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TOS forum

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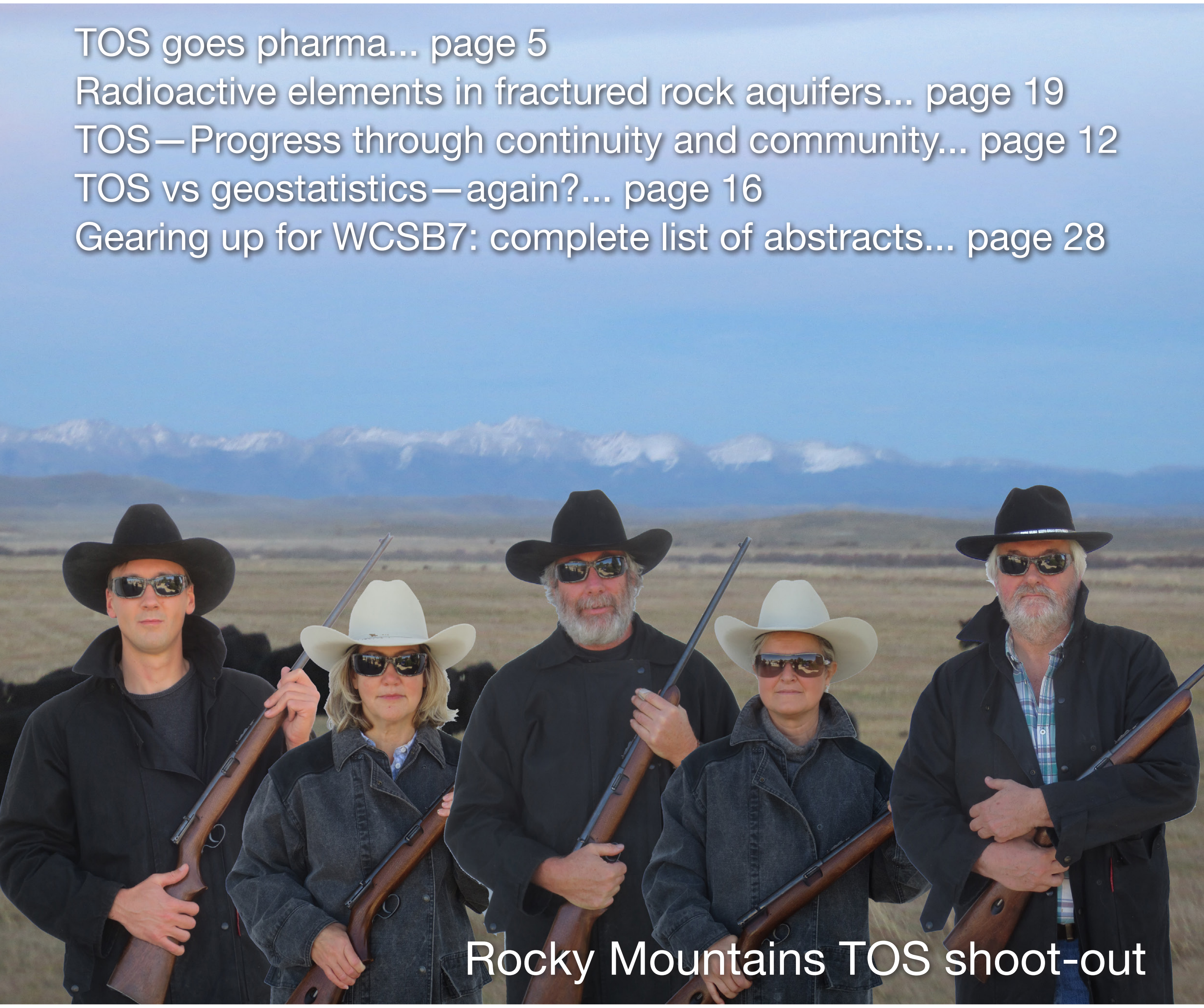

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WCSB7

7th World Conference on Sampling and Blending

10-12 june
Bordeaux, France

Centre de Congrès Cité Mondiale
18 parvis des Chartrons - 33080 Bordeaux

Dear potential attendee to WCSB7
It is only 75 days to the opening of WCSB7. Here is a report from the frontline, prepared by the chairmen and a few words to inform you about the status of the conference.

Organisation

Venue, logistics, hotels… all is going well. You may follow everything at www.wcsb7.com.

Registration

We need you! Registration has started very slowly—as for all conferences—but due the grave international economic situation with resultant changes in many company policies, we need to be more active to promote this event. The conference needs your active help.

Please use your personal networks to raise your colleagues' interest to attend our important conference. Our two conference chairmen will give you all the assistance you may require:

Stephane Brochot (s.brochot@caspeo.ne) Philippe Davin (philippe.davin@iteca.fr)

Sponsorship

We are pleased to welcome the following partners for sponsoring and support:

- Platinum Sponsor: FLSmidth
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- Media Partners: Bulk-Online, EuroBulkSystems, Gecamin, Granulats.fr, IM Publications, TOS forum and World Cement
- Sponsor: Multotec

We are very grateful to these sponsors; they all know that the conference is the best opportunity to meet a large audience. This goes for both good times as well as for the present times.

Nevertheless, we are still looking for more partnerships and sponsors, there are still many opportunities for part-sponsoring available: gala dinner, lunches, coffee breaks and Wi-Fi are still available; they each give broad visibility during the event. Don't miss this opportunity to be seen! Please consult the homepage at www.wcsb7.com.

Proceedings

All is going well, very well. WCSB7 is committed to delivering a printed copy of the Proceedings to every conference delegate upon arrival (with the unavoidable very strict production schedule and deadlines), and we are actually ahead of plan. At this point in time, more than 85% of all manuscripts are already accepted in their revised final form. The conference plan calls for publication both as a printed hardbound special issue of *TOS forum* (to be handed out to every participant upon signing in), as a USB stick and as an open access internet depository freely available to everybody after the conference. Having this aspect of the conference well "in the bag" gives relief to the chairmen's committee.

Many thanks for your understanding and your active help!
Looking forward to seeing you in Bordeaux!
Stéphane Brochot, Phillipe Davin, Florent Bourgeois, Kim H. Esbensen

www.wcsb7.com

doi: 10.1255/tosf.35

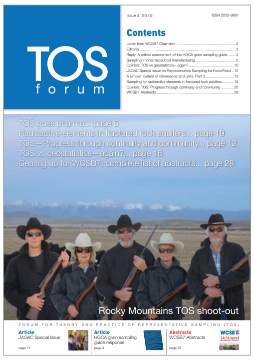
Editorial: Carrying on... with a special focus on WCSB7

With this issue *TOS forum* carries on its role as the designated *communication forum* for the world community of samplers. In addition to scientific papers, this issue has a particular focus on the 7th World Conference on Sampling and Blending (WCSB7), 10–12 June 2015, in Bordeaux. This issue also carries opinion pieces intended to further and facilitate debate amongst samplers all over the world, certainly not least at WCSB7. It is perhaps not necessary to iterate (but the editor does it anyway) that this platform is open for all kinds of contributions, opinion pieces (formal, informal) and other reflections on issues and events. There is a whole *forum* out there which only has the possibility to hear it from *you* at two-year intervals, but why not tell us "now"…

It is with distinct pleasure the editor can introduce this fourth issue. There is a full spread of articles and features:

- Francis Pitard continues his journey into "A simpler system of dimensions and units"
- Gaathier Mahed concludes his mini-series with "Development of a sampling protocol for radioactive elements in fractured rock aquifers"
- Romañach and Esbensen take TOS to the pharmaceutical industry (surprisingly for the first time)
- We bring a response to an earlier critique of the HGCA grain sampling guide
- Opinion pieces abound in this issue, viz. Bongarcon and Pitard/Esbensen/Paoletti
- Gearing up for WCSB7, you will find in here the complete list of submitted abstracts, from which you can appreciate that all is well regarding the interest from around the world to present results and developments to the conference of all samplers worldwide. A total of 56 abstracts were received, all of which were carefully assessed and graded by the scientific committee. Only one was rejected at this stage, the rest were partitioned into two categories dependent on the accumulated scores from the 12 committee members, which led to 30 contributions rated for oral presentation and some 16 to be presented as posters.
- The sole reason for bringing this comprehensive list of abstracts is for the world community of samplers, and indeed everyone engaged in sampling in science, technology and industry is to offer all the information you need to decide on attending the 7th World Conference on Sampling and Blending (WCSB7), which we hope very much. Welcome to WCSB7!

It has been an interesting two-year journey since the launching of *TOS forum*. Lessons have already been well learned, i.e. that four issues between conferences is just about right. It is a welcome experience that that there has been no shortage of papers, reports, PhD summaries etc. While *TOS forum* in its present form makes no pretention to be a full-fledged, peer-reviewed scientific journal, this steady influx of papers points to an easy need for communicating results and ideas to our community between publishing in proper scientific journals, as many of us also do. These are but a few manifestations of a continuing satisfactory development of the *organised* interactions between samplers. It has also been learned that our community, while happy to receive a free copy of *TOS forum*, is apparently not (yet) ready to contemplate taking out a subscription for this facility across the full board of current recipients. This was indeed foreseen, and so it is necessary to provide one or two more years of service to our community before we may hope to sway this attitude—it is certainly worth a try! Which just makes it all the more important to locate and garner the interest of major (and minor) companies in which the importance of proper, representative sampling is recognised, of OEM companies or consultancies for supporting the very reasonable *TOS forum* production costs against effective community-wide advertising possibilities. Again—it is certainly worth a try! The editor and the publisher have decided to forge ahead with this endeavour and will report again at WCSB8. Meanwhile—we hope to see as many as possible of you in Bordeaux!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A group of samplers, regulators and educators met in Nov. 2014 to write a Special Guest Editor Section of the *AOAC Journal*. Terminology harmonisation is notoriously difficult across well established disciplines. The background for the "resolution" attempt depicted on the this issue's frontpage can be found on p. 12.

Be part of the next issue of *TOS forum*!

We welcome contributions to *TOS forum*: articles, letters, comment, news or news of PhD projects for the PhD Presentations column.

TOS forum Editor, Kim Esbensen, would be pleased to discuss any ideas you may have and to receive your contributions.

EDITOR
Kim H. Esbensen (Geological Survey of Denmark and Greenland (GEUS), Copenhagen, and ACABS research group, Aalborg University, campus Esbjerg, Denmark; ke@geus.dk)

PUBLISHER
Ian Michael (ian@impublications.com)

6 Charlton Mill, Charlton, Chichester,
West Sussex PO18 0HY, UK.
Tel: +44-1243-811334;
Fax: +44-1243-811711;
E-mail: subs@impublications.com

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TOS forum will be available on subscription in 2015. Visit www.impublications.com/tos-forum for details.

Editorial correspondence to Kim Esbensen, ke@geus.dk. All production correspondence should be sent to *TOS forum*, 6 Charlton Mill, Charlton, Chichester, West Sussex PO18 0HY, UK, Tel: +44(0)1243–811334, Fax: +44(0)1243–811711, e-mail: ian@impublications.com.

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A critical assessment of the HGCA grain sampling guide

Claas Wagner[a,*] and Kim. H. Esbensen[b,a]
[a]ACABS Research Group, Aalborg University, campus Esbjerg (AAUE), Denmark
[b]Geological Survey of Denmark and Greenland, Copenhagen, Denmark. E-mail: claas.wagner@googlemail.com

HGCA's grain sampling guide is assessed with respect to the principles for representative sampling as set forward in the Theory of Sampling (TOS). Sampling correctness, which requires the elimination of all Incorrect Sampling Errors (ISE), constitutes the only guarantee for valid, representative grain quality control; presence of ISEs causes a varying, uncontrollable sampling bias that cannot be corrected for. Contrary to a first superficial observation ("grain is grain"), many different species and varieties, as well as differences caused by soil types, availability of local nutrients, make "grain" a significantly heterogeneous commodity, which requires special attention when sampled at various process locations (from harvesting, storage until commercial intake). The present appraisal shows that most of the respected HGCA grain guide's recommendations do not comply with TOS principles of sampling correctness. The suggested sampling procedures constitute major error potentials, which strongly compromise sample representativity.

Introduction

The "Home Grown Cereals Author
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ties the latter two aspects (
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cases, not seldom due to inap
inadequate sampling procedure
such discrepancies causing se
nomic disputes, extraction of repr
grain samples is also crucial with
impurity detection (e.g. GMO quar
toxins), as regulated by internation
ards (e.g. ISO 24276:2006).[3]

The following critical assessm
HGCA's grain sampling guide serves to
evaluate whether

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acknowledges that such strict separa-
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For practical sampling the above must also hold for the operational unit, the "increment". The FSP condition is missing entirely with HGCA.

Dear *TOS Forum*,

Thank you for publishing the recent critique of the HGCA *Grain Sampling Guide*, which raises some interesting and thought-provoking issues for anyone involved with practical on-farm sampling.

We thought it might be helpful for your readers to explain HGCA's approach as set out in the Guide, which is focused on providing growers with a practical and cost-effective means of sampling—particularly at very busy times such as during harvest.

The methods outlined were developed to be suitable for growers in real, on-farm situations where time is constrained and resources are often limited.

The Guide was drawn up in close conjunction with the UK arable industry to reduce errors as far as practically possible and to provide growers with a realistic and basic level of information about the physical properties of their grain.

This information will help growers understand whether their grain meets contractual specifications on attributes such as moisture, protein levels, specific weight and Hagberg Falling Number.

The Guide's working assumption is that these attributes will follow a normal distribution, so the protocol is sufficient to give a basic, but useful, level of information about the farmer's crop.

In addition, grain coming from a single field can be regarded as reasonably homogenous because it is a single variety that has largely received the same agronomic management and has been exposed to the same soil and weather conditions.

This context is somewhat different to the Theory of Sampling principles to which you compare the HGCA Guide. These principles are very rigorous and are more suitable for finding contaminants present at a low inclusion rate, and is not necessarily what is required on-farm.

All the information within the guide was written to adhere to:

- BS EN ISO 24333:2009 Cereals and cereal products – sampling
- BS EN ISO 542:1990 Oilseeds – sampling

Growers and the UK grain industry will continue to work towards the common objective of providing an improved understanding of grain quality which meets both contractual and due diligence requirements.

As the UK industry moves forward, HGCA will ensure its *Grain Sampling Guide* is reviewed regularly and we will continue to look at how issues such as those raised in your article can be better reflected in our on-farm advice.

Yours sincerely
Dr Dhan Bhandari (HGCA) and Dr Ken Wildey (Technology for Growth)

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Sampling in pharmaceutical manufacturing—Many opportunities to improve today's practice through the Theory of Sampling (TOS)

Rodolfo J. Romañach[a] and Kim H. Esbensen[b,c]
[a]Department of Chemistry, University of Puerto Rico, Mayagüez, Puerto Rico
[b]Geological Survey of Denmark and Greenland, Copehagen, Denmark
[c]ACABS Research Group, Aalborg University, Campus Esbjerg (AAUE), Denmark

This overview discusses sampling at different stages of pharmaceutical manufacturing—and why. The pharmaceutical industry primarily uses grab sampling. In spite of the need to know exactly the status of pharmaceutical processes and products, there are only a very few pharmaceutical applications where principles in TOS has been applied so far and representative sampling solutions are consequently often lacking. But this translates into many opportunities to improve pharmaceutical manufacturing. The authors have embarked on a large-scale programme to introduce proper sampling approaches within this important industry sector.

Introduction to pharmaceutical manufacturing

Pharmaceutical manufacturing is generically first concerned with production of a drug, usually referred to as the drug substance or *active pharmaceutical ingredient* (API), which is followed by a process where the API is mixed with excipients to manufacture the *dose units* of the drug product. API production typically includes reactions, crystallisation, solvent washes, centrifugation and drying steps. This may involve synthesis of a small molecule API, a fermentation process for an antibiotic, or the bioprocessing of large proteins. In-process characterisation of the API production constitutes the first stage of sampling in the five pharmaceutical processes shown schematically in Figure 1.

The second sampling is located at the end of the API production process. Sampling is here performed on a drug substance with a high purity. For example, many "small molecule" products are characterised by purity higher than 99% (w/w) to avoid possible secondary effects from impurities. Even though API purity is high, these are *not* "homogeneous products" and their detailed characterisation is essential in terms of both chemical and physical properties. The API must be analysed very carefully to determine its chemical properties, for their concentration of *impurities*, water content or and solvent *residues*.

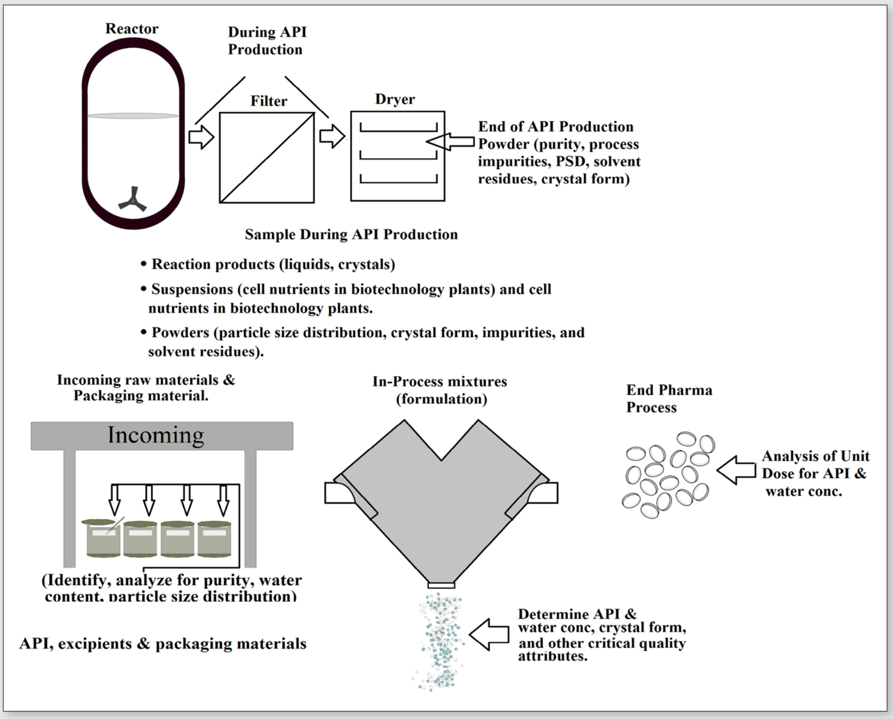

Figure 1. Flow path of the generic pharmaceutical manufacturing process with the principal sampling locations indicated.

Note that instead of what could appear to be a trivial case for sampling (a high purity substance) the focus is on the most difficult case: very low concentrations of impurities, necessarily with a significant heterogeneous distribution. The physical properties, i.e. particle size and crystal form are also needed. Many API have limited solubility, for which reason a reduced particle size is needed to improve the rate of dissolution. Crystal form also affects solubility as exemplified by the well-known *Ritonavir* case, involving a drug which failed key dissolution tests and for which the original crystal form could not be obtained after production of 240 lots—which caused a drug shortage of a life-saving medicine.[1] The Ritonavir case was likely caused by a low-level degradation product that served as a template for the lower solubility form. Thus, even if the drug was greater than 99% (w/w) pure, differences in low level impurities, water content or crystal form throughout the lot may very well have serious effects on the product's *performance*.

The API is usually transported to a separate facility where the drug product, or *formulation*, is manufactured. The dose unit, which a patient receives, is only rarely the pure API. Instead the API is typically *mixed* with *excipients* to develop a formulation that is called the drug product. The third stage of sampling (Figure 1) is performed to identify the API *before* it is used at the manufacturing facility where the formulation is prepared. Sampling is also required here to identify and characterise the excipients that will be mixed in to obtain the desired formulation, and all packaging materials that will come in contact with the pharmaceutical product must also be characterised. The API and excipients are frequently identified by mid-infrared spectroscopy since each compound has a unique spectrum in this wavelength region.[2]

Near infrared (NIR) spectroscopy is used extensively in pharma to identify and characterise incoming *raw materials* even though the differences in NIR spectra are more subtle than those observed in mid-IR spectroscopy. This is a task which is greatly helped by involving chemometrics, especially applying multivariate calibration and proper validation.[3,4] NIR spectroscopy is also able to discern between raw materials on the basis of the differences in their physical properties.[5] The sampling and identification of these materials is a required cGMP regulation, and Section 211.84 (a) states: *"Each lot of components, drug product containers, and closures shall be withheld from use until the lot has been sampled, tested, or examined, as appropriate, and released by the quality control unit."*

History has proven that this sampling stage is vitally important. In 2006, at least 100 citizens (mostly children) tragically died in Panama after consuming cough syrup prepared with di-ethylene glycol instead of the specified glycerin. One mid-infrared or NIR spectrum could have avoided this tragedy, but none of the five companies that brought the material from China to Panama analysed the material.[6] We here emphasise this incident, as a stark reminder that proper sampling and proper analysis are key components of due diligence. TOS certainly has a key role to play within the pharmaceutical industry.

After they are satisfactorily identified, *excipients* play a major role in pharmaceutical formulations. For context, some API are extremely potent and 1 mg may be sufficient to obtain a therapeutic effect. But 1 mg as a direct drug delivery is not handled easily by a patient, which is why excipients are used as *diluents* to obtain a dose unit with a greater tablet mass. Pharmaceutical formulations very often involve mixing of excipients and one or more API; sampling of these *mixtures* constitutes the fourth stage of sampling in the pharmaceutical manufacturing pathway. Approximately 80% of pharmaceutical dose units sold are solid oral dosage forms (tablets, capsules), due to the convenience of administration of this type of drug delivery. The solid form is also important to obtain a drug product with a longer date of expiration, as API are typically more stable in the solid state than in the liquid state. It is typically *powder mixtures*, the most prevalent results from the mixing of the API and excipients that are used to form tablets and capsules. Sampling of in-process powder mixtures as well as of the final dose units are *mandated* by the current good manufacturing practices (cGMPs), and the API concentration must be determined in both stages.

The final drug product or dose unit is also analysed. Sampling of the drug product at the unit dose constitutes the final stage of sampling in pharmaceutical manufacturing. Dose units from throughout the entire production batch are sampled and sent to the quality control lab for analysis. Most of the analyses are mandated to be performed with High Performance Liquid Chromatography (HPLC), which requires breaking up tablets and capsules for extraction of the API from the formulation. These sample preparation steps require time and only 10–30 dose units are usually analysed per lot (typically a lot can have 3,000,000 or more tablets/capsules). The traditional discussion of sampling for final dosage forms characterisation has very much been focused on the number of samples that are needed to fully evaluate the drug content of the individual units. These are areas in which traditional statistics is well applied, but it is unfortunately not always the case that the analytical data supplied to statistical treatment are proven to be representative—TOS to the fore.

The role of sampling in pharmaceutical manufacturing

Within pharma the importance of sampling is clearly acknowledged, e.g. by Brittain, "Samples are therefore defined as the units upon which a program of testing is conducted."[7] The effectiveness of all quality control activities depends on the samples acquired, or, in clear text: if ever there were a context in which only representative samples are acceptable, the pharmaceutical manufacturing pathway must rank among the most important examples—health and lives are at stake.

But in spite of this general recognition, application of the Theory of Sampling (TOS) in pharmaceutical production is very limited.[8–10] Brittain does make reference to Gy's work in his widely accessible article, but TOS may in this, as well as in many other industrial sectors, often have been perceived as relating more to the mining and metallurgical industries, and not to pharmaceutical applications because at that time the major successful examples and case histories mostly still came from this sector. Regardless of the reasons and the very few articles that apply TOS to pharmaceutical formulations, TOS is unquestionably a critical asset also for pharmaceutical manufacturing as discussed further in this article and in several companions to be presented at WCSB7.

Regulatory requirements

This section describes the regulatory requirements in the current Good Manufacturing Practices and European Commission Rules related to sampling. There are many similarities between these regulations and those of the World Health Organisation and other agencies. Pharmaceutical cGMP and European regulatory requirements emphasise that "written procedures must be followed to obtain representative samples". The procedures must specify the number of containers to be sampled, the amount of material to be taken, and the need for appropriate statistical criteria for component variability, confidence intervals, and the degree of precision required. The cGMPs also indicate that if it is necessary to sample a component from the top, middle and bottom of its container, these sample sub-divisions should *not* be composited for testing.[11] The European rules indicate that *"the identity of a complete batch of starting materials can only be ensured if individual samples are taken from all the containers and an identity test performed on each sample."* [12] These requirements are quite understandable given concerns for the identity of incoming raw materials. Finally, the materials shall be withheld from use until the samples are analysed by the quality control unit.

In the cGMPs a representative sample means a *"sample that consists of a number of units that are drawn based on rational criteria such as random sampling and intended to assure that the sample accurately portrays the material being sampled."* The European rules do *not* define a representative sample, however. Representativeness criteria, as detailed in TOS, are missing in these regulations.[11,12] The cGMPs also never discuss "sampling correctness", and never make a distinction between samples and specimens. However, the cGMPs (CFR 210.1) does clearly specify that the regulation contains the *minimum* current good manufacturing practice. Thus, additional emphasis and scientific approaches proven (otherwise, elsewhere) to lead to unambiguous representative sampling, such as described by the Theory of Sampling, are principally not beyond the scope of the regulations.

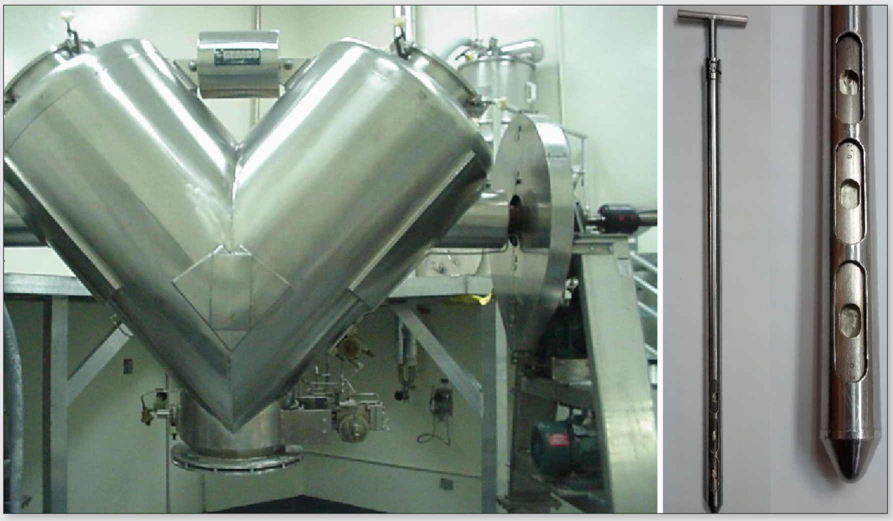

Figure 2. Sampling thieves are used extensively to extract single samples from blenders with various fixed geometrical schemes.[13] Left: large V-blender used in pharmaceutical industry; right: expanded view of sample thief and die cavity.

Sampling associated with *sample* thieves—and its many difficulties

Adequate analysis of excipients and API powder mixtures is required by cGMP regulations. Powder mixtures are extracted from blenders, an operation that overwhelmingly has been performed with the use of sampling *spears*, called sample *thieves* in the pharmaceutical manufacturing realm. Figure 2 illustrates the traditional approach for using thief sampling from a V-blender. Usually a fixed number of samples are required (6 or 10); we treat the details of thief blender sampling in a WCSB7 contribution.[13] The sample thieves employ pre-set cavities to assure that the powder mixture extracted has approximately the mass of a single dose unit, which from a "consumer" point of view appears as a very reasonable demand: the analytical result must pertain to the dose unit the patient receives, but see Reference 13 regarding the fundamental sampling error (FSE).

The use of sample thieves emanates from the understanding that there *could* be "dead spots"—areas of incomplete mixing and drug agglomerates within the blender.[14] The emphasis has been on protecting the patient from a possible over-potent or sub-potent dose unit and identifying these units within the blender, and then improving the blending process to minimise the risk. The Blend Uniformity Work Group composed by members of industry, academia, and the FDA developed the stratified sampling guidance to address these concerns. Stratified sampling was defined as "the process of selecting units deliberately from various locations within a lot of batch or from various phases or periods of a process to obtain a sample.[33] Stratified sampling of the blend and dosage units specifically targets locations either in the blender or throughout the compression/filling operation, which have the higher risk of producing failing content uniformity results."[15]

It will come as no surprise for the TOS community that careful evaluation of sample thieves has shown that they are most often unable to furnish representative samples. Thus, there are many opportunities to improve the sampling and evaluation of powder mixtures through the use of TOS with respect to eliminating ISE and/or FSE.

TOS has for too long not been recognised as an essential component in modern pharmaceutical manufacturing implementations. The present authors are currently collaborating extensively in this endeavour, focusing on the liberating opportunities of basing process monitoring (mixing process in particular) on a rational basis of introducing variographic analysis and characterisation.

Sampling in PAT—sampling with non-destructive methods

In 2004, the FDA published the famous Process Analytical Technology (PAT) Guidance, starting a well-planned effort to bring the latest science and engineering principles into pharmaceutical manufacturing to improve the quality of pharmaceutical products.[16] PAT requires careful study of the API or formulation processes to understand what process parameters can affect the quality of the product. These *critical parameters* are then measured during the process with sufficient frequency so that the information obtained can be used for feed-forward process control and quality assurance. Such PAT measurements can be simple, e.g. as concerns a reaction where the critical parameters are temperature or pH, and these can then be controlled. They may, of course, also be more complex and typically require spectroscopic methods for determination of drug concentration in a powder mixture or suspension for example.[3,17] Spectroscopic methods are often described as real-time, non-destructive methods, since they are able to provide measurements quickly and do not require dissolving samples (which is common for the majority of chemical analyses).

Being able to perform measurements precisely of the critical process, or product parameters constitute a continuous quality assurance process. PAT is now seen as part of the wider Quality by Design (QbD) initiative since the objective is to *design* processes to achieve quality and avoid relying on inspection and reliable removal of non-compliant products.

PAT represents significant progress in pharmaceutical manufacturing. However, in this realm of "advanced manufacturing" the basic principles of TOS are still important,

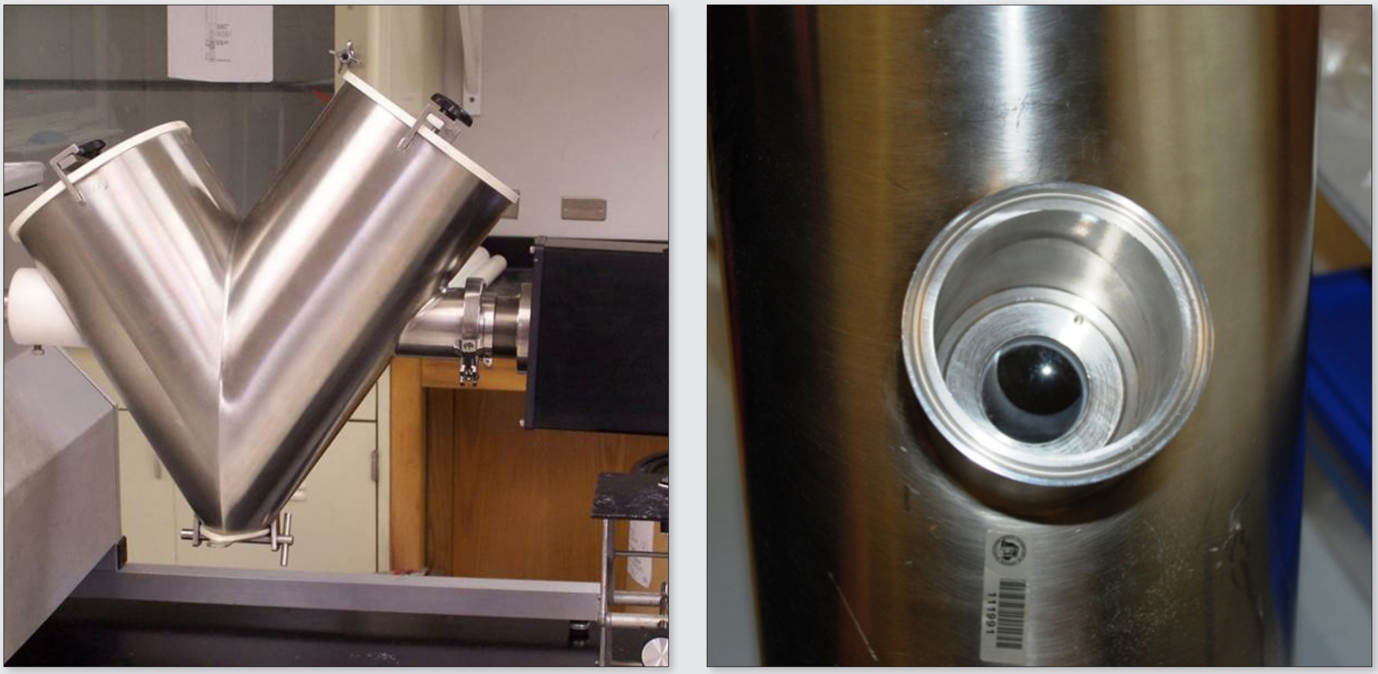

Figure 3. The "no sampling" fallacy in PAT. The NIR spectrometer is optically sampling the powder within the blender through a sapphire window. Left: tumble blender and wireless NIR spectrometer that rotates with the blender. The spectrometer obtains a signal for the material but only to a depth of less than 2 mm below of the window shown on the right. The remaining part of the material is not analysed. The assumption is that the vigorous mixing/blending allows for a meaningful averaging of the signal characterisation of the whole volume. This is a lab-scale system; typically manufacturing tumble blenders are much larger, which introduces ever greater scale-up issues.

and sadly, still almost lacking.[3] A spectroscopic method is still analysing only a very small part of the mass of the entire lot. Thus, the spectroscopic method is in effect doing "optical sampling" of the lot, through the interaction of electromagnetic radiation with a particulate matter, but the acquired spectra represents nothing but grab sampling of very small masses; the likelihood of a significant FSE is very high indeed. Figure 3 shows a wireless NIR spectrometer affixed to a tumble blender. The NIR method is able to obtain spectra of the powder passing across the sapphire sensor window but only to a depth of approximately 2 mm. Spectroscopic signal acquisition is eliminating the physical process of removing a sample from the process, but does *not* at all eliminate sampling errors to influence the final analytical results. The issue revolves around to which degree a "signal" represents a full cross-section or the pertinent volume of the moving matter, which has been treated in detail elsewhere.[3]

The system shown in Figure 3 leads to a very interesting situation since the heterogeneity of the system is being reduced as the blending progresses. Although the system is not able to sample the entire cross-section, as blending progresses new material will reach the window of the spectrometer. To the degree that blending is sufficiently effective, the Grouping and Segregation (GSE) error will be significantly reduced.

Regulatory agencies will also expect an estimate of the sample mass analysed. This sample mass may be estimated taking into consideration the depth of penetration of the light, the density of the sample and the number of spectra that are averaged in the analysis.[8]

The location and placement of the spectroscopic equipment and its interfacing with the process is essential for the success of any PAT implementation. The resulting spectra could be sampling only the materials next to the interface while the bulk (inner) composition is not analysed (a clear breach of the fundamental sampling principle, FSP). The spectroscopic method would then be analysing some of the sample all the time generating an increment delimitation error (IDE), opening up for an inconstant sampling bias. If this happens the spectroscopic sampling is again no better than physical grab sampling. There is a real need to improve the installations for the spectroscopic methods, and install systems capable of evaluating an entire cross-section of the material.[3]

Assuming a spectroscopic signal can be made representative, each would then correspond to an *increment* (classical TOS style). Now the spectroscopic sampling approach is opened up for a strategy of aggregating several increments to form a problem-dependent *composite sample*; all spectroscopic methods permit averaging any number of spectra ("scans"). This opens up for regular process sampling approaches, well-known from TOS, in which variographic analysis allows estimating the necessary number of increments to be composited to force the total sampling error (TSE) below a desired threshold (fit-for-purpose representativeness), e.g. References 18–21.

The PAT initiative has brought significant challenges in the validation of these non-destructive, real-time methods. Regulatory authorities require that analytical methods be validated. Validation is the term used in the pharmaceutical industry for the study and documentation of method accuracy, precision, range and scope of use of the method—which is precisely the total analytical error (TAE) in TOS parlance. Valid and reliable determination of TAE is a challenge for any dynamic process where samples are continuously changing, such as a mixing, drying or milling processes. Validation will involve efforts to compare the results of the real-time method to those of an off-line method where samples are sent to the lab. This comparison appears simple, but too often the sample analysed with the PAT method is not the same that is brought to the lab.[9] Examples of this particular issue are legion in many PAT implementations in industry, where the focus has all too often mostly been on the new on-line analytical possibilities and their effective calibration/validation within a chemometric context.[3]

Current PAT methods include thorough evaluations of the total analytical error (TAE), but not of the minimum possible error, MPE, which includes the much more dominant TSE (total sampling error). Thus, there are many opportunities for improving PAT approaches through the use of *variographic analysis* providing estimates of the nugget effect and thus the sum-total (TSE + TAE). TOS has not at all been recognised as an essential component of modern pharmaceutical applications.

The present authors intend to change this perception by a systematic innovation program collaboration, three presentations of which will appear at WCSB7.[13,22,23]

Conclusions

TOS has not been incorporated in the pharmaceutical industry to any significant degree—yet. There exist numerous opportunities for improving existing manufacturing practices, e.g. by eliminating bias-generating errors (ISE) both regarding physical sample extraction and/or when the PAT initiative is brought to bear. The most immediate advantage would appear, though, to be introduction of *variographic analysis* for optimal process monitoring and TSE + TAE control.

In the longer term we expect to see PAT methods where the entire cross-section of moving streams of matter is analysed. This will require careful design of instrument sample interfaces and improvements in the design of spectrometers.

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TOS vs geostatistics—again?

Dominique Francois-Bongarcon and Kim H. Esbensen

Introduction

In a paper presented by the first author at the WCSB1,[1] the intimate relationships that exist between the theory of sampling of broken material (TOS) and the discipline of geostatistics were examined for the first time. In a nutshell, if TOS cannot be mentioned without reference to Pierre Gy's lifetime fundamental contributions, it can neither be fully understood if outside the geostatistical reference frame. TOS calls for geostatistical concepts at the small scale (through Gy's formula and the liberation factor), mixes with it at medium scale (sampling regime of one-dimensional flows) and is also very much needed by larger scale geostatistics (data quality in view of estimation, conditional simulations).

Indeed, in the 1950s, motivated by a growing need for better grade estimation methods in the mining industry worldwide, the late Professor G. Matheron developed the Theory of Regionalized Variables, a.k.a Geostatistics.[2] Pierre Gy was at the same time busy developing his Theory of Sampling, but when his first work was officially published and generally applauded, a certain skepticism also rose about his central statistical demonstrations, it was to Matheron that he turned to validate his numerical development. In a seminal paper,[3] translated to English (and which will be presented in this language for the first time at the WCSB7 in Bordeaux in June 2015), Matheron indeed approached the problem of the calculation of the sampling variance with a fresh eye using a tedious but more rigorous demonstration based on probability calculus, which fully validated the results of Gy's developments.

Geostatistics was at this time "fresh out of the oven", so to speak, and its practical applications were just beginning to be figured out. So when Gy introduced the use of the *variogram* to tackle and analyse the behaviour and sampling of one-dimensional material streams (process), it was with a tool that was not yet fully understood.[4] Decades later, when Francois-Bongarcon established the missing models for the predictive use of the liberation factor,[5,6] it was thanks to a modern understanding of geostatistical concepts.

It is felt important that the relationship between TOS and Geostatistics needs to be examined again, and as always with a critical eye if we are to influence the way TOS is to develop in a proper manner.

The need for a complete solution

Bad vocabulary

"Sampling"! A small word but a full world! While geologists "sample" rocks and mineral deposits using hammers and core drilling, laboratory operators around the world are busy "sub-sampling" crushed material during sample preparation for analysis and metallurgical processes, or in industry a lot of "sampling" is carried out using automatic devices. Meanwhile, surveys are done on human population "samples", for example, for which statisticians have defined proper collection rules. So, is "sampling" a universal human activity?

The truth if the matter is these varieties of sampling are not all equivalent, but the vocabulary has been used freely without much precision, with one single verb (*sampling*) being used to describe very distinct and very different endeavours.

- There are at least three different concepts we can identify under this one verb, which must never be confused: statistical sampling (statistics of independent variables)
- physical sampling of broken ore (TOS) (sampling of heterogeneous matter in general)
- *in situ* sampling (i.e. measurement and interpolation theory, aka geostatistics)

Leaving statistical sampling aside, many parties in technology and industry usually refer to the two latter categories as "sampling" synonymously, as if they were indeed based on, and using the same theories and tools.

In the particular case of the mining and minerals processing industry, indeed there is a need for a complete theory covering both broken ore sampling and *in situ* sampling. That wonderful theory, surprisingly, has not been written yet, and for the time being, TOS is only one important half of it. For the other half, thanks to Matheron, all the tools exist in geostatistics (and many of us are using them in *ad hoc* manners), but no one has ever bothered putting them into a practical theory for the perusal of exploration geologists. This unifying work still needs to be undertaken, and it is definitively not of the resort of TOS alone.

In the meantime, the confusion between the two survives, and misapplications keep appearing, tragically, and apparently on a regular basis.

Erroneous uses of TOS

In this context, there are two classical mistakes, which are repeatedly committed:

- Using TOS's famous variance prediction formula, "Gy's formula", to calculate the precision of sampling *a process* with increments collected *along time*.
- Preparing and assaying the complementary split of a drill hole core interval, to calculate the precision attached to "sampling the half core" (thinking the variance value derived from these pairs of "duplicate samples" can contribute to characterise the precision of the final assay result.

As pointed out in Reference 4, these errors all stem from the implicit use of probabilistic models for which the attached probability space (or, often, even the mere meaning of that concept) is not understood, making any variance calculation a futile, purely mechanical exercise with no usable meaning.

In order to be able to make sensible decisions about the future direction of TOS, it appears advantageous to establish a clear foundation for possible discussions at WCSB7 for example (or here in *TOS forum*). In this context it is essential to weigh the pros and cons of both approaches (TOS / geostatistics). This means that future applications TOS should be carefully examined to make sure that such confusions as above are eliminated, missing theoretical links are developed and implemented in practise. In other words, we need to decide if we want to grow TOS into a complete theory of both *in-situ* and broken ore sampling, or if we prefer to clean up the existing practice from its potentially misleading features and leave it for the geostatistical community to properly figure this out separately, if it ever will.

TOS' future: two options

Status quo–separation

In the "separation" option, the status quo of TOS is maintained, albeit with *some* cleaning-up of concepts and practises, especially making sure the difference between *in-situ* sampling and broken ore sampling can be, and will be better, distinguished by the practitioners, not shying away from relying on proper methods mainly used outside TOS to tackle category 1 above, i.e. not being afraid to call on professional geostatistic collaboration wherever, whenever required. This amounts to "Giving back to Caesar what belongs to Caesar", and hopefully geostatisticians would soon jump on board to study process streams (essentially 1-D geostatistical problems) using state-of-the-art geostatistical methods as a substitute for Gy's sometimes slightly invalid variographic analysis procedures. These include using experimental variogram values instead of a smooth model and the erroneous splitting of variance components along oblique lines in a variogram plot. It is recognised that many colleagues are content and satisfied with the first item, using experimental variograms for heterogeneity characterisation, and process interpretation alone. This is where a healthy debate may find one of its foci (even DFB and KHE do not agree entirely on this matter).

The "pro" of this option would be to collaborate better regarding what can be achieved in terms of understanding, characterising and diagnosing such streams. One may imagine that powerful, more modern geostatistical tools and concepts could provide much more elaborate results than was possible in the 1960s. The "con" option would be, sadly, that a swathe of contemporary activity and experience would escape to another profession.

Integration

Should we decide to opt for integration efforts, then we only need to revamp and modernise our methods whenever they need geostatistical involvement. This will include:

How to handle duplicate half-cores in QA/QC.

- The most important issue is that we should vehemently refrain from considering a half-core as a bona fide sample of the full core (sic).When used by geostatisticians, the data gives the same results and procedures, as it is transparently handled through the nugget effect of the variogram. In fact, often, the practitioner may think he/she is using full core, of which he/she has taken a primary sample, but in reality, he/she is only ever using data defined on a half-cylinder support. The full core is not present anywhere and is not supporting any part of the modelling. There is already a big clue here!
- But when used in QA/QC, it is a different story. Indeed, there is a complete duality between geostatistical auto-correlations and broken ore segregation. Should one be interested in the half-core selection process, even though there is often no good reason for it (see above), then, to be correct, the auto-correlation that exists between a split half core and the other half should be used when quantifying the (useless) variance that one can calculate from such pairs of alledged "sample duplicates" and which includes both sampling and assaying errors, plus the geostatistical nugget effect (auto-correlations). The calculation should treat this as a segregation, but within TOS we do not have the tools to do it—yet.

How to properly calculate/predict the precision attached to the estimation of an average over a period of time from (pseudo-)periodic increments collected from **a 1-D stream**. The variogram should be calculated experimentally, and *then* be *modelled* using a smooth "allowable" function (there are strong geostatistical reasons why doing so is necessary for meaningful results),[2] then a non-illusory estimation variance can be calculated using a kriging program.

How to analyse and diagnose a 1-D stream. The variogram is a naturalistic tool that gives important information on the behaviour of streams. Sills and nugget effects provide key information for those who are in-the-know about the rules of interpreting variograms. Its periodicities can be assessed and important conclusions derived.

But it is possible, with correctly handled geostatistics, to go much further. For instance, the stream can be simulated geostatistically, with formidable benefits in terms of testing certain strategies, whether for the increment collection or within the frame of other types of variability studies.

- **The handling of segregation in large stockpiles** can advantageously be the objective object of geostatistical handling, although this would be a matter of research for the time being. Much work remains here; we have only started this particular strand.

■

Conclusions

While TOS is unquestionably being applied more and more successfully, witness the series WCSB1–WCSB7 and in many other situations in all of science, technology and industry, it is proposed that a cleaning exercise, as suggested above, would condition the integration effort with great advantage. If this takes flight, it can be started and executed rather quickly and better tools will be developed as a result.

It is hoped that the present opinion piece can serve as a start of a healthy debate about these central issues.

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Journal of AOAC International (*JAOAC*) Special Issue on Representative Sampling for Food and Feed Materials: A Critical Need for Food/Feed Safety

A special collection of papers on all aspects of food and feed safety sampling—to be used in risk assessment, process control in a food/feed manufacturing environment, foodborne disease outbreaks, and regulatory compliance—is now available as an open access publication on the *Journal of AOAC International*'s (*JAOAC*'s) website. Visit http://aoac.publisher.ingentaconnect.com/content/aoac/jaoac for 11 fully refereed papers in the March/April 2015 issue.

These papers are the result of a groundbreaking trans-Atlantic collaboration between researchers, samplers and regulators from Europe and the United State, a true first within the sampling world. The authors gathered for a week in Windsor, Colorado in October 2014 to collaborate and write.

The papers in this Special Guest Editor Issue introduce the Theory of Sampling (TOS) as relevant for all aspects of food and feed safety sampling—the principles governing representative sampling apply universally. The papers are written and composed to interact with each other, providing a comprehensive, yet compact overview of the criteria that must be followed to ensure representative sampling.

The guest editors were: **Kim H. Esbensen**, Geological Survey of Denmark and Greenland, and Aalborg University, Denmark; **Claudia Paoletti**, European Food Safety Authority Parma, Italy; and **Nancy Thiex**, Thiex Laboratory Solutions, and Agricultural Materials section editor for the Journal.

The target audience includes all food/feed protection personnel: field sampling operators, academic and industrial scientists, laboratory personnel, companies, organisations, regulatory bodies and agencies that are responsible for sampling, as well as their project leaders, project managers, quality managers, supervisors and directors. In the United States alone, there are an estimated 45,000 federal, state and local food/feed regulatory personnel, not including industry or laboratory personnel.

"We hope to trigger a long overdue discussion and awareness regarding the need for global harmonization of representative sampling approaches for food and feed commodities", it is stated in the section's introduction. "As a collection, these papers represent a leap forward with respect to a valid sampling-plus-analysis approach for the entire food and feed area. A highpoint concerns the extended framework in which TOS remain the essential tool, the formal system definition, revolving around the concept of Decision Units (a new issue not often considered in TOS)".

The SGE issue includes the following contributions:

- "Food and Feed Safety Assessment: The Importance of Proper Sampling" by **Harry Kuiper** and **Claudia Paoletti**.
- "Towards a Unified Sampling Terminology: Clarifying Misperceptions" by **Nancy Thiex**, **Kim H. Esbensen** and **Claudia Paoletti**.
- "A Systematic Approach to Representative Sampling" by **Charles Ramsey** and **Claas Wagner**.
- "Sample Quality Criteria" by **Charles Ramsey** and **Claas Wagner**.
- "Materials Properties: Heterogeneity and Appropriate Sampling Modes" by **Kim H. Esbensen**.
- "Theory of Sampling—Four Critical Success Factors Before Analysis" by **Claas Wagner** and **Kim H. Esbensen**.
- "Quality Control of Sampling Processes—A First Foray; From Field to Test Portion" by **Kim H. Esbensen** and **Charles Ramsey**.
- "Considerations for Inference to Decision Units" by **Charles Ramsey**.
- "Distributional Assumptions in Agricultural Commodities—Development of Fit-for-Decision Sampling Protocols" by **Claudia Paoletti** and **Kim H. Esbensen**.
- "Critical Practicalities in Sampling For Mycotoxins in Feed" by **Claas Wagner**.
- "Considerations for Sampling Contaminants in Agricultural Soils" by **Charles Ramsey**.
- "Considerations for Sampling of Water" by **Charles Ramsey**.

Transatlantic Special Section taskforce, October 2014, Windsor, Colorado (left to right): Nancy Thiex (Thiex Laboratory Solutions); Kim H. Esbensen (Geological Survey of Denmark and Greenland & ACABS Research Group, University of Aalborg); Charles Ramsey (EnviroStat, Inc.); Claas Wagner (Wagner Consultants); Claudia Paoletti (European Food Safety Authority, Parma, Italy). The authors brought strong opinions and traditions from very different fields to the meeting and had to work hard to reach a consensus, but met with success in the end. Although at one time widely different terminology usages and traditions almost had to be resolved by the American way to solve disputes in the Wild West (see front cover).

The open access Special Guest Editor Issue is available online at http://aoac.publisher.ingentaconnect.com/content/aoac/jaoac.

This work was supported, in part, by the Association of American Feed Control Officials (AAFCO), the Association of Public Health Laboratories (APHL) and by Grant No. 1U18FD004710 from the US Food and Drug Administration (FDA). Its contents are solely the responsibility of the authors and do not necessarily represent the official views of AAFCO, APHL or FDA. Claudia Paoletti is employed by the European Food Safety Authority (EFSA). The positions and opinions presented in this special session are those of the author alone and do not necessarily represent the views or scientific works of EFSA.

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A simpler system of dimensions and units, Part 3

Francis F. Pitard

In Parts 1 and 2 (*TOS forum* Nos 2 and 3) it was demonstrated that time, mass, permeability and permittivity are relative concepts originating in the human imagination and it was postulated that they do not necessarily require units of their own. This continues to suggest that a simpler system of fundamental units could be useful to perform serious science. Unless we are willing to make some changes, necessary changes, science as it is done today is unnecessarily complicated, and therefore ambiguous. This seems unacceptable to this passionate scientist.

Heat and temperature

Historically, heat has been regarded from two points of view; as a calorific quantity and as a dynamic quantity. The unit of heat is the calorie; it is the quantity of heat that is required to raise the temperature of one gram of water from 14.5° to 15.5° centigrade.

Thermodynamics, on the other hand, regards heat as equivalent to energy, with dimensions

$$[H]=\left[\frac{L^2\cdot M_i}{T^2}\right].$$

A conversion factor, J, converts a number of calories to a number of Joules.

$$[H]=\left[\frac{L^2\cdot M_i}{T^2}\right]=\left[P\cdot L^3\right]=J\cdot M\cdot K \qquad (1)$$

The gas equation $P\cdot V=R\cdot T$ must be rewritten here as $P\cdot L^3=R_g\cdot K$ to avoid confusion. The thermodynamic T is replaced by K, and the gas constant R is replaced by R_g. Dynamically

$$[K]=\left[\frac{L^2}{T^2}\right].$$

It follows that $[R_g]=[M]$. If K has the dimensions of energy, R_g is defined by the gas-kinetic equation and R_g is dimensionless. In the $LP\rho C$ system, $[P\cdot L^3]=[R_g\cdot K]=[\rho\cdot L^3\cdot C^2]$. This presents the possibility that the proper dimensions for K are $[K]=[C^2\cdot L^3]$, and the proper dimensions of R_g are those of density.

$$[R_g]=[\rho] \qquad (2)$$

and

$$[K]=[C^2\cdot L^3] \qquad (3)$$

Problem: Find an expression for the thermal conductivity of a gas in terms of the properties of its molecules, supposing the direction of heat conduction is parallel to the x-axis of the apparatus. The following seven physical quantities are involved: thermal conductivity, k; molecular mass, m; number of molecules per unit volume, N; mean velocity of molecules, v; mean free path, l; gas pressure, p; thermal capacity per unit mass, C_u. Conversion of the *LMTK* dimensions of these *SI* quantities to $LP\rho C$ proceeds through the following relationships:

$$[M_i]=[\rho\cdot L_x{}^3] \text{ (heat transfer parallel to x-axis)} \quad \text{(see notes below)} \qquad (4)$$

$$[M_g]=[\rho\cdot L_x\cdot L_y\cdot L_z] \qquad (5)$$

$$[K]=[C^2\cdot L_x\cdot L_y\cdot L_z] \qquad (6)$$

$$[L]=[L_x] \text{ (see notes below)} \qquad (7)$$

$$\left[T^2\right]=\left[\frac{\rho\cdot L^2}{P}\right] \qquad (8)$$

$$[H]=\left[\frac{L^2\cdot M_i}{T^2}\right]=\left[L_x^3\cdot P\right] \qquad (9)$$

(see notes below)

$$[k]=\left[\frac{L\cdot M_i}{T^3\cdot K}\right]=\left[L_x^2\cdot L_y^{-2}\cdot L_z^{-2}\cdot\rho^{-1/2}\cdot P^{3/2}\cdot C^{-2}\right] \qquad (10)$$

$$[m]=[M_g\cdot L^3]=[\rho\cdot L_x\cdot L_y\cdot L_z] \qquad (11)$$

$$[N]=[L_x{}^{-1}\cdot L_y{}^{-1}\cdot L_z{}^{-1}] \qquad (12)$$

$$[v]=[L_x\cdot T^{-1}]=[L_x\cdot\rho^{-1/2}\cdot L_x{}^{-1}\cdot P^{1/2}]=[\rho^{-1/2}\cdot P^{1/2}] \qquad (13)$$

$$[l]=[L_x] \qquad (14)$$

$$[p]=[P] \qquad (15)$$

$$[C_u]=\left[\frac{H}{M_g\cdot K}\right]=\left[L_x\cdot L_y^{-2}\cdot L_z^{-2}\cdot\rho^{-1}\cdot P\cdot C^{-2}\right] \qquad (16)$$

Notes, with:

$$k=c\cdot m^a\cdot N^b\cdot v^c\cdot l^d\cdot p^e\cdot C_u{}^f \qquad (17)$$

$$L_x{}^2=L_x{}^{a-b+d+f} \text{ with } a-b+d+f=-2 \qquad (18)$$

$$L_y{}^{-2}=L_z{}^{-2}=L_y{}^{a-b-2f} \text{ with } a-b-2f=-2 \qquad (19)$$

$$\rho^{-1/2}=\rho^{a-\frac{c}{2}-f} \text{ with } a-\frac{c}{2}-f=-\frac{1}{2} \qquad (20)$$

$$P^{3/2}=P^{\frac{c}{2}+e+f} \text{ with } \frac{c}{2}+e+f=\frac{3}{2} \qquad (21)$$

$$C^{-2}=C^{-2f} \text{ with } 2f=2 \qquad (22)$$

$$a=1,\ b=1,\ c=1,\ d=1,\ e=0,\ f=1 \qquad (23)$$

$$k=c\cdot m\cdot N\cdot v\cdot l\cdot C_u \qquad (24)$$

Since $m\cdot N$ is the gas density, d, and v is proportional to K,

$$k=c\cdot d\cdot K\cdot l\cdot C_u \qquad (25)$$

Experiment confirms that thermal conductivity is proportional to absolute temperature. Surprisingly experiment also confirms that thermal conductivity is independent of pressure ($e=0$).

The *SI* "amount of substance", the mole, Avogadro's number, N_a, has a relation to mass, M. Scrutiny of the "dimensional independence" of M would be incomplete without investigation of N_a.

Avogadro's number and mass

Avogadro's number, N_a, is defined as the number of atoms in a gram-mole of carbon-12. In *SI* parlance it is "the amount of substance in a system that contains as many elementary entities as there are atoms in 0.012 kilograms of carbon 12". An *SI* directive gives as an example "1 mole of H_2 contains about $6.022\cdot10^{23}$ molecules or $12.044\cdot10^{23}$ H atoms". The *SI* value for N_a is listed (2011–2012) as $6.02214179(30)\cdot10^{23}\,\text{mol}^{-1}$.

There is an obvious contradiction here. A hydrogen atom does not have exactly 1/12 the mass of a carbon-12 atom. The ratio $12(M_h/M_c)$ is about 1.00782503207(10). The number of atoms in 1 gram-mole of H_1 is not the same as the number of atoms of C_{12} in 1 gram-mole. It takes fewer hydrogen atoms to make a gram-mole of hydrogen. To deal further with this complication, it is first necessary to establish a **new unit (*NU*) of mass**, introduce a constant *t*, the **time thickness constant**, and develop an alternative to Avogadro's number on a new unit of mass, *NU*[*M*].

We have suggested that the gas constant, R_g, has the dimensions of density.

$$\left[R_g\right]=[\rho]=\left[\frac{M}{L^3}\right] \tag{26}$$

In *SI* units, $R_g = 8.314472(15)$ Joules/mole/°K. Because a conversion factor from *NU* to *SI* has been established, there is the possibility of approximating a mass conversion factor (*M*). The new unit (NU) of length is by definition the radius of a unit vacuole, $r=1=1NU[L]=1(L)$. The square-bracketed [*L*] is simply a dimensional statement. The (*L*) in parentheses is a conversion factor from *NU* to *SI*.

From Equations (35) and (36) in publication #2, since $(L)=5.006148\ldots\cdot 10^{-13}\,\mathrm{m}$, $(M)R_g\cdot L^3$ and $(M)=(8.314472\cdot 10^7)$ $(5.006148\ldots\cdot 10^{-13})^3 = 1.043147\ldots\cdot 10^{-23}$ grams. This supposes, of course, that $1NU[\rho]=1$. If we chose 2π as a $NU[\rho]$ (good reasons for this!), $(M)=1.6602\ldots\cdot 10^{-24}\,\mathrm{g}/NU[M]$.

The inverse of this (approximate) mass conversion factor (*M*) is $6.02337\ldots\cdot 10^{23}$. If we assign the letter *N* to this inverse mass, $N/N_a = 1.0002$. This **"coincidence"** will be developed further as the speculative source of this writing is developed.

The time thickness constant *t*

In exploring the dimensions of length [*L*], we made use of the dimension-less fine-structure constant, $\alpha = 7.2973525376(50)\cdot 10^{-3}$ (from 2011–2012 *CRC Handbook*). Arguments not presented at this stage require development of the concept of a time-thickness of the 3-dimensional (3-D) Universe in which we find ourselves. If we regard time as a fourth dimension right-angled to up-down, east-west and north-south in a 4-D space, we can recognise that our perception of time is not instantaneous. There is a distance in time, very small, but real, that appears subjectively as **the duration of the present instant**. In finding a conversion factor *NU*[*T*] to m/s, the velocity of light was used to convert centimetres to seconds and vice versa, **giving a dimension-less value for light velocity as a ratio between two units of length**, the metre and the second. $c = 2.99792458\cdot 10^8$ is a conversion factor from seconds to metres.

Using thermal quantities, we estimated a conversion factor $M = 1.6602\cdot 10^{-24}$ grams/*NU*[*M*]. We have also found a conversion factor $L = 5.0061\ldots\cdot 10^{-9}\,\mathrm{m}/NU[L]$. From these, we estimated a conversion factor $\rho = 1.3233\cdot 10^7\,\mathrm{g\,cm^{-3}}/NU[M/L^3]$ or $\rho = 1.3233\cdot 10^{13}\,\mathrm{g\,m^{-3}}/NU[M/L^3]$ and an estimate of the gas constant $R_g = 8.3144\cdot 10^7\,\mathrm{g\,cm^{-3}}/NU[\rho]$.

A sphere with mass *M* and radius *L* has a density with dimensions $[\rho]=[M/L^3]$ and a surface area with dimensions $[L^2]$. If the time thickness referred to above has dimensions [*L*], it must be related to the radius of the unit sphere by a dimension-less constant. If the time thickness reveals itself as a measured wave length, *l*, of electromagnetic character, $l=t\cdot d$ or $2\cdot t\cdot r$, where *d* is the diameter and *r* the radius of the unit sphere.

As a speculative hypothesis, put $l=l_{ec}$, the Compton electron wave length (aka the Dirac wave length). Then

$$l_{ec}=2\cdot t\cdot r \tag{27}$$

and

$$t=\frac{l_{ec}}{2r}=\frac{2.4263102175(33)\cdot 10^{-12}}{2\cdot 5.006148\cdot 10^{-13}} \tag{28}$$
$$=2.42332\ldots$$

Equation (27) is the basis for our discussions later on in subsequent publications.

The time thickness constant is related to the fine structure constant, α:

$$t=\frac{1}{2\cdot 3^2\cdot\pi\cdot\alpha}=2.423322 \tag{29}$$

and can replace α in calculating the conversion factor (*L*):

$$L=2\cdot 3^2\cdot\pi^2\cdot\alpha^2\cdot a^0=\left[\frac{a^0}{2\cdot 3^2\cdot t^2}\right]= \tag{30}$$
$$5.006148\cdot 10^{-13}\,m\,/\,NU[L]$$

Selection of carbon-12 as the basis for a unit of "amount of substance" is completely arbitrary. Avogadro's number, N_a, can be replaced with any reasonable number without loss of truth or meaning. Accordingly, we suggest that N_a be replaced through the relation *M*:

$$M=2^7\cdot t^3\cdot m_e=2^7\cdot t^3\cdot[9.10938215(45)\cdot 10^{-28}]g/NU[M] \tag{31}$$

The following factors *NU* to *SI* have now been established:

$$t=2.423322 \tag{32}$$

$$L=5.006148\ldots\cdot 10^{-13}\,m/NU[L] \tag{33}$$

$$T=1.669872\ldots\cdot 10^{-21}\,s/NU[T] \tag{34}$$

$$M=\rho\cdot L^3=1.659629\ldots\cdot 10^{-24}\,g/NU[M] \tag{35}$$

$$N=1/M=6.02337\cdot 10^{23}\ \text{unit spheres/g} \tag{36}$$

$$P=M/(L\cdot T^2)=1.188888\ldots\cdot 10^{28}\,\text{pascal}/NU[P] \tag{37}$$

$$\rho=M/L^3=1.322817\ldots\cdot 10^{13}\,g/m^3/NU[\rho] \tag{38}$$

$$\text{Gas constant } R_g=2\cdot\pi\cdot\rho=8.311523\ldots\cdot 10^{13}\,g/m^3/NU[\rho] \tag{39}$$

$$\text{Electron mass } m_e=2^7\cdot t^3NU[M]=9.10938215(45)\ldots\cdot 10^{-31}\,kg \tag{40}$$

The constants of physics

It is now possible to calculate *NU* values for the constants of Physics and their *SI* equivalents using the relationships:

$$L_{ec}=2\cdot t\cdot L=\frac{h}{m\cdot c} \tag{41}$$

$$\alpha=\frac{1}{2\cdot 3^2\cdot\pi\cdot t}=\frac{2\cdot\pi\cdot e^2}{h\cdot c} \tag{42}$$

$$N=\frac{1}{M}=\frac{1}{2^7\cdot t^3\cdot m} \tag{43}$$

$$c=\frac{L}{T} \tag{44}$$

From (41): $$h=2\cdot t\cdot L\cdot m\cdot c \tag{45}$$
From (45):

$$m=\frac{1}{2^7\cdot t^3\cdot N} \tag{46}$$

Substituting (44), (45) and (46) in (41):

$$h=\frac{1}{2^6\cdot t^2}NU\left[\frac{L^2}{N\cdot T}\right]\ \text{or}\ NU\left[L^4\cdot\rho\cdot C\right]=2.660711\ldots\cdot 10^{-3}NU \tag{47}$$

$$h=2.660711\ldots\cdot 10^{-3}$$
$$[L^4\cdot\rho\cdot C]=6.62606896(33)\cdot 10^{-34}\,js$$

Substituting (44) and (45) in (42):

$$e^2 = \frac{h \cdot c}{2^2 \cdot 3^2 \cdot \pi^2 \cdot t} = \frac{1}{2^8 \cdot 3^2 \cdot \pi^2 t^3} NU\left[\frac{L^3 \cdot M}{T^2}\right] \tag{48}$$

Thus 1*NU* of quantity of electricity, *Q* is:

$$Q = e = \frac{1}{\sqrt{2^2 \cdot 3^3 \cdot \pi^2 \cdot t}} = \frac{1}{\sqrt{2^8 \cdot 3^2 \cdot \pi^2 \cdot t^3}} NU\left[\sqrt{\frac{L^3 \cdot M \cdot k}{T^2}}\right] = 1.757887 \cdot 10^{-3} NU\left[L^2\right] \tag{49}$$

$$Q = e = 4.803204\ldots \cdot 10^{-14}\, mgsSI \quad \text{taking } k = 1 \tag{50}$$

Compare the 2011–2012 *SI* value $1.602176487(40) \times 10^{-19}$ C.

There is no need for a unit of quantity of electricity in the *NU* system.

The conversion factor (L^2/P) is necessary instead of (L^2) because, while k has dimensions $[1/P]$, its numerical value is 1. The difference between N_a and N which is $(N/N_a) = 1.0007204$ shows up in all quantities with N in dimensional statements; for example, the Faraday, $F = e \cdot N$, the Boltzmann and Stefan constants and all other thermal quantities, sometimes in subtle ways that are difficult to detect. It happens that if Cesium-133 had been chosen instead of Carbon-12 in calculation of N_a, the ratio N/N_a would be 1.000009, about 9 parts in a million difference.

It seems that the attempt to establish an exact scale of atomic mass units is a mistake. This provides a reason to doubt that mass is a "dimensionally independent quantity" and supports the proposition that the proper dimensions of mass are $[\rho \cdot L^3]$.

Dimensions and conversion factors

In the *NU* system, physical quantities are written in the form:

$$\text{Mass of brick} = m_b = 1.205\ldots \cdot 10^{27}\, NU[M]$$

This should be read "the mass, m_b, of the brick is 1.205 times 10^{27} new units of mass, expressed to four-figure precision. The $[M]$ in square brackets is a dimensional statement. To convert from *NU* to *SI* or other system requires the use of conversion factors. These have been estimated for length, density, pressure and (secondarily) for mass and time. Conversion is written thus:

$$m_b = 1.205 \cdot 10^{27}\, NU[\rho \cdot L^3] = 1.205 \cdot 10^{27} \cdot (\rho \cdot L^3)\,\text{g} \tag{51}$$

The conversion factor $(\rho \cdot L^3)$ has been estimated at $1.659 \cdot 10^{-24}$ grams per *NU*[*M*]. The mass of the brick (remember it?) is then $m_b = 1.205\ldots \cdot 10^{27}\, NU[M] = 1.205\ldots \cdot 10^{27} \times 1.659\ldots \cdot 10^{-24}\,\text{g} = 2000\ldots$ g.

In some instances, the dimensional statement and the conversion factor are not exactly the same. An example is the statement for unit charge, *e*.

In *SI*,

$$[e] = \left[\frac{\sqrt{L^3 Mk}}{T}\right]$$

In *NU*, $[e] = [L^2]$

But the conversion factor from *NU* to *SI* is $(L\sqrt{P})$.

This is due to the substitution of $\sqrt{(1/P)}$ for $\sqrt{k}$, as explained previously. Another example is the conversion factor for the gravitational constant, *G*. In SI,

$$[G] = \left[\frac{L^3}{M \cdot T^2}\right].$$

In *NU*,

$$[G] = \left[\frac{1}{P \cdot L^2}\right],$$

but the conversion factor is

$$\left(\frac{C^4}{P \cdot L^2}\right),$$

with a correction N/N_a.

In this case C^4 is numerically the unity, but must be included for dimensional homogeneity. Necessity for the correction factor involving $N = 1/M$ is due to the arbitrary selection of carbon-12 as the basis for the *SI* unit of "amount of substance".

Avogadro's number, N_a, and $(1/M) = N$

Avogadro's number, N_a, "the number of elementary entities as there are atoms in 0.012 kilograms of carbon-12" and $N = 1/M$ both have dimensions (number/mass). There are, however, subtle differences. Avogadro's number is best measured by electrolysis of a silver solution, not of a carbon solution. The ratio of atomic mass to mass number for carbon-12 is exactly 1.0000… This ratio for silver is 0.9991… For hydrogen-1, the ratio is 1.0079… The number N_a

Table 1. The many values of *N*.

Element or constant	*U* or *f*( )	$N \cdot 10^{23}$
^{o}n (neutron)	1.0086649	5.970404
^{1}H (Hydrogen-1)	1.007826	5.975379
p+ (proton)	1.0072765	5.978633
$G = 2[(N \cdot T^2)/L] = 6.67428(67) \cdot 10^{-11}\,\text{m}^3\,\text{kg}^{-1}\,\text{s}^{-2}$ *SI* units		5.98966 (see note 1)
$k = 2 \cdot \pi(\rho/N) = 1.3806504(24) \cdot 10^{-23}\, JK^{-1}$ *SI* units		6.01894 (see note 2)
$\sigma = (2^{23} \cdot \pi^3 \cdot t^6)/15(D^5/C^5) = 5.670400(40) \cdot 10^{-8}\,\text{Wm}^{-2}\,\text{K}^{-4}$ *SI* units		6.01941 (see note 3)
^{12}C (Carbon-12)	12.00000000	6.0221367… (N_a)
^{207}Bi (Bismuth-207)	206.98037	6.0227023
^{133}Cs (Cesium-133)	132.905429	6.0264218
$N = 1/M$	1.0007204	6.0264751 (see note 4)
^{127}I (Iodine-127)	126.904473	6.0266698
^{59}Co (Cobalt-59)	58,933198	6.0289629

Note 1: *G* the gravitational constant depends on the cosmic abundance of the elements, which are mainly hydrogen and helium

Note 2: *k* is the Boltzmann constant

Note 3: σ is the Stefan Boltzmann constant

Note 4: *N* is the number of unit vacuoles per gram. N_a is the number of atoms in a gram-mole of Carbon-12 per mole. *N* may be assigned differing values depending on the elements or functions in which it is used. $1/N$ may replace *M* when appropriate differs from $N=1/M$ in that it is an arbitrary constant unrelated to the mass of the particles it counts, whether they be atoms or molecules… or ships or shoes!

The ratio $N=1/M$ would be identical to N_a only if masses of all atoms were independent of their mass numbers, and if an elemental isotope were chosen (e.g., to replace carbon-12) for an elemental standard with a ratio (i.e., atomic mass/mass number) such that the new value for $N_a=1/M$. A decision that the conversion factor $M=1.659345\ldots\cdot10^{-24}\,\mathrm{g}/NU[M]$ be derived from the electron rest mass was, of course, also arbitrary. First efforts to find a best value for M took place when the oxygen-16 base was in favour. Then, $N_a=6.025\ldots\cdot10^{23}\,\mathrm{g\,mol^{-1}}$. Now $N_a=6.022\cdot10^{23}\,\mathrm{g\,mol^{-1}}$. This approach led to complications, but also to awareness of subtle difficulties. In electromagnetic, N_a is useful. In thermal and dynamic situations it is better to recognise that mass is essentially a secondary approximate unit, and that its components must be considered in any fundamental scheme.

Table 1 shows the many values of N. The symbol (*) attracts the attention that the gravitational constant depends on the cosmic abundance of the elements, largely hydrogen and helium; k is the Boltzman constant; σ is the Stefan Boltzmann constant; N is the number of **unit vacuoles** (defined in a later publication) per gram; N_a is the number of atoms in a gram-mole of carbon-12. N may be assigned differing values depending on the elements or functions in which it is used. $1/N$ may replace M when appropriate.

Comparison between the 2-dimensional systems $LMTkN_a$ and $LP\rho CN$

At this stage, useful physical quantities should be summarised and their dimensions compared, as they will have many applications; see Table 2. The *LPρCN* system more clearly reflects the nature of many of the quantities, especially electromagnetic quantities.

The constants of physics (e.g., $t=2.423322\ldots$)

Table 3 shows useful physical constants with conversion factors into new units *NU*, in which dimensions of Time [*T*] and Mass [*M*] no longer play a direct, structural role. In the new system *NU*, all values for the fundamental physical constants are absolute, with the exception of the time-thickness constant.

Table 2. Comparison of dimensional systems.

Physical quantity	$LMTkN_a$	$LP\rho CN$
Action (angular momentum)	$(L^2\cdot M)/T$	$L^4\cdot\rho\cdot C$
Avogadro's number	N_a	
Bohr magneton	$(L^{5/2}\cdot M^{1/2}\cdot k^{1/2})/T$	L^3
Density	M/L^3	ρ
Electric charge	$(L^{3/2}\cdot M^{1/2}\cdot k^{1/2})/T$	L^2
Electric current	$(L^{3/2}\cdot M^{1/2}\cdot k^{1/2})/T^2$	$L\cdot C$
Electric permittivity	k	$1/P$
Electric resistance	$T/(L\cdot k)$	$\rho\cdot C$
Energy	$(L^2\cdot M)/T^2$	$M\cdot C^2=L^3\cdot P$
Gravimetric constant	$L^3/(M\cdot T^2)$	$L\cdot N\cdot C^2$
Inductance	$T^2/(L\cdot k)$	$L\cdot\rho$
Inverse mass		$1/(\rho\cdot L^3)$ or N
Length	L,L_x,L_y,L_z	L,L_x,L_y,L_z,L_t
Magnetic field strength	$(L^{1/2}\cdot M^{1/2}\cdot k^{1/2})/T^2$	$P^{1/2}/\rho^{1/2}=C$
Magnetic permeability	$u=1/c^2k$	ρ
Mass	M	$\rho\cdot L^3$
Potential difference	$(L^{1/2}\cdot M^{1/2})/(T\cdot k^{1/2})$	$L\cdot P$
Pressure	$M/(L\cdot T^2)$	P
Surface tension	$M\cdot T^2$	$L\cdot P$
Temperature (dynamic)	L^2/T^2	C^2
Temperature (kinetic)	1	1
Time	T	$\rho^{1/2}/P^{1/2}=L/C$
Velocity	L/T	C/c

Table 4 may help the reader when comparing *NU* values with values from the *SI* system.

Electronic charge, *e*

Conventional dimensions of *e* are $[e]=[\sqrt{(L^3Mk)}/T]$ or $[\sqrt{(LM)}/u]$ with L = length, M = mass, T = time, k = electric permittivity, u = magnetic permeability.

The later exposed Vacuole Hypothesis puts the proper dimensions of *e* at $[L^2]$. Solving the equality:

$$L^2=\frac{L^{3/2}\cdot M^{1/2}\cdot k^{1/2}}{T}=\frac{L^{1/2}\cdot M^{1/2}}{u^{1/2}} \qquad (52)$$

gives:

$$[k]=[1/P] \qquad (53)$$

and

$$[u]=[\rho] \qquad (54)$$

Permittivity has dimensions [1/Pressure], permeability has the dimensions of density and

$$c^2=[1/(u\cdot k)]=P/\rho \qquad [55]$$

For this reason P and ρ replace M and T as primary dimensions.

Gravitational constants G_n and G_r

Dimensions of the Newtonian constant G_n, $[L^3/(M\cdot T^2)]$ and the relativity constant G_r, $T/(L\cdot M)$ differ by $[1/c^4]$ or $[T^4/L^4]$. If one takes $c^4=1$, converting to the $LP\rho$ system gives the conversion factor listed above. The value given N_g derives from the fact that the universe contains much more Hydrogen and Helium than Carbon-12.

Table 3. New units *NU* and conversion factors.

Physical quantity	Value in *NU*	Conversion factor	Official Value in *SI* units (2011–2012)
Bohr magneton, u_B	$\frac{1}{2^5 \cdot 3 \cdot \pi^2 \cdot t^{1/2}} = 6.7798922 \cdot 10^{-4}$	$L^3 \cdot P^{1/2}$	$927.400915(23) \cdot 10^{-26} JT^{-1}$
Bohr radius, a_0	$2 \cdot 3^2 \cdot t^2 = 1.057054613 \cdot 10^2$	L	$0.52917720859(36) \cdot 10^{-10} m$
Boltzmann Constant, k	$2 \cdot \pi$	ρ / N	$1.3806504(24) \cdot 10^{-23} JK^{-1}$
Electron charge, e	$\frac{1}{2^4 \cdot 3 \cdot \pi \cdot t^{3/2}} = 1.757883944 \cdot 10^{-3}$	$L^2 \cdot P^{1/2}$	$1.602176487(40) \cdot 10^{-19} \mathrm{C}$
Electron g-factor, g	1.001159652193	1	1.001159652193
Electron radius, r_e	$\frac{1}{2 \cdot 3^2 \cdot \pi^2} = 5.628954647 \cdot 10^{-3}$	L	$2.8179402894(58) \cdot 10^{-15} m$
Electron rest mass, m	$\frac{1}{2^7 \cdot t^3} = 5.489751035 \cdot 10^{-4}$	M	$9.10938215(45) \cdot 10^{-31} kg$
Faraday, F	$\frac{1}{2^4 \cdot 3 \cdot \pi \cdot t^{3/2}} = 1.7578839 \cdot 10^{-3}$	$L^2 \cdot P^{1/2} \cdot N$	$96485.3399(24) Cmol^{-1}$
Fine structure constant, a	$\left[0.5 - \left(0.25 - \frac{1}{137^2 \cdot g^{1/2}}\right)^{1/2}\right]^{1/2}$ $= 7.2973525376 \cdot 10^{-3}$	1	$7.2973525376(50) \cdot 10^{-3}$
Inverse mass, N N_a	1.00000000	$1/M$ $N_{avogadro} =$	$6.02337 \cdot 10^{23} g^{-1}$ $6.02214179(3) \cdot 1\text{-}^{23} mol^{-1}$
Light velocity, c	1.00000000	L/T	$2.99792458 \cdot 10^8 m/s$
Planck constant, h	$\frac{1}{2^6 \cdot t^2} = 2.66069507 \cdot 10^{-3}$	$(L^2 \cdot M)/T$	$6.62606896(33) \cdot 10^{-34} Js$
Rydberg constant, $R_{¥}$	$\frac{1}{2^4 \cdot 3^4 \cdot \pi^2 \cdot t^3} = 5.4936105667 \cdot 10^{-6}$	$1/L$	$10973731 \cdot 568527(73) m^{-1}$
Stefan constant, σ	$\frac{2^{23} \cdot \pi^9 \cdot t^6}{15} = 3.337615 \cdot 10^{12}$	$\rho^5 \cdot C^5$	$5.670400(40) \cdot 10^{-8} Wm^{-2} K^{-4}$
Time thickness, t	$\frac{1}{2 \cdot 3^2 \cdot \pi \cdot a} = 2.423322$	1	2.423328345 preferred value (see References 4 and 5 in vacuole hypothesis paper from COI)
Time thickness,	$2 \cdot t = 4.846658901$	L	$2.426308377 \cdot 10^{-12} m$
Unit of density, ρ	1.00000000	$(M/L^3) = \rho$	$1.32259236 \cdot 10^{13} g/m^3$
Unit of length, L	1.00000000	$1/(2^4 \cdot 3^4 \cdot p^2 \cdot t^3 \cdot R)$	$5.00614635 \cdot 10^{-13} m$
Unit of mass, M	1.00000000	$2^7 \cdot t^3 \cdot m$	$1.659344784 \cdot 10^{-24} g$
Unit of pressure, P	1.00000000	$M/(L \cdot T^2) = P$	$1.18868673 \cdot 10^{28} pascal/NU[P]$
Unit of time, t	1.00000000	L/C	$1.66997068 \cdot 10^{-21} s$

Note that the conversion factors do not always show the actual dimensions of the quantities reported. Explanations are summarized in the following sections.

Temperature dependent constants, k_b

The Vacuole Hypothesis assigns dimensions $[(P \cdot L^3)/\rho]$ to temperature. This gives the gas constant the dimensions of density and $k = 2 \cdot \pi \cdot NU[\rho/N] =$ $1.3806504(24) \cdot 10^{-23} JK^{-1}$ *SI* units on the Carbon-12 scale.

Conclusion

In the new suggested system, all values for the "fundamental" physical constants are absolute, with the exception of the time-thickness constant, t. Planck's constant $h = 1/(2^6 \cdot t^2)$, electron charge $e = 1/(2^4 \cdot 3 \cdot \pi \cdot t^{3/2})$, electron rest mass $m = 1/(2^7 \cdot t^3)$, light velocity $c = 1$ etc. A "best value" for t, 2.42332945…

Table 4. New units *NU* and conversion factors to *SI*.

To convert from	To	Multiply by
NU[*L*]	Centimetres	$5.00614634 \cdot 10^{-11}$
centimetres	*NU*[*L*]	$1.99754448 \cdot 10^{10}$
NU[*M*]	grams	$1.65934478 \cdot 10^{-24}$
grams	*NU*[*M*]	$6.02647512 \cdot 10^{23}$
NU[*T*]	seconds	$1.66987067 \cdot 10^{-21}$
seconds	*NU*[*T*]	$5.98848770 \cdot 10^{20}$
NU[*P*]	pascals	$1.8868673 \cdot 10^{27}$
pascals	*NU*[*P*]	$8.412645544 \cdot 10^{-28}$
NU[ρ]	Grams cm^{-3}	$1.32259236 \cdot 10^{7}$
Grams cm^{-3}	*NU*[ρ]	$7.56090864 \cdot 10^{-8}$

has been estimated from the electron g-factor, experimentally determined to 10^{-5} ppm. Using these values, the fine structure constant $a = (2 \cdot \pi \cdot e^2)/(h \cdot c) = 0.00729735308\ldots$ The 1986 value is 0.00729735308(33).

A simple example may demonstrate the advantage of using the *LPρC* system instead of the *LMT* system. Solve the following:

Problem: Using the method of dimensions, determine the mass of viscous fluid flowing per second through a round tube.

Solution using the LMT system

A complete summary of parameters is given in Table 5.

Dimensionally, we have:

$$[M \cdot T] = \left[\frac{M}{L^2 \cdot T^2}\right]^x \cdot \left[\frac{M}{L^3}\right]^y \cdot \left[\frac{M}{L \cdot T}\right]^z \cdot [L]^w =$$

$$p^x \cdot d^y \cdot n^z \cdot r^w$$

whence

$$x + y + z = 1$$
$$2x + z = 1$$
$$w - 2x - 3y - z = 0$$

We have three equations and four unknowns. The best result we can find is:

$$x = 1/2 - z/2$$
$$y = 1/2 - z/2$$
$$w = 5/2 - 3z/2$$

We must guess that $z = -1$ to obtain the correct solution.

Table 5. *LMT* system.

Physical quantity	Symbol	Dimensions
Mass per second	m	M/T
Pressure gradient	p	$M/(L^2 \cdot T^2)$
Density of liquid	d	M/L^3
Coefficient of viscosity	n	$M/(L \cdot T)$
Radius of tube	r	L

Table 6. *LρC* system.

Physical quantity	Symbol	Dimensions
Mass per second	m	$L^2 \cdot \rho \cdot C$
Pressure gradient	p	P/L
Density of liquid	d	ρ
Coefficient of viscosity	n	$(P \cdot L)/C$
Radius of tube	r	L

Solution using the *LPρC* system

A complete summary of parameters is given in Table 6.

Dimensionally, we have:

$$\left[L^2 \cdot \rho \cdot C\right] = \left[\frac{P}{L}\right]^x \cdot [\rho]^y \cdot \left[\frac{P \cdot L}{C}\right]^z \cdot [L]^w$$

whence

$$w + z - x = 2$$
$$z = -1$$
$$y = 1$$
$$x + z = 0$$

and $x = 1$, $y = 1$, $z = -1$, $w = 4$

giving the correct solution, mass per second $m = (\text{a dimension-less constant}) \times (p \cdot d \cdot r^4)/n$.

The reason for success of the *LPρC* system is that it automatically takes the difference between inertial mass M_i and gravitational mass M_g into account.

Epilogue

This concludes our initiating long journey that demanded three publications in *TOS forum* setting the background for a simpler system of dimensions and units. We have now reached a point where I must make an attempt to offer a vision about what could be the implications as we "sample" the Universe in which we live. Obviously we shall make an attempt to enlarge the concept of sampling as we explore the unknown. This new journey will start by breaking certain paradigms that have stood in our way for too long, making progress in science difficult—it is a daring journey.

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Development of a sampling protocol for radioactive elements in fractured rock aquifers using a case study from South Africa

G. Mahed

Bioresources Engineering Research Group, Faculty of Applied Sciences, Cape Peninsula University of Technology, Cape Town, South Africa, 8000. E-mail: gaathier@gmail.com

This work outlines the methodology employed in order to develop a sampling protocol for radioactive elements in fractured rock aquifers. This has included the analysis of previously developed sampling protocols, historical data as well as the field application of a draft protocol to the area around Beaufort West in South Africa. The selected test site is showcased and the developed protocol is outlined in order to better understand the application of sampling in fractured rock aquifers. This includes the pre-sampling procedures, purging of the well, sampling devices, *in situ* methodologies as well as sampling frequency. Furthermore, the Theory of Sampling applied to a study of this nature is outlined in order to properly contextualise the work. Thereafter, the future outlook for improvements related to this specific protocol is highlighted within the context of Theory of Sampling.

Introduction

Water resources are of the utmost importance due to the fact that water is required in order to aid in the effective functioning of our daily lives. Groundwater resources are very important, because they constitute the larger percentage of the total available fresh water resources.[1] Therefore, studies related to the preservation and judicious use of groundwater resources are critical.

Groundwater can be defined as the water contained in the pore spaces below the surface, excluding the soil moisture in the unsaturated zone.[2] The media within which groundwater occurs could either be of primary porosity, like sand, or of secondary porosity. The latter is due to the fracturing of consolidated sediments. We thus find that fractures occur and these, as well as the rock matrix, are able to store groundwater.[3]

The fractured rock environment underlying the South African landscape has been extensively studied by Woodford and Chevallier.[4] The authors have compiled all the work related to the hydrogeology, geology, remote sensing and water chemistry completed in the South African section of the Karoo. The numerical treatment of the physical parameters of these aquifers can be seen in Botha and Cloot.[5] This includes the rock mechanics as well as applied models to groundwater flow in fractured rock. The determination of Karoo aquifer parameters has further been analysed by Bredenkamp *et al.*[6] and Van Tonder *et al.*[7] These studies have all focused on the geological and hydraulic parameters of these fractured rock aquifers.

The need has arisen for an in-depth understanding of the groundwater geochemistry of these aforementioned aquifers, specifically in areas of limited water supply. This will aid in understanding water quality and in turn help in effective water resource management and allocation.

It is with this in mind that the Water Research Commission decided to fund a study related to Uranium and radioactivity in groundwater in the region of Beaufort West, South Africa. One of the products developed from this study included a sampling and monitoring protocol for radioactive elements in fractured rock aquifers. This document is the first of its kind developed globally and is outlined in brief.

Background

In recent times various studies have characterised the extent to which natural radioactive contamination is occurring within groundwater.[8–10] Unfortunately there seems to be no standard sampling and monitoring protocol for radionuclides within secondary aquifers.[11] A document of this nature is important due to the fact that a major part of South Africa is underlain by hard rock aquifers and they supply numerous towns with potable water for various uses.[12]

It is also important to note that Uranium and its daughter products have adverse effects on human health. This is due to the radioactive nature of the parent material as well as the decay products released over time, more commonly known as daughter products. In order to minimise these impacts the sampling and monitoring of these radionuclides has to be done in an effective standardised manner.

Weaver *et al.*[13] suggests that groundwater sampling is done for the following reasons:

- Assess groundwater quality for fitness of use
- Understanding hydrogeology of an aquifer
- Investigating groundwater pollution
- Water quality monitoring

These reasons are all important and thus the development of a protocol in order to provide a methodology for radioactivity sampling in fractured rock aquifers is just as critical.

Methodology

The methodology used in order to develop the sampling and monitoring protocol presented in Xu *et al.*[14] is outlined in this section. The abridged work presented highlights of the salient points of the developed protocol. An in-depth analysis and presentation of the work can be viewed in the aforementioned literature.

Historical data sets

These data sets aided greatly in understanding applicable methodologies for sampling radioactivity in fractured rock aquifers. The methods used to generate this historic data also contributed towards the development of the protocol. Brunke[15] conducted the initial work relating to the groundwater geochemistry within the vicinity of the

Uranium channels of Beaufort West. The aim of the study was to investigate the possible relationship between Uranium and other trace elements in groundwater in the region. Brunke[15] suggested that the water quality is mainly a function of residence time and extent of rock/water interaction. It was further observed that waters with higher salinity values were enriched in SO_4 and Cl. The sub-surface waters were generally well aerated and had a positive Eh. These conditions favoured the leaching of Uranium, which also had a positive correlation with Total Dissolved Solids (TDS).

Scholtz[16] assessed the potential toxic influence of Uranium trail mining in the Karoo Uranium Province. The study revealed localised elevated values for U, Mo, Pb, Cu, As and Fe in surface- and groundwater, soils, sediment and crops. Scholtz[16] concluded that the U concentration in the groundwater was acceptable. Unfortunately the author did not purge the wells and thus sampled stagnant groundwater. Purging can be seen as the removal of stagnant water from the well. Purging is essential in order to gain a sample which is representative of the *in situ* conditions, especially in fractured rock aquifers.[3]

Sami and Druzynski[17] looked at the predicted spatial distribution of Uranium, Arsenic and Selenium within the borders of South Africa. This report yielded numerous maps for the occurrences of the aforementioned elements in groundwater throughout the country, including the proposed study area. The authors also extensively examined the health hazards, geology, physico–chemical properties as well as sources of Uranium. This is an excellent study, which outlines the theoretical aspects of Uranium migration in the sub-surface as well as deposition of the aforementioned elements. Thereafter, we have thoroughly examined all the aforementioned data relating to the occurrence of radioactivity within the Karoo. We have concluded that the overall water quality is poor, with most of the datasets showing TDS concentrations above the allowable limit of 450 mg L^{-1}. Despite this fact it has been shown, by means of historic data sets, that the levels of Uranium in the groundwater were generally acceptable.

Field work design

Previous reports as well as maps of the area were consulted in order to determine the boundaries of the study area (Figure 1). The geology and hydrogeology were carefully examined to properly understand groundwater flow. Lastly, boreholes in the vicinity of known Uranium deposits were earmarked for radioactivity sampling.

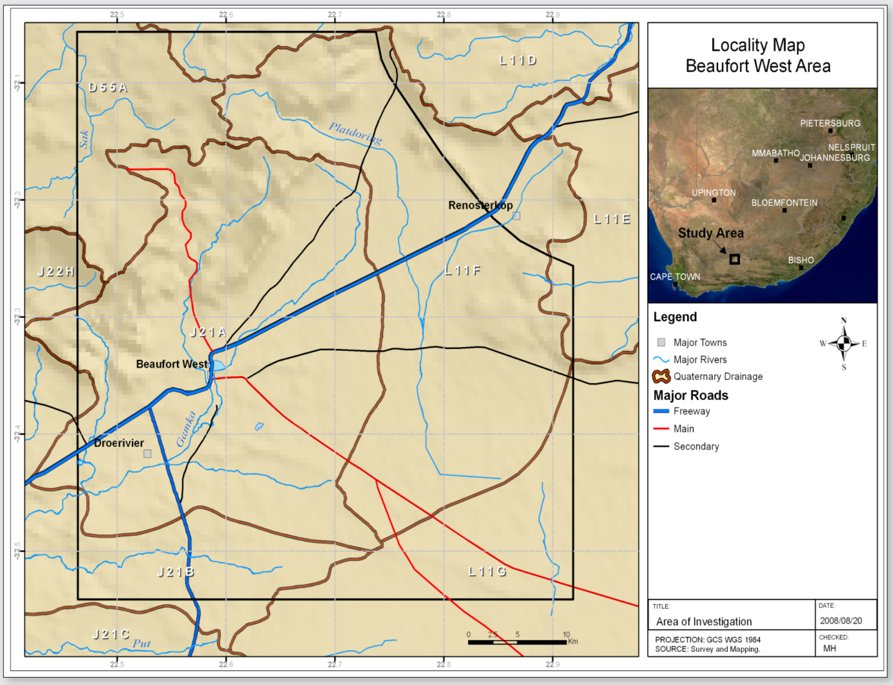

Figure 1. The study area, which is in the vicinity of the Karoo town of Beaufort West.

Sampling

The sites, which are located within the vicinity of the town of Beaufort West, were visited in order to carry out a groundwater sampling exercise. The proposed methodology for sampling radioactive elements was in line with that of heavy metals, as shown below.[13]

The samples were filtered through 0.45 µm filter paper and placed in HDPE sample bottles. The sample which was to be analysed for heavy metals was filtered into a 250-mL plastic bottle and spiked with 10% HNO_3, in order to prevent the heavy metals from precipitating. The radioactive sample, which was filtered into a 5-litre bottle, was also spiked with 10% HNO_3. These radioactive samples were then placed in a cooler box and promptly sent to the laboratory at NECSA for analysis.

In the case of windmills, the sample was taken as close to the outlet pipe as possible. Furthermore, it was assumed that the hole was purged due to the fact that the wind powered pump ran the whole day. With the pumps on the other hand, we find that they are permanently installed, thus making it difficult to determine the depth of the hole as well as the static water level. Therefore, these pumps were allowed to run for a few minutes before being sampled. In many cases the pumps were run prior to the arrival of the team on-site.

Protocol development

Prior to venturing into the field for sampling, a draft sampling protocol was developed in order fully to understand processes and applications which should be implemented for sampling. This process was completed by assessing all the best practices from across the globe, as well as in South Africa, and outlining possible options.

Upon returning from the field, an entire new outlook was required due to the fact that certain applications were not suited for local conditions. Therefore, the protocol was re-evaluated and then refined in order to be more locally applicable and relevant.

Study area

The study area is located in the vicinity of the town of Beaufort West (Figure 1), which lies at approximately 930 m above sea level.[18] At this altitude the majority of the precipitation occurs during the summer months due to a high pressure system dominating the inflow of moisture-filled air into the escarpment.[19] Average precipitation in the vicinity of the town is 235 mm per annum.[20]

The area itself is fairly flat with scattered mesa's and butte's predominating as one draws closer to the Nuweveld mountains in the north, which basically controls groundwater recharge in the area. The major bush types populating the barren soils have been classified by Acocks[21] as being False Karoo and Karroid Bushveld. Furthermore, cattle farming seems to be the dominant agricultural activity with sheep and cows being the major livestock. Satellite imagery has also shown that certain plots of land are also being cultivated along the Gamka, Hans and Kwagga rivers to the south of Beaufort West. The Game reserve, which is located in close proximity to the town, also houses varieties of buck and wildlife.

Hydrogeology

Woodford and Chevallier[4] have extensively examined the hydrogeology in the vicinity of the study area, on a macro scale by means of GIS. The remote sensing methods used to map the dolerite dykes has shown the extent to which these structures impact the landscape. The dykes and sills are major geological features caused by the upwelling of magma. The magma in turn solidifies and causes an impermeable barrier, vertical or horizontal in nature, as well as fracturing in the host rock.

With regards to the town of Beaufort West, we find numerous hydrogeological reports assessing the well fields, which are located north of the town (Figure 1) for municipal supply. Those reports up until 1980 have been compiled and assessed.[22] Kotze *et al.*[20] have utilised this data and shown short-term water level fluctuations in the municipal well fields, but there is a definite decline in water levels in general.[23]

Vogel *et al.*[8] also proved that localised recharge, which is the addition of water to groundwater, occurs in the immediate vicinity of the town. Rose and Conrad[24]concur with this and prove conclusively, by means of isotopic analysis, that surface water and groundwater supplies are not linked. Furthermore, groundwater to the south of the town is more saline than the groundwater in the well fields to the north.[8] This also suggests that the two groundwater systems are separated by the town dyke.

More recently, Nhleko and Dondo[25] looked at regional flow of groundwater in the vicinity of the town of Beaufort West. Correlations of geological logs, digital elevation models and three-dimensional cross-sections were all utilised in order to understand the hydrogeological setting of these three aquifers. The study highlighted the fact that groundwater resources in the area are slowly depleting and more research is required in order to fully understand the aquifers and thus maximise their use.[25] It was also shown that flow is generally in a southerly direction and that both the town dyke and Hansriver dyke in the area appear to act as flow barriers to groundwater, which compartmentalises the groundwater dynamics into north, middle and south regions. Moreover, the three compartments are linked by the Gamka River and its tributaries which overflow the dykes. Nhleko and Ndondo[25] also suggested that all the data for boreholes should be captured, specifically water strikes, as this plays a major role in determining which aquifers are being intersected as well as their yield.

Results

The results from the radioactivity analysis do not highlight any anomalous points of interest (Table 1). Steenrotsfontein's higher radioactivity values could be attributed to the fact that the sample is located within a region of anomalously higher Uranium. These values should have been expected considering the fact that the majority of the previously mentioned hydrogeochemical data sets allude to this.[16] Furthermore, it has been shown that the uranium deposits are of a "marginal" grade and this must be the reason for the minimal amounts of Uranium being liberated into the groundwater.[15]

The concurrence with previous data sets proves that the methods of sampling and analysis used in the field are acceptable for radioactivity sampling and could be used for further studies.

Table 1. Radioactivity results stemming from the study area (values in $\mathrm{mBq\,L^{-1}}$).

	Radioactive elements tested for in sample										
Sample name	^{238}U	^{234}U	^{230}Th	^{226}Ra	^{210}Po	^{235}U	^{227}Th	^{223}Ra	^{232}Th	^{228}Th	^{224}Ra
Steenrotsfontein	641	1380	15.1	12.9	4.86	29.5	6.79	10.9	2.3	13.9	6.94
Town Spring	184	465	7.9	1.6	5.68	8.49	7.3	4.85	2.83	3.9	1.6
Blydskap 1	123	554	7.9	9.49	6.56	5.68	2	–1	1.3	1.8	3.18
Blydskap 2	158	584	6.3	16.4	6.91	7.3	2.4	–1.5	0.81	2.2	1.5
Scheurfontein	135	380	6.8	6.07	0.98	6.51	2.5	0.47	1.27	0.42	0.68

Sampling protocol

The protocol was developed using the inputs from the methods previously outlined. Furthermore, the results from the field sampling exercise played a major role in interpreting and understanding the possible application of the protocol within a South African context. The most important aspects of the protocol are outlined below in order to showcase its efficacy. The entire protocol can be examined in Xu *et al.*[14]

Screening methods used to determine radioactivity in fractured rock aquifers

These methods make use of the detection of Radon gas in order to ascertain whether the groundwater is radioactive. This aids in determining whether a sample should be sent for further laboratory analysis for radionuclides. Thus costs could be minimised and no unnecessary work is done. The screening methods also give the individual an opportunity carry out *in situ* analysis and thus reduce the probability of incorrect sample analysis, due to prolonged storage periods, degassing or transportation. Some of the most commonly used methods are:

- Alpha Card Method
- Alpha scintillation counting
- Electret Ion Chamber (EIC)
- Liquid scintillation counting (LSC)

Zhou *et al.*[26] made use of alpha scintillation counting in conjunction with a Radon bubbler. Thus the gas was stripped from the groundwater sample by the bubbler and an alpha counter was used to determine the Radon concentration. This seems to be an effective combination of two methods.

Lin[27] has utilised the alpha card method in the Table Mountain Group, South Africa. Wu *et al.*[28] extensively explain the field operation procedure of the aforementioned machinery. It works on the principle of stripping the Radon gas from the vadose zone gas, the equipment is also able to bubble the Radon gas out of water. The emanating gas is then measured in a gas proportional counter. Lin[27] states that the count is termed pulse number in the alpha card instrument, from which the concentration of the radon gas can be estimated by means of the following equation:

$$C_{\mathrm{Rn}} = JN_{\mathrm{RaA}}$$

where C_{Rn} is the concentration of Radon, N_{RaA} is the pulse number measures and J is the coefficient of the Radon concentration which is a constant and is fixed by the measuring equipment.

Amrani *et al.*[29] have compared the LSC and EIC methods. The former method measures the Radon concentration in units per time. Thus a conversion is required in order to acquire the reading in Bq L^{-1}. The latter measures voltage and then the original Radon concentration in the water is inferred. The LSC method allows the equilibration of the Radon gas into an organic "cocktail", whilst the EIC allows the Radon to enter a chamber by passive diffusion.

Pre-sampling procedures

Weaver *et al.*[13] outlines a comprehensive planning programme which delves into pre-sampling procedures. This includes a list of field equipment and general groundwater sampling procedures. These practical tips are of the utmost importance when preparing to venture into the field.

Another important aspect is acquiring permission from land owners. In many instances, boreholes are located on private property and it is crucial that farmers or landowners are consulted prior to sampling. This process is also helpful in the hydrocensus, which is the initial phase of data collection, due to the fact that the land owner could provide valuable information with regards to numerous environmental factors in the area as well as history, and the location of wells and springs.

Last, it is necessary to liaise with the laboratory in order to ascertain which containers, preservatives and reagents are to be used when sampling for radionuclides.[13] Wilde *et al.*[30] suggest that a 1-L polyethelyne bottle be acid rinsed and then the sample should be preserved to pH < 2 using HNO_3. Levin,[31] on the other hand, states that sample bottles should be thoroughly rinsed with 10% HCl and then emptied and rinsed thrice with de-ionised water.

Previously used bottles should be rinsed with acid and soaked in de-ionised water for a few days before sampling.[13] New sample bottles, on the other hand, should be field rinsed with water directly from the sampling device.[30] Finally, the sample bottle should preferably be plastic, due to the fact that glass could break and thus leakage would occur and therefore sample integrity would be questionable.[31]

Downhole logging

Prior to purging it is suggested that downhole logging is done. This will help to identify fractures within the sub-surface.[3] Anomalous increases in certain parameters infer the location of a fracture within the borehole. This would only occur if the well is screened at various intervals, or is entirely uncased. Furthermore, various *in situ* parameters such as temperature, pH, electrical conductivity, dissolved oxygen as well as some dissolved ion concentration could be determined in the borehole, depending on the type of logging tool used.[13]

Purging

Before taking a sample, the well should be purged. This is done in order to remove the stagnant water. Cook[3] has compared sampling prior to purging as well as post purging. The author has concluded that the Radon concentration within the well varies greatly due to the ability of the gas to diffuse. Thus a sample taken from an unpurged well would not be representative of *in situ* conditions of the aquifer. This is especially true in fractured rock aquifers due to preferential pathways (Figure 2).

Also the well should be purged using a low flow approach.[32] This minimises the oxidation of the sample and thus the alteration of *in situ* chemical conditions. After the borehole has been purged the fractures would then be de-watered, followed by the matrix.[3] This has important implications for chemical analysis as the conditions within a fracture differ to those of the matrix. It is especially important with regards to radionuclides due to the fact that we find an increase in Radon within these fractures.[33] Cook[3] has shown that the volume of water which should be purged must equate to two well volumes. It is critical to note that low flow sampling does not equate to purging.[13]

After purging the well, the use of a flow-through cell would be advised. This is done in order not to expose the sample to the atmosphere and thus alter its chemical or physical state.[13] The flow-through cell seems to be the best tool for direct field measurements, due to the ability of the device to measure multiple parameters.[30] When taking the sample the utmost care should be taken in order not to contaminate the sample.

Some parameters are measured in the field for the following reasons:[13]

- to check the efficiency of purging
- to obtain reliable values of those measurements that will change in the bottles during transport to the laboratory
- to obtain some values that may be needed to decide on the procedure or sampling sequence immediately during the sampling run

The parameters which are normally taken *in situ* include pH, Eh, temperature and electrical conductivity.

Sampling devices

It is also of the utmost importance that the acquired sample is representative of the *in situ* conditions.[30] Thus the devices used in order to sample the groundwater are very important.

Puls and Barcelona[32] strongly recommend that low flow sampling, in conjunction with packers, should be carried out in fractured rock aquifers. This approach should only be attempted after identifying the water bearing fractures and thus the sampling zone can be isolated.

Depth specific samplers have also been proposed as a viable option.[13] These are lowered into the borehole in order to gain a sample at the fracture or other area of interest. Unfortunately, this method could artificially elevate turbidity in the well due to it disturbing the water while it is submerged.[34]

A relatively new method for sampling is known as Diffusive Gradient in Thin Films (DGT). These are based on the use of a

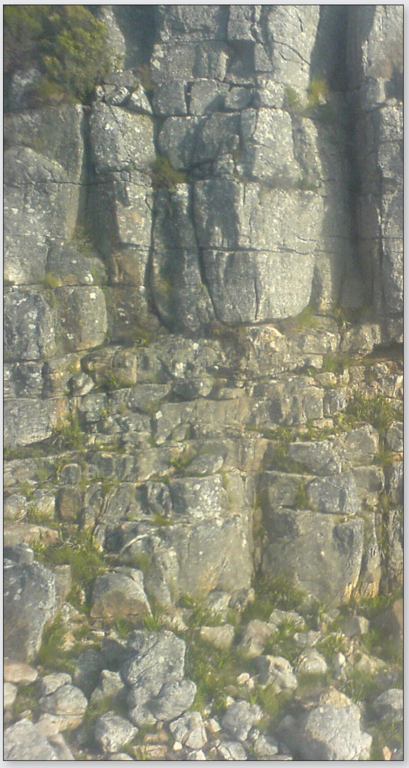

Figure 2. Vertical and horizontal fractures in sedimentary rocks act as preferential pathways for groundwater recharge and flow.

chelator, which is an iron binding complex, in order to sample metals over a time period of a few days. Numerous case studies have been outlined and these show the applicability as well as the functioning of this specific method.[35] Furthermore, a phosphate-based DGT has been developed specifically for radioactive elements.

Sampling frequency

EPA[36] promotes the hourly sampling of fractured aquifers for field determinands. This protocol was developed specifically for nuclear waste facilities and the parameters which would be measured on an hourly basis would include those which a data logger could determine. These include temperature, TDS and water level. This would aid in determining whether leakage has occurred from the storage facility and also aid in determining anomalous inflows of contaminants in groundwater, in a natural setting. The aforementioned could be inferred from fluctuations in readings and the parameters would act as indicators for the contamination of groundwater.

A statistical analysis could also be done in order to effectively ascertain sampling frequency. This would mean that a substantial amount of data would be required and it would have to stem from the area of interest. As a crude guideline you need about five samples from groundwater source with seasonal variation to indicate variability.[37]

The purpose of trend analysis, in statistical terms, is a determination of whether the probability distribution from a series of observations has changed over time.[38] The simplest statistical method which could be used to ascertain this variability would have to be based on historical data, as previously mentioned.[39]

The theory of sampling applied

Petersen *et al.*[40] has extensively examined the Theory of Sampling (TOS) in relation to data analysis and unbiased results. Helsel and Hirsch[38] have highlighted the use of statistical methods in order to examine data, graphically represent data and include aspects of quality control of data for error mitigation in interpretation. The latter text was included in the protocol whereas the former was unfortunately not.

The TOS, as a science, could add an extensive value to this protocol. It is felt that the major point being driven home by Petersen *et al.*[40] is the fact that the quality control of a sample is the responsibility of everyone within the entire analytical chain. This point is taken quite lightly in sampling for groundwater due to the fact that certain laboratories are negligent of cross-contamination and sample storage. This in turn has an adverse effect on sample integrity and in turn the results. This is known as the Increment Preparation (IPE) error in TOS and includes every step after extraction.

The Fundamental Sampling Error (FSE) as well as Grouping and Segregation Error (GSE) are common, especially in the hydrological sciences. It has been shown that *in situ* practices, especially in surface water, still advocate grab samples which are in no way representative of the lot.[41]

Conclusions

A groundwater sampling protocol for radioactive elements in fractured rocks, which was developed using international best practices as well as local methodologies, proves that previously utilised methods are extremely effective. This protocol covers a wide range of methods for pre-sampling, sampling and post-sampling processes. Historical data in conjunction with the newly generated data set, stemming from this study, conclusively prove that the methods outlined by Weaver *at al.*[13] for sampling radioactive elements are applicable to fractured rocks.

Unfortunately, due to limited infrastructure as well as field conditions, not all the methods outlined in the protocol could be tested. Therefore, it is suggested that the other methods outlined in the document should be applied in the field and the efficacy thereof should be scrutinised in future studies. A methodology for this could be utlilising multiple methods, like low flow sampling as well depth specific sampling on a single well and then comparing the results in order to check whether the radioactivity results are similar.[32,8]

TOS should also be applied to the development of future manuals in order to align sampling in the hydrological sciences with sampling as a science. Petersen *et al.*[40] have shown that sampling as a science is still developing due to the fact that it is merely 50-years old. In order to better the science geostatistical applications such as variographic analysis of time series type data, which is a practical tool for optimising the sampling frequency of heterogeneous sampling targets and could be applied in future studies.[4]

The exercise was also hindered by the fact that many mines have bought prospecting rights from farmers in the area. Thus farms which are currently being explored for uranium could not be accessed for research purposes. Despite this, a framework for a sampling protocol was developed in order to aid in better sampling practices.

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TOS: Progress through continuity and community

Francis Pitard, Kim H. Esbensen and Claudia Paoletti

Dominique François-Bongarçon's piece in *TOS forum* issue 3 offered a clear view of the status of the TOS community, summarising where our present knowledge stands, how it is applied today and the challenges ahead. Here we want to continue this effort and share our considerations on how we can go from former knowledge, tradition, to new knowledge and scientific development, without fear of progress and innovation. We also reflect on some more worrisome experiences from the world community of samplers, our scientific duties and on the problem of individualistic pursuits.

World Conference of Sampling and Blending—a resounding success

For the 12 years WCSB has been in existence, there is absolutely no doubt that these events have been beneficial to TOS and its practitioners in many ways:

- Through six WCSB conferences samplers finally had ample opportunities to meet and discuss with each other, creating an intellectually fertile context where new ideas and projects started to develop naturally.
- The WCSB has offered, and continues to offer, the future generation of sampling practitioners, educators and experts a rich training environment to learn, grow and challenge ideas; thus, creating a framework to ensure the future of the TOS community.
- The full spectrum from the academic community to industry and equipment manufacturers are pleased and have gained respect for this forum, its activities and the very relaxed form of communication that allows direct and efficient problem solving.
- Through WCSB the world's top experts in sampling today know each other much better, and rely on a biannual opportunity to share knowledge and experiences according to the fundamental principles of scientific discourse: open and honest dialog, where also disagreement can be constructively addressed.

All is not just good, however

Thus, there is one delicate issue that needs attention: respect for former knowledge. If, today, knowledge from the past may appear less relevant (and perhaps even obsolete), its historical context was never-the-less fully correct for its time, and it provided the necessary foundation to achieve what we have today. This is no different than what we are doing today; constructing the basis for tomorrow's progress that includes new ways of understanding and using former and historical knowledge. Such knowledge, even if applied in ways that are now no longer frontline, should not be forgotten in the light of today's progress. It is of essential value precisely because it reflects the past intellectual achievements and provides a snap-shot of what was available at a certain point in time, when it represented the best guidelines available to the sampling community. It would be unfair to judge such knowledge only in today's timeframe—just as it would be unfair not to acknowledge that inevitably over the course of time new knowledge arises, opening novel scenarios for the theory and practice of TOS.

Our mission here is to call attention to this mature view of scientific progress in the light of certain occurrences of personal grandstanding observed at several of the recent WCSB conferences as well as behind the lines of our everyday work.

As is the case with history, different approaches can be taken when confronting scientific progress:

1) *The former knowledge and the way it was applied gets completely dismissed*—in the fashion: "Get this old work out of the way, my new approach is far superior (and I am the only one who knows what I am talking about)". This is a destructive approach, a favourite of egocentrics, never leading to real progress for a scientific community, unless we are talking of a true paradigm shift. Former knowledge was novel at its time and many practitioners in industry could solve their problems in a reasonable way—because there was indeed *some merit* in the ways things were done earlier. As a prominent example of what we are pointing to, take Pierre Gy's rudimentary, graphical variographic analysis of processes for which we will borrow our late friend Pedro Carrasco's words: "*Since we expanded the use of the variogram to study process variability, as suggested by TOS, we made significant progress understanding different sources of variability. Now we are in a much better position to effectively control our processes from rock to cathodes*." As a matter of fact, Pedro Carrasco had plenty of extremely successful economic case studies demonstrating his conclusions. So does, for example, Hilde Tellesbø (Weber Saint-Gobain) and very many others (see the entire set of WCSB Proceedings), who have presented many practical TOS applications at all levels of complexity for specific process industries with equally important results for efficiency, economic profitability—or for the pure satisfaction of engineering solutions to problems that could not even be identified before the first application of variographic analysis. Whether these applications are simple or complex does not matter. Today's deeper understandings are just as much a consequence of the intellectual path defined both by such applications as well as new, impressive theoretical developments. The point is that our community grows in scientific maturity only because of such *continuity* between former and present knowledge: *continuity* between theory and practice.

2) *The former knowledge and the way it was applied is considered as a vehicle for establishing a new way*. This is precisely what was attempted (perhaps in an imperfect way …history will judge) when the 2009 doctoral thesis by Francis Pitard made an attempt to reconcile Gy's TOS with Visman and Ingamells' works. At first glance, many were of the opinion that either the one or the other, but not both, could be integrated with TOS. However, this first reaction could not be farther from the truth, because the in-depth analysis presented actually showed not only many similarities, but also several complementary ideas that actually came to fit one another quite well.

We firmly believe, as demonstrated over and again by the history of science, that all progress is rooted in past experiences. Therefore our emerging scientific community must be able to acknowledge established knowledge and constructively build on it—without blasting away everything that is “former”.

Another challenge we are facing today within TOS is effective communication to the outside world. During the past two decades, TOS has transgressed several scientific boundaries and its applicability is now discussed, albeit not universally implemented, in several disciplines that were not on the agenda when TOS originated, but where sampling plays a definitive role never-the-less: chemistry, agriculture, food and feed safety, a continuing spread of process industries, the geo-and environmental sciences, international trade… We like the phrase “in science, technology and industry”, because it is difficult to consider much valid activity across all of this realm without some basis in proper sampling.

But it is a fact that the dialogue with other communities has not always been easy, effective and smooth—in fact surprisingly often the contrary. Why? Terminology has something to do with this—it must be admitted that some of the terms used in TOS have not always been well understood nor well received in several other important fields (see further below). The lack of universal terminology for sampling leads to the perception (valid, fair or *not*) that TOS was a creation understandable only by experts from the sampling realm. Obviously this situation is beneficial to nobody’s interest. Fruitful developments and endurable progresses, in TOS and beyond, can only be achieved if we continuously improve our communication, if we strive to develop a common language,[a] [[a]For example JOAOC Special Guest Editor Section (see page 12 in this issue).] and if we are open for and welcome samplers from all other disciplines and traditions who can in fact challenge and enrich us by broadening TOS’ application fields. Indeed, this objective was one of the main drivers behind the development the world’s first horizontal sampling standard, DS 3077 (2013).[1]

The TOS vs MU debacle

Esbensen and Wagner[2] presented an in-depth analysis of the complex Measurement Uncertainty (MU) concepts, ending in a call for reconciliation between TOS and MU. Here is the essence of their critical analysis: Figure 1 (right panel) shows a standard “fishbone diagram” depicting the full complement of uncertainty sources of an analytical measurement process. Note that all uncertainty sources connected to sampling, i.e. both sample extraction and those preparation stages involving sampling, are disregarded. It is conveniently *assumed* that the analytical sample, which ends up as the test portion, has been extracted and mass reduced in a representative fashion. How nice this would be, as long as somebody was responsible! But who? Remarkably, every time the procedures to obtain the test portion in any type of analysis were investigated, it was realised how the responsibility to ensure representativeness was simply missing. Alas, as everybody in the TOS community knows only too well, if the appropriate TOS approaches have not been involved, the resulting uncertainty estimate of the analyte concentration of the test portion is of little value as it unavoidably will be too small to an unknown, but significant, degree. It is structurally flawed and *invalid* as a proper fit-for-purpose MU estimate. This state of affairs was understandably criticised by the authors.[2,3]

It is necessary to add-in the effects related to all preceding sampling stages. This can in fact be done easily and in a perfectly seamless fashion; furthermore, there is no need to change anything regarding $\mathrm{MU}_{\mathrm{analysis}}$, because the $\mathrm{MU}_{\mathrm{sampling}}$ framework is supplied by TOS. It simply falls to TOS to be responsible for delivering the analytical aliquot for a proper $\mathrm{MU}_{\mathrm{analysis}}$ estimation. Which is why many from our community are involved in education enterprises with this and related objectives. Who could possibly object to that? Well, many… it turns out.

Sometimes an outreached hand is not respected

Here follow two citations from a review of the work that eventually was published by Esbensen & Wagner.[2] For readers of this forum there is no need to comment, the citations speak loudly for themselves about the attitude one may experience directed towards TOS specifically and our community’s efforts in general.[b] [[b]There is more documentation, but for here these two citations will suffice; a full account of this unilateral unfriendliness can be found in Appendix 7 in Wagner (2013)[4]]

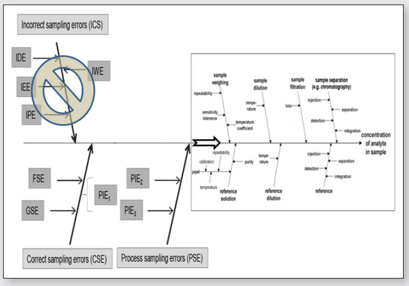
“…there is no need for reconciliation between these two issues, but if this is needed it cannot be done as suggested by the authors by amending a fishbone diagram for the estimation of MU with error terms from TOS that largely are not amenable to quantification, but—as the authors contend themselves—have to be eliminated first.”

“Something that must be regarded very strange is the frequent reference to VIM and the VIM-defying language such as “incorrect sampling errors” and “correct sampling errors”: there is no such distinction in metrology, but it presumably dates back to the times when Pierre Gy made up English expressions for his lack of command of this language, a fact he never attempted to deny in personal contact. Nobody has ever come across a “correct error”, but it may be argued that this is a way for TOS freaks to avoid introduction of the notion of random and systematic effects/errors in sampling. Why this is so—except as a reverence for Gy—is completely in the dark.”

“TOS freaks”—indeed.

While these, and similar, transgressions of proper reviewer decorum were duly debunked, and the journal allowing such reviewing left with significantly reduced credibility, the present authors are saddened by such unprofessional, hostile attitude representing a top reviewer from within the MU community. We have at several occasions made a deliberate outreach to this community—alas, mostly with similar results as evidenced above. We shall nevertheless continue to do so on behalf of all of the TOS community. The worrying issues here are both the arrogance (which we must assume is rather a personal, not an institutional character trait) as well as the distinct unwillingness to address sampling issues in a scientific way, first and foremost in the form of how to deal comprehensibly and effectively with *heterogeneity* in all its myriads of manifestations.

Why is this? Most likely because ensuring representative sampling is considered so



The standard analytical fishbone diagram with conventional MU measurement uncertainty sources (right panel) with preceding TOS uncertainty sources (right panel), see Esbensen and Wagner[1] for details.

"difficult" that is preferable to ignore the problem rather than facing it. Our TOS community has a specific responsibility in this context and must devote significant resources to reach out the samplers outside the present community to offer didactic solutions directly oriented towards the specific sampling needs of various disciplines, and to continue to enlarge and enrich the educational literature on TOS—not that there is any lack hereof, witness our plentiful literature.

What can be learned from the above? There is still a vast, largely ungrateful task ahead of us in communicating our science beyond current boundaries. Our energies should converge and complement each other in this mission—and various types of lament sometimes expressed *sotto voce* at conferences, for example, regarding worries for "broadening out beyond mining" is only going to slow down not only the fulfilment of our joint scientific responsibility, but also TOS' scientific progress in general.

LinkedIn sampling discussion groups and Wikipedia

Recently, we were struck by a saddening and difficult-to-gasp attitude in the business social medium, LinkedIn. Here one finds many discussion groups overwhelmingly most of which of very high value, in which discussions are usually held in a proper tone and format; but there are also many fora here, which mainly seem to exist only to create a sounding board for *opinionating* (no further comments needed).

However, we were blown away by one discussion group with a particularly interestingly title: "Theory of Sampling"—with more than 2500 members. The discussion strand referred to below has 45 entries; if you spend 30 minutes here—and we really recommend this—it gives an incredible insight into the kind of discussions the present opinion is directed at. There is so much animosity lack of respect for the historical TOS, indeed often a lack of even the most fundamental of understanding, that it a.o. provoked an entry of our own:

> "*I found some time to get a jour with the various discussions on sampling in the LinkedIn forum during the holiday season just concluded. I was taken aback with the willingness to join the Pierre Gy-bashing crowd in this particular discussion strand. Sadly I found very little in the way of a comprehensive understanding of the tenets of the Theory of sampling (TOS), Gy. Instead all manner of substitute justifications for not being willing to do the work needed in getting a full understanding of all the elements in TOS. Since Geoff Lyman has been one of the pivoting centers in this discussion, I would like to direct attention to a joint work recently addressing much of the kind of 'critiques' as is leveled in this discussion, which is published in* TOS forum*, No. 1 (p. 28–31) http://www.impublications.com/tos-forum. Observe here a very different, open attitude regarding what constitute scientifically legitimate ways to critizise TOS.*"

We encourage *TOS forum* readers to find time to peruse this discussion, which you'll find here: http://linkd.in/1N70ytB

Where do we go from here?

Before answering this question, we need to take a decision. Scientific progress happens, it is unavoidable. This is embedded in the nature of *Homo sapiens*. Experienced/senior scientists can either choose to focus inward and draw themselves into an easy comfort zone relying exclusively on secure and already established developments, or to constantly welcome new challenges, being willing to risk one's comfort zones with the humble attitude that learning and developing is a life-long quest. The latter are typically the same scientists demonstrating knowledge of, and encouraging respect for "former knowledge", because they are well aware of being a part of a broader path that was there before them and that will also be there after them. A successful and scientific challenging future of TOS can only rely on such attitudes.

After 12 years of ever-increasing positive development for our community, signs are beginning to crop up of a more-or-less frantic search for "alternatives" to TOS, including grave examples of declarations that TOS is wrong because it is not founded on conventional statistics—or, slightly more on the less dangerous side, that "TOS is too difficult to be practical". A full confrontation of such claims is beyond our limits in this opinion piece, but certainly within the possibilities of further debate in *TOS forum*. And real scientific progress will never happen on a basis of fear of complexity.

We should always be ready to listen and to accept challenges to TOS, but only on the basis of documentable, scientific argumentations. Conventional statistics is a good example of a complacent comfort zone, difficult to leave perhaps because it offers the certainty of a very well-developed theory of universal fixture: what is the first course in any natural science, technological or engineering curriculum at university? Statistics 101. We do not criticise this state of affairs—but we do point out that heterogeneity is not well covered with standard statistical distributions. Heterogeneity is, uncomfortably for some, more complex than this—this may be an inconvenient truth, but not one our community should shy away from.

At the microscopic level, from our own little circles, we find the evergreen discussion on the apparently unending intricacies involved in the famous "Pierre Gy's formula" which seems never to die—and the number of extreme *abuses* of this formula are legion, if for nothing else because people who apply it right away have not invested even a modicum of the effort needed to understand it historicity, and its very clear application limits. Limits which very easily are pointed in poignant examples of contemporary critiques of TOS, but which are to be found self-claimed in the pertinent historical literature. Also here one finds more discord, in-fight and divisiveness than a constructive, joint enquiry.

There are thus a growing number of reasons to worry that as a community we are not completely up to the task of stewarding the development of TOS as a joint undertaking. WCSB7 in Bordeaux is our next opportunity to contribute jointly to TOS' development and future. Let us focus on a journey made together in full respect of past, present and future work and contributions by our entire community, equally welcoming the full historical view as well with complete openness to all new developments and challenges.

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The application of an integrated software library for controlling and monitoring ISO sampling systems

C S W Adams[a] and T T Neidel[b]
[a]Senior Technical Advisor, FLSmidth Pty Limited, 58-60 Dowd Street, 6106 Welshpool WA Australia.
E-mail: craig.adams@flsmidth.com
[b]Engineering Manager, FLSmidth Pty Limited, 58-60 Dowd Street, 6106 Welshpool WA Australia. E-mail: tore.neidel@flsmidth.com

There exists an industry need for an integrated system to monitor and control ISO compliant sample stations. This paper discusses the development and application of a control system toolbox to deliver complete ISO compliant functionality.

Traditionally automated sampling systems have often relied on generic equipment control standards to operate individual sampling components. The design of the sampling equipment in these systems may comply with ISO requirements but does the complete integrated system meet these same conditions?

The development of a software library that integrates ISO sampling standard requirements with customised equipment control units via a supervisory control module bridges this gap.

The application of standardised libraries, based on over 30 years of combined sampling, electrical and control engineering experience, has led to the seamless integration of standalone sampling devices into ISO compliant sampling systems. All components have well-defined interfaces, common functional control and reporting mechanisms. The result is a fully integrated sample station that performs as a cohesive quality system which harmonises with appropriate ISO standards.

The benefit of a standardised and integrated sample station is the consistent production of reliable and accurate results. Trustworthy sample data gives QA analysts, technicians and plant management a high degree of confidence that they have a full understanding of their material's properties and commercial worth.

Confidence in sampling results is essential as the quality of the material is inexorably linked to a company's reputation as a reliable supplier of quality products and, ultimately, to their bottom line.

Blast hole sampling in two areas of the same deposit

Marco Alfaro
Head of Civil Mining Engineering, Catholic University of Valparaíso, Chile. E–mail: marco.alfaro@ucv.cl

The Rio Blanco ore deposit is a porphyry copper, located in the central zone of Chile, it is a planetary anomaly of copper and molybdenum. It contains resources identified in 20,000 million tonnes at 0.59% Cu and 0.016% Mo.

The deposit is divided in two zones exploited through open pit mining by two different companies, Codelco (Andina) and Anglo American (Los Bronces). In Andina and Los Bronces the blast hole grade is essential for mine planning. Each company has its own method for blast hole sampling.

This paper numerically compared and analyzes the blast hole sampling results in the two areas of the deposit, using as reference the grade of diamond drill holes composites for copper, molybdenum and arsenic.

Iron ore ROM sampling

Juvenal Barbosa, Louise C Cinquini and Luana L Pacheco
Mariana Mine

This study aims to evaluate bias and precision errors of the sampling process of ROM (Run-Of-Mine) from three pits of iron ore located in Minas Gerais, Brazil, Alegria Mine Complex. Firstly, during formation of ROM piles, it was done a manual sampling by little scoop (flatted with 5x5cm) inside a truck with about 140 tons. It was collected an increment for each twenty trucks during a period of 6 hours. During same period, about 120 trucks dump ore to compose piles that feed two ore dressing installations. Then, three increments with about 2kg each one were collect as a sample by installation. The partial results from piles formation are used to measure adherence of piles 'programming based on the geological model in order to achieve the specifications of process and product.Actually the results have shown a difference about 0.5% for monthly mean iron ore content (absolute error regarding a 90% confidence interval).To estimate the bias due to the finer material losing were collected two samples with about 5 kg each increment in the piles dumped by the trucks for each twenty trips along six hours. During a month it was evaluated the error associated to the sample pairs (A= originals x B= duplicates) collected in different depths of the piles by a backhoe. One pair of duplicates was collected during six hours and forty during a month to supply information about accuracy of the method.

Evaluating Gy's formula accuracy for bauxite

Daniel Armelim Bortoleto,[a] Ana Carolina Chieregati[b] and Raiza Cavalcante de Oliveira[c]
[a]Process Supervisor, Alcoa World Alumina, Juruti, Pará, Brazil.
E-mail: daniel.bortoleto@alcoa.com.br
[b]Professor, Department of Mining and Petroleum Engineering, University of São Paulo, São Paulo, Brazil.
E-mail: ana.chieregati@gmail.com
[c]Mine Engineering, University of São Paulo, Brazil.
E-mail: raiza_cavalcanti@hotmail.com

Quality control in the mining industry context is directed to the extraction of natural resources with reliability, effectiveness and minimum cost. The understanding and application of the Theory of Sampling (TOS), developed by Pierre Gy, integrated with process management, is essential for reaching this objective. Samples will never present exactly the same characteristics of the lot from which they are selected because of the constitutional heterogeneity, which generates the fundamental sampling error. Each stage of the sampling process produces an error which must be known for determining the reliability of the estimates. In this context, the heterogeneity tests are an essential tool for knowing the natural variability of the deposit, and to conduct sampling in a correct way in order to generate representative samples. The present work studies the heterogeneity of a Brazilian aluminum ore and compares the results obtained from Gy's formula calibrated by the heterogeneity test with the ones obtained from the formula using the factors for bauxite, i.e. shape, mineralogical, liberation and granulometric factors. Results validate the factors proposed by Pierre Gy for this particular Brazilian bauxite.

Relative efficiency of four common splitting procedures for bauxite

Daniel Armelim Bortoleto,[a] Ana Carolina Chieregati,[b] Antonio Henrique Rietra Pereira,[c] and Raiza Cavalcante de Oliveira[d]
[a]Process Engineer, Alcoa World Alumina
E-mail: daniel.bortoleto@alcoa.com.br
[b]Professor, University of São Paulo (USP)
E-mail: ana.chieregati@gmail.com
[c]Technical Manager, Alcoa World Alumina
E-mail: antonio.h.pereira@alcoa.com.br
[d]Production Supervisor, Alcoa World Alumina
E-mail: raiza.oliveira@alcoa.com.br

According to Pierre Gy, all components of the overall sampling error result from the existence of one form or another of heterogeneity. The reliability of analytical results is often affected by uncontrolled sampling errors that result from the constitutional and the distributional heterogeneity, associated to the fundamental sampling error and the grouping segregation error, respectively. As a consequence, the probability of obtaining a sample which perfectly represents the parent distribution is remote. In addition, it is very rare for reduction from bulk to analytical sample to be carried out in just one operation. Laboratory assays have to be conducted using a small fraction from the whole lot. For this reason, sampling is a subject that should interest analysts, professors and students of analytical chemistry. In order to achieve the best possible mass reduction, the operator needs an appropriate technique to minimize the preparation error in the laboratory under the Theory of Sampling (TOS) sense. There are four sampling procedures commonly used for a representative mass reduction: cone and quartering; table sampling; rotating splitting and riffle splitting. This paper compares the relative efficiency of the four sampling methods using aluminum ore and presents the results in statistical terms.

The added-value of sampling

Florent Bourgeois[a] and Geoffrey J Lyman[b]
[a]Laboratoire de Génie Chimique, Université de Toulouse / Materials Sampling & Consulting, Toulouse, France
[b]Materials Sampling & Consulting, Southport, Queensland, Australia 4215

Determination of the complete sampling distribution (Lyman, 2013 & 2014), as opposed to estimation of the sampling variance only as per current sampling practice, represents a leap in sampling theory. This is the link that has been missing for sampling results to be used to their full potential for quality assurance purposes. Indeed, access to the complete sampling distribution provides opportunities to bring all the concepts and risk assessment tools from statistical process control into the production and trading of mineral commodities.

The paper will present the way by which sampling theory, via the complete sampling distribution, interfaces with statistical process control theory and practice. Illustrative examples, through calculation of operating characteristic curves in particular, will establish the causal relationship between sampling precision and quality assurance trading risks. The case will be made that the added-value of sampling lies not only for production of minerals, but also, and perhaps more significantly for commercial risk assessment and trading. The paper foresees that sampling is expected to become a real source of competitiveness, hence revenue, for mining companies.

Placer gold sampling—the overall measurement error when using gravity concentration on particle size ranges during sample treatment

Stéphane Brochot[a] and François Mounié[b]
[a]Scientific and Technical Manager, Caspeo, Orléans, France.
E-mail: s.brochot@caspeo.net
[b]Manager, IDM Guyane, Rémire Montjoly, Guyane France.
E-mail: idmguyane@hotmail.fr

Placer deposit are generally characterized by low grade of free gold. This is the case in French Guyana where the main placer deposit are in the river bed. Most of them have been already exploited by very small mining companies with sluices. If this

technology is efficient for coarse gold, it releases fine gold in the tailings. During these last years, studies have been performed on various sites and the recoveries have been estimated between 40 and 60% depending on the size distribution of gold particles and of the quality of the sluice configuration.

A lot of recent or ancient tailings are available with a non-negligible quantity of remaining gold, offering retreatment opportunities. They are generally disposed as a sand heap with the frame of a dejection cone at the discharge of the sluice. Due to the resulting large heterogeneity of distribution, it is necessary to take many samples at various locations. These samples have to be large enough to be representative of the neighbouring material. As gold is mainly liberated, traditional sample treatment with successive size reductions and sub-samplings is not efficient and can be very expensive. Another approach using sieving and gravity concentration per particle range have been preferred.

The paper, after the presentation of the sampling and measurement protocol, focuses on the calculation of the overall measurement error including sampling stages, mass measurement, and gold analysis errors. Various cases of tailings are presented for which the decision of retreatment depends on the obtained level of confidence in the estimate of the quantity of recoverable gold.

The overall measurement error – TOS and uncertainty budget in metal accounting

Stéphane Brochot
Scientific and Technical Manager, Caspeo, Orléans, France. E-mail: s.brochot@caspeo.net

Metal accounting is one of the main tools for financial and technical management of metal production industry. It is based on measurements and has to manage the uncertainty inherent to the measurement process. The uncertainty in the metal accounting generates financial risk. The accuracy of the metal accounting results is directly linked to the accuracy of the material balance and then to the accuracy of the mass and content measurements. Estimate the overall measurement error, through its probability distribution or its first and second moments (mean and variance), can contribute to the enterprise decision making.

The overall measurement error can be calculated and analysed by establishing the uncertainty budget. If this approach has been mainly introduced to calculate the analytical error (cf. ISO GUM), it has to take into account the sampling procedure. Even though it is not explicitly named “uncertainty budget”, the same approach is proposed in the Pierre Gy’s Theory Of Sampling, where the various components of the overall error are well identified and described with their properties and their relative weights.

The present paper propose a methodology to build such uncertainty budgets in the frame of the implementation of a metal accounting system. It can be applied to an existing measurement system, analysing the results in order to find some ways for improving the measurement accuracy. In addition, it can be used to define a new measurement procedure with an objective of accuracy. Various real examples illustrate both applications.

Comparing different heterogeneity tests for gold

Ana Carolina Chieregati,[a] Rafael Senefonte[a] and Thiago de Oliveira Nunan[b]
[a]Department of Mining and Petroleum Engineering, University of São Paulo, São Paulo, Brazil. E-mail: ana.chieregati@gmail.com, rafaelsenefonte00@gmail.com
[b]Mineração Serra Grande S.A., Crixás, Brazil. E-mail: tonunan@serragrande.com.br

Estimating the heterogeneity of gold ores is one of the biggest challenges for the mining engineers and geologists who work with tonnage and grade estimation. The calculation of the minimum sample mass to represent a given ore at a given comminution size is based on the estimation of the constant factor of constitutional heterogeneity, IH_L, which can be derived by different heterogeneity tests. Two tests are well known in the mining industry: the Heterogeneity Test (HT) and the Duplicate Sampling Analysis (DSA). In 2011, Minnitt, Pitard and François-Bongarçon proposed a third test named Segregation Free Analysis (SFA), where the Grouping and Segregation Error (GSE) is to be eliminated. The tests often show different results, especially when it comes to gold ores. These differences are due to many reasons, but one of the main reasons is the analysis technique chosen for gold content estimation. Other reasons include the fragmentation mechanism when generating the fractions for the heterogeneity tests and, primarily, the difficulty of collecting a representative sample for the test, especially when dealing with high cluster and nugget effect deposits. This paper analyses and compares two different heterogeneity tests – HT and SFA – and two different fragmentation mechanisms for the same gold ore. The sample was comminuted using a jaw crusher whose main fragmentation mechanism is compression, as well as using the drop weight testing device whose main fragmentation mechanism is impact. First results show the complexity of estimating the heterogeneity of gold ores and highlight the importance of using different approaches to estimate the minimum representative sample mass for gold ores.

Validation of reverse circulation drilling rig for reconciliation purposes

Ana Carolina Chieregati,[a] Thammiris Mohamad El Hajj[a] and Carla Fernanda Imoto[b]
[a]Department of Mining and Petroleum Engineering, University of São Paulo, São Paulo, Brazil. E-mail: ana.chieregati@gmail.com, thammiris.poli@usp.br
[b]MultiGeo, São Paulo, Brazil, Mining and Minerals. E-mail: carla.imoto@gmail.com

Taking representative samples of ores containing precious metals is a very difficult task. The more the grade decreases and the nugget and/or cluster effect increases, the higher the difficulty of selecting samples which are both accurate and precise. Reconciliation practices can be used as an effective tool to evaluate sampling accuracy throughout grade control processes. However, a proper reconciliation system must be based on reliable data and, therefore, the optimisation of sampling techniques is a must for the development of a reliable reconciliation system. This paper is a result of an extensive reconciliation study carried out at a copper and gold mine in Brazil, where a significant reconciliation problem took place while using manual sampling for grade control and short-term modelling. After analysing several sampling equipment and sample selection techniques, the authors suggested the use of a reverse circulation (RC) drilling rig with automatic sampling system for grade control sampling. The samples generated by this automatic system were compared with the samples generated by the previous percussion rotary air blast drilling rig, with manual sampling after completion of the drill hole. Moreover, three pairs of twin holes were drilled in order to validate the reverse circulation drilling rig. Results allowed measuring the bias related to the Increment Weighting Error (IWE) generated by manual sampling and showed that the RC rig eliminates significant sampling biases, improving sample representativeness by increasing both sample precision and accuracy.

Improvement in short term mining planning with soft data

Cristina da Paixão Araújo, João Felipe Coimbra Leite Costa and Vanessa C. Koppe
Mining Engineering Department, Federal University of Rio Grande do Sul, Porto Alegre, Rio Grande do Sul, Brazil.

Short-term mining planning typically relies on samples obtained from blastholes in mining operation. These samples may carry a large sampling error. The aim of this paper is to evaluate the impact of the sampling error in mining recovery. This paper presents a case study about a gold mine, where there were two different data types, Au grades collected by diamond drilling (hard data) and Au grades collected by reverse circulation (soft data). Two methodologies were investigated in order to estimate the Au grade of each block to be mined: Ordinary kriging considering data from diamond drilling and ordinary cokriging considering the two different data types. The results showed that samples with poor sampling protocols, even being biased, improved the estimates, compared to retaining only precise and unbiased samples (but in smaller number)s for estimation purposes.

A multi-parameters approach for process variograms

Q. Dehaine and L.O.Filippov
GeoRessources,Universitéde Lorraine,CNRS,UMR7359, 2 ruedu DoyenMarcelRoubault,TSA70605, F54518,Vandœuvre-lès-Nancy, France. E-mail: quentin.dehaine@univ-lorraine.fr, lev.filippov@univ-lorraine.fr,

In the theory of sampling, the variogram have proven to be a powerful tool to characterise the heterogeneity of 1-dimensionallots. Yet its definition and application in sampling for mineral processing have always been limited to one variable,typically ore grade. However this definition is not adapted to some cases,often encountered in mineral processing, where samples need to be representative for a large range of parameters,i .e. variables, such as multiple element grades, grain size, etc.For such cases the multivariable variogram, originally developed by Bourgault and Marcotte (1991) for spatial data analysis,can be used to summarise time variation of the multiple variables (e.g.ore characteristics which are important for theprocess) and highlights the multivariate time auto-correlation of these variables. Different metrics can be used to compute the multivariable variogram, commonly the identity matrix (Euclidean distance) or the inverse of the variance-covariance matrix (Mahalanobis distance) depending on the requirements of the sampler. A case study of a low grade ore show the potential of the multivariable variogram compared to the classical approach which do not take all the variables of interest into account.

Sampling considerations for characterization of radioactive contamination using geostatistics

Serge Antoine Séguret
Paris School of Mine

At the end of process equipment dismantling, the complete decontamination of nuclear facilities requires the radiological assessment of residual activity levels of building structures or remaining materials. Similar considerations also apply to remediation of contaminated land and groundwater. As stated by the International Atomic Energy Agency: "Segregation and characterization of contaminated materials are the key elements of waste minimization".

In this framework, the relevance of the geostatistical methodology relies on the presence of a spatial continuity for radiological contamination, characterized through the variographic analysis. Geostatistics then provides reliable methods for activity estimation, uncertainty quantification and risk analysis, which are essential decision-making tools for decommissioning and dismantling projects of nuclear installations.

The objective of radiological characterization is to find a suitable balance between gathering data (constrained by cost, deadlines, accessibility or radiation) and managing the issues (waste volumes, levels of activity or exposure). Results should demonstrate sufficient confidence without multiplying useless data. Then the spatial structure of radioactive contamination advantageously enables the optimization of sampling effort (type, number and position of data points). Geostatistical methodology can help determine the initial mesh size and reduce estimation uncertainties, in particular with the false negative, in which an area is declared to be below the threshold using estimate results, but in reality exceeds the threshold.

In addition, the impacts of the information support (size of the measured or sampled area) and the estimation support (punctual, block or global estimates) are addressed, respectively on spatial structure interpretation and on waste classification.

Applications of sampling theory in bulk commodities: an iron ore case study

Oscar Dominguez and Kathleen Smith
BHP Billiton Iron Ore

Iron Ore supply is outpacing global demand, reinforcing the importance of product quality and reliability as critical factors that distinguish Iron Ore producers in a competitive market. This expectation calls for a dramatic shift in industry attitudes toward sampling in bulk commodities, beginning with a greater emphasis on optimisation of sampling protocols from Exploration to Port. Quantifying the Fundamental Sampling Error (FSE) of the sampling protocol is a minimum requirement to achieve this and should be preceded by experimental calibration of the sampling constant K and the exponent alpha (α).

Here, we present a case study in which calibration methodologies proposed by Francois-Bongarcon and Minnitt were comparatively used to determine K and α for a Channel Iron Deposit (CID) and a Brockman Iron Formation-hosted Bedded Iron Deposit (BID) from the Pilbara region of Western Australia. Following experimental calibration of K and α, liberation size was calculated for iron oxides and deleterious minerals using Gy's formula. The results were then critically compared against QEMSCAN analysis, thus the Qemscan approach to heterogeneity is put into context.

Although agreement was achieved between calibration methods, the QEMSCAN results raise questions about liberation size calculated using the experimentally derived K and α. Furthermore, the QEMSCAN results highlight uncertainty around mineralogical assumptions made in calculations of FSE. These observations emphasise the importance of validation when assessing FSE. The case study presents an industry perspective on the learnings, opportunities and caveats associated with applications of sampling theory in response to an increasingly competitive Iron Ore market.

Sampling protocol development in a coarse gold deposit

Dr Simon Dominy
Visiting Professor – Camborne School of Mines, University of Exeter, Cornwall Campus, England. E-mail: s.dominy@exeter.ac.uk

The occurrence of coarse gold particles leading to grade complexity and sampling challenges is a common feature of many gold deposits. Poorly designed sampling protocols applied to these deposit types can lead to an excessively high Fundamental Sampling Error. Together with other errors, the Fundamental Sampling Error contributes to the nugget effect. Proper sample collection, preparation and assay protocols are required to minimise this error, and hence reduce the total nugget effect.

On a practical level, half core cutting of coarse gold mineralisation frequently leads to grade uncertainty given that the remaining half may or may not contain a material gold particle. This is frequently evidenced by the very poor precision between duplicate core half assays. In addition, further uncertainty is introduced where the assay of a half core sample is based on a single fire assay result.

A case study from the Ballarat East gold mine in Victoria, Australia is presented, which is characterised by notable quantities of coarse gold (>50% +100-micron gold) hosted in multiple-quartz veins. Diamond drilling provides a reasonable measure of gross geological continuity at drill a spacing of 15-25 m along strike and 5-10 m down-dip. On vein development with face sampling, together with detailed geological studies are undertaken during the resource delineation phase.

A number of different sampling and assay options have been trialled at Ballarat over its recent project history. The current drill core sampling protocol utilises whole core; using 2 kg LeachWELL assays after logging and photography.

This contribution describes the nature of the Ballarat East deposit, its gold particle size characteristics, how sampling and assay protocols have developed with time, application of Gy Sampling Theory and its calibration, and how the data is subsequently applied to grade estimation.

Analysis of granite's roughness using stratified random sampling for the evaluation of radon gas emanation

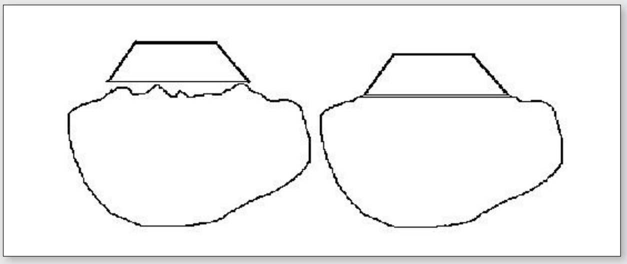
Thammiris Mohamad El Hajj,[a] Homero Delboni Jr,[a] Ana Carolina Chieregati,[a] and Mauro Gandolla[b]
[a]Department of Mining and Petroleum Engineering, University of Sao Paulo, Sao Paulo, Brazil
[b]Università della Svizzera Italiana: USI, Lugano, Switzerland

There are three natural radioactive families according to their decay, which are: the uranium series (^{238}U decreasing to stable ^{206}Pb), the actinium series (^{235}U decreasing to stable ^{207}Pb) and thorium series ($^{236}U \rightarrow {}^{232}Th$ decreasing to stable ^{208}Pb). The three series have radon gas as an intermediary element, each with a different atomic mass (^{222}Rn, ^{219}Rn and ^{220}Rn). The three isotopes are inert gases at ambient conditions and they are alpha particles emitters. Thus, soils naturally emanate these radioactive gases in variable concentrations depending on the location. The radon radioactive emanation is a mass flow composed of radionuclides emitted to the atmosphere from the surface of the material or transported to it. In the case of the elements on the surface, the emanation depends on the amount of radon atoms formed from the decay of radium and surface roughness. This study aims to analyse the roughness of granite plates using simple stratified random sampling of an area in order to minimize the analysis time. To validate the sampling method, stratified sampling results were compared to the measure made in the whole area, presenting a good adherence of both data. It is concluded that the measurements can be conducted just in a few points using stratified random sampling, significantly reducing the time for obtaining granite's roughness.

Handheld XRF analysis (hXRF) — field sensor sampling representativeness and development of a prototype FRAT (field rotary abrasion tool)

Kim H. Esbensen[a,b,d], Martin Holding[c,a], Munim Mehors[d]
[a]**Geological Survey of Denmark and Greenland (GEUS). Copenhagen. Denmark. Email: ke@geus.dk**
[b]**ACABS Research Group, Aalborg University, Denmark**
[c]**Department of Geosciences and Natural Resource Management (IGN), Copenhagen University, Denmark**
[d]**ACRG Research Group, Telemark University College, Norway**

Handheld X-Ray Fluorescence instrumentation ('field hXRF') is used with increasing frequency within geology, mining, prospecting and metals processing providing real-time *in-situ* measurements that can aid scientific interpretations in the field, industrial processing and decision-making. hXRF is by its nature less powerful than laboratory XRF and a.o. precision is claimed to suffer as a result. We investigate to which degree this is the case, but much more importantly: what about accuracy (bias)? hXRF is subject to several types of sensor sampling errors as only a small field-of-view is measured (8 mm) and the specific outcrop morphology is critical, creating very uneven XRF path lengths. Multivariate (chemometric) prediction models have been created on the basis of a representative master training set, comparing the fidelity of measurements acquired from raw outcrop surfaces to those from cut (sawed) and *abraded* surfaces[1,2]. A new handheld, battery-operated "Field Rotary Abrasion Tool (FRAT) has been developed[2], intended to improve the field sensor signal acquisition. Abraded surfaces yield significantly more accurate and precise results (53% -73% improvements) compared to today's raw field surfaces[1]. When implemented these feasibility studies will allow *improved* field hXRF measurement quality for geological outcrops and other material surfaces with *similar* compositional characteristics, provided relevant and appropriate calibration data sets.



Schematic drawing of variable XRF path lengths on raw outcrop surfaces (left) compared to uniform path distances for abraded surfaces (right)[1]

Improved surface hXRF fidelity resulting from application of the newly developed Field Rotary Abrasion Tool (FRAT)[2]

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Proper sampling, total measurement uncertainty, variographic analysis and fit-for-purpose acceptance levels for pharmaceutical mixing monitoring

K.H. Esbensen[a] and R.J. Romañach[b]
[a]**Geological Survey of Denmark and Greenland (GEUS). Copenhagen. Denmark-E-mail: ke@geus.com**
[a]**University of Puerto Rico, Department of Chemistry, Mayagüez, PR-E-mail: rodolfoj.romanach@upr.edu**

Process monitoring in technology and industry in general, in pharmaceutical batch and continuous manufacturing in particular, is *incomplete* without full understanding of all sources of variation. Pharmaceutical mixture heterogeneity interacts with the particular sampling process involved (by physical extraction or by PAT signal acquisition) potentially creating four Incorrect Sampling Errors (ISE), two Correct Sampling errors (CSE) plus the analytical error (TAE). In the highly regulated pharmaceutical production context it is essential to eliminate, or reduce maximally, all unnecessary sampling contributions (TSE) to the total measurement uncertainty (MU) in order to be able to meet the regulatory stringent blend - and dose uniformity requirements. Current problems a.o. stem from inadequate understanding of the challenges in sampling of powder blends. In this endeavor the Theory of Sampling (TOS) forms the only reliable scientific framework from which to seek resolution. We here present a variographic approach with an aim to conduct problem-dependent TSE error variance decoupling and to show how to develop *fit-for-purpose* acceptance levels in powder blending process monitoring. The key issue is shown to be the nugget effect, which contains all non-optimised [ISE, CSE] plus TAE contributions to the total Measurement Uncertainty (MU_{total}). A large nugget effect w.r.t. the sill is a warning that the measurement system is not tuned in, and must be improved. Regulatory guidances have called for sampling from within blenders, leading to sampling errors associated with the insertion of sample thieves (a.o. spear-sampling from blenders). Instead of blender sampling we call for on-line variographic characterisation of the blender outflow stream. Practical case histories are described in a parallel contribution to WCSB7 ("TOS to the rescue").

Calculating the sampling constant of particulate ore samples — examples from base metal ores

C.L. Evans
Senior Research Fellow, The University of Queensland, Sustainable Minerals Institute, Julius Kruttschnitt Mineral Research Centre
40 Isles Road, Indooroopilly, QLD 4068 E-mail: c.evans@uq.edu.au

The challenges presented in the sampling of particulate materials in mineral processing operations was one of the drivers for Pierre Gy to develop his sampling theory and this challenge continues today. Gy's simplified formula is frequently used in designing appropriate sampling protocols for the representative sampling of fine particulate ore materials from process streams. One of the key parameters required in Gy's simplified sampling equation is the Liberation Factor and the variable nature of ores means that the value of this factor can change significantly as the ore texture changes. Ideally the liberation factor should be calculated for each ore and Lyman and Schouwstra[1] have developed a method to do this which uses the mineralogical data for individual particles in polished sections, data which are readily available from automated mineralogy measurement systems.

This paper applies the method developed by Lyman and Schouwstra[1] to a number of base metal ores with a range of textural characteristics and examines how the sampling constant varies across these different ore types over the range of particle sizes typically found in mineral processing operations. The work also calculates the liberation factor for each particulate sample and examines how this changes as particle size changes.

Reference

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Pre-crusher stockpile modelling to minimise grade variability

J.E. Everett[a], T.J Howard and K. Jupp
[a]Emeritus Professor, Management and Organizations, school of Business — Adjunct Professor, Centre for Exploration and Targeting, School of Earth and Environment, The University of Western Australia

The use of pre-crusher stockpiles for storage and buffering to control quantity variations is usually well recognised and managed. However, a third function of these stockpiles, to reduce variations in the grade of ore entering the crusher, is often given insufficient attention. Well designed stockpiles and a disciplined approach to building and reclaiming are essential to systematically reduce short- term grade variation.

Pre-crusher stockpiles are commonly built and reclaimed with little or no regard to where the ore is dumped to or reclaimed from. Consequently, the full potential to reduce short-term grade variability is diminished as well as losing the ability to reconcile mine/blast block grades with crusher grades.

It is important to acknowledge that the pre-crusher stockpiling procedures referred to in this study are not those used for long-term storage of ore but those which facilitate the short-term buffering and flow-through of ore.

This paper reports the conclusions from studies simulating the reduction of grade variability by a range of alternative models, and quantifies the benefits achievable in reducing the grade variance by building stockpiles of appropriate dimension using systematic methodologies. The models considered cover a range of stockpile configurations, including stockpiles built with single and double layers, and reclaiming in directions perpendicular or parallel to the build direction.

Building confidence intervals around the true value of a sample

Dominique François-Bongarçon
Agoratek International Consultants Inc., Vancouver BC, Canada

Common practice in sampling for the TOS erudite consists of using the sampling variance obtained from Gy's numerical theory to build confidence intervals around the true sample value. This is usually done to characterize the 'precision' of the sample, and, by centering that interval on the sampled value, one states for instance that *"the true value has 95% chances of being between values x and y"*, those two values usually being centered on the sampled value". The somewhat naïve rationale behind this practice is reviewed in some details and criticized. It is suggested the confidence interval of real interest to the user of the sampled value, is more difficult to define and more delicate and indirect to build. Some methods for doing so are examined and a methodology is recommended.

Gy's theory of sampling: applications and limitations

Dominique François-Bongarçon
Agoratek International Consultants Inc., Vancouver BC, Canada

The achievements of modern Theory of Sampling (TOS) to date are reviewed and the focus is then put on their limitations, examining the question: "Are we always using TOS within its domain of validity?" Specific examples from common practice are examined with the aim of producing a best practice guide for using TOS, with emphasis on the meaning and epistemology of using mathematical models.

Proper field sampling and laboratory processing for archæometric discrimination between cultivated and fallow Bronze-age fields on Bornholm, Denmark — TOS meets chemometrics meets archeology

Bastian Germundsson,[a,c] Anders Pihl,[b] Kim H. Esbensen[c,d,e]
[a]Department of Geosciences and Natural Resource Management (IGN), Copenhagen University, Denmark.
E-mail: bgermundsson@gmail.com
[b]Bornholm Museum, Rønne, Denmark
Email: ap@bornholmsmuseum.dk
[c]Geological Survey of Denmark and Greenland (GEUS). Copenhagen. Denmark. Email: ke@geus.dk
[d]ACABS Research Group, Aalborg University, Denmark
[e]ACRG Research Group, Telemark University College, Norway

Archeologically it is interesting to be able to predict whether a particular Bronze-age field has been cultivated or not based on soil chemistry characteristics augmenting traditional archeological evidences. A field sampling campaign was carried out in the summer 20014 on the island of Bornholm with the objective to discriminate between documented cultivated and fallow Bronze-age agricultural fields based on multivariate data analysis (chemometrics) of metal concentrations (ICP-MS) in soil. The experimental design (Fig. 1) was directed towards investigating the degree to which *proper* field sampling (TOS) plays a significant role a.o. including replicate sampling at three levels. Fig. 1 shows the geographical layout of one cultivated field (JP01-JP10) and a nearby fallow field (JP11-JP19), termed “D1” and “Ud” respectively (all samples originate from the same depth corresponding to the paleo-cultivated layer or the equivalent depth in fallow fields). Applying Principal Component Analysis (PCA), the t_1-t_3 scores plot (right) corresponds to 54% of the most discriminative variance in the 11 variable/19 sample X-matrix containing the ICP-MS metal concentrations. Another cultivated field (D2), located 1 km away, also appears in Fig.2. It is highly satisfying that the first and third PC-component is able to delineate a complete discrimination [Ud] vs. [D1,D2]; PC component no. 2 models other, general soil chemistry features that are *compensated* for in the PCA solution.

We present the TOS-specifics pertaining to the critical field sampling procedure, including the hierarchical three-level experimental design used for quantifying all contributions to the total Measurement Uncertainty (MU) budget in the field-to-analysis pathway (grab vs. composite field sampling, local replicate site-sampling, replicate sub-sampling in the laboratory, replicate test portion extraction as well as σ^2(TAE), in order to better understand the discrimination achieved. Five elements appear to be particularly involved in the discrimination [P, Fe, Mn, Zn, Pb], currently undergoing paleo-agricultural/geochemical interpretation. Based on these first results we plan a full *test-set validation* campaign in 2015 – which will be the ultimate performance test for this type of archæo-chemometric discrimination. This contribution illustrates the versatility and power of multivariate data analysis (Chemometrics) applied to data with a substantial proportion of potential sampling errors.

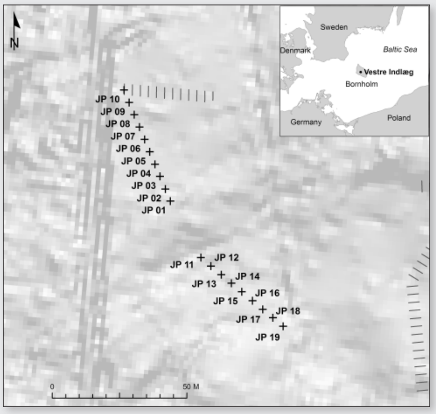

Figure 1.

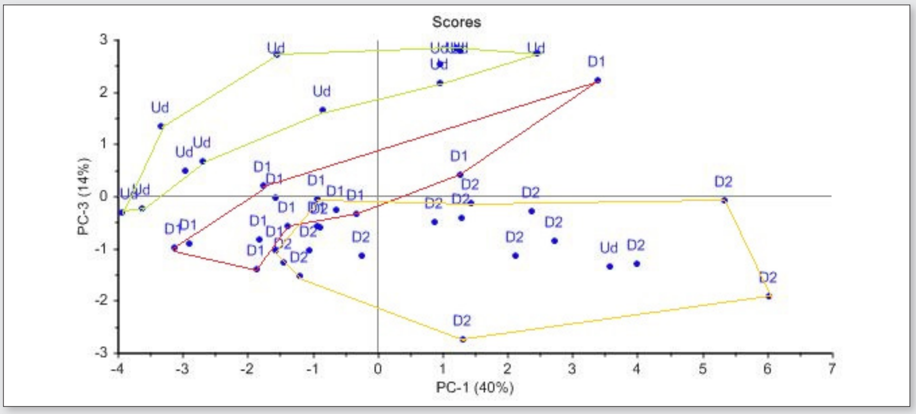

Figure 2.

Using an optimisation algorithm to determine a stockpiling and blending strategy for iron ore

Zita Harber
Advisian, South Africa. E:mail: zita.harber@advisian.com

WorleyParsons RSA conducted a feasibility study on the development of an open-cast iron ore mine in South Africa. As part of the study the team needed to determine how many stockpiles of run-of-mine ore should appear before the crushing section, how the mined material should report to the stockpiles and what is the maximum mass of saleable iron ore that could be blended from the stockpiles. The specifications obtained from the client stated that the blended iron ore product has to contain at least 58% iron (Fe), with a maximum content of 10% silica (Si), 3.5% aluminium oxide (Al_2O_3), 0.07% phosphorous (P), 0.05% sulphur (S), 0.3% alkali and 0.5% manganese (Mn), respectively. A mine plan model showed that batches of run-of-mine (ROM) ore would report to the surface on a weekly basis over the life of mine and also indicated the associated concentrations of Fe and other contaminants. This data was obtained from a geological model of the ore body and showed a great variety in the concentrations of all elements. These varying characteristics necessitated the development of a strategy to ensure that the maximum amount of saleable product and minimum amount of waste will originate from the operation.

A numerical score was calculated for each batch of ROM ore that reported to the surface, based on its Fe and Si concentrations, as predicted in the mine plan. Based on this numerical score the material was allocated to different stockpiles, where the most ideal stockpile had the highest Fe and lowest Si concentrations, respectively. Conversely, the least ideal stockpile had the lowest Fe and highest Si grades, respectively. At each time step, a multivariable optimisation algorithm in Matlab® (fmincon) calculated the maximum amount of saleable product that could be formed through the blending of material from all available stockpiles, while adhering to constraints on the concentrations of all elements. Another set of constraints were formed by specifying that neither the masses taken off the stockpiles nor the actual stockpile levels can take on non-negative values. The result of performing the stockpiling and blending algorithm for a selection of between four and 12 stockpiles resulted in estimated weekly production data over the life of mine, as well as the associated stockpile levels and the concentrations of Fe and all other contaminants. Out of all scenarios it was found that 12 stockpiles allow for the greatest flexibility for blending run-of-mine ore which leads to the highest mass of saleable material with the least amount of waste material left over at the end of life of mine. The algorithm also allows the user to lift any or all of the restrictions on the concentrations of contaminants and it was found that production over the life of mine can be increased by 11% if only Fe and Si constraints are considered in the optimisation algorithm.

Sample station design and operation

Ralph J Holmes
Mineral Resources Flagship, CSIRO, Clayton South, Australia.
E-mail: Ralph.Holmes@csiro.au

Accurate sampling practices in the mineral industry are critical to determining the chemical, mineralogical and physical characteristics of ores and mineral products for resource evaluation and utilisation, feasibility studies, process design and optimisation, quality control, metallurgical accounting, and ultimately commercial sales. Sampling is the first step in the measurement chain and is where the measurement process all begins, so if the sample that is collected is not representative, then the whole measurement chain is compromised at the outset. However, frequently the responsibility for sampling is entrusted to personnel who do not fully appreciate the significance and importance of collecting representative samples for analysis, and everyone seems satisfied as long as some material is collected and returned to the laboratory for analysis. In the case of sample stations, cost is often the main consideration rather than sampling correctness. Clearly this is unacceptable and needs to change.

The paper will provide guidelines for the correct design of sample stations, which will be illustrated with a range of examples of good and bad designs, eg, the design of primary cutters, the operation of secondary cutters, crusher performance, sample mass and ease of inspection. It is important that sampling experts are involved at the design stage to avoid design flaws and the subsequent need for expensive retrofits to address major problems. Furthermore, ongoing audits of performance need to be conducted to ensure sample stations are adequately maintained and continue to conform with correct sampling principles. Provision also needs to be made for duplicate sampling to monitor the precision achieved in practice on an ongoing basis for quality assurance purposes.

PFTNA logging tool and its contributions for boreholes in situ elemental analysis

P. Jeanneau and V. Flahaut
Sodern

Nowadays, nuclear geophysical techniques are used extensively for boreholes characterization with main demand from oil well logging exploration. The Oil and gas industry has made large efforts to develop high tech components that can withstand great depths severe conditions. PFTNA (Pulsed Fast and Thermal Neutron Activation) is one of those nuclear elemental analysis techniques that gained great benefits from innovation in scintillator detectors and reliable and safe electrical neutron sources introduced in oil well logging. Sophisticated methods, sustained by ever more powerful computers, also enable simulation for optimum instrument design and advanced data processing.

Relieved from major challenges as high stress in temperatures and shocks, the technology can be simplified, and reasonably priced, for the mining industry where boreholes elemental analysis receives increasing interest either in exploration or mining. PFTNA method is currently applied for in situ measurements of the elemental composition of the rock surrounding the hole. It can also derive some physical properties as density. Traditionally, borehole material is collected in various size and shapes upon drilling techniques from solid continuous cores to cuttings surface recovery and then sent to laboratory for assay. This provides desired information about boreholes, but the whole process usually extends over several weeks, delaying as much any decision to proceed. PFTNA Nuclear logging is able to provide information almost instantaneously for major elements. Proposing different tradeoffs in response time and performance, laboratory analysis of samples and PFTNA in situ elemental logging should be implemented accordingly. The two approaches should also not be opposed in regards with theory of sampling (TOS). If physically inaccessible, samples volume measured by nuclear PFTNA can be yet investigated in details by Monte Carlo simulations. Effective measured samples with this contactless methods is yet found rather complex to establish. Nuclear signals depth of penetration in the material is usually roughly defined and submitted to the influence of material properties themselves. But physical sampling methods could also be severely hindered by classical source of errors attached with samples recovery or handling operations. Representativeness of those samples remains also limited to infer surrounding material composition especially in heterogeneous deposits. The volume of rock sampled each meter by nuclear PFTNA borehole logging is in the cubic meter range and thus provides very good sampling statistics.

Through the case of a recently developed instrument, this paper describes first the latest in design of PFTNA nuclear logging tool. If the heart of the physics of the instrument lies in a high resolution gamma scintillator detector coupled with a recent compact electrical neutron source, the whole system is discussed such as the benefit of modern digital electronics, surface to tool data transfer and user interface. The paper will then discuss the outcome of elemental analysis with PFTNA and how it is interrelated and mutually supportive with traditional sampling method

Improved counteracting soil heterogeneity sampling designs for environmental studies – TOS meets chemometrics

Zahra Kardanpour[a,b], Ole Stig Jacobsen[b], Kim H. Esbensen[a,b,c]
[a]**ACABS Research Group, Aalborg University, Denmark.**
E-mail: zka@geus.dk
[b]**Geological Survey of Denmark and Greenland (GEUS).**
Copenhagen. Denmark
Email: ke@geus.dk
[c]**ACRG Research Group, Telemark University College, Norway**

This project aims at development of an improved soil heterogeneity characterization methodology for ‘next generation’ sampling/monitoring and spatial modeling practices a.o. allowing consideration of realistic pesticide variability in environmental contaminant assessment studies. Within the environmental sciences there is a strong need for an integrated understanding of chemical contaminant transformations (e.g. pesticide degradation), spatial modeling and multivariate data analysis. All critical parameters are in need of effective counteraction of the variability related to inherent soil heterogeneity. This study evaluate a series of improved designs of field and laboratory sampling experiments at all stages from the primary field sampling to the final analytical sample preparation. The effect of soil heterogeneity at different scales critically affects the sampling/monitoring procedures involved. Soil samples were collected from the topsoil (A-horizon; 0-25 cm) of a typical sandy soil with an equidistance of 1 m along a 100 m long profile oriented parallel to plough lines intended for *large scale* variographic analysis; results for clayey soils will also be presented. Each sample contains 20-30 gram moist soil; the profile center included a *short scale* replication experiment. A large suite of 38 inorganic elements in addition to moisture, loss on ignition and bacteria counts (CFU) were analyzed, plus carbon-14 measurement of MCPA sorption and mineralization and glucose respiration. Contemporary sampling approaches in environmental/soil sciences makes little or no allowance for soil heterogeneity, often resulting in significant between-pot heterogeneity which unnecessarily endangers the discriminating power in laboratory pot experiments. Variographic analysis shows the advantage of using composite sampling locations with a distance below the pertinent minimum half-range for both organic and inorganic compounds based on the empirical soil sample autocorrelations. Synoptic overviews of the correlation data structure between 40+ chemical parameter, as well as between their variograms, were analysed by multivariate data analysis (chemometrics), allowing to quantify the combined covariance-spatial soil heterogeneity.

Review of a non-probabilistic sampler versus a vezin sampler on low weight percent solids slurries

Steve E. Kelly[a] and Francis F. Pitard[b]
[a]**Engineer, Waste Feed Delivery Technology Programs, Washington River Protection Solutions**
[b]**Francis Pitard Sampling Consultants, LLC**

The Hanford Tank Operations Contractor (TOC) and the Hanford Waste Treatment and Immobilization Plant (WTP) contractor are both engaged in demonstrating mixing, sampling, and transfer system capability using simulated Hanford High-Level Waste (HLW) formulations. This work represents one of the remaining technical issues with the high-level waste treatment mission at Hanford – the TOCs’ ability to adequately sample high-level waste feed to meet the Waste Treatment and Immobilization Plant (WTP) Waste Acceptance Criteria Data Quality Objectives. A full scale sampling loop was used at a cold test facility to evaluate sampler capability. The sampler under investigation for deployment is non-probabilistic but radioactive environment friendly. A Vezin sampler (probabilistic) was used to obtain reference samples and accurately characterize the simulant as it flowed through the test loop. The two samplers are located in series, allowing for multiple samples to be taken from both samplers over the same time period (sample pairs) and direct sample comparison. The Vezin sampler was modified to minimize material build up allowing for steady-state operation. This report discusses modifications made to the Vezin sampler and the results of sampler comparison.

A method to evaluate the possible sampling error of a multiple cutter metallurgical sampler

Janne Loimi[a], Pentti Minkkinen[b], Christian von Alfthan[a], Jarmo Lohilahti[a], Tapio Korpela[a]
[a]**Outotec**
[b]**LUT Chemistry/Faculty of Technology, Lappeenranta University of Technology**

The head loss caused by metallurgical sampling for the slurry stream can be reduced by metallurgical sampler design. When the process stream volumetric flow is sampled by vertical static cutters before the equal number of moving cutters, the installation requires less installation head space and is easier to accommodate at a suitable location in the process. Low head loss reduces the building costs for the processing plant and operational costs during the life time of the plant.

The presence of a possible systematic bias in the particle size distribution or the chemical composition between the vertical static cutters caused by segregation in the metallurgical sampler can be estimated by a sampling campaign where sub samples are cut from each of the moving cutter sample streams simultaneously. The sub sample assay results can be evaluated by the F test to reveal if there exists significant variance between the cutter assays.

The heterogeneity and minimum possible error caused by the sampling and analysis system can be estimated by performing a sampling campaign where spot samples are collected at equal intervals to perform a variographic experiment to study the heterogeneity of the process stream and a minimum possible error by estimating the V_0 intercept. V_0 is the variability of a single measurement and is an indication of the minimum practical error (MPE) and also the minimum sampling variance expected in practice.

MPE includes the fundamental sampling error, the grouping and segregation error, the analysis error including preparation errors and the possible incorrect sampling errors.

In this paper we present how above mentioned methods can be used to evaluate the possible errors of an economical metallurgical sampler.

Complete sampling distribution for primary sampling, sample preparation and analysis

Geoffrey J Lyman
Materials Sampling & Consulting, Southport, Queensland Australia 4215

Following from the author's recent paper at Sampling 2014 which presented a method for calculation of the sampling probability density function due to the particulate heterogeneity (density function of the fundamental sampling uncertainty), it is possible to apply the same characteristic function method to arrive at the overall sampling distribution for any sampling protocol and analysis method.

This paper develops the application of the method of characteristic functions to the overall sampling problem including the uncertainty which derives from the primary sampling from a process stream. The assay distributions in a process stream or of impurities in the flow of a final product can be governed by non-Gaussian, serially correlated distributions. The paper shows how such circumstances can be dealt with to arrive at robust solutions.

The paper represents an end-point in the theory of sampling as it provides a means of determining the entire distribution function for a sampling system. Such a determination has not previously been possible and having determined the entire distribution function, the statistics of the sampling process are completely determined.

Determination of the precision of sampling systems and on-line analysers

Geoffrey J Lyman
Materials Sampling & Consulting Southport, Queensland Australia 4215
James Asbury
Realtime Group Limited, Mackay, Queensland Australia 4740

There is a simple and inexpensive way of determining the precision of sampling systems and on-line analysers when a data base of output values from the sampling system or on-line analyser can be accessed and there exists serial correlation in the data sets. Basically, if it is possible to construct a variogram for the data set, it is possible to extract the precision estimate as the variance is simply given by the intercept (nugget variance) of the variogram.

The method is much superior to doing interleaved sampling, which gives incorrect estimates of the precision when serial correlation exists. It is rare to find that there is no serial correlation in the data.

This paper outlines the method and illustrates the procedure with a number of data sets from various areas. It also demonstrates by simulation why the interleaved sampling method is incorrect. When variogram estimation is made using maximum likelihood methods, a confidence interval for the precision can be calculated.

The weighting error: a study by simulation

Geoffrey J Lyman
Materials Sampling & Consulting, Southport, Queensland Australia 4215

In Gy's theory of sampling, estimation of sampling error due grade variations in a process stream is carried out under the assumption that the mass flow is constant. Gy's work does not provide quantitative analysis of the impact of variations in the mass flow. In the same way as the grade variations are treated as a random function characterised by a variogram or covariance function, mass flow variations can be characterised.

A formal analysis of the impact of mass flow variations uncorrelated with the grade variations leads to complex expressions. Armed with a means of efficiently creating realisations of random functions, it is a simple matter to study the impact on sampling variance by simulation. The simulation method provides exact results for a given set of conditions as long as a sufficient number of simulations are used. Simulation can also deal with cross- correlation between the mass flow and the grade variations.

The paper explores the analysis of the weighting error both analytically and by simulation with the objective of indicating at what magnitude the flow variations begin to cause the sampling uncertainty to increase significantly. Bias in sampling due to cross-correlation is also investigated.

Sampling of cereals : development of a protocol for mycotoxins analysis

Brigitte Mahaut, Guislaine Veron Delor
ARVALIS-Institut du végétal

European directives (UE) 401/2006 and (UE) 691/2013 for official controls of some contaminants such as mycotoxins set methods for sampling and analysis.

The composition of batches of cereals is rarely homogeneous and, in particular, certain contaminants like Fusarium-mycotoxins are distributed in a non-uniform way. Sampling therefore is a procedure which requires a great deal of care, and it is necessary to get a representative sample before initiating any analysis.

In order to harmonize sampling procedures and to determine the best way to prepare a homogenous and representative laboratory sample, studies have been undertaken by a French working group associating storage organizations and suppliers of sampling devices.

The aims of these studies were:

- To evaluate the mycotoxines distribution in cereal batches,

- To compare different sampling protocols including the European directive,
- To determine the relationship between the number of samples and the uncertainty of the analysis result, and
- To define an acceptable sample weight for the laboratory.

The results obtained concerned different toxins (DON, fumonisins, zearalenone). They came from trials in large storage silos on flowing or static grains. They showed that the heterogeneity of the batch increases with the level of contamination.

According to the data, it is possible to reduce the number of samples to be taken during sampling without a significant impact on the result. Finally, the studies showed that the weight of the sample sent to the laboratory for the detection of Fusarium-mycotoxins could be reduced.

These results supported the standard EN ISO 24333, Cereals and cereal products – Sampling and more recently allowed an evolution of the European directive.

Comparison between samples with constant mass and samples with constant fragment population size

by G. Matheron
Translated from French to English, clarified and further commented by Dominique François-Bongarçon[1] and Francis Pitard[2]
[1]Agoratek International Consultants Inc., Vancouver BC, Canada
[2]Francis Pitard Sampling Consultants, LLC, Broomfield, Colorado, USA

In his essay “l’echantillonnage des minerais en vrac” that could be translated as “sampling of particulate ore” published in 1967 in France by the Revue de l’Industrie Minerale, Pierre Gy suggests a calculation of the variance associated with samples with a constant number of fragments. In practice, samples with a constant mass are instead collected, which may seem at first like a contradiction. In this mathematical development it is clearly demonstrated that these two kinds of samples lead to variances that are similar within well-established mathematical limits.

Comparison of sampling methods by using size distribution analysis

Pentti Minkkinen[a], Lari Ruotsalainen[b], Jesse Auranen[b]and Ilpo Auranen[c]
[a]LUT Chemistry/Faculty of Technology, Lappeenranta University of Technology, Lappeenranta, Finland
[b]Mine On-Line Service, Espoo, Finland
[c]IMA Engineering, Espoo, Finland

Pierre Gy [1,2] has derived an equation, which can be used to estimate the relative variance of the fundamental sampling error of size distribution results given as mass fractions for each size class. This theory is used in this study. Heterogeneity invariant, ***HI***, is the relative variance of the fundamental sampling error extrapolated to a sample size of a unit mass (usually 1 g). ***HI*** can be estimated from a sieve analysis for each size class ***i*** from Eq. 1.

$$HI_i = \left(\frac{1}{a_i} - 2\right) v_i \rho_i + \sum_{i=1}^{n} \rho_i a_i v_i \tag{1}$$

Here $\boldsymbol{a_i}$ is the mass fraction of size class $\boldsymbol{i}$, v_i the average particle size in class $\boldsymbol{i}$ and ρ_i the density of particles in size class $\boldsymbol{i}$. Given $\boldsymbol{HI_i}$, the relative variance of the fundamental sampling error, S^2_{FSE}, can be estimated for different sample sizes to be sieved from the test material:

$$s^2_{FSE} = HI_i \left(\frac{1}{m_s} - \frac{1}{m_L}\right) \tag{2}$$

Here $\boldsymbol{m_s}$ is the sample size to be sieved and $\boldsymbol{m_L}$ the size of the lot from which the sample is taken.

If the sampling methods performs correctly and is able to minimize the segregation effects, always present when material consisting of fragments or particles having a wide size distribution, the observed variance of replicate samples should be close to that obtained by using the above equations and it is possible to calculated confidence interval for a given size distribution.

In this study a newly developed sampler was tested by sampling blast hole drill cuttings and the results were compared to other sampling methods currently in use. Part of the samples were also sent for chemical analysis to see if the analytical results correlate with the size classes. A convenient way to summarise and compare size distribution results and analytical results is carry out Principal Component Analysis (PCA) on both size data and analytical data. These results will be presented WCSB7.

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Empirical evidence for a simplified version of Gy’s qquation for low grade gold ores

RCA Minnitt
JCI Professor of Mineral Resources and Reserves, School of Mining Engineering, University of the Witwatersrand, South Africa. E-mail: Richard.Minnitt@wits.ac.za

Classically Gy’s equation for the Fundamental Sampling Error takes the form:

$$\sigma^2_{FSE} = \frac{Kd_N^3}{M_S} \tag{1}$$

Later work by Francois-Bongarçon (1995) led to a modification of Gy’s formula, particularly for low grade gold ores that takes the form:

$$\sigma^2_{FSE} = \frac{Kd_N^\alpha}{M_S} \tag{2}$$

Where the exponent to d_N is replaced by alpha (α) rather than 3 as given in the original equation by Gy. Francois-Bongarçon (1995) further showed that the sampling constant K and the exponent alpha can be calibrated for a given ore-type and that the calibrated constants could then be used to provide the ideal solution for stages of comminution and mass reduction in the sampling nomogram for that particular ore.

The calibration method suggested by Francois-Bongarçon (1995) has been carried out numerous times by various sampling practitioners and is a well-established procedure in the literature. The procedure is referred to in the literature as the Duplicate Sampling Analysis (DSA) method and is clearly described by authors who have undertaken this type of calibration. Another type of calibration procedure referred to as the Segregation Free Analysis (SFA) method produces results similar, if not identical, to that suggested by the DSA method of Francois-Bongarçon (1995). All the calibration experiments carried out in low grade gold ores have produced values for K that vary between 70 and 170 and have yielded values for alpha in the range 0.97 to 1.30. The range of values for alpha suggests strongly that the average value for alpha in low grade good ores may in fact be 1, rather than 3 as originally proposed by Gy (199?) (Equation 1) or the 1.5 proposed by Francois-Bongarçon (1995) (Equation 2).

It is suggested that for low-grade gold bearing ores that the equation for the Fundamental Sampling Error should take the form:

$$\sigma^2_{FSE} = \frac{Kd_N}{M_S} \tag{3}$$

Such an equation for the variance of the Fundamental Sampling Error greatly simplifies the characterisation of gold ores which now only required the calibration of K for a given mass and established fragment size.

Food and feed safety assessment: proper sampling is imperative

Claudia Paoletti[a] and Harry A. Kuiper[b]
[a]European Food Safety Authority (EFSA), Parma, Italy
[b]Institute of Food Safety (RIKILT) Wageningen UR, Wageningen, The Netherlands

The general principles for safety and nutritional evaluation of foods, feed and associated hazardous compounds have been developed by FAO and WHO and further elaborated in the EU funded project SAFE FOODS. Nevertheless, the crucial role that sampling has in foods/feed safety assessment has never been explicitly recognized. High quality sampling should always be applied to ensure the use of adequate and *representative* samples as test materials for hazard identification, toxicological and nutritional characterization of identified hazards, as well as for estimating quantitative and reliable exposure levels of foods/feed or related compounds of concern for humans and animals. The importance of representative sampling is underlined through examples of risk analyses in different areas of foods/feed production. The Theory of Sampling (TOS) is recognized as the only frame to ensure accuracy and precision of all sampling steps involved in the field-to-fork continuum, necessary to monitor foods and feed safety. As such, it is emphasized how TOS must be integrated in the well-established FAO/WHO risk assessment approach in order to guarantee a transparent and correct frame for the risk assessment and decision making process.

Practical case: representative sampling for full-scale incineration plant test

Jan Hinnerskov Jensen and Peter Bøgh Pedersen
Danish Technological Institute, Kongsvang Allé 29, 8000 Aarhus C, Denmark,

Today all impregnated wood waste in Denmark is exported. The Danish Environmental Protection Agency needed knowhow in order to investigate whether wood waste could be incinerated in an environmentally safe way in Demark.

Therefore, the Danish Technological Institute was commissioned to execute a full-scale test, including the measurement of all waste streams on an already existing incineration plant.

For the test, 600 tons of impregnated wood waste was gathered. For mass balance purposes, a representative sample of this wood waste was necessary.

Prior to the incineration test, a procedure for sampling was prepared. The plan involved successive steps of sample mass reduction in the waste deposit site, including shredders and front loaders. The reduction of the 600 tons of wood waste resulted in a 10 kg sample. The further sample preparation, including further mass reduction, was handled in the laboratory.

A project funded by the Danish Environmental Protection Agency

Sample system designs for the new NSPS standards

Dewey Ponthieu
Triad Control Systems, Baton Rouge, Los Angeles, USA

In 2015 all flares in the United States which have sour gas feeds will be required to meet the requirements of 40 C.F.R. Part 60 Subpart Ja. The need to meet this rule has required companies with flares that fall under the guide lines to determine how best to implement the rule at their facility.

Triad Control Systems designs and builds analytical systems for the petrochemical industry. For the past year we have been very involved in the design, construction and implementation of systems designed to meet the requirements of Subpart Ja.

This paper will review several different ways companies in the Gulf Coast region of the United States have chosen to address the requirement of Subpart Ja. Focus will be on the analytical equipment chosen and the sampling techniques devised to meet the stated requirements of the ruling. Additional emphasis will be give to the safety issues involved in working with high concentration H2S samples.

Layout, sampling methods and equipment used in the Continuous Environmental Monitoring systems (CEM's) to monitor the amounts of Hydrogen Sulfide (H2S) and other sulfur compounds sent to the flare will be reviewed. Additionally, methods to monitor the flow through the flare will be addressed.

H2S is a very toxic chemical and must be handled very carefully in order to prevent injury to personnel. Many of these flares during upset conditions can see H2S concentrations go from 0 to +60% very quickly. How to address these safety issues will also be covered.

The decision unit – a lot with objectives

Charles A Ramsey
EnviroStat, Inc., Fort Collins, CO, USA

Sampling is more than shoveling material into a bucket. It is even more than using adequate mass, increments, and tools. Sampling is a systematic process that incorporates everything from development of objectives through final decision-making. Many sampling protocols currently in use focus only on the physical sample collection and ignore the preceding steps in the sampling process. The ignored steps include the development of the objectives, integration of sufficient quality control, inferences from test portion to lots, and final decision making, statistical or otherwise. Without this supporting framework, it is impossible to ascertain the validity of the sampling protocols when needs or objectives change. Often, the same sampling protocol is implemented year after year without any consideration to its appropriateness.

Proper Sample Quality Criteria (or Data Quality Objectives) are to be determined from the objectives of the project and must be an integral part of any sampling campaign. The major components of the Sample Quality Criteria are 1) Question, 2) Decision Unit, and 3) Confidence. The Decision Unit is the specific material to which an inference from the analytical result is made and ultimately to which a decision is made. If the Decision Unit is not precisely determined and integrated into the development of the sampling protocol, the resulting decisions will be incorrect or, at a minimum, not cost effective. This contribution will address development and integration of the Decision Unit into the sampling protocol framework.

The role of inference in food safety

Charles A. Ramsey
EnviroStat, Inc., Fort Collins, CO, USA

People have been trying to determine the safety of their food since ancient times. In ancient times, people themselves were the ultimate test of food safety, but as humans progressed other techniques such as sensory perception and experimentation on animals were used. Today sophisticated analytical techniques and models are available to measure and predict food safety. These sophisticated techniques and models are dependent not only on the quality of samples that are collected and analyzed but also on how inferences are made from the analytical results to the food being sampled. Unfortunately, the Theory of Sampling and the role of inference have not been fully integrated into prediction of food safety.

The basis for many "modern" food sampling protocols was developed prior to the development of the Theory of Sampling. Many of these sampling protocols were based on concepts of acceptance sampling procedures and associated inference. The Theory of Sampling enables the representative sampling of bulk materials and eliminates the reliance of acceptance sampling as the only method for the characterization of food and utilizes a different type of inference than for acceptance sampling. This contribution addresses the differences between inference for acceptance sampling and inference for the sampling of bulk materials and the implications of these differences for food safety.

TOS to the rescue: estimating TSE for near infrared spectroscopic analysis of pharmaceutical blends

Rodolfo J. Romañach, Barbara Alvarado, Andres Román Ospino, Kim H. Esbensen

The results of a **replication experiment**[1] of a five component pharmaceutical blend are presented. Replication experiments represent a new approach to the analysis of pharmaceutical blends and to estimating sampling and measurement uncertainty. The current protocol for routine analysis for pharmaceutical blends preclude use of replication experiments, they being either too labor-intensive or they may alter the powder mixture every time that samples are extracted from a lot or batch. The blends analyzed here are similar to many pharmaceutical formulations since they include lactose monohydrate and microcrystalline cellulose, the two most common excipients in the pharmaceutical industry and include acetaminophen (APAP), a widely used active ingredient. APAP is a very cohesive powder and pharmaceutical formulators are challenged to break drug agglomerates to achieve the desired drug distribution. This experiment also sheds light on current 'mixing efficiency' issues, which is a subject of intense discussion in pharmaceutical manufacturing. In this present research sampling is performed with near infrared spectroscopy (NIRS), which brings a number of advantages to the fore. The principal advantages of NIRS stem from its non-destructive nature and rapid analysis times, which may range from a few milliseconds to 30 seconds, depending on the spectrometer used. These features facilitate the use of a replication experiment. Measurement repeatability was determined by focusing the NIR beam on a single analysis footprint of the powder mixture, taking many consecutive measurements at identical conditions. This part of the experiment furnishes an estimate of the Total Analytical Error (TAE). Subsequently the replicate experiment is also deployed analyzing one extracted test portion of the blend multiple times; subsequently several aliquots were extracted as close to one-another as possible. Finally, similar analysis of multiple aliquots from the lot were performed to determine the Total Sampling Error in a pattern dictated by the current regulatory protocols. The resulting hierarchical variances are subtracted from one-another allowing a complete decomposition of the individual error contributions in the chain primary sampling errors, secondary ditto, test portion extraction error and var(TAE) respectively. This experiment was repeated but now carried out on the output material stream exiting the mixture blender upon mixing completion (on its way towards tableting), i.e. conducted as a *variographic experiment*. These experiments provide critical information to develop adequate regulatory expectations based on a quantitative comparison between these two principal approaches – always subject to the degree that the laboratory simulations can be shown to be identical to routine manufacturing practice (scaling-up issues). In the pharmaceutical industry there is today a strong desire to move towards 'sampling-free' approaches such as PAT (Process Analytical Technologies), but NIR is not a panacea, the main limitation being that the mass analyzed by the NIR radiation is not known – this is conventionally *assumed* to be comparable, if not constant. The analyzed volume, i.e. sampled volume, or mass, can be estimated however; we present a new approach for this critical part of the NIR analytical approach. The sampling volume may also be reduced or increased as a function of the spectral acquisition parameters. At this time a complete understanding of PAT ‘sampling’ and the associated analytical error for NIR analysis of powder blends is not available however - TOS and the **replication experiment** provide a critically needed contribution forward.

Reference

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When “homogeneity” is expected – TOS in pharmaceutical manufacturing

Rodolfo J. Romañach, Adriluz Sánchez Paternina, Andres Román Ospino, Barbara Alvarado, Kim H. Esbensen

Pharmaceutical manufacturing contains an expectation, indeed a regulatory demand that powder blends that precede tablets and capsules be “homogeneous”. This term is a first collision between TOS and pharmaceutical industry quality control (QC) practices. Here “homogeneous” does not imply a perfect mixture where the distribution of particles is strictly identical throughout the lot however, but is used to communicate that heterogeneity is sufficiently low that patients will receive a product with the strength “it purports or is represented to possess”. These “homogeneous” unit doses are usually required a relative standard deviation (RSD) of less than 5%. Quality control units in pharmaceutical manufacturing have a strong interest both in determining the average concentration of a blend, and an equally strong interest in determining how the drug varies throughout a lot (*so much for homogeneity in TOS’ fashion*). The pharmaceutical industry has traditionally relied on *grab sampling* (using sampling spears) to obtain the desired information in this context, which to any informed TOS-entity appears as Mission Impossible; indeed a significant number of publications have described the problems that have resulted. Industrial strategies have sought to find “dead spots” in blenders with incomplete mixing that could lead to an over or under-dose. This traditional pharmaceutical QC area is now being addressed with a new TOS-based approach: i) It is futile to continue searching for documentable heterogeneity in blenders, which are emptied onto conveyor belt immediately after sampling anyway; ii) variographic analysis (for both batch and continuous mixing) are being brought to bear. Real-time analysis of drug concentration is now performed by near infrared spectroscopy, a non-destructive analytical method applied to blender output streams (what else?). Replicate experiments will be presented and evaluated. The quest only to rely on *relevant* total Measurement Uncertainty systems (MU) of pharmaceutical blends has started: TOS meets pharma!

Geostatistical comparison between blast and drill holes in a porphyry copper deposit

Serge Antoine Séguret
Paris School of Mine

Diamond drill holes grades are known to be of a better quality than blast holes ones, is it true? We present a formal study of a porphyry copper deposit in Chile where the 3 meter length drill hole samples variogram is compared to the 15 meter length blast hole ones and we show that the blast holes can be considered as a regularization of the punctual information deduced from the drill holes, up to a nugget effect proper to the blasts.

In fact the blast drilling length is approximately 17m and to restore the requested 15m, 5 cm of the material is removed by hand from the envelop of the blast cone, leading to another question: could the error proper to the blasts be due to the arbitrary removal of this material and the blast length variability? Extension variances show that the answer is no and the blast error belongs to the set of Pierre Guy sampling errors. In the study, the drill information is taken as reference because:

Referring to the blast is not possible, the blast nugget effect is too important,

We are in an full heterotopic case where there is no spatial location where blast and drill are both known and could make possible the calculation of cross variograms,

The variograms present a linear component which forbids the use of cross co-variances.

Consequence is that we could not model an eventual error proper to the drills and the blast error pointed out is a minimum. The maximum could be 50% more important if there is no “natural” nugget effect (i.e. micro structure).

The first conclusion is that the blast holes in this mine are of much better quality than one generally believes, justifying the short term planning and the ultimate selection based on them.

Design advances and operational studies for the True Pipe® Sampler: a symmetry based unit for reliable sampling of pressurised particulate streams

R.H. Steinhaus and A. Fouchee
Multotec Process Equipment (Pty.) Ltd.

Obtaining representative samples with minimised sampling errors, is critical for calculating accurate metallurgical mineral balances on process plants. A challenging situation exists, where no acceptable, robust or economically viable sampler has been commercialised for sampling of one-dimensional pressurised slurry pipelines yet. The design of the True Pipe® in-line sampler is based on the principle of symmetry, as described by Dominique François-Bongarçon (2005), and operates on a fail-safe principle for control on the synchronous opening and closing of valves for the sample chamber. Previous test work on the True Pipe® in-line sampler indicated that the prototype sampler is reliable within certain tolerances, initially indicating the concept could well be a viable design option. This paper presents the results from further test work, which mainly investigated three sampling phenomena in more detail, by examining classical one dimensional sampling, with the aid of an automated valve actuator. Firstly, the transient effect, which originates from the disruption in laminar particle flow. Secondly, the effect of split sampling, where the portion of the stream is sampled as well as the full stream. Thirdly, the effect of symmetry is confirmed. The expected accuracy level of the True Pipe® in-line sampler is also evaluated for varied material conditions. Advances on the design include the ability to sample the entire pressurised particulate stream in a safe operating condition, by making use of a mechanical actuator for synchronous opening and closing of the sample chambers, as well as improved control on the valve opening and closing cycles.

Practical use of variographics to identify losses and evaluate investment profitability in industrial processes

Hilde Tellesbø[a] and Kim H Esbensen[b,c]
[a]Weber Leca Rælingen, Saint-Gobain Byggevarer AS, Rælingen, Norway, Plant Manager, E-mail: hilde.tellesbo@weber-norge.no
[b]Geological Survey of Denmark & Greenland (GEUS), Copenhagen, Denmark. Research Professor, E-mail: ke@geus.dk
[c]ACABS Research Group, Aalborg University campus Esbjerg (AAUE), Esbjerg, Denmark. E-mail: kes@bio.aau.dk

The first example concerns production of light-weight expanded clay aggregates ('LECA'), produced in cement-like rotary kilns. Clay raw material is heated to 1150°C to be expanded. A periodicity was observed in a specific plant cooler regarding fluctuations in the material height (level). This influences the amount of air passing through the cooler and thereby amount of air and the pressure in the kiln. Periodicities in the pressure in the kiln cause periodicities in the level of expansion and thereby output from the kiln. A lower expansion means a smaller amount (m^3) of material produced from the same amount of raw material, i.e. higher production costs (sales are valued by m^3). This problem can be resolved by a more stable level in the cooler, which could be engineered by a small investment of about 20,000 Euro. A variogram characterization was carried out to evaluate the amplitude of the periodicity, and thereby the quantities involved (losses), which were finally used to calculate the pay-back time of the investment. From the variogram it was observed that the lowered kiln output was at least 0.4%. During one year with improved cooler level control this translates into savings of about 50,000 Euro, i.e. a pay-back time will be less than 6 months. The other example is from a LRM-project (Loss and Reduction Model) at a plant producing pre-mixed mortars, in which the variance of the weight of the produced bags was found to be consistently too large. A variographic analysis is applied with an aim to identify the root cause(s) of this problem (previous work has identified several potential factors contributing to this variance). Investment caution rules the day, e.g. it is futile to invest in expensive equipment to level the filling degree if the main problem turns out to be a high nugget effect v(0) caused by inaccurate scales. In such a case, investment should instead be directed at upgrading the scales or to change the scale control routines. This investigation is currently ongoing; final results will be presented at WCSB7. Variographic analysis is a powerful tool for industrial technicians, for process engineers - and industrial managers as well, in the present case for evaluating investment profitability in industrial processes.

JAOAC special guest editor section: representative sampling for food and feed materials: a critical need for food/feed safety

N.Thiex[a], C. Paoletti[b] and K. H. Esbensen[c,d]
[a]Thiex Laboratory Solutions LLC, Brookings, SD, USA. E-mail: nancy.thiex@gmail.com
[b]European Food Safety Authority, Parma, Italy E-mail: claudia.paoletti@efsa.europa.eu
[c]Geological Survey of Denmark and Greenland, Copenhagen, Denmark, E-mail: ke@geus.dk
[d]ACABS Research Group, University of Aalborg,Campus Esbjerg, Denmark, E-mail: ke@geus.dk

A special collection of papers on all aspects of food and feed safety sampling - to be used in risk assessment, process control in a food/feed manufacturing environment, foodborne disease outbreaks, and regulatory compliance -is now available as open access on the Journal of AOAC INTERNATIONAL's website. Visit http://aoac.publisher.ingentaconnect.com/content/aoac/jaoac for 11 fully refereed papers in J. AOAC Int.'s March/April 2015 issue.

These papers, with unrestricted online access, are the result of a ground-breaking trans-Atlantic collaboration between researchers, samplers, and regulators from Europe and the United States, a true first within the sampling world. Indeed, the authors gathered in Windsor, Colorado in October 2014 to collaborate and write. The authors brought strong opinions to the meeting and worked hard to reach a consensus. (jokingly referred to as the 'shootout'.)

The papers in this Special Section introduce the Theory of Sampling (TOS), which is relevant for all aspects of food and feed safety sampling, as the principles governing representative sampling apply universally. The papers are not independent; they were written and composed to integrate with each other, thus providing a comprehensive overview of the criteria that must be followed to ensure representative sampling.

The guest editors were: Kim Esbensen, Geological Survey of Denmark and Greenland and Aalborg University, Denmark, Claudia Paoletti, European Food Safety Authority Parma, Italy and Nancy Thiex, Thiex Laboratory Solutions, and Agricultural Materials section editor for the Journal.

The target audience for this Special Section includes all food/feed protection personnel: field sampling operators, academic and industrial scientists, laboratory personnel, companies, organisations, regulatory bodies and agencies that are responsible for sampling, as well as their project leaders, project managers, quality managers, supervisors, and directors. In the United States alone, there are an estimated 45,000 federal, state and local food/feed regulatory personnel, not including industry or laboratory personnel.

"We hope to trigger a scientific discussion and awareness towards global harmonisation of representative sampling approaches for food and feed commodities," it is stated in the section's introduction. "As a collection, these papers represent a leap forward with respect to a valid analytical methodology for the discipline."

The Special Guest Editor Section includes the following contributions:

- “Food and Feed Safety Assessment: Proper Sampling is Imperative” by Harry Kuiper and Claudia Paoletti. A free online appendix of terms used in key sampling standards and documents is included.
- “Towards a Unified Sampling Terminology: Clarifying Misperceptions” by Nancy Thiex, Kim H. Esbensen and Claudia Paoletti
- “A Systematic Approach to Representative Sampling” by Charles Ramsey and Claas Wagner
- “Sample Quality Criteria” by Charles Ramsey and Claas Wagner
- “Materials Properties: Heterogeneity and Appropriate Sampling Modes” by Kim H. Esbensen
- “Theory of Sampling—Four Critical Success Factors Before Analysis” by Claas Wagner and Kim H. Esbensen
- “Quality Control of Sampling Processes—A First Foray; From Field to Test Portion” by Kim H. Esbensen and Charles Ramsey
- “Considerations for Inference to Decision Units” by Charles Ramsey
- “Distributional Assumptions in Agricultural Commodities—Development of Fit-for-Decision Sampling Protocols” by Claudia Paoletti and Kim H. Esbensen
- “Critical Practicalities in Sampling For Mycotoxins in Feed” by Claas Wagner
- “Considerations for Sampling Contaminants in Agricultural Soils” by Charles Ramsey
- “Considerations for Sampling of Water” by Charles Ramsey

The Special Guest Editor Section is now available online at http://aoac.publisher.ingentaconnect.com/content/aoac/jaoac

The Special Guest Editor Section is scheduled for the March/April 2015 print issue of J. AOAC Int. For additional information on publication of this special section, please contact Catherine Wattenberg at cwattenberg@aoac.org

Figure 1. Transatlantic Special Section taskforce, October 2014, Windsor, Colorado (left to right): Nancy Thiex, Thiex Laboratory Solutions; Kim H. Esbensen, Geological Survey of Denmark and Greenland and ACABS Research Group, University of Aalborg; Charles Ramsey, EnviroStat, Inc.; Claas Wagner, Wagner Consultants; and Claudia Paoletti, European Food Safety Authority, Parma, Italy.

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Claudia Paoletti is employed by the European Food Safety Authority (EFSA). The positions and opinions presented in this special session are those of the author alone and do not necessarily represent the views or scientific works of EFSA.

Critical practicalities in sampling for mycotoxins in feed- heterogeneity characterisation

Claas Wagner
E-Mail: cw@wagnerconsultants.com

The presence of mycotoxins, in particular aflatoxin B1, can cause significant health problems as well as severe economic loss, and are therefore regulated with respect to maximum acceptable concentration for various feed- and foodstuffs. International regulatory authorities have recognized the importance of representative sampling, and sampling guidelines have been formulated which only partly comply with the Theory of Sampling (TOS). In particular, practical guidance regarding sampling, including correct design and operation of sampling devices and explanation on how to develop sufficient sampling protocols are lacking in current guidelines. These are critical practicalities of main importance, especially when dealing with trace concentrations and/or concentrations that are irregularly distributed - as is the case for mycotoxins. Furthermore, heterogeneity characterization, which is a necessary requirement to be able develop valid sampling protocols or validation assessments of existing sampling operations, is currently not mentioned in the existing guidelines. The present paper focuses on heterogeneity characterization with respect to sampling of mycotoxins for 1–D and 3-D feed decision units. Structural guidelines for correctly designing experimental heterogeneity characterizations are presented, allowing evaluation of sampling representativeness and determination of optimal number of increments per composite sample.

A European standard for sampling of waste materials: EN 14899

Philippe Wavrer,[a] Bernard Morvan[b] and Sébastien Louis-Rose[c]
[a]Waste Sector Manager, Caspeo, Orléans, France, E-mail: p.wavrer@caspeo.net
[b]Traidema, Rennes, France. E–mail: bmorvan.traidema@numericable.fr
[c]AFNOR, La Plaine Saint-Denis, France. E-mail: sebastien.louis-rose@afnor.org

Wastes are materials, which the holder discards, or intends or is required to discard, and which may be sent for final disposal, reuse or recovery. Such materials are generally heterogeneous and the testing of them allows informed decisions to be made on the appropriate way in which they should be treated or not, recovered or disposed. In order to undertake valid tests a representative sample of the waste may be required.

The European Standard EN 14899, developed for the characterisation of waste by the European Committee for Standardisation and published in December 2005, specifies the procedural steps to be taken in the preparation and application of a waste Sampling Plan. The Sampling Plan describes the method of collection of the laboratory sample necessary for meeting the objective of the testing programme. The principles or basic rules outlined in this European Standard, provide a framework that can be used by the user:

- to produce standardised sampling plans for use in regular or routine circumstances (elaboration of daughter/derived standards dedicated to well defined sampling scenarios),
- to incorporate the specific sampling requirements of European and national legislation,
- to design and develop a Sampling Plan for use on a case by case basis.

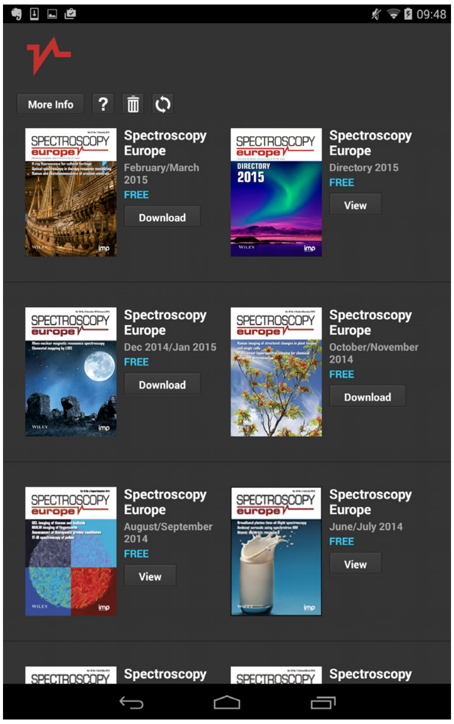
This European Standard is accompanied by five Technical Reports dealing with sampling techniques and procedural options and providing essential information and instructions for its application.

Innovative sampling solutions for the mining industry

Maurice Wicks
IMP Group P/L. E-mail: maurice@impgroup.com

While online analytical systems are continuously improving the mine site laboratory remains the benchmark. The laboratory is expected to produce high quality information, so the sampling process is critical. Process managers demand high quality, timely produced results from the laboratory. Mine managers and shareholders are demanding that the process, analytical results and productivity is optimized maximize return on investment. These demands conflict with traditional sampling and laboratory routines which are frequently slow, labor intensive and frequently involve potentially dangerous, not to mention unscientific methods and work practices.

For more than a quarter of a century, working with the world's largest mining companies. Over this time, IMP has teamed with its partners and likeminded customers, to challenge conventional sample collection and processing techniques. In doing so we have developed ground breaking innovative automated sampling and laboratory solutions for the mining industry. This paper will introduce you to a selection of the automated sampling and laboratory solutions that we have developed. It will achieve this by presenting case studies, including but not limited to, a time based and mass based automated sampling and laboratory solutions for lump and fines, powder sampling and analysis techniques and slurry sampling and analysis solutions.



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