slag is produced per cycle, meaning that the value of precious metals in a single slag cycle would have to be greater than US$57,000 to make re-cycling through the furnace feasible. If samples can be collected and analysed before the slag is poured, then remedial actions such as increasing the residence time in the furnace can be performed. In this case precision of the result is not as crucial as the sampling-to-analysis turn-around time so this is where the focus for the project was placed, and rightly so. But if the furnace charge is analysed before smelting it is possible to modify the charge and reduce the risk of precious metals reporting to the slag. In this case the precision is more critical to the process as small variations in the charge can affect the smelt efficiency.

Reducing the loss of precious metals in the slag to less than 5 ppm would result in an additional precious metal production of over US$400,000 per annum. This figure, based on historical data gathered from the smelter, compares the actual gold content of processed slag with what it should have been if the Au grade was maintained below 5 ppm. Assuming a three-year return on investment, a sampling solution costing less than US$1,200,000 would indeed add value. This example illustrates the necessity of understanding the economic and logistical implications, limitations and the effect of improved sampling *before* proposing a sampling-to-analysis solution.

A less than perfect sampling solution may still add value

A less than perfect sampling solution was observed at a phosphate fertiliser production plant where phosphate slurry is mixed with H_2SO_4 in a reactor vessel to produce phosphoric acid. *Dip samples* are taken between 50 cm and 500 cm below the slurry surface (sampling experts would collectively frown severely!). Concentrations of free sulphate, measured by titration, and phosphoric acid cannot be quantified in the complete vessel with any certainty using this imperfect sample type, but some knowledge of the concentrations is critical for controlling processes in the reactors.

In this case, time is of the essence. It is critical that the sample be filtered and analysed as soon after extraction as possible because the reaction in the sample container continues as the sample cools, affecting the analytical results significantly. To improve the integrity of the sample, an insulated sample container should be used to collect the sample (Craig Ritchie, 2018, *personal communication*). In addition, rapid transport to the laboratory using a pneumatic air tube conveyance was strongly suggested.

Too many compromises invalidate the sampling point

When faced with tight deadlines and minimal budgets, project managers and engineers often must make compromises in correct sampling to complete a project. Although some compromise is almost always required, too many can completely invalidate the sampling solution being used. For each compromise made, the total effect on the result should be established to understand the ultimate financial impact on the plant accountings. This is also where the project owners must know what is needed as a minimum to achieve the required sampling precision and to meet all the operational requirements to ensure that the sampling solution providers they are using do not lead them astray. Using internal resources or external specialists to define what is needed for sampling installations is one method to achieve this, which is a lot more cost effective than attempting to investigate and repair "what went wrong" **after** the system has been implemented.

Good sampling to analytical practices

At critical operations, such as port loading facilities, correct sampling together with rapid sample preparation and measurement can have massive financial rewards for the company.

As an example of this, in a well-designed iron ore port facility every reasonable effort was made to minimise SPM errors in the facility. This, together with the addition of automated sample preparation and analysis, not only makes the system more precise but also offers the value of rapid preparation and analysis. For this facility, even though the sampling building did not have enough head room to fit a standard traditional cross-stream sampler, an

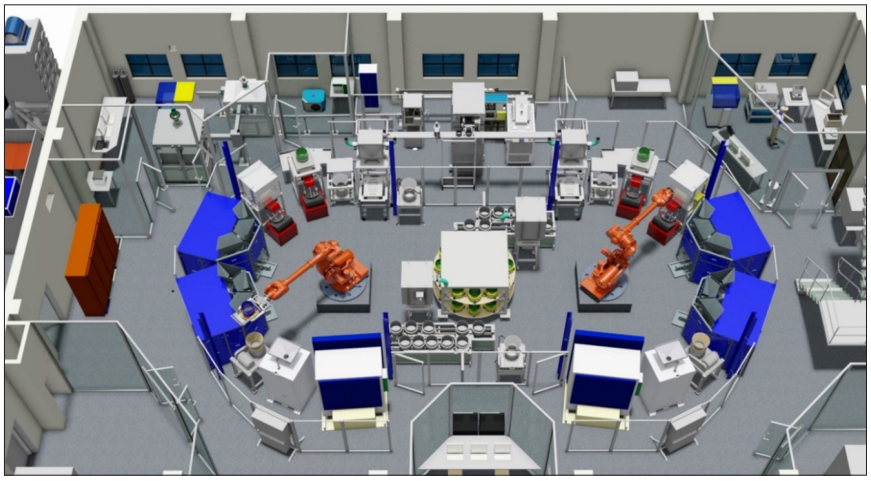

Figure 1. Robotic automation for sampler preparation and analysis for chemical, PSD and moisture conveyor.

innovative alternative was developed (which involved a long radius swing arm which crossed the stream and lifted the sample material to the floor above). This key contribution required that both the client and supplier had a strong understanding of the sampling requirements and worked together to find a feasible solution. The result of this is a turnaround time on results of less than 6 h after the completion of the ship being loaded, with precision of less than 0.15%.

Value of investment

The iron ore producer has not released the actual value of the investment to make this facility perform as it does today, but the following available information will suffice.

1) The final analysis is available 6 h after ship loading is complete; this was previously a minimum of 48 h. The benefit is that the lot can be invoiced nearly two days earlier than before, resulting in an estimated gain of US$5500 per 270,000 ton shipment on *interest* alone.
2) For large lots, the laboratory can release data during ship loading with a precision of less than 0.15%. This data is used to adjust the blend between low- and high-grade ore to control the final blended grade being loaded.
3) The iron ore producer can use the high precision as proof of the quality of its product thereby giving them a commercial advantage over their competition (*bragging rights*).
4) Reduced risk of penalties due to deleterious elements exceeding upper specification limits of the lot, or lower than specified Fe content.
5) Disputes over the quality of the ore loaded through this terminal are quickly settled due to the overall compliance of the complete facility with the relevant laboratory and material specifications.

This plant has proven that rapid analysis with consistently high precision is possible, so the producer is currently investigating upgrades and expansions of this facility to increase sampling and analytical capacity with the aim of optimising in-ship grade blending.

Conclusions

A full understanding of the complete mineral production and sales process before and after the sampling point is essential. Such insights allow one to appreciate the current usage of the sampling results, as well as identify other potential uses and added value opportunities, especially if the quality of the sampling can be improved. Ascribing a monetary value to a sample in a process or procedure is an important asset. An understanding of the levels of precision or sampling correctness of a sample, as well as the turn-around time to analysis will influence the value. An appreciation of various constraints, such as applicable standards or specifications, physical space available, accessibility for inspections, maintenance and sample collection, plant down time available for the installation, distance of sampling point to the laboratory must all be taken into consideration to create a fit-for-purpose sampling solution.

In the process control domain, fit-for-purpose sampling has a wider scope as compromises can be made in various aspects of sampling to suit the application, provided the consequences of these compromises are understood. In the product control domain, where the same compromises cannot be made, fit-for-purpose sampling can still be applied when considering how the sampling will affect other aspects of the facility such as material throughput and the value of faster sampling-to-analysis. Using a cross-stream sampler will not affect loading rates, whereas a stop belt sampler will; therefore, the cross-stream sampler is fit-for-purpose in this case.

The feasibility of motivating and actioning an upgrade process required by a facility to exploit the expected value-add from the specified sampling solution also requires insight and understanding. Some of the actions can include automated sample collection and transport systems to increase turn-around time from sampling to laboratory. Other actions could include upgrades to the laboratory to accommodate the sampling solution and an upgrade to standard operating procedures. The result of such actions would enable the facility to respond to improved sample information to achieve added value possibilities.

It is important that project owners communicate their needs to sampling equipment suppliers in a way that ensures the supplier provides the best solution for their application. Lowest cost procurement should not govern the choice and selection of critical success equipment, of which sampling equipment range very high, as this is likely to turn out to be a costly error of judgement. A policy of lowest cost procurement is short-sighted as it may mean not only inferior equipment selection, but also incorrect sample extraction that

introduces costly bias associated with poor sampling.

The greatest deterrent of decisions to install appropriate or improved sampling solutions is that the benefits are *invisible*, while the adverse costs are *obvious*. No financial statements tell CEOs what the benefits from proper, FFP or indeed fully representative sampling are. The only indications might be increases in the costs of reagents and consumables. When presenting a sampling solution to an executive committee, with the hope of getting approval, the primary motivational factor should be a clear demonstration of the *monetary benefits* the solution can offer. The basis of the motivation should be a comparison of cost-to-implement against the long-term expected returns on investment. All mathematical and other technical aspects of the proposed solution should be kept as straightforward as possible with only key results presented, but which are verified by a well-respected specialist in the field.

Caveat

Of course, there always also is the option of being able to *explain* adequately more of the essential technicalities in a manner that is fully understandable, so that management, CEO's board members, investors … actually gain an increased factual knowledge. This will always be part of a *best* business case. This challenge still leaves *room* for the diligent, competent, didactically motivated fraction of the international community of sampling experts, who not all necessarily need to rush off to get a MBA degree—team collaboration will always go a long way!

The ideal management commitment

The reader is referred to an earlier Sampling Column addressing the key issue of awareness and commitment on the part of management: Theory of Sampling—an approach to representativity offering front line companies added value and potential substantial savings.

F. Rendeman, J.R. Pedersen and K.H. Esbensen, "Theory of Sampling—an approach to representativity offering front line companies added value and potential substantial savings", *Spectrosc. Europe* **32(3),** 23–26 (2020). https://doi.org/10.1255/sew.2020.a1

SAMPLING SPECIAL SECTION

Sampling quality quantification: the key to support business decisions

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Introduction

Current practices to evaluate the operation of sample stations that support processing and metallurgical balance are typically based on visual inspections. For example, material build-up on cutters, sample spillage, reflux while sampling, pegging on sizing screens and worn cutter lips are all most unwanted discoveries. But, being subjective observations, these do not allow quantification of the impact on the samples collected, production process or on the reliability of metallurgical balancing when deviations are found. For this reason, they are traditionally just considered as "good practice" recommendations or, N.B., as an **extra cost for the business**. Because they are only qualitative observations, it is quite difficult to generate and quantify a business case related to their impact with which to support an investment in better, i.e. more reliable, sampling systems. To complement the current visual regimen from a sampling and QA/QC perspective, this contribution illustrates the value of also using process monitoring practices, results and controls to proactively quantify the quality of the sample information, especially at the primary sampling stage. This allows the desired business cases to be completed with quantitative cost estimations.

Variability

Several papers have been published regarding the applicability of variograms as a useful tool to quantify industrial processing variability,[1–3] including new developments with variograms targeting *continuous monitoring of measurement system performance*.[4]

This "proactive approach" includes the use of daily production grade information in variograms for control process to quantify the variability of each of the sampling points deployed in, for example, a metallurgical process.[4,5] The most important advantage of this methodology is the use of the *additional* available information without extra budget requirements. This leads to higher monitoring relevance and reliability, because this augmented process modelling can be performed more frequently and the results will better reflect "day-to-day" variability in the process—which allows better insight in the process variability. The ultimate aim is to calculate the variographic nugget effect, $V(0)$, better; i.e. the viewpoint where "a sample is compared against itself", because this represents the total sampling-and-measurement error (expressed as a variance).

Bias testing

In industry, bias tests are often suggested, or contractually mandated, to compare a production sample obtained against the material it supposed to represent at the control point. Many international standards recommend bias testing—almost universally.

But bias tests require *interruption* of the regular production process in order to extract material from the conveyor belt with a mutually accepted "reference sampling" method. For this reason, bias tests are in reality not popular in industry ("we lose a lot of money and time having to interrupt our process many times") and are, therefore, usually performed only reluctantly, or not at all! Because of this, companies are unavoidably exposed to higher risks than necessary, since it is simply assumed that the processes involved are not affected by a monitoring (i.e. sampling-and-analysis) bias. For this reason, "data quality representativeness" is an unknown characteristic. However, sadly, unchecked data obtained by process monitoring with un-evaluated methods are nevertheless very often still assumed to be the "truth". There is a demonstrable loss of potential process information here and the ultimate question is not difficult to formulate: "what are the hidden costs involved for allowing this complacency?".

Under the reasonable demand that a representative sample is one that accurately represents the "DNA of the lot material" by including *all* the components in the lot in their *correct* proportions, the "augmented proactive approach" to be presented below includes the use of grade–grain size distribution curves of the samples obtained daily. These can then be used as convenient reference information for process control. The following case example contains some technical details, which can be skipped if interest is solely in the economic consequences hereof.

Case example

This is an industrial example where a quality programme (QA/QC and QM) has enabled a new level of observation and quality quantification, developed and implemented after serious information gaps were determined by visual inspection.

1) Visual field inspection of a key sample station revealed consistent deviations in the operations (Figure 1): a) the primary cutter is too narrow for coarse material, b) the secondary cutter is not working, the sample goes straight to the bucket, c) lumped material is not crushed, d) samples are not collected as per time requirements (electrical issues)

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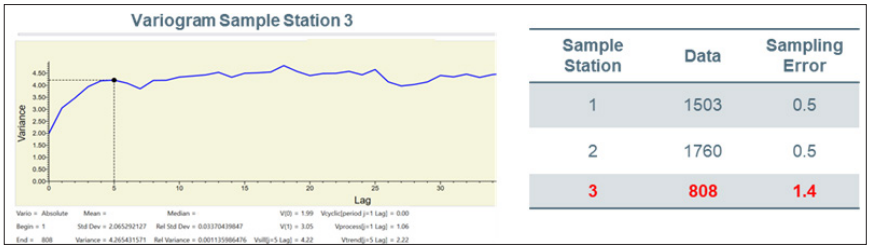
Figure 1. Quantified field evidence (right) collected after a visual inspection of the primary sample station shown on the left. The deviation between the expected nominal top particle (10 mm) and the factually observed size is dramatic.



Sample Station	Data	Sampling Error
1	1503	0.5
2	1760	0.5
3	808	1.4

Figure 2. Variograms performed for the three sample stations at the key site shown in Figure 1. Sample Station 3, the one identified and highlighted by visual inspection, clearly shows the largest Total Sampling Error. Variogram analysis is consistent with the visual inspection, and now *quantified*.

and e) while the expected Nominal Top Size is 10 mm, the real Nominal Top Size 60 mm!

2) Despite these deviations being correctly reported, the site team was struggling with communicating and getting the attention of senior levels, because the impact for the business calculations could not be *quantified*.
3) Appropriate variogram analysis was performed over the three sample stations at the site (Figure 2), which showed that the error of the singular failing station was three times *larger* than for the other two. Thus, the impact on sampling variability was finally quantified, the consequence of which is an increased risk for a non-compliant product, endangering the bottom line.
4) In terms of Bias, the grain size distribution of the failing sample station 3 was compared against the same material sampled at the loading port, and a preferential trend towards collecting more fine material on site could be observed. This allowed the quantification of the *underestimation* of the grades reported from this sample station (Figure 3).

Quantification at last

Variograms and grain size distribution analyses are here suggested to be used as the base for a proactive approach in production. Where performed, the impact of the deviations originally observed by on-site visual inspection only, could now be better *quantified and communicated to the organisation*. In terms of variability, the market always values long-term stability in the product, where any consistent variability reduction can represent an opportunity for a higher price during contract negotiation. For the mass product industry this represents a very important revenue opportunity due to the millions of tonnes produced in general by mining companies. This is why a continuous monitoring and

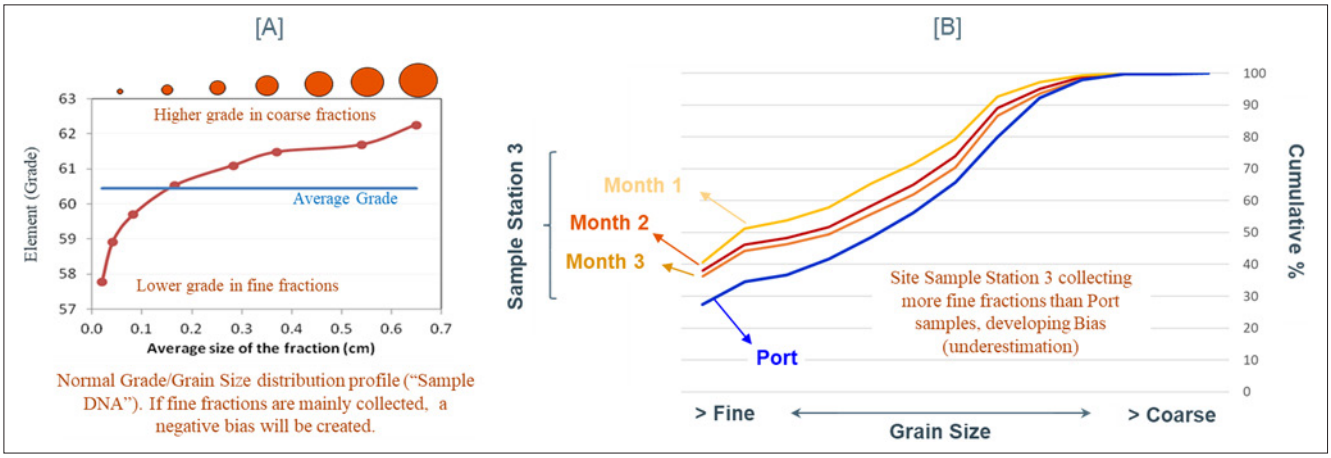


Figure 3. [A] Normal grade/grain size distribution profile (the "sample DNA") shows the impact on the overall sample grade if a preferential extraction of fine, or coarse, fractions prevail—this will assuredly generate a bias. [B] Grain size distribution analysis performed on samples from the faulty sample station 3, as compared with the same material sampled at the loading port, attesting to the same biased extraction of *too much* fine material.

quantification can lead to these, easily utilised opportunities.

In terms of bias, percentage deviations as small as 0.1–0.5 % bias are normally just considered as "minor" in some production environments. However, and due to the number of tonnes produced, these "minor" differences can represent a huge business impact. For example, for a mine producing 10 M tonnes, a 0.1 % Fe and 0.5 % Fe bias can represent an impact of **US$1.6 M** and **US$8 M**, respectively (assumptions: iron ore fines are based on the 62 % index, with an average price of US$100).

Conclusions

International Standards (depending on the commodity) are used to establish the methodology to be followed to setup and operate sample stations, but these requirements are normally only inspected or audited visually, compromising a full quantitative assessment of sample stations performance.

The risk for companies relying only on visual, qualitative assessments is creation of a potentially "false sense of security", where no detrimental issues are noted, or, when major defects are detected, impacts and risks are very hard to quantify to develop a relevant remedial "business case".

This contribution presented a case example showing the importance of implementing a QA/QC and QM programme on sample stations, as a *complement* or *enabler* of a sustainable compliance to International Standards. But also to further the opportunity of quantifying the performance of sample station performance, and to provide a "proactive approach" regarding deviations in the mining plan. This will potentially reduce operative costs, e.g. optimising the ore processing circuit), or optimising a blending process a.o. all of which will lead to an improved and optimised resource value.

Never underestimate the value of even a "minor bias"—your extra costs may be anything but minor!

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SAMPLING SPECIAL SECTION

Sampling in society, environment, public health, pharma, trade

Section contents

SAMPLING SPECIAL SECTION

Food and feed sampling: balancing ethics and money

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I first accepted the editor's invitation to contribute to this special issue on "economic arguments for representative sampling" with great enthusiasm. Alas, a few hours later, the enthusiasm started to fade because the many experiences of resistance to putting the Theory of Sampling (TOS) into practice in the food and feed sector came back to me. However, upon considerable soul searching, there may still surely be hope!

A personal statement

I have devoted about 20 years of my professional career to studying and regulating food and feed sampling standards and normative documents.[1–8] The good news is that many of them (though not all) claim that sampling *should* be representative. The bad news is that almost none goes as far as claiming representativeness as a *mandatory requirement*, the only exceptions being DS 3077,[9] Recommendation EC 787[10] (2004) and prEN ISO – 21568 (2005). The unavoidable result is that these standards fail when applied in practice, creating a breach between the principles behind the TOS's goals (good) and its application to everyday reality in the food and feed arena (bad). Thus, sampling is often felt as a necessity to be fulfilled to collect material for analytical investigation—clearly not knowing or reflecting on how important this information is for making societal decisions about public nutrition and health. However, reducing to a minimum the time devoted to sampling ("the faster the better") and minimising the associated costs ("the cheaper the better") will sooner or later sacrifice sampling quality and reliability. As for everything else in life, quality does not go together with speed and lack of resources.

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Setting a constructive scene

Since the present focus is on economic arguments for doing the right thing, instead of repeating that non-representative sampling is useless by definition, and that every penny spent on collecting *specimens* and analysing them is wasted, I would rather tackle the issue from the other end, exploring what happens when "something wrong" is detected in a food or feed product.

Looking rationally at the costs involved

When a food or a feed product turns out to be non-compliant with *a priori* established quality/safety criteria, the product needs to be *removed* from the market. What are the costs of removal? Per product the overall financial losses include all production, distribution and selling costs already sustained before the decision to pull from the market. Plus the costs necessary to i) map the supply-distribution followed to place the product on the market; ii) removal of the product from every supermarket counter and storage room across all the regions, countries and possibly continents to which the product was distributed; iii) costs to destroy the product. Arguably, these total costs are much, much higher than the cost required for the *a priori* application of a TOS-compliant sampling method, allowing the analysis of representative samples to support well-substantiated and informed decisions *before* market release.

When we total up the costs for this, grave problems become evident. Because of the vast amounts and tonnages involved, the costs are in fact so massive that they cannot even be estimated with reasonable precision, but they are guaranteed to be **huge**.

Scientific and technological understanding does not hurt

Under a less catastrophic scenario, a reliable understanding of human and animal *exposure* to certain substances (e.g. pesticides) is an important and wise requirement under many jurisdictions. The earlier it is understood that *only* representative samples reduce the possibilities of either *mis*-estimating actual exposure levels for humans and animals or, worse, *under*-estimating the risks for consumers to exceed tolerable intake levels, the better for society. This is also important in the case of foods and feed with nutritional benefits, where under- or over-estimating intake levels may lead to nutritional or deficiency problems. This also plays a critical role regarding surveillance of foods and feeds with unintentional contaminants or intentional adulterations, due to their often-low concentration levels and highly heterogeneous distributions. Watching out for these societal risks ranks among the prime objectives of national and international regulating authorities charged with *consumer safety*. These are goals worthy our most ardent efforts. But are we doing well enough?

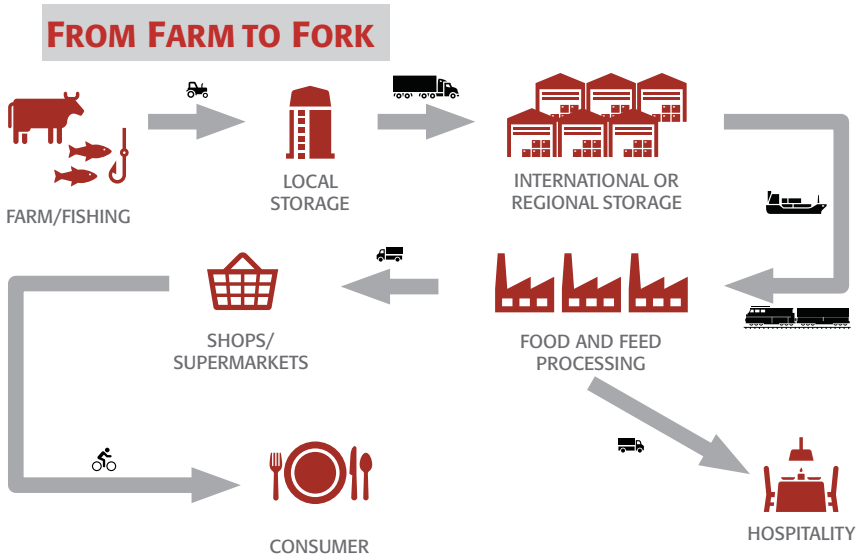
Reality check: very different objectives and usages of the TOS

Well, in today's food and feed arena, sampling continues to be perceived more as an economic *burden* and a technical necessity to be fulfilled because of regulatory demands, rather than a need to *ensure* proper citizen and/or animal protection.

Also, readers of this column could well be staggered, and maybe confused,

by the completely different attitude towards sampling between, for example, the mining/minerals/cement and the food & feed industry sectors. In the world of geological resource-based businesses, incorrect sampling means huge economic losses as value, cost and profitability estimates can be made precisely because the TOS is available. Here the TOS can be seen as the operative element safeguarding the business endeavours, see examples from the wide history of TOS applications, well substantiated in the annals of the world sampling community. Whereas in the food and feed business, sampling is a scientific tool to verify the accuracy of specific product claims, or to search for possible contaminants, or toxins, allergens, pollutants etc. Here, in essence, sampling means *searching* for possible *problems*, or verifying their absence to a certain degree of confidence (the concept of "risk assessment").

This contra-positioning is a key point for samplers, process engineers, managers, regulators, investors: *IF* from a practical point of view, exploration and searching for metalliferous resources and ores[a] is not so different from searching for, e.g., aflatoxins in a 60,000-ton shipment of grain kernels, or searching for accidental manufacturing residues across millions of chocolate bars (or a thousand barrels of pet food)—in practice the *motivations* for investing in correct sampling are markedly different. In the mining/minerals sectors the better the sampling the better for business (better in a straight economic optimisation sense), whereas in the food/feed sectors the better the sampling, the higher the risk of lot rejection or similar, which always carries a heavy *negative* economic penalty. What is good for one type of business is bad for another—what is good for one type of societal enterprise, is bad for others—the gamut of TOS applications in the last 20 years documents this dichotomy.



The food supply/production pathway: "From field to fork".

Balancing the opposites

The need for *balance* between integrity and financial gain opens up a quite different discussion on a higher level: one about direct use and benefits vs indirect and intangible disadvantages of the TOS involvement, which in the main goes beyond the purpose of the specific topic of this column, but here is at least the gist of it.

When sampling is executed to check for compliance with legislation requirements (i.e. regulatory sampling) it should be of crucial importance to ensure a high degree of confidence that the survey is accurate (unbiased) and that the compound sampling error is as small as indeed possible, within specified economic and workload boundaries. Specifically, if there is a legal threshold limit set for acceptance of the presence of a specific substance, all adopted sampling protocols must ensure that such threshold is respected with the specified degree of confidence. Of course, the lower this limit is, the greater the demands will be upon the sampling procedures and plans—and this cannot avoid being associated with *some* added costs.

Europe has established a very stringent approach to food and feed safety, monitoring products throughout all the steps of their production chain, "from farm to fork". Embedded into such a solid and ambitious safety strategy, and almost always out of sight, there is a high demand for accurate and precise, i.e. representative, sampling procedures, capable of ensuring reliable estimations throughout this entire pathway, leaving very little space for shortcuts behind the cheap and fast collection of meaningless (i.e. non-representative) *specimens*.

Where does this leave us—Trust!

In the food and feed sector, however you look at sampling, it is *never* only about money: it is about ethics **and** money. Correct sampling is not a money maker as in other sectors. Appropriate sampling is about being accountable for the *trust* that society puts into governmental and inter-governmental control systems for the safety of food and feed products. Society has no other choice!

After reading this article, you will sooner or later open the refrigerator and eat food that you bought at a supermarket. You *trust* it as safe. You *trust* that the control system worked to protect you. Consciously or unconsciously you *trust* the sampling adopted by such a control system was appropriate, i.e. representative, meaning that the safety decision taken applies also to the portion you

[a]Please don't *just* think of gold or diamonds, which geologically are kind of atypical resources—distinguishing themselves only by the societal agreement that they *represent* great value. The value of the much more voluminous base metals a.o. commodities, is vastly greater.

have in your refrigerator. If you again think of the dimensions of the global market, this is extremely far from being a trivial personal issue—the job to ensure for food and feed safety for all consumers is enormous! Ultimately, the money invested for correct sampling is money invested *for* the citizens who have neither the means, nor the knowledge, to verify. This *trust* should have much more exposure within and especially beyond our scientifically and technically driven community. This *trust* should become the root reason to ensure a continuous and open dialogue between TOS experts and *those* who decide what ultimately is allowed on the market: the *consumers* eat what reaches supermarket shelves.

After 20 years—my last effort?

Allow me to borrow Dr Vogel's statement (elsewhere in this column): "If 'representative' is removed from the sampling process, all 'piece of mind' goes away!".

The worst situation is that as long as nobody finds *problems*, everybody lives happily. Alas, everybody lives, but *blindly*! Are we ready to deal with these topics—going beyond profitability—transparently and honestly? Until now this would not appear to have been greatly successful.

Hopefully, the future debate will fuel more active measures, including reactions to this multi-authored contribution, surprising us!

Disclaimer

The author declares no competing interest. Claudia Paoletti is employed by the European Food Safety Authority (EFSA). The positions and opinions presented in this article are those of the author alone and do not necessarily represent the views of scientific works of EFSA.

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SAMPLING SPECIAL SECTION

The costs of hidden bacteria: challenges for representative sampling and measuring bacterial loads in an industrial slaughterhouse

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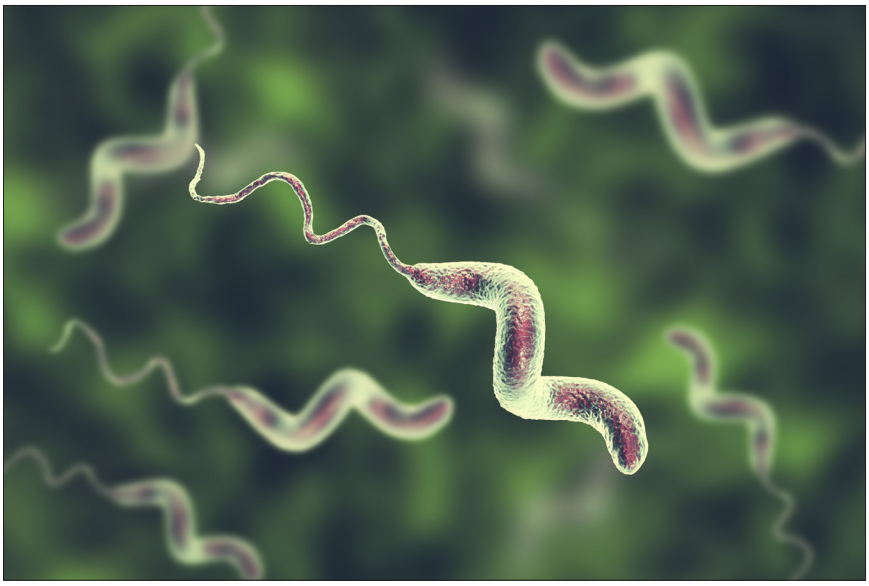
The European Union has adopted an integrated approach to food safety, termed "from farm to fork", by providing independent scientific support and advice on food safety-related aspects of *Campylobacter*. Chicken meat is responsible for 20–30 % of all cases of gastroenteritis, while 50–80 % of the cases can be related to chicken reservoirs of bacteria. There exists a Process Hygiene Criterion (PHC) of the European Commission Regulation 2017/1495 of 23 August 2017,[1] amending Regulation (EC) No. 2073/2005 for *Campylobacter* spp. The objective of the PHC is to control contamination of chicken carcasses during the slaughtering process through monitoring and taking corrective actions when the mandated targets are breached. Satisfactory monitoring results (EU PHC criterion: 1 January 2020) means that, after chilling, no more than 15 out of 50 sampled carcasses may have counts above 1000 Colony Forming Units per g. If this criterion is exceeded, improvements have to be made to the whole production line, i.e. taking appropriate biosecurity actions from the farms to a review of process controls in the slaughterhouse.



Campylobacter. Credit: Kateryna_Kon/stock.adobe.com

It all starts with representative sampling

How can the basics of sampling, as formulated in Theory of Sampling (TOS), be introduced in the field of microbiology? Measuring is knowing, and it all starts with representative sampling. In the Netherlands alone, 1.7 million chickens are slaughtered and processed every *day*. For a slaughterhouse capacity of 250,000 chickens a day, the mandatory checking rule for *Campylobacter* spp. of 50 carcasses sampled per week corresponds to a sample frequency of only 0.004 %. With such an *extremely low sampling coverage* the primary sampling must be totally reliable, so TOS-compliant sampling procedures are an absolute must. And when test samples are indeed fully representative, analysis procedures have to be likewise; the latter is "easy" to accomplish especially compared to the sampling tasks.

Microbiological paradigm shift

Microbiological analysis is performed by the gold standard of culturing microbes in Petri dishes. This time-honoured method has been used since 1886 following a publication by Theodor Escherich (*Escherichia coli* bacteria were named after him). Following this publication, along with the paradigm of the famous microbiologists Pasteur and Koch, only pathogenic bacteria have been cultured and examined.

However, a dramatic turning point came in 2005, when Eckburg, based on 16S rRNA sequence analysis, discovered hundreds of completely *unknown bacterial species* in the human digestion tract, exceeding even the most common culturable species in number. From this moment, culturing bacteria on Petri dishes has been criticised as "the great plate count anomaly". This standard method for bacteria detection in fact detects only 1% of all bacteria.[2]

Thus, the "Total Plate Count (TPC)" no longer corresponds **at all** to the real

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microbial populations of interest.[3–5] Despite this serious proviso, the Petri dish culturing method is still used as the pragmatic choice in the food industry.

Campylobacter and VBNC

When *Campylobacter* is cultured, it has to be done under very special conditions [micro-aerophilic and capnophilic atmosphere (5% O_2, 10% CO_2, 85% N_2) at 41.5°C] on a specific plate that inhibits its growth of other bacteria. The focus is on culturing *Campylobacter jejuni*, (*C. jejuni*) and *Campylobacter coli* (*C. coli*). However, this excludes other *Campylobacter* strains, such as *C. concisus* and *C. foetus*, which are responsible for many cases of gastroenteritis in the elderly.

The most important problem of the anomaly of the culturing method is it misses the *viable-but-not-culturable* (VBNC) cells. These bacteria are induced to temporarily stop reproducing, though they may become virulent in another, more favourable environment. In practice, this means that chicken meat may well test negative for *Campylobacter* at the control platform in the slaughterhouse, while testing positive at the retail level. These emerging and still not fully understood VBNC characteristics pose a serious risk to human health.

Serious microbiological impacts

A possible drawback of cleaning is an activation of genes resistant to chemical disinfectants, including chlorinated products. To make matters even more complicated, these genetic changes have also been found to promote resistance to a broad spectrum of antibiotics. This is the emerging, and potentially disruptive, problem of Multi-Drug Resistant *Campylobacter*.

The slaughterhouse provides multiple niches for reservoirs of all kinds of *Campylobacter* spp. *Campylobacter* exhibits great genetic diversity, finding different genotypes during processing in the slaughtering line. Culture-independent analyses, like multilocus sequence typing (MLST) and whole-genome sequencing, are uncovering the mechanisms of survival of *Campylobacter* bacteria.[6] This study is an example of how the boundaries and definitions of genetics are continuously evolving in the new era of post-genomic microbiology. The amount of novel microbial genomic information that is being generated on a daily basis is now so vast that multidisciplinary approaches, which integrate bioinformatics, statistics and mathematical methods are required to assess it effectively. All these challenges necessitate a highly targeted approach to representative sampling working closely with microbiological analysis. However, today, we are very far from this goal.

Modern genomics has revolutionised every aspect of microbiology. There is an urgent need for new rapid and reliable microbial detection techniques in all relevant sectors of life science and, especially, in the food industry. Microbiology is extremely complicated, but it all starts with proper sampling. A useful point of departure regarding food and feed was described in Reference 7, with a special focus on considerations with respect to water analysis.[8] The future for required innovations is challenging and there is good reason to be cautiously optimistic, however, there are threats looming at the horizon, especially as multi-drug resistant (MDR) bacteria proliferate at a rapid pace.

Economic impacts

Campylobacteriosis is the most commonly reported *zoonosis* disease (one which can be transmitted to humans from animals) with an increasing trend in the European Union. The impact of disease in people is conventionally quantified in non-monetary terms, usually in the form of what is called a "disability-adjusted life year" (DALY)—whereas losses due to disease in animals, particularly livestock, are quantified in monetary terms.[9] As an example, in the Netherlands, the burden of disease in terms of DALY is calculated as *1200 DALYs per year*.[10] The EFSA[11] calculated the costs of campylobacteriosis for public health systems and for lost productivity in the EU at approximately **€2.4 billion per year** (whether animal losses are included is unclear). Worldwide, campylobacteriosis is estimated to cause **500 million disease cases** in human society. What are the economic costs of this societal burden? How to break down such estimates on national levels?

Even approximate costs for all the industrial interventions and scientific research needed are hard to estimate. However, from a socio–economic perspective it is critically important to understand the interactions between the sectors of microbiota, animal welfare and pathogenesis in humans. There is so much more to do here—and working towards a better economic **cost calculus** is very high on the agenda, so that this aspect cannot be ignored in societal reckoning. Human diseases that can be prevented, as well as unnecessary deaths, are much too important!

This will get us nowhere if there is no representative sampling. The application of the TOS for the complex sampling of bacteria in the large-scale meat industry from chicken farm to slaughterhouse is challenging, however, it offers the possibility for profitable cooperation between the basic principles of the TOS and microbiology!

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SAMPLING SPECIAL SECTION

Sampling in pharmaceutical manufacturing: a critical business case element

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Editor's summary

Sampling can be seen from many viewpoints: technical, economical, managerial… Here, sampling is described as a critical success factor in business cases, broadening the viewpoints presented above and below.

Introduction

Leading pharmaceutical companies continuously acquire technology to develop a quality product and bring it to market in the shortest possible time, realising that the growth and health of the company depends on new sales. They do not want the lack of new technology to stand in the way of competition for market opportunities. Leading companies are also committed to meeting the demands of their supply chain. Once a new product is approved, they want to supply their customers and always meet the expected delivery date. The 2020–2021 pandemic has emphasised the need for pharmaceutical manufacturing and *timely* delivery of products to counteract COVID-19 and provide medications for related conditions.[1] Companies have invested heavily in Process Analytical Technology (PAT) to monitor and control processes, and in *continuous manufacturing*. They realise the need to consistently and rapidly monitor materials and interim products during production in which they increasingly rely on integrated, on-line analytics.[2]

To be able always to acquire *representative samples*, or representative PAT signals, is correctly viewed as one of the most challenging aspects in reliable process monitoring.[2] Key examples are presented below in which proper sampling is a critical economic success factor in business cases.

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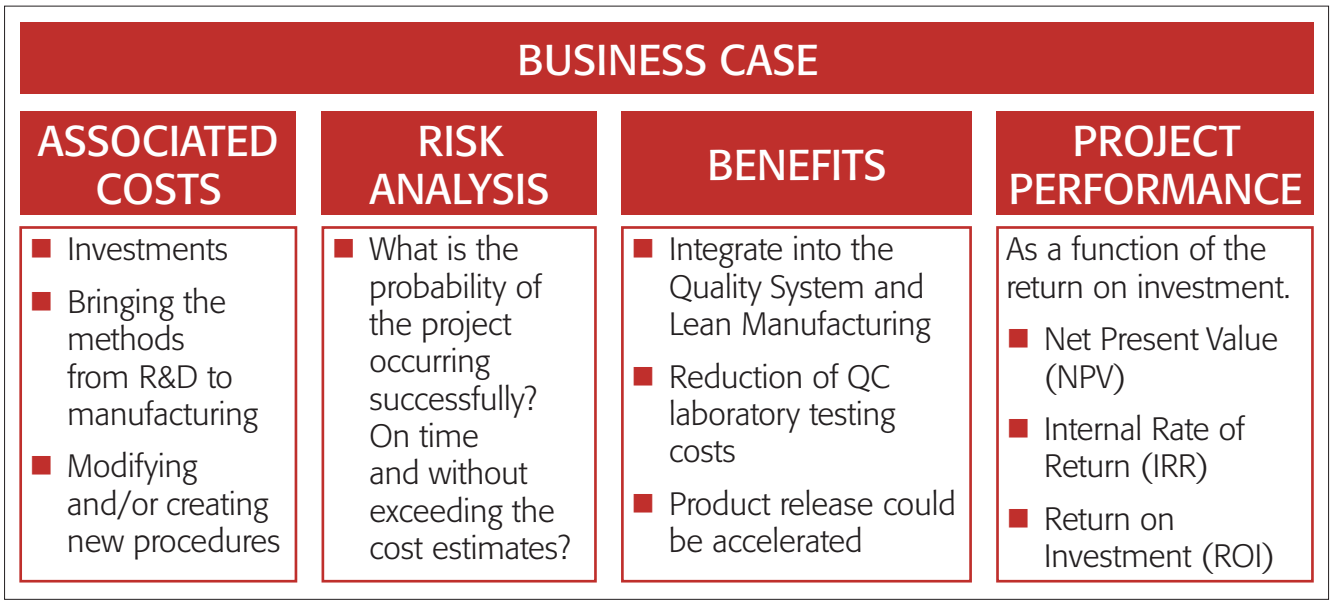
Pharmaceutical sampling: lots of positive economic opportunities

Pharmaceutical sampling is carried out to serve various critical purposes:

1) There are currently multiple efforts to eliminate manual sampling in the synthesis of small molecule drugs and in biotechnology-based products.[2,3] This interest is especially evident with cell culture media where manual sampling could result in contamination.[3] Automated sampling is seen as a way towards assured representative sampling.[2] Automated sampling systems are being developed for the synthesis of Active Pharmaceutical Ingredients (API), where the acquired samples have to be prepared (e.g. removing particulate material) before injection into an on-line chromatographic system.[2,4] Synthesis often involves sample extraction which, if performed manually, would be time consuming and impractical for long processes. Automated systems seek to eliminate the variability which could be introduced by different analysts, and avoid possible sample integrity problems.[4] The goal is to integrate representative sample acquisition with subsequent preparation for injection into a chromatographic system, data processing and to make the results obtained available for process control.[2,4] **These developments have obvious positive economic benefits and can readily be included and emphasised in business cases.**
2) Sampling is also performed to identify incoming raw materials.[5] The current Good Manufacturing Practices (cGMP) and other regulations require that *all* raw materials be identified before use in a pharmaceutical process. The identification method is currently performed through handheld Raman or near infrared (NIR) spectrometers at many manufacturing sites. The business case is here a significant reduction of time needed for analysis. The handheld systems permit reliable identification of raw materials directly at the warehouse where materials are received. Thanks to handheld systems, it is no longer necessary to transfer the material to a local or remote laboratory. Handheld systems also facilitate digital transfer of the identification results to Laboratory Information Management Systems, reducing the risk of errors associated with manual entry of results—**again with obvious economic benefits easily outlined in business cases**.
3) Very significant efforts have always been made to monitor the uniformity of powder blends.[6] Pharmaceutical blends are usually constituted by several excipients and one or more APIs. Pharmaceutical regulations require that the uniformity of blends be evaluated *before* tablets are compressed. It is of considerable professional concern that sampling of such blends is still usually done through thief sampling, which is nothing but *grab sampling*, and multiple serious problems occur at this stage.[6,7] Thief sampling requires interrupting the manufacturing process for several hours, and often requires special gowning and protection to reduce the exposure of personnel to potent drugs—**all of which cause severe additional costs**. Current good news, however, is that *all* of this *can* be avoided by



Key economic analysis tools for sampling.

judicious application of the Theory of Sampling (TOS).[6,7] **TOS becomes a valued integral element in any business case in Pharma.**

4) Simultaneous sampling-and-analysis. In recent years, NIR and Raman spectroscopy have been used to monitor drug concentrations at the feed frame, immediately before tablets are compressed.[8–10] The feed frame, and a stream sampler currently under development, are the main agents for meeting the Fundamental Sampling Principle (FSP) in which all parts of a moving lot must have the same opportunity of being sampled for analysis.[11] NIR and Raman spectroscopic methods are essential parts of real-time monitoring and control approaches within the field of PAT. These methods are non-destructive, analyse the material in their native state and thereby eliminate the use of *solvents* in analyses. Wider implementation of PAT methods will reduce the use of *solvents* significantly, avoid operator exposure to potent drugs, and will further improve the uniformity of the tablets manufactured. However, as thief sampling still remains the main method for sampling powder blends; a *stern call for caution* has been made,[6] **which has considerable positive economic opportunities.**

Sampling in business cases

All the industrial applications of defensible representative sampling described above have on one or other occasion required preparation and approval as part of a *business case*. Investments in automation, PAT and continuous manufacturing require the approval of a business case by company management. The business case is how all new technology is presented in the company and corporation regimen, describes the investments needed, the likely economic benefits as well as plans for risk management and avoidance.[12]

The pharmaceutical industry presents multiple challenges for sampling of products which may be liquids, suspensions, tablets, small molecules or proteins. It is difficult to estimate the specific monetary gain potentials in this highly varied scenario. However, the Center for Structured Organic Particulate Systems, University of Puerto Rico at Mayagüez is currently developing a template to present business cases for new investments in PAT, sampling equipment and continuous manufacturing to pharmaceutical industry leaders.[12] This novel template has provided new insights into the adoption of new technologies in the pharmaceutical industry, including sampling. **A business case template will significantly add to the persuasion power of involving proper sampling wherever needed.**

Acknowledgement

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SAMPLING SPECIAL SECTION

Sampling expertise for the accounts department, CEOs and board members

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Money out the window—either way

Here is a perfect example of how everything works out at the accounting level, where value is measured in monetary units. Picture a business selling a commodity under the contract specification that the product contains 27.45 % of a critical compound (this is measured by the seller's own "home" laboratory). For the sake of argument, let us assume that this is exactly what is reported for a consignment in question. So, the seller is apparently in the clear, and the buyer will, therefore, get exactly what is stipulated on the product specification sheet. This is the ideal case for both parties: the seller does not give away a higher concentration of the valuable commodity than promised, and the buyer only has the correct amount of valuable goods paid for.

However, the buyer wishes to exercise his testing privilege (relying only on his own preferred laboratory of course)… The whopper: before the day is out, the seller is being sued by the buyer's lawyers—since the control laboratory reports a concentration of 23.40 % *only*. Is the seller employing an inferior laboratory? Or, is this newly discovered disparity a result of the buyer's laboratory inferior performance? Or worst, should the seller be suspected of trying to swindle the buyer? Suddenly both stakeholders experience uncertainty and doubt—who, what is to blame? Today's tradition is overwhelmingly to look for *causes* to such control differences only *within* the realm of analytical laboratory performances (both *could* be wrong in principle, but this conclusion has only a snowman's chance in Hell, since both laboratories are, no doubt, properly certified, so this conclusion will be ignored). Nevertheless, with today's most often used approaches, what happens instead is a totally unnecessary amount of *extra* laboratory work (see Example 2 above).

Most unfortunately, in the overwhelming number of such cases, the root cause lies miles away from the certified analytical laboratories. The sampling + analysis spread is the real culprit!

Because of the inevitable sampling + analysis spread, Figures 1–3, which was reported as 27.45 % *could* alternatively (from a second sampling) just as well have turned out as, say, 23.20 % in the case of significantly heterogeneous materials. A difference of 4.20 % in concentration of the valuable analyte will very likely be unacceptable. But less can be equally bad, if the intrinsic value of 1 % point is higher. Depending on the intrinsic % point value, the magnitude of the concentration difference, and the so-far ignored weight determination uncertainty as well (yes, there is also a weighing spread lurking in the wings, but more on that later), as one ranges over all the World's traded raw materials, commodities and volumetric goods sooner or later there will be a threshold on the other side of which such differences will not be acceptable because of the accumulated *value losses* (loss in material, loss of revenue, loss of reputation…).

Here is the principal situation, in terms of the money lost for the one party… or gained for the other. For the sake of argument, assume a nominal commodity price: EUR 850 / 1 % point / ton: 4.20 % deviating concentration is equal to EUR 3570 / ton; if tonnage is, say, 250 ton, **EUR 892,500**.

(It should be factored in that industrial weighing is most certainly also fraught with measurement errors, just as is analytical determination, which will only add to the sum-total uncertainty. However, the weighing uncertainty influence(s) will be treated specifically in its own right in several examples below.)

The intrinsic value of raw materials, commodities and goods as characterised w.r.t. composition and the value by volume (mass) of course display an extreme range. For the "lower end" of things, the consequences of analytical differences will not constitute major deviations—while as soon as the *ICV* is *higher* and/or the tonnages involved are, the accrued loss of revenue for the seller (or the "extra commodity received at no payment" for the buyer) will meet with severe disapproval at accounting and management levels.

For the sake of argument, assume a constant tonnage of 250 ton, with changing intrinsic commodity value per % point (*ICV*) and changing analytical difference (*AD*), the gross economic consequence in the form of the resulting *value gain or loss* (*VGL*) for this example commodity is shown in Table 1.

This tally will, of course, take on quite other manifestations, some less drastic, others very much more so, depending on what *your* commodity *ICV* is, *your* tonnage involved and what the operative between-laboratory analytical difference

Table 1. How it always adds up...

AD	*ICV*	*VGL* (EUR)
1.00 %	850	212,500
1.00 %	1700	425,000
2.50 %	850	531,250
2.50 %	1750	1,002,500
5.00 %	850	1,062,500
5.00 %	1750	2,125,000

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(*AD*) happens to turn out to be. There is no need to insult anybody's intelligence by producing *similar* tables as the one above for a slew of other materials, lots and products (some less valuable, many very much more so). Anybody on the business side of the principal transaction used in the example above, will have got the picture long ago:

WHY do such hidden discrepancies occur within our business?

WHY has nobody told management about this risk long ago?

WHO is accountable for this lack of due diligence w.r.t. proper risk management?

WHAT can we do about this?—Immediately!

Traditionally, knee-jerk reactions and solutions to the above desirability has been to pour a lot of new money into improved analytical performance, either upgrading one's own lab or finding a better commercial laboratory with a better reputation etc. Alas, as has been made abundantly clear above, that this will very likely *not* solve the issue, Figures A–D in the Editor's Introduction.

This is the very reason the TOS *has* to be invoked. This is the fundamental reason a minimum of the TOS understanding *must* be mastered at all relevant levels, including those formerly only responsible for the business side of operations. Of course, that should also include proper **risk management**.

Conclusion

There are ample economic, pure business-related reasons to make sure that TOS knowledge is part of your operations, company, corporation and organisation—and absolutely no reasons not to…

"The costs of sampling errors and bias in the mining industry"

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Abstract. "South Africa's mineral commodities generate approximately R420 billion per annum from export earnings. Of that amount coal (28.1%), gold (15.2%), iron ore (14.5%), and platinum (21.7%) account for 80%, and together with chrome and manganese account for 88% of the earnings. Payment for these products is based on the metal content, and in the case of coal, the energy content. Traders rely on the analytical results from samples of the products to obtain a fair price and true value of the sale. This paper covers three main issues. Firstly, the thrust of interest in sampling of particulate materials is shown to be primarily due to the financial implications of poor sampling and the vibrant trade in these mineral and metal products in the USA between the 1850s and 1940s. The importance of correct engineering for cutter operation and good maintenance of cutters in general in the sampling of bulk commodities is emphasised. Secondly, simulation of a low-grade iron ore deposit demonstrates that the principal offending factor in sampling events is the sampling bias, rather than the sampling error. Whereas sampling error may account for as little as 0.0016% error in the mean grade, sampling bias, which can be positive or negative, may affect the mean grade by as much as 10%. Thirdly, the contribution of individual particles of iron ore, particularly those in the larger fractions of the size distribution, is investigated. Relatively small changes in mean grade of about 0.106%Fe can result in losses to the supplier of about US$11 600 per 100 000 t shipment of iron ore, a substantial amount of nearly seven million dollars per annum. Together the three aspects, principles of correct cutter operation, the effects of bias on the mean grade of samples, and the effect of size distribution on sample extraction error, contribute to potential financial losses in the bulk commodities trade."

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SAMPLING SPECIAL SECTION

Appropriate sampling—a critical success factor for sustainability

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UN Sustainability Development Goals

The UN sustainability goals are now spreading throughout society, showing us the way to the future. Everybody wants to contribute to a more sustainable world. Sometimes, actions to support sustainability are presented as easily comprehensible tasks for society, i.e. saving energy and lower emissions. It would appear that almost all companies' management can present a portfolio of sustainability related projects with a clear understanding of which sustainability development goals (SDGs) they support.

It takes time … and insight

Sometimes, however, other tasks are necessary to move this development demand forward: more insight and knowledge. Sometimes such tasks are *hidden* in the background of more pressing everyday needs (pandemic, climate crisis, inequality etc.). This is precisely the situation for *appropriate sampling*, which is, nevertheless, a *critical success factor* for sustainability.

Some companies, unfortunately, show a lack of recognition of the importance of appropriate sampling and only see this as an unnecessary expenditure. It is necessary to be able to point out how correct sampling can contribute to reach our common, as well as the individual company's, sustainability goals. All companies, of course, seek to run their production efficiently, but far from all prioritise the quality of the data necessary to optimise this business goal. And, if so, new investments are typically much more easily allocated to better analytical systems in the laboratory, sadly foregoing or neglecting the importance of the first step of all analytical processes, *appropriate sampling*. But as one strives for a lean production, optimisation of processes, more efficient use of resources and fast correction of process deviations are highest on the prioritisation agenda. Therefore, it should be a no-brainer to see appropriate sampling as an important foundation to reach such goals.

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Appropriate sampling must be brought in

To bridge the gap between the science behind the TOS and applied industrial procedures, let's connect appropriate sampling to four of the 17 SDGs:

4 Quality education

Recognising the importance of applying the TOS in *your* company is the first step. This can be done most efficiently by educating employees, on any relevant level, to understand better the quality of the data that is being used for process monitoring and control (QA/QC), i.e. knowing the *origin* of the valuable data, as well as their *uncertainties*. Increased knowledge on sampling error contributions is crucial here—all is not only analytical uncertainty! Investing just a little for this purpose will immediately enable increased sound critical thinking around current procedures.

9 Industry, automation, infrastructure

A mind set aiming for continuous improvements should a.o. contain the willingness to *rethink* current sampling procedures in any company or organisation. Sampling protocols should not be static, but dynamic, in order to follow increasing knowledge and experience in the TOS arena and the most recent technological developments. New emerging industries, especially, should have a clear mission including optimal sampling.

12 Responsible consumption and production

A key factor is process understanding and optimisation. For this, it is necessary to have trustworthy sampling schemes, which ensure that the data utilised are indeed correct (representative) and can be used to follow all relevant process improvements. If this is not the case, the righteous chase for improvements will include many *unnecessary* trial-and-error loops, unavoidably also leading to lower motivation in the organisation and to quite unwarranted data distrust.

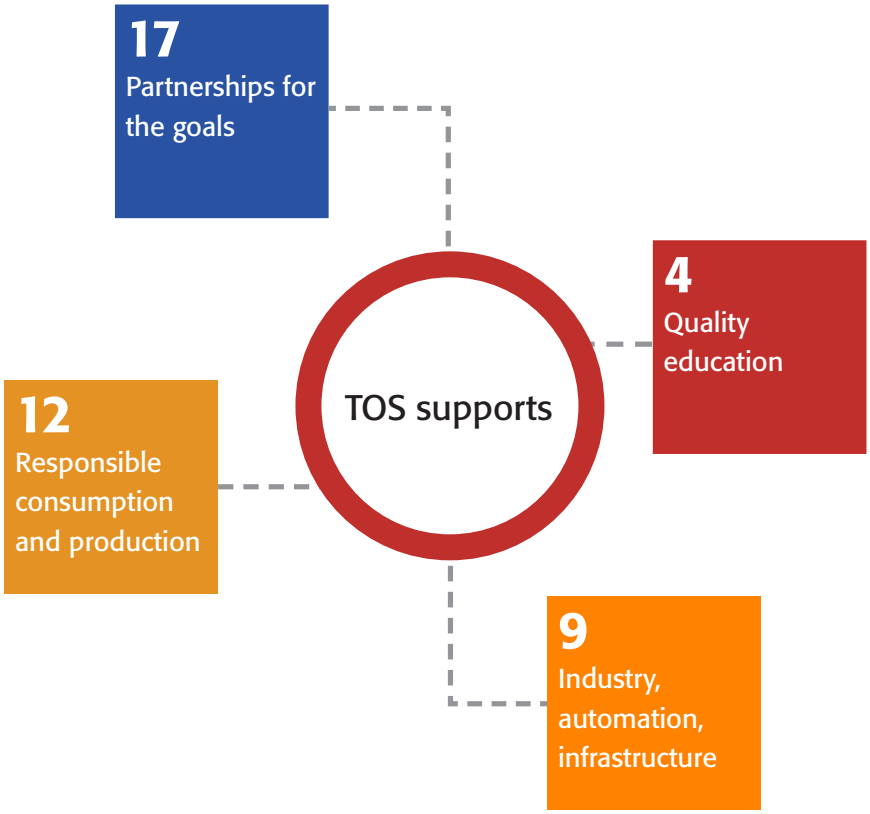
17 Partnerships for the goals

Creating awareness around the existence and application of the TOS is the ultimate goal of the International Pierre Gy Sampling Association (IPGSA), which has been put into action by the biannual World Conference of Sampling and Blending (WCSB) series, by the magazine *TOS Forum* and by a regular sampling column in *Spectroscopy Europe/World*. Networking individuals, companies and organisations and regulating authorities in these fora in the last 20 years have spawned immense activities, very fruitful discussions and learning across all almost sectors in science, technology and industry.

How to reach the SDGs most efficiently?

We have *all* the right tools at hand for appropriate sampling.[1–9] The TOS has been out there for seven decades, although its impact has been especially effective since the change of the Millennium. This work is very well under way.

In the last two decades, ten World Conferences on Sampling and Blending



have promoted the TOS to a continually broadening community, far from all sampling experts "by birth", and has connected users and suppliers of sampling equipment in a highly efficient way. Also, many educational courses from sampling experts have been given, making the TOS' principles much more approachable to "common users" in technology and industry. Very many articles have been published that highlight the importance of a basic understanding of what makes sampling representative. And standards and guiding documents have been approved to lead the way towards representative sampling, e.g. the *de facto* international standard DS3077.[1]

A personal impression: Compared to the extensive literature that is now available at all levels,[1–7] from introductory (very easy to understand by all) to the highest textbook level,[8–9] the marked impression regarding the heading: "How to reach the SDGs most efficiently?" is …. that relevant individuals, scientists, company employees, organisational personal, management etc. DO NOT HAVE THE TIME, OR DO NOT SET ASIDE THE NECESSARY TIME FOR CONTINUING SELF-EDUCATION (please observe that the effect hereof is one-and-the-same). Here is a call to all involved in the sampling business: We are all individually obligated to start *doing better*—not much is required for a first step!

Still, today, there would appear to be a lack of focus on appropriate sampling across many sectors in technology and industry. There is much focus on process improvements and innovation, but little, far too little, on how the crucial **data** with which to control the process are obtained. Sampling and its related activities is a critical success factor and a vital support function for production processes, which should never be forgotten or neglected. And, N.B., the TOS is valid both for traditional physical sample extraction and for process analytical technology extracting sample characteristics through appropriate sensor technologies. Any chain is only as strong as its weakest link!

So, dear CEOs, managers, supervisors …

- Strengthen your sustainability drive(s) and start actions to control the crucial aspect of sampling!
- It is what you run your processes with!
- Your bottom line depends on it!
- The current planet is in danger—and requires appropriate action!
- Remarkably, appropriate sampling has a role to play even in this vastly larger perspective!
- It all starts with me and you!

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SAMPLING SPECIAL SECTION

IPGSA indicates a member of the Council of the International Pierre Gy Sampling Association

My name is Abel Arkenbout (MSc), toxicologist educated at the University of Utrecht, the Netherlands. In the nineties, I developed educational programmes for the Ministry of Health on transmissible diseases and the risks of illegal drugs markets. Together with a team, I set up a consultancy for information and education on these topics in Amsterdam, which has now become a national advisory body. As a scientist, I develop crowd-based and funded research programmes together with my colleagues, since 2013 for the ToxicoWatch foundation. This concerns biomonitoring projects on Persistent Organic Pollutants (POPs) such as dioxins (PCDD/F), dl-PCBs, SCCPs and PFAS related to waste incineration. In our multi-year biomonitoring studies, we use vegetation (mosses, pine needles and leaves) and eggs from backyard chicken as relevant biomarkers. With the help of innovative analytical bioassays like the DR CALUX, FITC-T4 and PFAS CALUX, POPs in the environment can be detected in the small quantities of picograms. ToxicoWatch Consultancy focuses more on the analytical challenges in microbiology and investigates the potential of microbial degradation of Persistent Organic Pollutants.
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SAMPLING SPECIAL SECTION

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SAMPLING SPECIAL SECTION

Mr Martin Lischka (MSc Geosciences and Environment) has more than ten years of experience in the field of sample taking and sample preparation. He is currently working in the R&D department at HERZOG Maschinenfabrik GmbH & Co. KG. Projects he is involved range from special sampling systems, large scale raw material applications, down to final aliquot preparation—like pulverisation, pressed pellet preparation, borate fusion for XRF analysis and many more. His recent activities focus on precious metal recycling, copper-related commodities and sensoring methods applied to sample taking and preparation routines as a quality measure.
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Geoffrey Lyman has worked widely in mineral processing research and mathematical modelling for many decades. His current work is in sampling of particulate materials, through his company Materials Sampling & Consulting Pty Ltd, which also provides courses to in-house groups or at Conferences. He has worked on sampling in a wide variety of industrial sectors, i.e. in the food industry, the grain industry and widely in minerals sampling (gold, platinum group elements—concentrators, smelters and autocatalyst recycling—coal, iron ore and base metals). He has many authored leading papers in the statistical theory of sampling over the last five years. He has recently developed a means of calculating the entire probability distribution for the sample analyte content. A major new textbook was published in 2019, in which he takes a final step forward past the sampling theory of Gy.
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Duncan Aldwin Vogel (born in the Netherlands, 13 October 1973) is a global expert in weighing, sampling and testing of traded commodities. Already during his study in business management at the International School of Economics, Rotterdam, Aldwin started building his pedigree in the renowned family inspection business Hoff & Co. Services BV that became part of Bureau Veritas in 2010. From September 2011 to August 2013 Aldwin was based in Houston, USA, seconded as acting Director, Steel and Energy Products. Returning to Europe and the Metals & Minerals Trade Business Line in September 2013, Aldwin is now responsible for Technical Governance of Bureau Veritas' Commodities Trade services globally. His expertise covers all aspects of inspection, sampling and analysis starting from green field prospect requirements to fully implemented turn-key projects. Embracing augmented inspection services through IoT and smart communication, Aldwin recently also came out as inventor and patent holder of several novel inspection solutions. He is highly experienced at all aspects of testing for Transportable Moisture Limit and was leader of the TML workgroup of the TIC Council. Aldwin is a delegate of the Netherlands on ISO Technical Committee 102 (Iron ore and direct reduced iron) and TC183 (Copper, lead, zinc and nickel ores and concentrates) where his focus is on sampling, sample preparation, moisture determination and TML.

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TONY DAVIES COLUMN

Finding data in today's information age: the Bayer COLID system

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It is said we live in an information age. Some say we live in a mis-information age. We certainly enjoy easier access to a multitude of information sources to support our work than at any time in history. However, at what stage does the shear enormity of the information we are presented with mean that our ability to filter good from bad or even deliberately misleading is overwhelmed? Then we start making worse decisions than in earlier times when limited peer-reviewed information feeds were all we could rely on.

There are, of course, many Internet search engines available to you, and you will certainly have a favourite "go to" engine on which you rely for the majority of your information quests. However, companies can influence the results you are presented with, by paying the search engine providers or employing specialists whose job it is to understand how the search engines rank the information they have scraped from the Internet. Stand in front of a mirror and look yourself squarely in the eye and admit how many pages of search results you are prepared to scroll down through, and how often do you access multiple results pages to make an informed decision on the problem you are researching.

Finally, let's add a complication in that there may well be some superb work carried on within your own company which should certainly influence your decision making, but it was carried out in a division whose information is not available to common Internet search engines for obvious company confidentiality reasons. There is nothing worse than working on a problem for six-months only for someone at a corporate event to ask you "didn't you talk to Sheila in Formulations; she did some superb work on exactly these active ingredients working out of Brisbane and found a solution back in 2015 with all the confirmatory spectroscopic data you will ever need!".

Evolving solutions in a digital world

Even where we have access to well-curated and indexed archive solutions, the route into each archive is often very specific to each technique. Even where we have, for example, chemical structure information associated with specific data sets in the individual collections, they may well be in formats or encoded in a way which is fine for the specific data source but is missing content which makes comparison of information across sources problematical. This has already been partially covered in a recent column where we showed many of the various ways that NMR spectra can be found in different data sources—fine in their own environment but a real problem if you want to compare them against one another.[1] So, imagine you want to search for a specific item in a museum—clearly the museum's catalogue would be a great starting point—hopefully detailing not only what is on open display but what they have hidden away in the archives. Now expand that question to all museums around the world and all their archives… and you get some idea of the problem we are facing. Additionally, of course this isn't a static problem—the archives and information resources are also evolving and expanding even as we search.

Fortunately, there are digital solutions evolving to meet the expanded challenges of a digital world. Instead of a printed catalogue for a physical world meet the digital Finding Aid for the information age. In a subsequent article we will look at the exciting work which is currently ongoing within IUPAC on the use of Finding Aids to interrogate digital archives of supplementary information for spectroscopic data and associated chemical structures and metadata, but in this column, we will look at one which you can have access to for free to build your own Finding Aid, the Bayer COrporate Linked Data (COLID) system.

COLID not COVID!

Many years ago, I met Rolf Grigat who has been working on spectroscopic data systems for most of his active career, and we even worked in the same organisation at Creon•Lab•Control and Waters Corporation for four years. He is now working in Bayer in Leverkusen, Germany and has been the product owner for

DOI: 10.1255/sew.2021.a52

TONY DAVIES COLUMN

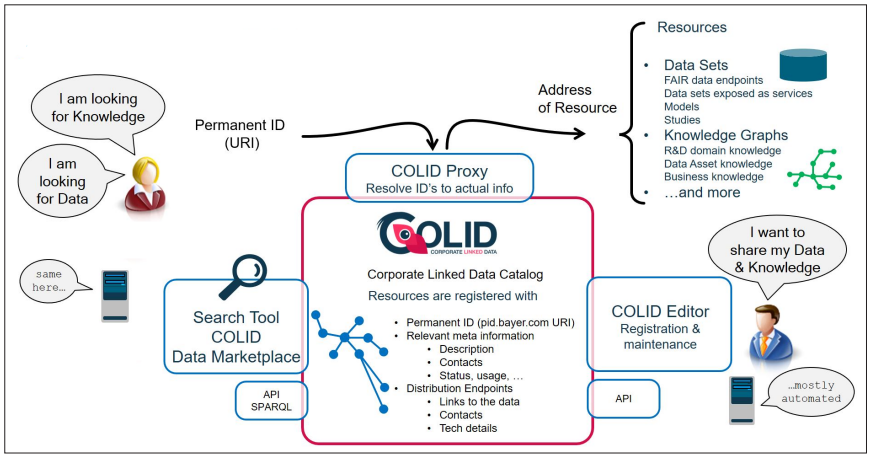

Figure 1. Highlights of the definition of data consumers user requirements for the COLID system.

the COLID data and information catalogue for more than three years. This is a solution which is designed to meet the challenge of making data and information assets FAIR[2] and linked for all data consumers (human and computerised) from both internal and external information sources. Rolf collected concrete requirements from the various business units and started the implementation as a cloud native application (built with cloud tools rather than taking a classical client–server application which is hosted in the cloud, which is more efficient and easier to maintain!). Figure 1 shows graphically the results of the data consumers' wishes.

COLID has been fully operational for two and a half years and is used cross-divisional and remarkably has been published (without company confidential content of course!) as a well-documented open source GITHUB project so that anyone can host their own COLID service.

How does COLID work?

Well, COLID is essentially a "catalogue of catalogues" collating any data source with which it is connected. Metadata is harvested for all the content it finds within the data source—all of which are provided with permanent Uniform Resource Identifiers (URIs). These information sources can be both internal and external unifying information retrieval in one uniform access application. Such a Finding Aid is ideal for collecting and providing metadata about basically any resource that you want to incorporate and a) link endpoints, such as spectra, in a repository or details in a chemicals database and b) link it semantically with any other related resource. So COLID could be simply be spelt as "F" in FAIR!

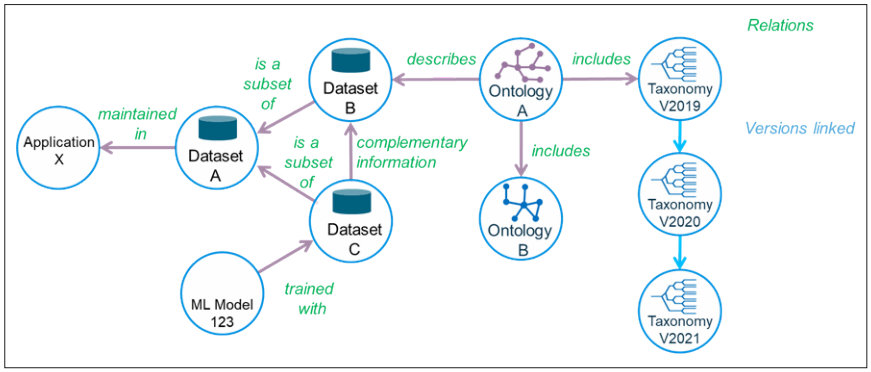

Figure 2. Simplified resources and relationships model for COLID showing the maintenance of linked versioning, transparent to the end user through the COLID applications.

A modified version of one of Rolf's simpler published explanatory graphics is shown in Figure 2.

So, if we were to take the available functionality and apply it to our use case outlined in the third paragraph, we might build something that looks like the outline system in Figure 3 with the taxonomies providing standardised classifiers for better comparison of the information entries.

My hope for the future is, of course, that Sheila in Formulations, who has such wonderful spectra, successfully registered her project, the spectroscopic data and the chemical entities involved in her work into a repository which is linked to my COLID Finding Aid. If so the chances that I would miss her work would hopefully be pretty much reduced to zero as my access application will find the corporate knowledge through spectral searches, chemical entity searches for any of the APIs not to mention reported intermediates. Hopefully, I will find all this out on the first morning of my new project and be enjoying reading about all the experimental results and associated project information, made available to me through the permanent URIs, in the same afternoon. Much better than waiting to find out six months later that my team have been wasting their time and Sheila in Brisbane beat us to it, on the other side of the planet, six years ago!

And stay informed!

Now we are happily informed about what Sheila achieved through our new Finding Aid, our work is supported further by keeping us up-to-date on any changes to the entries we have subscribed to. What we quickly discovered, for example, is that Sven's Applications Team in Västerås, Sweden is currently working with the same active ingredients, but different excipients, on a project very similar to ours but for a totally different client grouping. So there seems to be enormous potential to support each other and get both our projects over the line faster and cheaper than was originally budgeted for. Oddly enough, a small research group from the University of Mälardalen has also published some peer-reviewed papers from a local

TONY DAVIES COLUMN

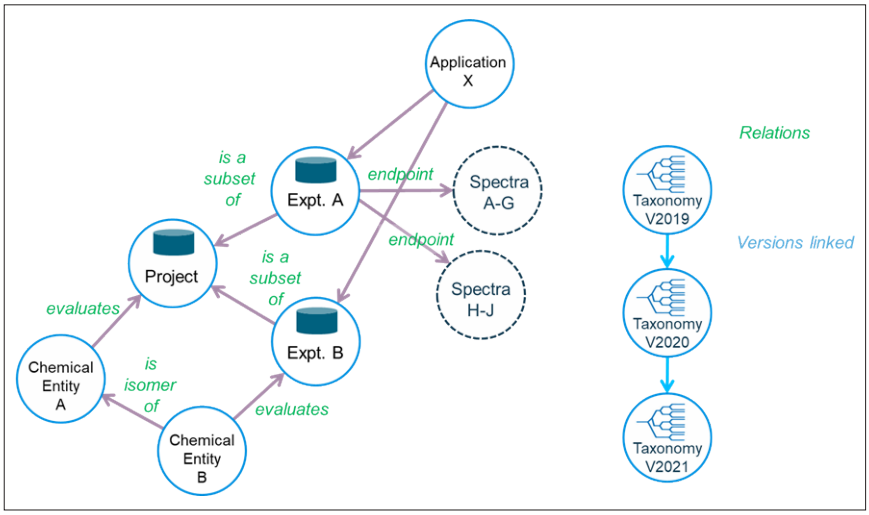

Figure 3. Potential COLID deployment capturing project, experiment, chemical and spectroscopic data with all associated metadata and relationship information.

conference in Swedish, including some of the chemistries we plan to explore—I would never have spotted these papers without the help of the Finding Aid. We will be keen to see how much freedom to operate we have in both our projects!

Conclusions

In the beginning of the article, I painted a deliberately grim picture of, to be quite honest, how I really feel about the way information is being made available to us in this information age. There are far too few fast, helpful tools to support us in our decision making and the sheer volume of information at our fingertips is often swamped by data of uncertain pedigree. Reading about functionality of these Finding Aids like COLID and following the excellent work being done within IUPAC on a Finding Aid aimed at supplementary spectroscopic information from peer-reviewed publications gives me hope that we have a brighter, more informed future ahead. Of course, as Rolf pointed out to me recently, the actual data sources are often highly confidential in nature so "F"inding out that information exists somewhere is not the same as actually having the permissions allowed to access it—which makes our Sheila and Sven example somewhat idealistic!

If you think you may have a requirement that may be met by a COLID deployment have a look at the documentation in the Github site[3] or even look to some information published by the Pistoia alliance.[4]

Figure 4. COLID logo.

References

1. R.M. Hanson, D. Jeannerat, M. Archibald, I. Bruno, S. Chalk, A.N. Davies, R.J. Lancashire, J. Lang and H.S. Rzepa, "FAIR enough?", *Spectrosc. Europe* **33(2),** 25–31 (2021). https://doi.org/10.1255/sew.2021.a9
2. https://www.go-fair.org
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4. https://fairtoolkit.pistoiaalliance.org/methods/fairification-workflow/

Tony Davies is a long-standing *Spectroscopy Europe* column editor and recognised thought leader on standardisation and regulatory compliance with a foot in both industrial and academic camps. He spent most of his working life in Germany and the Netherlands, most recently as Lead Scientist, Strategic Research Group – Measurement and Analytical Science at AkzoNobel/Nouryon Chemicals BV in the Netherlands. A strong advocate of the correct use of Open Innovation.
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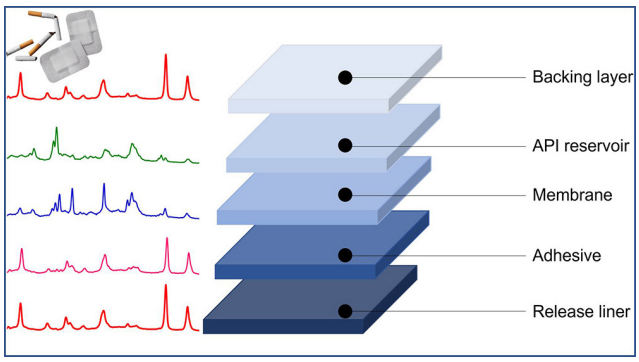
antony.n.davies@gmail.com

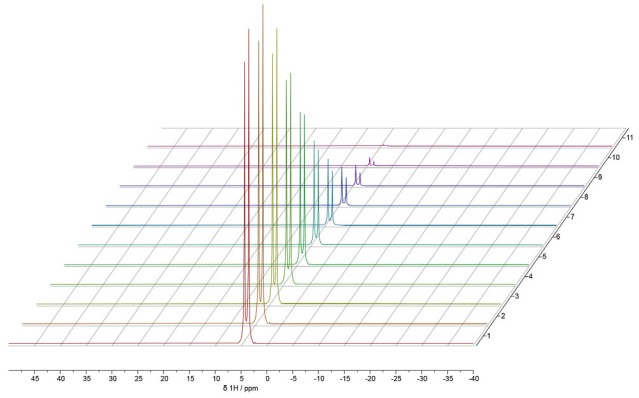


3D Raman mapping of a transdermal patch

A transdermal patch is a method of drug delivery through the skin into the bloodstream. The patch contains a drug which absorbs into your skin when attached to you and it releases a consistent and controlled amount of medication into the body over long periods of time. One of the most common uses of transdermal patches is to combat nicotine addiction. This application note studies a nicotine patch to reveal the active pharmaceutical ingredient as well as the polymer layers encapsulating it using confocal Raman microscopy.

Edinburgh Instruments

- Download Application Note



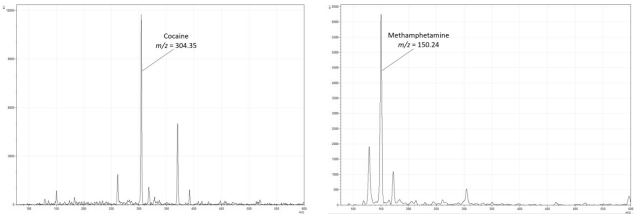
Multinuclear benchtop NMR for electrolyte design

Benchtop NMR enhances electrolyte design by enabling rapid and routine measurement of key performance parameters including electrolyte composition, diffusion coefficients of each component, conductivity, transference number and viscosity. Hence, it provides critical data for the design of new electrolyte formulations and optimisation of their performance. This application report outlines practical approaches for NMR electrolyte analysis and how the measured parameters can affect performance using examples from lithium battery R&D.

Electrolytes, which consist of anions and cations in a solvent system, are a key component in battery performance. Rechargeable lithium-ion (Li-ion) batteries offer high energy density and have become extremely popular, providing energy storage for electronics, medical devices and electric vehicles. Current battery technologies use small-molecule liquid organic solvents, such as ethylene carbonate (EC), dimethyl carbonate (DMC), coupled with small Li^+ and hexafluorophosphate ($[PF_6]^-$) ionic species. However, new electrode formulations such as Li-metal, lithiated silicon or lithium sulfur, require new electrolyte chemistries. Optimising the electrolyte performance delivers improvements in power output, longevity and safety, making development of new systems a high priority.

Oxford Instruments

- Download Application Note



Controlled substance detection

The landscape of controlled substance analysis is changing with compact mass spectrometers. No longer do the samples need to go to the lab, but now the lab can go to the samples. With the growing risk of exposure to fentanyl and its analogues, there is a need in law enforcement and decontamination services for analysis that is fast, dependable and can be operated with little to no training. Law enforcement agencies have been using chemical field tests as a presumptive test for the presence of controlled substances for decades. Not only are the field tests unreliable and not admissible in many jurisdictions, but it has become increasingly relied upon to negotiate plea deals. Additionally, there is now an increased risk of exposure in performing the tests on site. Instead of a preliminary analysis, some agencies are opting to send the samples directly to a laboratory, where there can be a significant delay for results. Sites undergoing decontamination are rendered unusable until the remediation process is complete. If the site is contaminated, numerous sample sets will be sent to a laboratory for a single site until the contamination is below a set threshold, costing both valuable time and money. Each time a sample set is sent to a laboratory, the results need to be obtained before proceeding, costing yet more time and financial resources.

Bayspec

- Download Application Note

APPLICATIONS

MIMS application in determination of N_2 and Ar levels in marine biological denitrification processes

The deviation of the N_2, Ar concentrations from equilibrium are known to be indicative of the important biological and physical processes taking place in the marine and aquatic biological environments and can be measured by membrane inlet mass spectrometry (MIMS).

Hiden Analytical's HPR-40 DSA has been used to perform fast response, high precision measurements of dissolved N_2 and Ar in water. The deviation of the N_2, Ar concentrations from equilibrium are known to be indicative of the important biological and physical processes taking place in the marine and aquatic biological environments. The HPR-40 DSA has measured the precision (co-efficient of variance) of N_2, Ar and the N_2/Ar ratio as: $Cv(N_2) \leq 0.26\%$, $Cv(Ar) \leq 0.25\%$, and $Cv(N_2/Ar) \leq 0.058\%$ respectively. Such high-precision measurements are important, in particular, in the study of the sensitive marine biological process of denitrification: $NO_3^- \rightarrow N_2$.

Hiden Analytical

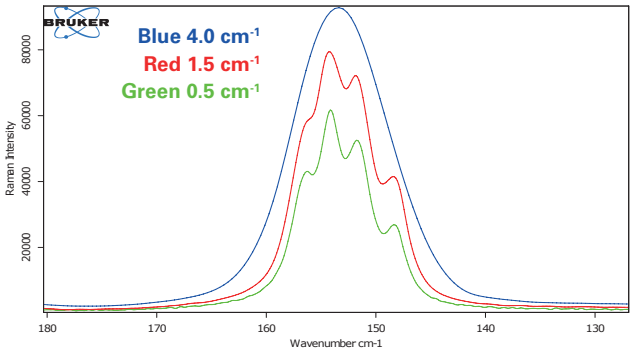
Download Application Note

Confocal Raman and photoluminescence microscopy for forensic investigations

Forensic samples may need analysis with multiple techniques; confocal Raman and photoluminescence microscopy are well suited to deal with such samples. Only microscopic amounts are required, and the techniques are non-destructive and non-contact: essential for further analysis of forensic samples. No sample preparation is required, and the results provide chemical and spatial information on sample components.

Edinburgh Instruments

Download Application Note



Spectral resolution in Raman microscopy

Selecting the right spectral resolution is of decisive interest to all Raman users. This applies to the purchase as well as the daily work with a Raman microscope. In most cases, the user's application and studied materials determine the final choice in spectral resolution. For example, narrow Raman lines, such as those found in highly crystalline materials or gases, require higher spectral resolution. In contrast, high resolutions are not required for the identification of amorphous solid material or liquids. This paper discusses how and why the spectral resolution required for dispersive Raman microscopy depends on the intended application and the sample material.

Bruker Optics

Download Application Note

Product Focus on Raman Spectroscopy

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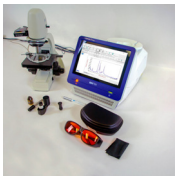
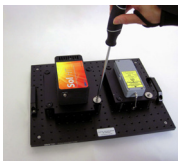
Tel: +1.855.MY.BWTEK
marketing@bwtek.com
www.bwtek.com

PRODUCT: PTRam
APPLICATIONS: Pharmaceutical development ▪ Bioprocessing ▪ PAT/ QbD applications ▪ Polymerisation ▪ Catalysis investigation
KEY FEATURES: 785-nm Raman system with fibre-optic sampling ▪ Self-calibrating and self-monitoring to ensure the validity of each measurement ▪ Long lasting, rock solid laser ▪ Rugged high performance, 24/7 real-time monitoring ▪ Rack mount package

PRODUCT: i-Raman® Prime
APPLICATIONS: Materials science ▪ Chemical analysis ▪ Bioscience and medical diagnosis ▪ Pharmaceutical analysis ▪ Process monitoring (PAT) ▪ Forensic analysis ▪ Geological and mineralogical research
KEY FEATURES: High sensitivity and low noise detector combined in Raman with choice of 532, 785 or 1064-nm laser excitation ▪ High-throughput spectrometer ▪ Flexible fibre-optic-probe based sampling ▪ Comprehensive package of sampling accessories ▪ Touch screen interface

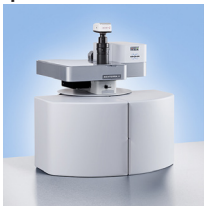


PRODUCT: DIY Raman Building Blocks
APPLICATIONS: Material science ▪ Food safety and quality determination ▪ Pharmaceutical ▪ Silicon wafer testing ▪ Teaching
KEY FEATURES: Multiple flexible configurations for application prototypes ▪ Fibre optic sampling flexibility ▪ Patented CleanLaze® Technology for laser stabilisation ▪ Easy configuration and installation ▪ Customisation



Bruker Optik GmbH
Tel: +49 (0)7243-504 2000
info.bopt.de@bruker.com
www.bruker.com/optics

PRODUCT: Confocal Raman microscope SENTERRA II
APPLICATIONS: Forensics ▪ Pharma ▪ Cultural heritage ▪ Polymers & plastics ▪ Material science ▪ Environmental studies
KEY FEATURES: Fully automated hardware ▪ One-click switching of 4 built-in lasers ▪ SureCal™ calibration technology ▪ Fast 3D Raman imaging ▪ Laser safety class 1



PRODUCT: Stand Alone FT-Raman Spectrometer MultiRAM
APPLICATIONS: Quality control ▪ Pharmaceutical products ▪ Routine analytics ▪ High throughput measurements (HTS) ▪ Research & development
KEY FEATURES: Spectral range of 3600–50 cm^{-1} (Stokes shift) ▪ RockSolid interferometer ▪ High sampling flexibility ▪ 2nd excitation line available ▪ Microscope coupling available ▪ 21 CFR Part 11 compliance

PRODUCT: Handheld Raman Spectrometer BRAVO
APPLICATIONS: Pharma ▪ Materials identification ▪ Incoming goods control
KEY FEATURES: SSE™—Patented fluorescence mitigation ▪ Duo LASER™ excitation ▪ IntelliTip™—Automated measuring tip recognition ▪ Pharma compliance ▪ Laser Class 1 in all operation modes

Edinburgh Instruments
Tel: +441506425300
alison.winn@edinst.com
https://www.edinst.com/

PRODUCT: RMS1000 Raman Microscope
APPLICATIONS: Bio sciences ▪ Pharmaceuticals ▪ Chemicals ▪ Polymers ▪ Nano materials
KEY FEATURES: Truly confocal ▪ Five-position grating turrets ▪ Two spectrograph options ▪ Four simultaneous detectors ▪ Photoluminescence microscopy, Time-resolved measurements, Fluorescence lifetime imaging (FLIM)

PRODUCT: RM5 Raman Microscope
APPLICATIONS: Bio sciences ▪ Pharmaceuticals ▪ Chemicals ▪ Polymers ▪ Nano materials
KEY FEATURES: Truly confocal ▪ Integrated narrowband Raman lasers ▪ 5-position grating turret ▪ Integrated detectors

Ocean Insight
Tel: +31263190500
info@oceaninsight.com
www.oceaninsight.com

PRODUCT: Ocean HDX Raman Spectrometer
APPLICATIONS: Authentication of spirits ▪ Analysis of cannabinoids ▪ Identification of polymers ▪ Characterisation of pharmaceutical ingredients
KEY FEATURES: Great value and accessibility—high-performance 785 nm Raman for affordable, non-destructive measurements ▪ Compact footprint—small size and light weight are ideal for use in the lab or integration into other products ▪ Raman shift—from 150 cm^{-1} to 3400 cm^{-1} ▪ Preconfigured options—versions available

PRODUCT FOCUS

PRODUCT: QE Pro Raman+ Spectrometer
APPLICATIONS: Materials analysis of chemicals, pharmaceuticals, and food and beverages ▪ Trace level detection of illicit drugs and explosives ▪ Concentration level analysis, in combination with custom algorithm development ▪ Industrial process monitoring
KEY FEATURES: Portable—small footprint, light weight, fibre optic-based spectrometer ▪ Sensitive—3× sensitivity improvement and wider spectral range ▪ Powerful—signal-to-noise ratio of >1000 : 1 ▪ Raman shift—150–3000 cm^{-1} and 0–3000 cm^{-1} ▪ Stable—cooled detector allows low light detection

Pro-Lite Technology	Tel: 01234436110 info@pro-lite.co.uk https://pro-lite.co.uk/

PRODUCT: Wasatch Photonics: WP 830 Raman Spectrometer
APPLICATIONS: A general purpose excitation wavelength ▪ Pharmaceuticals ▪ Glucose monitoring ▪ SERS ▪ Reduced fluorescence
KEY FEATURES: 250–1850 cm^{-1} Raman range ▪ High NA, f/1.3 optical design for superior sensitivity and SNR ▪ Interchangeable slit to adjust resolution & sensitivity ▪ Free operating software, SDKs & matching libraries

PRODUCT: Wasatch Photonics: WP 785 Raman System
APPLICATIONS: Most popular excitation wavelength ▪ General purpose system for pharmaceuticals & narcotics ▪ Industrial applications ▪ Medical diagnostics ▪ SERS
KEY FEATURES: Turnkey Raman system, 270–2000 cm^{-1} range ▪ High NA, f/1.3 optical design for superior sensitivity and SNR ▪ Integrated 785 nm, 450 mW multimode laser ▪ Integrated sampling optics with 22 mm working distance ▪ Free operating software, SDKs & matching libraries

PRODUCT: Wasatch Photonics: WP 532 XL Raman Spectrometer
APPLICATIONS: Best for inorganic materials–carbon nanomaterials ▪ Semiconductors ▪ Minerals ▪ SERS
KEY FEATURES: Choice of input aperture: f/1.5 for maximum signal or f/2.0 for resolution ▪ Internal opto-mechanical shutter for automated optical dark collection ▪ User-configurable input coupling, interchangeable slit & cage system interface options ▪ Internal opto-mechanical shutter

Shimadzu Europa GmbH	Tel: +49 203 76 870 shimadzu@shimadzu.eu www.shimadzu.eu	SHIMADZU Excellence in Science

PRODUCT: IRSpirit
APPLICATIONS: Pharmaceutical ▪ Chemical and food industries ▪ Academic institutions
KEY FEATURES: Space-efficient due to very small footprint ▪ IR Pilot Program with 23 application-specific workflows ▪ Easy and quick analysis even for unexperienced users ▪ Large choice of accessories

PRODUCT: IRTacer-100
APPLICATIONS: Near, mid and far infrared range for pharmaceutical ▪ Chemical ▪ Food ▪ Environmental and microanalysis (crime, forensics)
KEY FEATURES: Outstanding sensitivity obtains high quality data quickly and easily ▪ High-speed scanning of 20 spectra in a second in rapid scan mod ▪ Expandability through software and hardware options

PRODUCT: IRAffinity-1S
APPLICATIONS: For routine Applications ▪ Research and development
KEY FEATURES: S/N ratio 30,000 : 1 ▪ Easy maintenance by built-in auto dryer ▪ Contaminant analysis and identification test program ▪ Smart design ▪ Wide range of accessories

PRODUCT: AIM-9000 Infrared Microscope System
APPLICATIONS: Micro sample analysis in electricals and electronics ▪ Machinery and transportation ▪ Pharmaceuticals and life sciences ▪ Petroleum and chemicals
KEY FEATURES: Signal-to-noise ratio of a staggering 30,000 : 1 ▪ Automatic zoom-in from eye-size to contaminant-size ▪ Automatic contaminant recognition function ▪ Automatic identification of the spectrum ▪ wide range of accessories

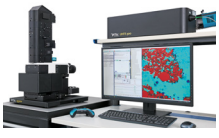
PRODUCT: LabSolutions IR Software
APPLICATIONS: Food ▪ Pharmaceutical ▪ Petroleum ▪ Chemical and other fields where contaminants analysis is performed
KEY FEATURES: Network-enabled ▪ Library of approx. 12,000 spectra as standard ▪ High-performance search function ▪ macro functions provide automation and labour-savings

WITec GmbH	Tel: +49(0)731 140 700 info@witec.de https://www.witec.de/	WITec focus innovations

PRODUCT: alpha300 R Confocal Raman Imaging System
APPLICATIONS: Materials research ▪ Pharmaceutics ▪ Semiconductors & battery materials ▪ Life science ▪ Geosciences ▪ Coatings & Thins films ▪ Polymer research ▪ Low-dimensional materials
KEY FEATURES: Unmatched sensitivity, speed & resolution (simultaneously) ▪ Confocal setup: highest spatial resolution (200 nm) and depth profiling ▪ Acquires a complete Raman spectrum at each image pixel ▪ 3D chemical imaging ▪ Upgradeable to AFM and/or SNOM ▪ Particle analysis option available

PRODUCT: TrueSurface Microscopy
APPLICATIONS: Large-area investigations ▪ Characterisation of rough & inclined surfaces
KEY FEATURES: Topographic confocal Raman Imaging ▪ Precise tracing of the true surface while acquiring Raman imaging data in a one-pass measurement process ▪ Virtually no sample preparation of large samples

PRODUCT: alpha300 apyron automated Raman Imaging System
APPLICATIONS: Materials research ▪ Pharmaceutics ▪ Forensics ▪ Life science ▪ Geoscience
KEY FEATURES: Push-button principle for high performance 3D Raman imaging ▪ True-Power automated absolute laser power determination ▪ Outstanding spectral and spatial resolution ▪ Drastically reduced time required to become familiar with the operation of the instrument ▪ Remote operation easily possible



PRODUCT FOCUS

PRODUCT: RISE Microscopy—Raman SEM Imaging
APPLICATIONS: Materials research ▪ Pharmaceutics ▪ Nanotechnology ▪ Life science ▪ Geoscience
KEY FEATURES: Correlative Raman-SEM imaging integrated in one system ▪ Quick and convenient switching between Raman and SEM measurement on the same position ▪ Correlation of the measurement results and image overlay

PRODUCT: alpha300 Ri inverted Raman Imaging microscope
APPLICATIONS: Life sciences ▪ Biomedical research ▪ Living cell analysis ▪ Aqueous samples
KEY FEATURES: Inverted beam path allows liquid samples to be placed on the stage for quick and repeatable measurements ▪ Compatible with other microscopy techniques including: fluorescence, DIC, phase-contrast ▪ Non-destructive imaging technique: no staining of fixation of the sample required

Wasatch Photonics	Tel: +1 919-544-7785 info@wasatchphotonics.com https://wasatchphotonics.com/

PRODUCT: WP Raman XL-Series
APPLICATIONS: Spectroscopy ▪ Raman
KEY FEATURES: High throughput optical bench design based on our patented VPH gratings ▪ Compatible with ultra-cooled scientific cameras for extremely low-light Raman signals & long measurement times ▪ Fingerprint or extended range ▪ User-configurable input coupling & slit ▪ Internal opto-mechanical shutter

NEW PRODUCTS

ATOMIC

Compact spark-OES metals analyser

Bruker has launched the new Q4 POLO, a compact spark optical emission spectrometer. In addition to the large element range from lithium to bismuth, the Q4 POLO enables applications previously not addressable by such compact instruments: high precision, particularly on light elements; excellent results in the challenging analysis of cast iron; reliable analysis of nitrogen at low ppm levels in low alloyed steels; and analysis of oxygen in copper. The Q4 POLO also has long-term stability: the absence of thermal- and contamination-based drifts reduces the need for cleaning and recalibrations. Bruker's patented Automatic Ambient Compensation (AAC™) ensures that the optical system keeps its focus by eliminating thermal drift. The new ArgonShield™ prevents contamination of the optical window during measurements. The active sensing digital SmartSpark™ source further improves analytical precision and long-term stability, enabling shorter measurement times. The coverage of the full elemental range is achieved by a unique electromagnetic light junction as core component of the MultiVision™ optics.

Bruker AXS

https://link.spectroscopyeurope.com/2415-P1-2021

LUMINESCENCE

New pulsed light sources for time-resolved photoluminescence spectroscopy

Edinburgh Instruments has introduced new pulsed light sources for time-resolved photoluminescence spectroscopy. The VPL, VPLED and HPL series of pulsed diode lasers and LEDs expand their range of compact, monochromatic sources, while the AGILE supercontinuum laser provides tuneable picosecond pulses across the visible and NIR regions.

The HPL diode lasers are designed for time-Correlated Single Photon Counting (TCSPC) from picoseconds to microseconds. They are suitable for samples with low brightness, thanks to high repetition rates up to 80 MHz and high-power output mode. For longer decay times, the VPL and VPLED series are available. The pulse width of these sources can be varied from 50 ns to 1 ms so they are suitable for Multi-Channel Scaling (MCS) measurements, providing higher pulse energies than picosecond lasers and LEDs. AGILE is a white-light picosecond pulsed laser available as a TCSPC source in the FLS1000 Photoluminescence Spectrometer. Coupled to the excitation monochromator in the FLS1000, its output wavelength can be tuned from <400 nm to >2000 nm removing the need for multiple monochromatic sources.

Edinburgh Instruments

https://link.spectroscopyeurope.com/670-P1-2021

NEW PRODUCTS

MASS SPECTROMETRY

Standalone quadrupole power supply

Extrel CMS has launched a new power supply, the 440 khz QPS, which offers a wider capacitance range compared to previous models, so it adapts to a broader range of quadrupole mass filters, octupole and hexapole ion guides, collision cells, and other RF devices—including non-Extrel products and custom-built, specialised vacuum systems. The power supply has a single input for control, and two power supply outputs to be connected to the RF device. The mass range is from 4 Da to 16,000+ Da, making large-ion research with a quadrupole mass spectrometer not only possible, but capable of achieving high resolution and sensitivity.

The 440 khz QPS is available as a standalone power solution, meaning it is a cost-effective alternative to expensive magnetic sector or time-of-flight mass spectrometers. Users can add the QPS to their existing quadrupole system without having to buy a new, complete mass spectrometer. It can also be combined with other powerful components from Extrel, including quadrupoles, octupoles, hexapoles, other ion guides, ionisers, benders, energy analysers, detectors and scan control systems.

Extrel CMS

- https://link.spectroscopyeurope.com/2431-P1-2021

SOFTWARE

ACD/Labs announces software updates

ACD/Labs has announced its annual updates for its Spectrus and Percepta platform applications. Key highlights include: a better integrated lab with hardware and software; democratised knowledge and accessible data; and expansion of functionality in browser-based apps. There is new functionality for particular areas. In MS, spectra can be annotated with fragment structures to capture and share knowledge, and there is an updated peak integration algorithm. In NMR, there is improved chemical structure verification functionality and the introduction of new tools to determine absolute molecular configuration. In property prediction, there is more at-a-glance data for bulk predictions to help assess the quality of results, and significant enhancements to the interpretability of compound safety assessment in support of decision making for regulatory submissions involving ICH M7 guidelines.

ACD/Labs

- https://link.spectroscopyeurope.com/660-P2-2021

DIARY

Conferences

2021

31 October 2021, Philadelphia, PA, United States. **69th ASMS Conference.** https://www.asms.org/conferences/annual-conference/future-annual-conferences

28 November 2021, Online, Poland. **EUROPT(R)ODE 2021.** http://europtrode2020.eu

12 December 2021, Rio de Janeiro, Brazil. **23rd International Mass Spectrometry Conference. https://www.imsc2020.com/**

16 December 2021, Honolulu, Hawaii, United States. **The International Chemical Congress of Pacific Basin Societies 2021.** https://pacifichem.org

2022

17 January 2022, Tucson, United States. **2022 Winter Conference on Plasma Spectrochemistry.** wc2022@chem.umass.edu, https://icpinformation.org/

26 January 2022, Ghent, Belgium. **17th International Symposium Hyphenated Techniques in Chromatography and Separation Technology.** htc17@kuleuven.be, http://www.htc-17.com

21 February 2022, Seattle, United States. **AAFS 2022 Annual Scientific Conference.** tdelozier@aafs.org, https://www.aafs.org

28 February 2022, Moscow, Russia. **13th Winter Symposium on Chemometrics (WSC-13).** wsc13@chemometrics.ru, https://wsc.chemometrics.ru/

5 March 2022, Atlanta, United States. **73rd Pittcon 2022.** pittconinfo@pittcon.org, http://www.pittcon.org

20 March 2022, Diego, United States. **American Chemical Society (ACS) National Spring 2022 Meeting.** service@acs.org, https://www.acs.org/

3 April 2022, Vienna, Austria. **EGU General Assembly 2022.** secretariat@egu.eu, https://www.egu22.eu/

20 April 2022, London, United Kingdom. **Photoelectron Spectroscopy and the Future of Surface Analysis Faraday Discussion.** https://www.rsc.org/events/detail/45900/photoelectron-spectroscopy-and-the-future-of-surface-analysis-faraday-discussion

8 May 2022, Honolulu, Hawaii, United States. **2022 Materials Research Society (MRS) Spring Meeting & Exhibit.** info@mrs.org, https://www.mrs.org/spring2022

9 May 2022, Pau, France. **SPECTRATOM 2022.** contact@spectratom.fr, https://www.spectratom.fr/

22 May 2022, Chiba City, Japan. **Japan Geoscience Union Meeting 2022.** http://www.jpgu.org/

30 May 2022, Gijon, Spain. **Colloquium Spectroscopicum Internationale (CSI) XLII.** csi2021@csi2021spain.com, https://www.csi2021spain.com

31 May 2022, Kristiansand, Norway. **10th World Conference on Sampling and Blending (WCSB10).** contact@wcsb10.com, https://wcsb10.com

5 June 2022, Minneapolis, Minnesota, United States. **70th ASMS Conference.** https://www.asms.org/conferences/annual-conference/future-annual-conferences

12 June 2022, Leon, Norway. **10th Nordic Conference on Plasma Spectrochemistry.** yngvar.thomassen@stami.no, http://nordicplasma.com/

19 June 2022, Dublin, Ireland. **12th International Conference on Clinical Spectroscopy.** http://spec2022.org

20 June 2022, Prague, Czech Republic. **29th Symposium on Plasma Physics and Technology.** sppt2020@plasmaconference.cz, https://www.plasmaconference.cz/

27 June 2022, Online, United Kingdom. **BNASS 2022.** https://www.rsc.org/events/detail/40623/bnass-2022-the-20th-biennial-national-atomic-spectroscopy-symposium

24 July 2022, Chicago, United States. **2022 American Association for Clinical Chemistry (AACC) Annual Meeting.** https://www.aacc.org/meetings-and-events/annual-meeting-dates-and-locations

8 August 2022, Kingston, Canada. **64th ICASS Conference on Analytical Sciences and Spectroscopy.** diane.beauchemin@chem.queensu.ca, http://www.csass.org/ICASS.html

21 August 2022, Chicago, United States. **American Chemical Society (ACS) National Fall 2022 Meeting.** natimtgs@asc.org, https://www.acs.org/content/acs/en/meetings/acs-meetings/about/future-meetings.html

26 August 2022, Scottsdale, United States. **AOAC International Annual 2022 Meeting and Exposition.** meetings@aoac.org, https://www.aoac.org/events/2022-aoac-annual-meeting/

4 September 2022, Singapore. **SETAC 8th World Congress/12th SETAC Asia-Pacific Biennial Conference.** barbara.koelman@setac.org, https://singapore.setac.org/

2 October 2022, Cincinnati, United States. **Annual Conference of Federation of Analytical Chemistry and Spectroscopy Societies (SciX 2022).** facss@facss.org, http://www.scixconference.org

9 October 2022, Denver, United States. **2022 Geological Society of America (GSA) Meeting.** meetings@geosociety.org, http://www.geosociety.org

12 December 2022, Chicago. **2022 AGU—Advancing Earth and Space Science Fall Meeting.** meetinginfo@agu.org, https://www.agu.org/Events/Meetings/Fall-Meeting-2022

2023

29 January 2023, Ljubljana, Slovenia. **2023 European Winter Conference on Plasma Spectrochemistry.** http://www.ewcps2021.ki.si

Exhibitions

2021

3 November 2021, Madrid, Spain. **Farmaforum 2021.** https://farmaforum.es/

15 November 2021, Dubai, United Arab Emirates. **ARABLAB 2021.** info@arablab.com, https://www.arablab.com

2022

4 April 2022, Frankfurt, Germany. **ACHEMA.** https://www.achema.de

27 April 2022, Basel, Switzerland. **Lab Vision.** https://www.spectaris.de/analysen-bio-und-labortechnik/labvision/

24 November 2022, Istanbul, Turkey. **Turkchem.** http://www.chemshoweurasia.com/

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