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TOS forum

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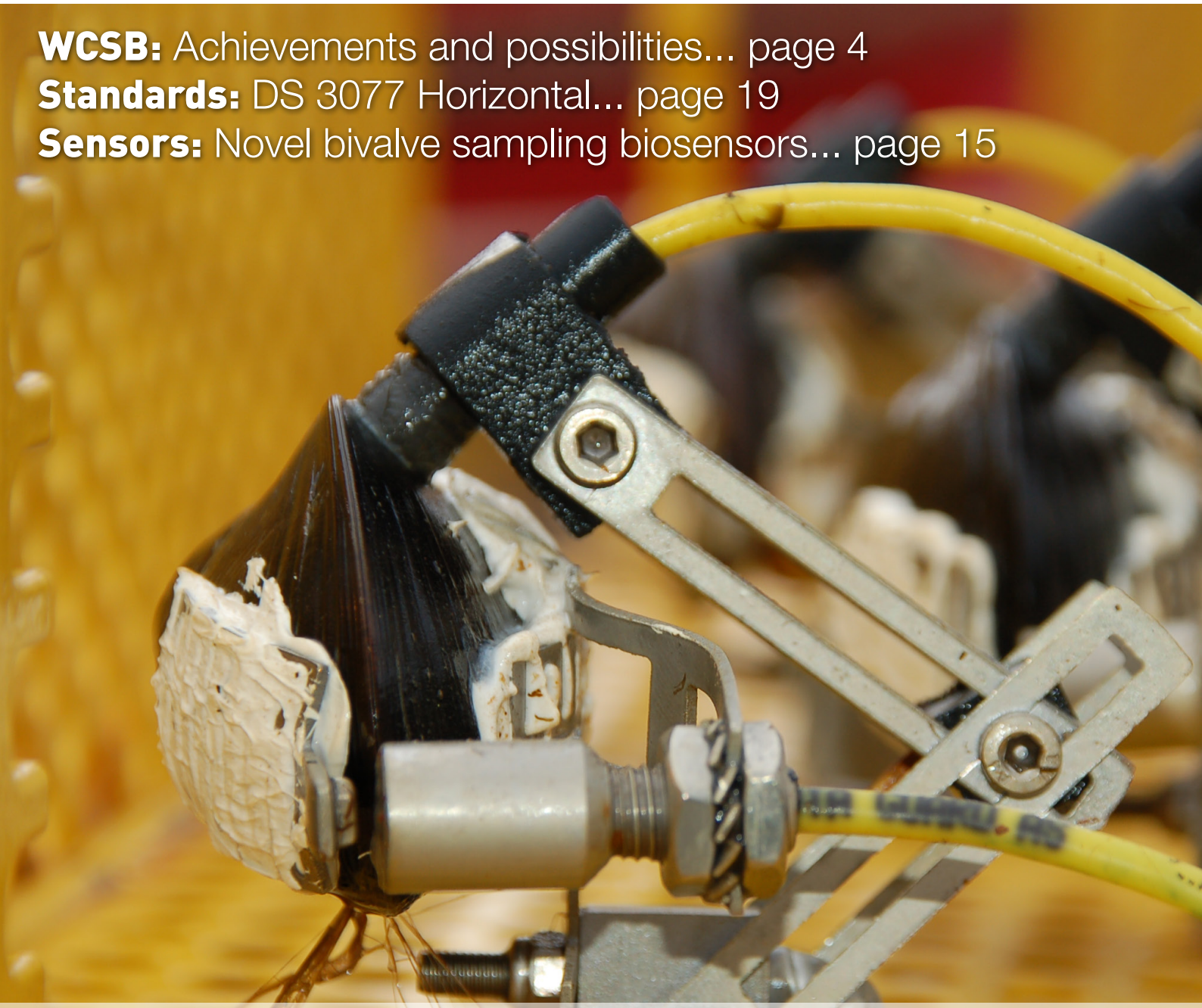

FORUM FOR THEORY AND PRACTICE OF REPRESENTATIVE SAMPLING (TOS)

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Q-Interline Sampling Award 2013

As has happened at previous international NIR spectroscopy conferences, Q-Interline handed out the Q-Interline sampling award in Montpellier, France, during the NIR-2013 conference. The scientific committee behind the award, headed by Professor Kim Esbensen, did a careful review of all posters and orals. Nominees were all poster and orals where sampling issues had been dealt with in a proper and professional manner, acknowledging that what comes before analysis may have a huge impact on the results.

This year's winner is Industrial Pharmacist Dr Lizbeth Martinez and her team, with poster #091, "Mixing of particulate material studied by near infrared spectroscopy". Dr Martinez and the team has made an important contribution to the understanding of how chemical and physical attributes affects the optical sampling situation, and that sampling can have a huge impact on the analytical performance.

Winners of the Q-Interline Sampling Award 2013. From left to right: Dr Lorenz Liesum, Dr Lizbeth Martinez and Dr Antonio Peinado.

Every other year, Q-Interline selects a person or a group to receive the Sampling Award. The achievement should focus on either fast analytical methods with critical consideration to the Theory of Sampling (TOS), or focus on critical, correct sampling in the area of Process Analytical Technologies (PAT). The sampling award can be given for fundamental studies, R&D or industrial implementation.

PANalytical NIR partners with ALS's CoreViewer

PANalytical NIR (formerly ASD Inc.) and ALS Mineral Services have announced that ALS's geochemical data management system CoreViewer will incorporate near infrared (NIR) mineralogy data collected from PANalytical's TerraSpec 4 to provide customers with greater comprehensive visual representation of their data.

Spectral mineralogy has long provided great benefits to mine operators for both mining exploration and production projects as thousands of spectra are often collected for each project. In addition to the spectral mineralogy, a plethora of additional data that is collected by geologists for projects can complicate the correlation, management and presentation of that data. The goal of this partnership is to provide seamless information flow from the collection and interpretation of the spectra, through integration with other geologic data and presenting it on the web for collaborative decision making.

Geologists can now submit TerraSpec data along with drill core photos into ALS' CoreViewer so spectral data can be plotted directly alongside the photograph, along with other relevant geological or geochemical data. This data is then viewable online.

More information from www.asdi.com

Martian sampling challenge

TOS forum has located a news item that will interest all readers. It concerns the world's decidedly largest and most refined effort to eliminate all possible IPE (Incorrect Preparation Errors, which in this case include "storage errors" and "cross-contamination errors"). The European Space Agency (ESA) have built a container to hold samples collected on Mars and return them to Earth (read the full story at http://bit.ly/16oLeH6).

This spherical container has been engineered to house samples to be brought back from Mars. Weighing less than 5 kg, this 23 cm-diameter sphere has been designed to keep Martian samples in pristine condition at a temperature of under –10°C throughout their journey back to Earth. The container hosts 11 sealable receptacles, including one set aside for a sample of martian air. Copyright ESA-Anneke Le Floc'h

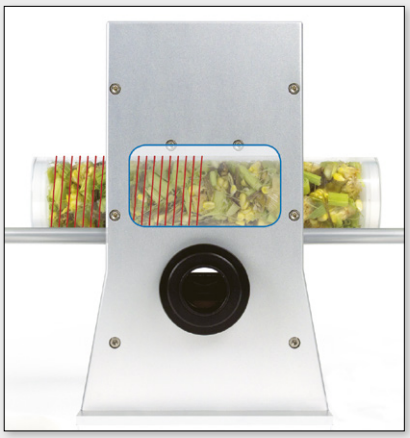
All readers of *TOS forum* will be able to locate a possible "weak spot" in the ESA article—but there may very well be a solution somewhere in the mission descriptions, regarding the all-important question:

- HOW will these 11 samples be taken? In a gravity field that is less than 1/3 of that on Earth? At temperatures which are generally below zero, and with an atmospheric pressure of 7.5 millibars only (less than 1/100 of that on Earth)?
- HOW does this influence our standard application of TOS?

Something to think about and ponder for all TOS afficionados ...

FT-NIR with Spiral Sampler

Q-Interline have launched a combination of their FT-NIR platform, the Quant, and a new patented accessory, the Spiral Sampler; together called the AgriQuant B8.



Q-Interline's Spiral Sampler acquires representative data from very hetergeneous samples.

The AgriQuant B8 makes it easy to acquire representative spectral data from very heterogenic samples with a high degree of reproducibility. Drying and grinding is no longer needed for many products and parameters, vastly reducing the total time spent from reception of the samples to the final result. Examples of target materials are wet forage, fresh energy crops and wood pellets, compost, cotton, flaky materials, big pellet materials and generally anything that does not fit well in a petri dish.

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Welcome to the inaugural issue of *TOS forum*!

The issue in your hands represents a constructive answer to some of the frustration which has existed in parallel with the first successful decade of WCSB conferences. The conferences function well, scientifically and socially, and they have all been organised and conducted with exemplary professionalism.

However, there has also been deep frustration—evidenced by a plethora of personal statements over all these years. The main issue is that while individual conference attendees unquestionably receive new knowledge and valuable personal inspiration at WCSB, there is very little inter-group activity *between* conferences (with the exception of existing personal networks, which mostly contain only a few individuals). A case in point: while proceedings' papers are a delight to read **after** each conference, there is simply no time for discussion of more than a few papers during the conference. This is a frustration for us all.

But, there is a way out of these frustrations, a way that will be able to serve the above complaints and desires. You hold in your hand the first issue of a new communication platform for all professionals dealing with sampling, the *TOS forum*, which has been created precisely to respond to all of the above in the form of a forum in which to present many types of contributions, e.g. discussions of proceedings papers from the WCSB series as well to publish minor original entries (research in progress etc.), news of people, products and events etc. In addition, *TOS forum* will also function as an everyday platform for interaction between all members of the international sampling community, and which could even also be a vector for an augmented outreach strategy beyond our already existing circles.

The International Council for Near Infrared Spectroscopy (ICNIRS) is a sister organisation, currently boasting approximately 500 delegates to its biannual world conferences. ICNIRS has similar needs and desires regarding scientific interaction and information-sharing in the periods between its international conferences, identical to those facing the TOS community. Within ICNIRS this vital issue has been solved with resounding success in a fashion that may well serve as a template for our present needs. Indeed by looking to ICNIRS, the TOS community may be able to "hit the ground running ...".

The publisher of *NIR news*, IM Publications, has agreed to replicate the print publication for our TOS community, but with a slightly different publication frequency defined by the TOS community's needs, initially suggested to be every 3 months.

An attempt has been made to produce a relevant, "typical" *TOS forum*, showcasing many of the types of articles and contributions that we hope will be of general interest—with one exception. In this issue there happens to be little that caters to the mining or minerals processing industries. This is a mere coincidence, likely brought about by the heavy representation of these sectors at WCSB6, indeed at the last several conferences, all for the best of reasons. However, here also, *TOS forum* will be able to come to the rescue by welcoming, indeed encouraging, contributions on all areas of sampling theory and practice.

The first edition of *TOS forum* (both printed and internet versions are available) is being handed out to all participants at WCSB6. This sample issue has been produced by an *ad hoc* working group. But this group is only supposed to be temporary. It is hoped that this issue will kindle the interest of a salient group of associate regional editors and many more active authors and contributors.

TOS forum is offered as new facility to aid us in the next decades of inspired work and significant achievements by our vibrant, healthily evolving community. Consider this Editorial as a cordial invitation to join in and to contribute!

Kim Esbensen

Bivalves are being used as sampling sensors to monitor pollution from oil and gas facilities. Find out more in the article starting on page 15.

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.

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The World Conference on Sampling and Blending (WCSB)—achievements and possibilities

Personal reflections by Francis F. Pitard

TOS forum has received many responses to the first call for contributions, some of which are published in this first issue, others will follow as soon as possible. The very first submission received, presented here, was from the extraordinarily active *éminence grise* of sampling, Francis F. Pitard, in the form of personal reflections on the achievements and prospects of the series of World Conferences on Sampling and Blending.

Introduction

At the event of WCSB6 I want to put some thoughts together, so as a Pierre Gy Gold Medallist I would bring my experiences and reflections on TOS, and contribute to making sure TOS grows in a rational way—in spite of its many distracters. Looking at recent comments made around the world, it is clear that many statisticians and empiricists promoting "Measurement of Uncertainty" (MU) strongly believe that the "Theory of Sampling" is something they can live without. Such antagonism is misplaced, unjustified and very unfair and I am aware of a heroic attempt to bridge the chasm between TOS and MU, which is on the verge of being crowned with success.[1] I also strongly believe the MU promoters need TOS, and vice versa, and perhaps, through WCSB if we could communicate in a more friendly way, we would be able to create the necessary foundation of many, better standards around the world. In this search for "peace" it would be perhaps advisable to go back to history.

A long time ago

We live in a heterogeneous world and all attempts to reach homogeneity are most certainly an exercise in futility. This was the starting point for the entire life's work by Pierre Gy that can be dated pretty accurately to the year 1950. But before Gy's work there were many authors, empiricists and theorists, who came up with good ideas and remarkable work. Gy's mission was to spend 10 years (late 50s early 60s) to make a monumental search of the existing literature on the subject of sampling particulate materials. In his historical documents[2–4] Gy always carefully referred to all the positive work he had found from theoreticians. Along the way he had been mostly impressed by the American school of thought, such as the remarkable works of D.W. Brunton, Kassel, Guy and especially R.M. Becker, and many others from other schools around the world. He also discovered the work of empiricists, such as Richards from MIT. It is fascinating to see that today empiricists still have a strong hold on how sampling problems should be approached and resolved. Gy's work is an integrated and comprehensive approach naturally based on ideas of many of these preceding workers. To this day, he is the only author who has created a complete coverage of what a Theory of Sampling must contain. All subsequent work carried out outside this framework rarely cover all sources of sampling errors in a logical way, and if they do, it is only an attempt to try to explain *how* Gy's theory is working.

Irrefutable facts

Gy breaks the total uncertainty manifestations down into eight sources of sampling variability which he called *sampling errors* (i.e., short-range errors FSE, GSE, IDE, IEE, IWE and IPE, plus a long-range error and a periodic error for dynamic measurements), to which other sources of uncertainty should be added such as laboratory analytical measurement error and the *in situ* nugget effect (e.g. for geologists and geochemists). MU experts and empiricists seem to resent such classification as they think the conventional statistical analysis of data alone is enough to detect sampling problems; in this there is a firm belief that all variability can be modelled by a systematic component (bias, acceptable or not) and a stochastic variance (precision, acceptable or not). However, detection is not cure, so MU should welcome TOS because it effectively pinpoints where problems are, and this is the cardinal issue, gives irrefutable solutions for minimising each source of excessive sampling uncertainty. As a quick reminder, TOS makes a clear distinction between *uncertainty* (i.e., **after** all sources of sampling biases have been minimised to a negligible level, and **after** precision has been reduced to an acceptable level relative to a pre-selected Data Quality Objective), and *error* when no attempts to minimise sampling correctness problems and unacceptable precision are made. The word "error" was selected by Gy because at the time, early sixties, in an overwhelming amount of cases sampling incorrectness and excessive precision problems were the rule of the day. These definitions in TOS may bother some MU experts, but I do not think they are totally incompatible with their ways of thinking either... So, let us negotiate together… within WCSB would be advisable.

Matheron's introduction of Gy's work

In the preface to Gy's historical publication (dated 15 January 1967),[2] released in *Revue de l'Industrie Minerale* (which only very few of today's sampling experts know of—and far less have read), the famous originator of the discipline of "geostatistics", G. Matheron stated (translated from the French by Francis Pitard):

"In this work that Pierre Gy asked me to present to his readers, we may see the characteristics of a accomplishment of reason and an intelligent synthesis trying to satisfy at the same time the necessary rigour of theoretical thinking, unity and coherence and the necessary efficiency in complex conditions often poorly defined in industrial practices. It is the first time it seems that such a synthesis is provided in the world of sampling, a domain where, as Pierre Gy mentions, some medieval practices from alchemists still remain. Such statement may be surprising, especially considering that the "Ratio Occidentalis" from the very

day it gave itself the mission of conquering the world, changed all the old ways of living and thinking, then radically transformed the way the planet where we live looks like; it is then difficult to comprehend the reasons why all techniques relative to the subject of sampling escaped, just by themselves, this new imperial order. Perhaps we would say that it is because too many difficult questions, for which too many inextricable factors may interfere with logical answers, are nearly impossible to be clearly expressed. Therefore, a fortiori *it is nearly impossible to submit these questions to the rigour of scientific analysis. This is why common sense, guided by experience and intuition, found their way for too long inside such a labyrinth… It is very clear that a theory that sits on an empty space will produce only chimerical thinking; but, inversely, common sense and experience do not have the right to dismiss reason as a dishonest servant."*

Identifying the theory of sampling (TOS)

Misconceptions

For TOS there are only so many fully initiated champions to go around, and sampling teams without one are doomed to bide their time on the treadmill of mediocrity. The fortunate teams have the duty to give guidance to sampling practitioners around the world, helping to establish operative, practical standards… However, such standards are not always open to new ways of thinking: too much conservatism, too much status quo and unwillingness to stand for what is right instead of simply following what the entire world is doing... is often the rule.

Many people around the world today think the TOS is the work of Pierre Gy alone; there is nothing further from the truth, however! TOS is the work of D.W. Brunton, Kassel, Guy, R.M. Becker and many others, sorted out in a logical way and, of course, significantly augmented by Pierre Gy. Later new works were brought to TOS by François-Bongarçon, Minkkinen, Holmes, Minnitt, Lyman, Esbensen and Pitard who integrated the valuable works of Visman and Ingamells in his 2009 doctoral thesis. Here it is shown that several of these individual theories are not necessarily incompatible, in fact, in this particular case they are indeed beautifully complementary.

A dynamic body

TOS is a dynamic body in a permanent state of flux and it is critically important it remains that way. WCSB would appear to be just the right platform to deliberate suggestions for new additions… I emphasise the word *additions*, because a lot of people think of subtractions, replacements, negative arguments—born in a complete ignorance of the valuable works done during the last 50 years. My advice to many of those ready to voice criticism of Gy's work is, spend some years to understand his work **in depth**, including many essential French publications, then and only then, we may talk again. I have little tolerance for those who read a short paper in diagonal and are already on a mission of critique. Einstein said "I have little patience with scientists who take a board of wood, look for its thinnest part, and drill a great number of holes where drilling is easy".

WCSB: A powerful meeting place for science and industries

TOS, through WCSB, brings together a forum of people who is interested in sampling theory, practice, experience, implications and standards, and these meetings offer powerful tools to academics, manufacturers, engineering firms and practitioners, so essential for many industries; this is our mission at WCSB. Equally important, at WCSB there is also a need for MU experts to be present; proponents of MU are very welcome and their ways of thinking should be respected because their work is important and necessary. MU is welcomed in the spirit of corporation laid down by Esbensen and Wagner.[1]

Main accomplishments of WCSB

The theory: attracting academics

University institutes that do not teach TOS have a huge handicap and it is fair to say they are managed with a deficient vision. Since WCSB was created, the academic world has been gaining momentum, however, both to learn about and to teach, and spread TOS. Along this slow process there are many obstacles; the new generation of teachers, professors and consultants often believe they can become experts overnight… We should accept such mistakes because they are the only ways for them to get better at what they are doing… and we all went through these steps ourselves.

Some young participants who faithfully participated to the WCSB conferences are now making huge progress; some prepared masters, doctorates and even post-doctorates on the subject of sampling and closely related subjects. Now, we have new teachers of the TOS in Denmark, Brazil, Mexico, South Africa and probably many other countries.

Pierre Gy's Gold Medallists, identified at each WCSB conference, are those who have been most effective and successful around the world to disseminate and promote TOS. This group of champions constitutes a formidable asset today as a unified body that is capable to teach, promote and make positive suggestions for a bright future as it was never done before.

Implications: Helping manufacturers and engineering firms

Manufacturers of sampling equipment are usually good engineers and excellent entrepreneurs: they know how to build good machines and sell them to the world. However, a good machine may easily transgress the most elementary rules of increment delimitation and increment extraction correctness, making it totally useless as a sampler as it is incapable of providing accurate and precise enough information. Actually, this problem is exactly where the word "uncertainty" should be replaced by the word "error"; it should be regarded as an *error* to produce machines that are obviously wrong (in TOS' sense), indeed outcomes from such "sampling" have no place in the world of "uncertainty" either. Several manufacturers of sampling equipment around the world found enormous value and guidance from WCSB to the point that they are willing to be valuable sponsors of the conference, which says it all…. For example, at WCSB4, Multotec, a well-known manufacturer from South Africa, allowed several of the best sampling experts to review their sampling systems and accept criticisms so they could greatly improve the correctness of their equipment. In a more discrete way, other manufacturers such as Essa FLSmidth, Ludowici FLSmidth, TecProMin and Rocklabs did the same and they undoubtedly, today, manufacture the best sampling equipment in the world.

Experience

To the empiricists: experience teaches nothing if you are not capable of a continuous and iterative learning process, and this is exactly why a dynamic and continuously updated TOS is important to all of us. We long passed the time when TOS was Gy's

product alone; today TOS is a scientific patrimony based on the talents and experiences of many experts worldwide. But TOS and its practitioners has its good and bad moments, as it should be, justifying the regular gathering at WCSB where, together, we may find the pathways to logical new breakthroughs.

Documentation, references and standards

Proceedings from WCSB conferences are extraordinarily valuable documents and many contributions herein can indeed be the object of new studies, new research and new breakthrough leading to additions that would allow standards committees to create dynamic, progressive iterative standards for industries and academics. As a first step, it is imperative that all WCSB Proceedings are easily available at all times, irrespective of whether this comes in the form of books or journals. Should other formats be decided upon, all proceedings papers must be freely, and easily available to the entire sampling community—especially to those who could not attend a specific conference. Without this option, the intended inter-communication will fail.

Making a united community from WCSB

Six WCSB conferences have taken place in the period 2003—2013. An enormous amount of valuable presentations have been featured and scores of Proceedings documents have been created and communicated to practitioners all around the world. Yet, there was no attempt to take all this information and *integrate* it in a logical way into TOS, as it was in 2003, prior to the creation of WCSB. This is perhaps understandable, as everybody was more than happy that the institution WCSB became firmly established. But this shortcoming must soon be corrected for otherwise the mission of WCSB will fade away and ultimately fail. One of the reasons for this status quo is because too many authors of good papers are far more interested in promoting themselves than helping to make TOS grow in a logical way, indeed there is a certain amount of grandstanding at every WCSB (perhaps unavoidable—but very nearly always counter-productive). Worse, too many are apparently interested in creating *their own* TOS, which is highly unfortunate as this goes nowhere in the broader perspective. Were such eager beavers only able to stand back a little, take a deep breath and refrain from such egocentricity, WCSB would be a forum ten times more powerful…

Figure 1. Three surviving Pierre Gy's Sampling Gold Medallists—very much aware of the responsibility to guide TOS along to grow in a united, rational and logical way. Left to right: Francis F. Pitard, Pentti Minkkinen and Dominique François-Bongarçon.

Publications

There are thousands of worthwhile references that can be found in all WCSB proceedings and this is precisely the point: how do we integrate all that knowledge into a single, dynamic, iteratively updated *oeuvre* of the greatest value for all, industries and academics alike?

Concluding remarks

Figure 1 allows me a few final reflections aimed at the future. There are today three survivors from a group of the five first Pierre Gy's Sampling Gold Medallists (Dominique François-Bongarçon, Pentti Minkkinen and Francis F. Pitard). We deeply regret and miss dearly our two friends and colleagues who have passed since the penultimate WCSB, Pedro Carrasco Castelli and Allen Royle—their contribution to the promotion and teaching of TOS were of the highest value; they will be forever remembered with fondness and love.

But we are not alone—this is our joint responsibility, the entire sampling community. There is no better way to ensure success for this endeavour than by contributing constructively to the series of World Conferences on Sampling and Blending (WCSB) and to the new *TOS forum*.

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Representative sampling in biomass studies—not so fast!

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Proper execution of representative sampling and laboratory mass reduction procedures are critical for the validity and reliability of chemical analyses of highly heterogeneous biomass fuels. In the study reported by Thy *et al.*,[1] it was demonstrated that faulty sampling had resulted in apparent ash compositions that differed from the true compositions by factors of two to three for many major oxides. Analytical results based on non-representative samples may thus not be representative for the specific fuel and processes being studied. Despite the general acceptance that accurate and representative compositions is a critical prerequisite for understanding reactions and elemental fractionation, the biomass energy community appears largely to have ignored the critical issues surrounding representative primary sampling. This can have resulted in misleading or faulty conclusions and may have restricted reliable predictive modelling.

Background

Knowledge of representative compositions of biomass fuels and their derivatives is critical for understanding reactions and elemental fractionation during thermal conversion such as fuel combustion. Achieving proper knowledge for highly heterogeneous biomass fuels is not a straightforward matter, but calls for careful considerations of the primary sampling procedures. Although the literature outside the biomass realm contains a wealth of established sampling principles, drying and ashing used as mass-reduction measures in fuel and combustion studies introduce further complexities. This mandates careful considerations also of laboratory procedures such as mass reduction techniques for secondary sampling of biomass byproducts in addition to the analytical procedures themselves. Despite the general knowledge in other fields that sampling errors can attain magnitudes of 20–50 times the analytical errors alone, in biomass studies the focus is all too often mainly on the precision of the analytical procedures alone, which is usually gauged by repeating the analytical procedure. Thus the quality of chemical analysis is typically evaluated by analysing as unknowns, well-characterised and compositionally similar standards. This approach only furthers the total analytical uncertainty for controlled samples, however (certified standards or in-house standards). But highly precise chemical analyses are of very limited blessing if the materials analysed are based on faulty or poorly documented and little understood sampling and mass reduction procedures. The main guarantee for accuracy of the analytical results rests with the documented representativeness of the entire sampling pathway.[2]

The biomass and energy community has unfortunately largely ignored or underestimated the effects of these problems. This can have impeded the ability to perform accurate predictive modelling, either experimentally or theoretically, of phase equilibria, elemental mobility and fractionation, and physical behaviour of residual silicate systems from thermal conversion of biomass materials.

This short note refers to a case study of the possible detrimental effect of non-representative chemical analyses on predicting relative element mobility during combustion of common wood fuel published by Thy *et al.*[1]

Wood fuel case story

This study reported attempts to characterise the inorganic part of a mixed conifer wood (mixed white fir and ponderosa pine), which was obtained from an operating power plant in California. The average grain-size of the fuel chips was inch-size (2–3 cm) and composed principally of solid wood with only minor bark, branches and foliage (Figure 1). The fuel was treated using standard methods of drying. The total air-dried mass of about 150 kg was stored in a closed master bin.

Three samples were taken from the master bin over the years of the duration of the study, two 1 kg primary samples (from which were produced 100 g of ashes for each). The analytical results in the present studies were elemental analyses of the ash fraction. These two samples were analysed twice by the same established commercial laboratory following accepted ASTM standard protocols. A larger primary fuel sample (25 kg) was also extracted from the same bin, which was milled to a finer 3-mm grain-size before being ashed in a similar fashion. This latter ash (~2500 g) was sampled after manual homogenisation, the analytical mass was 3 g and analysed by X-ray fluorescence techniques. The same ash was similarly sampled and analysed by the earlier used commercial laboratory mentioned following the same ASTM standard protocols previously used. Thus there is a basis for comparison of the analytical results based on this small experimental sampling design.

The four analyses summarised in Table 1 were all obtained with the purpose of representing the ash fraction of the same wood fuel. Since the particular purpose of the study was to evaluate alkali metal volatilisation as a function of temperature, see Reference 1 for details, an accurate knowledge of the ash composition was critical. NIST fly ash reference material was analysed concurrently with the unknown wood ashes and the results are also listed in Table 1 together with their recommended standard values.

Comparison of the results in Table 1 reveals very large discrepancies between the individual analyses. The content of the three main components varied unexpectedly by factors of two to three for the major constituents SiO_2, CaO and K_2O. The repeated results on the standard fly ash (last two columns) clearly show that analytical procedures were not the cause of these highly significant deviations, despite the two different analytical techniques used. Although the fly ash standard does not compare closely in composition to the wood ash, one would be hard pressed

Figure 1. Air dried wood chips used in the original study. Largest shards are approximately 1 inch (3 cm) in length. Although seemingly of uniform composition, the fuel actually consists of a mix of white fir and ponderosa pine. Grab-sampling of the pristine material will obviously give rise to severe sampling errors (FSE + GSE) if not guided by proper TOS-compliant principles, possibly aggravated by using significantly too small sample masses.

to attribute the highly diverse analytical results to analytical problems only. In this context it is particularly revealing that when the two different laboratories analyse the same ash, relatively consistent results were obtained.

These results forced us to reconsider the entire sampling–handling–subsampling–analysis pathway as implemented in the biomass energy community.

Implications

The study in the original 2009 paper in *Biomass & Bioenergy*[1] was motivated by a failed attempt to mass balance a set of high temperature, partial melting wood ash experiments.[3] The results led to the unexpected indication that appreciable amounts of silica were apparently lost during heating to temperatures of well above 1500°C. Because silica is known to be immobile at atmospheric pressure to very high temperatures, and indeed perhaps *only* volatile at conditions believed to have prevailed during formation of the primitive solar nebula, a second look at the data was warranted. This reconsideration clearly showed that the erratic results were caused by chemical analytical results that were not representative of the biomass investigated. We were able to rule out, using different analytical methods, the possibility that large analytical biases and errors were responsible (Table 1). The conclusion was inescapable: unwittingly large sampling errors were committed by basing our initial analysis on the results from a non-representative primary sampling process.

Because of the heterogeneous nature of the biomass, a grab sample, as is routinely used in this realm, is highly unlikely to be representative for the bulk fuel composition. When we later re-analysed the actual ash used in the experiments and used this composition in new mass balance calculations, we obtained reasonable results that indeed suggested that only the alkali metals were mobile at high temperatures simulating combustion as indeed reported by Thy et al.[3]

This experience prompted us to take a new look into available standard procedures and common practices in related and/or similar studies published in the scientific fuel and biomass literature. A brief survey of papers published in *Biomass & Bioenergy* between 1991 and 2009 showed that very few combustion studies have indeed made the effort to document, far less to ensure, that the biomass material being studied was representative with respect to a particular geographic region or specific location, plant species or the actual power plant fuel intake. Fuel material used in scientific studies is often obtained in limited quantity (~100 kg or less) from forest and agricultural harvest locations or from feedstock intake stations of commercial power plants. Such feedstock samples for forest materials are very unlikely to be representative and to be sufficiently well documented in all relevant aspects. Forest wood fuel is highly heterogeneous (segregated, stratified and contaminated) (Figures 2 and 3) typically composed of components such as pure wood chips, branch and root fragments, bark, foliage, as well as adhering soil. It is neither a simple practical nor an easy intellectual task, if not impossible, to aim for the proverbial statistically sound

Table 1. Duplicated analyses of ash fraction of wood fuel (normalised to 100%).

	AN 2002	AN 2005	AN 2006	AU 2002	NIST 1633a	Recom.
Sample size	100 g	100 g	25 kg	25 kg		
SiO_2	33.95	19.89	12.98	14.01	48.61	48.78
TiO_2	0.13	0.33	0.12	0.19	1.37	1.33
Al_2O_3	6.21	9.38	4.11	4.68	27.04	27.02
Fe_2O_3	2.43	3.60	1.40	1.71	13.63	13.44
MnO	2.01	1.99	2.66	2.64	0.02	0.02
MgO	4.33	10.05	7.02	7.39	0.79	0.75
CaO	35.67	23.92	47.40	48.04	1.56	1.55
Na_2O	0.58	0.60	0.63	0.58	0.21	0.23
K_2O	11.36	20.08	18.42	16.06	2.23	2.26
P_2O_5	3.33	10.18	5.25	4.69	0.38	0.38
Sum	100.00	100.00	100.00	100.00	95.84	95.76

Recommended composition of NIST 1633a (coal fly ash) are from GeoReM (2006) (http://georem.mpch-mainz.gwdg.de). Other analyses are from Thy et al.1

"random and representative" sample from such materials. This would require that the probability of all individual "elements" being sampled is exactly identical, irrespective of size, shape and their constituting elements (wood chips, bark, leaves, roots). In fact, the heterogeneity of biomass feedstock easily ranks among some of the most difficult materials to sample (Figures 2 and 3). In such a context, the unwitting quest for an intuitive and simple sampling procedure will always be on the agenda. This may have been a major scientific hindrance wherever reliable analytical results were essential for achieving a specific goal.

Without knowledge and respect for proper sampling principles, selection of supposedly representative samples all too often boils down to a personal intuitive judgement tied to the purpose of the particular study at hand, and this is almost invariably carried out by grab-sampling. If it is intended that the primary sample will represent the specific part of a forest, or a specific tree species, it may perhaps be possible to design a spatially random sampling strategy based on statistical knowledge from forest biomass surveys. Most likely it is more often desired that a sample should represent a specific biomass type and/or a seasonal average intake at a power plant (such as spring white pine wood). It is often possible to get sampling access to the feedstock at either an intake station at a power plant or from a conveyor belt prior to being admitted to the boiler. But to conduct representative sampling at such locations is still considered a daunting task for which most investigators often do not have the knowledge, patience or means to succeed. Because few fuel laboratories possess the required facilities for storing, preparing, ashing and sampling large fuel volumes for study and analysis, there is little doubt that truly representative samples are considered merely an ideal and unobtainable dream for many combustion studies of biomass fuels, whether originating from agricultural or urban sources.

Many investigators likely proceeded as was done in the original study: with the kind help of a plant fuel intake manager, we obtained a few, large plastic containers with wood chip feedstock claimed to be "as received" at the plant from a typical supplier. The information obtained in our case was that it represented mixed conifers (white fir and ponderosa pine) harvested from the north-eastern slopes of Mount Shasta, California. There is an almost unavoidable tendency to trust such claims regarding the provenance of primary samples, if not experienced regarding proper sampling principles, but this is most often a fatal trust. The fuel in our case was a high quality, whole-tree fuel composed of relatively clean wood chips with limited bark, branch and foliage parts. We proceeded to process about 100 kg of this fuel, which was the maximum that could reasonably be handled with the available facilities. We ashed a rather large proportion (25% of the primary sample mass) and were reasonably confident that the resultant ash after homogenisation and the sub-samples subsequently taken, represented the fuel, i.e. the secondary and tertiary sampling/mass-reduction steps were reasonably in control. There is no knowledge, however, of the degree to which the fuel truly represented the harvest biomass, the fuel received at the plant, the fuel conveyed to the boiler or combinations thereof. The primary sampling accuracy and hence the *representativity* may thus literally have been lost in the woods.

Discussion

The critical question obviously is whether the biomass field can live with this kind of uncertainty. Most of the scientific endeavours are designed toward understanding combustion and gasification processes and not toward obtaining absolute and truthful values representing the original feedstock fuel. The interest is most often to understand how certain elements behave during thermal conversion. The answers that we are seeking are thus typically relative to specific processes and not absolute with respect to original lot materials. Often secondary sampling from a primary sample (which may be more-or-less representative with respect to the primary lot) appears to provide an acceptable basis for this kind of specific studies, allowing us to gain insight

Figure 2. Typical fresh wood chips characterised by significant proportion of bark and foliage. Grab-sampling of this type of material will give rise to severe sampling errors (FSE + GSE) if not guided by proper TOS-compliant principles. Add hereto Incorrect Sampling Errors (ISE) if not considered.

Figure 3. Typical wood shard bio-fuel at a power plant intake. At this plant, routine primary sampling (for moisture determination), takes place following fully TOS-compliant procedures, see Reference 4 for details. An incremental primary increment sampler is shown (centre) just before being inserted into the lot (truckload); the sampler is closed when inserted. Three increments are used for composite sampling, i.e. from the top, middle and bottom level, respectively, with random sampling location in the X–Y plane.

into the central processes as long as fuel and products are sampled and handled in a sensible and identical representative manner from the secondary sampling stage onwards.

The seasoned experimentalists may advise that instead of trying to understand the behaviour of heterogeneous fuel systems, one may gain a better understanding of compositional variables by studying the individual components before embarking on the daunting task of examining experimentally the full complexity of realistic multi-component fuel systems. This way one can build an understanding of the complex system from knowledge of the behaviour of the individual components (bottom-up approach). Such an approach will also reduce the problem of obtaining representative components as long as we can sort and purify the material into its separate constituents. This bottom-up principle has been highly successful in phase equilibria studies of silicate systems, either simple or complex, and many other types of material science studies. However, at the end of this endeavour we are still left with the challenge of accounting for the total system in industrial use. In the understanding of biomass combustion, as well as in most other areas of science, the summation of all parts is often likely to be considerably more complex than a mere aggregation of partial results.

Thus, irrespective of method, scope and goal, it is critical for future biomass studies relying on analyses of experimental products that these be sampled only in a representative manner. This involves representativity in sampling of the primary lot, as well as for subsequent splitting of potentially large volumes (secondary sampling), milling of sub-samples to workable particle sizes and homogenising before the ultimate analytical aliquots are taken. In some cases it may be advantageous that sampling is done on ash fractions despite potential loss of elements during ashing, because smaller volumes and finer grain-sizes are easier to handle and ashes results in lower analytical detection limits. But relatively small grab samples of raw biomass or ash are, as shown also by our own experiences, prone, indeed likely, to be *non-representative* and may thus exhibit strongly diverse compositional variations. This is particularly true for the elemental composition of an ash fraction that only constitutes a minute proportion of the total sample (the ash fraction of clear wood is typically below 0.2). An increase in primary sample volume is often the only variable known that is believed to bring down these compositional sample-to-sample variations, but in fact this will only be true for samples approaching the total volume. A scientifically founded and improved sampling must counteract every feature of the complex lot heterogeneity, e.g. as per the principles presented in DS 3077.[2]

It is an essential, key insight in particular for all significantly heterogeneous materials, which cannot be freely mixed before the primary sampling stage (either too large and/or too heterogeneous lots), that composite sampling is the *only way forward*. A particularly relevant example is provided by Møller and Esbensen[4] for the primary characterisation of intake wood chips at a Danish power plant (Figure 3).

Conclusions and recommendations

Studies of biomass combustion processes are critically dependent on whether analyses of primary fuel (and ashes and slag) are conducted on samples that are demonstrably representative for the processes and materials being studied. The inherent problems in conducting traditional "statistically and sound sampling" of highly heterogeneous and stratified biomass critically restrict our ability to design valid and meaningful experiments of combustion processes. It is sometimes suggested, as a first alternative, that studies are conducted on the individual fuel components before multi-component fuel systems are being investigated, but this approach only dodges the ultimate purpose and will not necessarily address the full problem at power plant or incinerator plant scales. Consideration of proper mass reduction procedures (secondary sampling and sampling preparation) is still a prerequisite for the success of all biomass related studies. For this demand, as well as for primary sampling issues, a consistent theory of sampling is critically needed. There is an overwhelming TOS literature available to everybody's needs, a judiciously selected part of which can be found referred to in DS 3077.[2]

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The authors (Peter Thy, left): "WHOA—factors 2–3× wrong due to inappropriate sampling".

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Sampling conferences in South Africa

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In response to the rising interest in sampling in the minerals industry and the consistent educational input from international experts such as Francis Pitard, Dominique Francois-Bongarcon, Geoff Lyman and Kim Esbensen, three sampling conferences, forums for the expression of interest and research, have been held in South Africa over the past eight years. This has been a somewhat slower pace than that set by the Australian Institute of Mining and Metallurgy (AusIMM) who have arranged biannual sampling conferences in Perth since 2006. The first of the South African sampling conferences was entitled "Exploration, Mine, Met and Environmental Sampling" (EMMES 2005), held at the Eskom Conference Centre on 3–4 November 2005. The conference was presented under the auspices of the SAIMM in conjunction with the Geostatistical Association of Southern Africa (GSSA) and the Geological Society of Southern Africa (GSSA). The second conference specifically dedicated to sampling was the World Conference on Sampling and Blending 2009 (WCSB4) held in Cape Town in October 2009, and organised through the SAIMM. However, only 4 of the 35 conference papers presented were by South African authors, indicating that participation was very strongly skewed to the international community, whose support for this conference, by the way, was greatly appreciated.

The paucity of contributions from the South African sampling fraternity at WCSB4 emphasised the need for a local sampling conference at which those involved in day-to-day sampling activities on mines, in milling plants, in coastal loading terminals and in laboratories could be drawn to present the good work in sampling that they are doing. On this basis a third conference dedicated to sampling and entitled "Sampling and Analysis: Best-practice in African mining", with the sub-title "Reducing operational risk using sampling and assay" (SAIMM, Symposium Series S75), was proposed and organised. The conference was held at Misty Hills in the Muldersdrift area from 4 to 6 June 2013 with over 150 delegates registered for the conference. Of the 45 papers presented only three were by international speakers, namely Isobel Clark, Ralph Holmes (Keynote address) and Dominique Francois-Bongarcon.

For both of the non-WCSB conferences, Mr Hugh Bartlett was the Chairman of the Organising Committees. The substance and content of topics and papers presented between 2005 and 2013, as well as the progression of the level of research as recorded in the forewords to the conference proceedings (2005 and 2013), is noteworthy. In the foreword to the first conference, Bartlett (2005) emphasised that the conference was to be seen as a forum in which industry standards (of sampling) for exploration, mining and metallurgical processes for all commodities including coal, iron ore, diamonds, base metals, gold and platinum, could be discussed. He also emphasised that the application of sampling as the basis for resource and reserve estimation and metallurgical accounting had to be underpinned by good statistics. Questions such as the correctness of samples, ensuring unbiasedness, sample mass and methods for appropriate sample recovery and preparation were mentioned as being of utmost importance, and the reliability of assays, the use of certified reference materials and the issues surrounding quality assurance and quality control in the laboratory occupied an important place in the conference (Bartlett, 2005). In the foreword to the second conference Bartlett (2013) widened and deepened the scope of issues to be covered. He noted that sampling and sample analysis are the foundation of the minerals industry being essential at all stages of the value chain, from exploration and face sampling, to blast-hole sampling, in-mine grade control, ore processing and handling, metallurgical sampling, sub-sampling in the laboratory, as well as the analysis of standards and duplicates in maintaining quality control in the laboratory. The importance of sampling in trade of commodities, concentrates and residues for toll treatment was also highlighted.

Table 1. Major topics, papers presented and authors at the EMMES Conference, 2005.

QA/QC topics	**Standards and laboratory monitoring: Two key components of best practice assay quality control in the gold mining industry.** K. Kenyon, *AngloGold Ashanti Ltd* **Manufacture and use of reference materials.** M. McWha, *AMIS Mineral Standards* **Best practice—Methodology for production and use of reference materials for the platinum industry.** R. Sheets and D. Grant, *Applied Geology Services* and G. Chunnett, *Anglo Platinum* **Why mine/matrix matched certified reference materials.** C.J. Oats, *Anglo American PLC* **QA/QC at the Mineral Resource Management section of Sishen Mine.** J.H. Sullivan, *Sishen Iron Ore Mine* **Assay quality assurance—Quality control procedures at Goldfields Ghana Limited, Tarkwa Gold Mine.** S.D. Woods and R.N. Boryor, *Gold Fields Ghana Limited* **A practical quality assurance and quality control procedure for gold estimation in a deep level South African mine.** V. Govindsammy, *AngloGold Ashanti Ltd* **Analytical uncertainty component: The role of the laboratory.** V. Anderson, L. Duggan, S.H. Dry and R. Holdsworth, *Anglo Research* **Practical due diligence in fire assay.** D. du Preez, *Assay Tech*	9
Theory of sampling issues	**The imperatives for sampling and evaluation in SA mining industry.** P. Charlesworth, *Guest Speaker* **Determination of correct sample size and preparation method.** G.P.L. van der Linde, *Hotazel Manganese Mines* **An empirical assessment of GYs sampling constants K and Alpha using a broken rock model.** R.C.A. Minnitt, *Wits University* **The economic benefits of good sampling practices.** F. Pitard, *Guest Speaker* **Sampling standards.** C. Spangenberg, *AngloGold Ashanti Ltd* **Separation of errors in sampling and analysis.** H.E. Bartlett, *Hugh Bartlett Consulting* **Chemical measurement system analysis for a manganese metal production process.** R.C.A. Minnitt, *Wits University*, T. Gluck, C. Bothma and P.V. Savage, *Manganese Metal Co. (Ply) Ltd*	7
Sampling equipment	**Sampling tool project at AngloGold Ashanti Ltd.** R. Barnard, *AngloGold Ashanti Ltd* **Development and conceptual evaluation of a methodology for sampling for diamonds in broken ore.** S.J. Coward and J. Ferreira, *De Beers Mineral Resource Research and Development Unit* **Isokinetic emission testing.** R. Bissett and A. Jansen (presenting), *ECOSERV Environmental Consulting Services* **The use of radio frequency transponders in density tracers to conduct densimetric analysis.** D. van der Merwe and P. Fouche, *Kumba Resources* **An innovative and practical approach to sampling of slurries for metallurgical accounting.** R. Boyd, *Thermo Gamma Metrics (Ply) Ltd* **Cross belt sampler versus cross stream sampler.** W.S. Hefer, *Kumba Resources* **Development of a RF tracer for use in the mining and minerals processing industry, for ore tracking and blending.** P. Fouche, *Kumba Resources* (PRESENTATION ONLY) **The bulk sample preparation plant at Driefontein.** A. Fouche, *Gold Fields West Wits Analytical Laboratory*	8
Coal industry	**Sampling in the coal industry.** G.J. de Korte, *CSIR*	1
Metallurgy	**Sampling for cyanide in metallurgical processes.** P.W. Lotz, *Mintek* **An innovative and practical approach to sampling of slurries for metallurgical accounting.** R. Boyd, *Thermo Gamma Metrics (Ply) Ltd* **Improvements in metal accounting at Black Mountain.** J. Taylor, *Black Mountain*	3
Platinum	**The analysis of sulphur in the South African PGM smelting industry.** A.D. McKenzie, *Mintek* **Slurry sampling of toll PGE concentrates at Impala Platinum Ltd.** D. Adams, Impala Platinum and H.E. Bartlett, *Hugh Bartlett Consulting* **Confidences in metallurgical balances estimated from the errors in mass measurement, sampling and analytical determinations.** H.E. Bartlett, *Hugh Bartlett Consulting*	3
Diamonds	**Application of conditional simulation to optimise sampling diamond placer deposits.** S. Duggan, *De Beers Group Services* **Sampling considerations for determination of process efficiency within a diamond processing flow sheet.** R. Machowski, *De Beers Group Services (Ply) Ltd* **Correlations in dilution within the process plant at Snap Lake, De Beers, Canada—A practical sampling approach.** R. Machowski, *De Beers Group Services (Ply) Ltd* **Use of enterprise architecture in sampling programmes.** R.M. Irvine, *De Beers Group Services*	4
Environmental	**Environmental assessment, monitoring and interpretation.** J. Perkins, *Biotrack (Botswana) (Pty) Ltd* and M. Dangerfield, *Biotrack (Australia) (Pty) Ltd*	1

Conference content

A comparison of the content at each of the conferences is enlightening and interesting. The titles and authors of papers presented at the 2005 conference are listed in Table 1, with those for the 2013 conference listed in Table 2. Perhaps the most obvious difference in the conferences is the number of papers presented at each, 35 for the EMMES (2005) and 45 for the "Sampling and Analysis: Best-practice in African mining" (2013).

A simple comparison of the information in Tables 1 and 2 indicates that there is a growing interest between 2005 and 2013 in the topic of the theory and practice of sampling in South Africa. It also reflects a growing body of sampling "champions" in the industry, and a new-found awareness of the importance of sampling in the minerals industry. The scope of topics covered is also

Table 2. Major topics, papers presented and authors at the Sampling and Analysis: Best Practice 2013.

QA/QC topics	**Between laboratory biases; same sample, different answers. Guidelines?** M. McWha **Current practices in analytical laboratory QAQC.** N. Mackenzie **Quality control and quality assurance case studies for the analysis of precious and base metals**. K. Lomberg and R. Mckinney **A new control chart for QA/QC analysis.** D. Francois-Bongarcon **Best practice in quality assurance: determination of the sampling fundamental error.** G. Lyman, E. van Tonder and R. Schoustra	5
Sampling practice	**The "simulated chip-sample model" as a method for quantifying error and bias in sampling thin carboniferous reef types.** D. Fourie and R.C.A. Minnitt **Quality control and assurance of underground chip sampling at Kopanang Mine, South Africa.** A. Pillay, T. Flitton and B. Freese **Keynote address: Kumba iron ore product quality management systems.** N. Hannweg **Practical application of Venmyn Variance Towers to define data density and the number of boreholes needed.** A.N. Clay, T.C. Orford and J.A. Myburgh **Improved sampling of concentrate dispatched to smelter.** K. Tshimanga **Sampling of lumpy ore and ferroalloys manually by thin layer method.** M. Turner	6
Theory of sampling issues	**Keynote address: Sampling in the South African minerals industry.** R.C.A. Minnitt **Keynote address: Critical importance of sampling in trading mineral commodities.** R. Holmes **An overview of sampling best practice in African mining.** I.C. Spangenberg and R.C.A. Minnitt	3
Reporting codes	**The understanding and importance of sampling in the SAMREC code.** K. Lomberg **International reporting standards for exploration results, mineral resources and mineral reserves with particular reference to sampling techniques and data.** R. Dixon **Sampling—a critical component in delivering accurate and representative test results as the basis of trade in commodities and the role of relevant international standards and conformity assessment procedures and infrastructure.** G. Visser **Sampling for mineral resource definition.** H.F.J. Theart	4
Sampling equipment and software applications	**An overview of SGS Minerals Services' global geochemical laboratory quality management system.** R. Galow, J. Bowden, S. Khan, M. Labuschagne and V. Murphy **The evaluation of sampling and assay data via customized IMP programs.** H. de Roos **Managing a fully automated robotic laboratory: experiences from Anglo American Platinum's EBRL.** J.P. Le Roux **Mechanical sampling-a manufacturer's perspective.** R.C. Steinhaus and R.C.A. Minnitt **Challenges of retrofitting sampling equipment into existing belt conveyor transfers.** D. Stevens and H. Mostert **Pitfalls in Vezin sampling for finely crushed materials.** C. Kruger and E. van Tonder **Automated sampling and analysis of iron ore for export from the Saldanha iron ore terminal in South Africa.** P. Hofmeyr and D. Pretorius	7
Analytical procedures	**The use of XRD analysis in the sampling and materials balance of low-grade iron ores and sinters.** J.P.R. de Villiers **Advances in automated wet chemistry technology to enhance process control.** A. van der Westhuizen **Comparison of laboratory sub-sampling methods.** P. Qeqe and E. van Tonder **Best practice for weighted compositing: Introducing the VSSD.** E. van Tonder and Z. Marais **Comparison of Carius tube and microwave digestion of PGM concentrate and ICP-OES analysis.** D. Surender	5
Coal industry	**Sampling the coal chain.** P.E. Hand **Practical considerations for bias testing of coal sampling systems.** A.R. Johns	2
Gold	**Sample support size and spacing determination for resource development of a marine placer gold deposit.** P. Saravanakumar, G.J. Brown and G. Van Eck	1
Base metals	**The trials and tribulations of sampling on a copper concentrator.** C.B. Kohler and T.C. Brink	1
Metal accounting and metallurgy	**Metal accounting and corporate governance.** P.G. Gaylard, N.G. Randolph and C.M.G. Wortley **From metal to money: the importance of reliable metallurgical accounting.** D. Seke **Perspective on grade and tonnage reconciliation at Kopanang Mine, Vaal River District, South Africa.** D. Francois-Bongarcon and A. Johnson **Mine to metal: a practical balance for a large platinum producer.** M.J. Liebenberg and H.E. Bartlett **The allocation of gold production from multiple shafts feeding a common treatment plant using run-of-mine sampling of ore deliveries.** L. Korff, H.E. Bartlett and R.C.A. Minnitt **Gold accounting across CIUCIP circuits.** D. Clemente and H.E. Bartlett	6
Platinum	**Platinum group metals: Best practice sampling methods, assay techniques and quality control.** K. Lomberg **Mogalakwena Platinum Mine: world-class sampling for a world-class PGE, Cu, Ni mine.** R. Brazier	2
Diamonds	**Determination of sampling configuration for diamondiferous gravel occurrence using geostatistical methods applied to a probe drill platform.** J. Jacob, C. Prins and A. Oelofsen	1
Environmental	**Keynote address: Environmental sampling—overview.** E.M. Cukrowska, H. Tutu and L.K. Chimuka	1
Uranium	**Uranium exploration analysis.** D.R. Young	1

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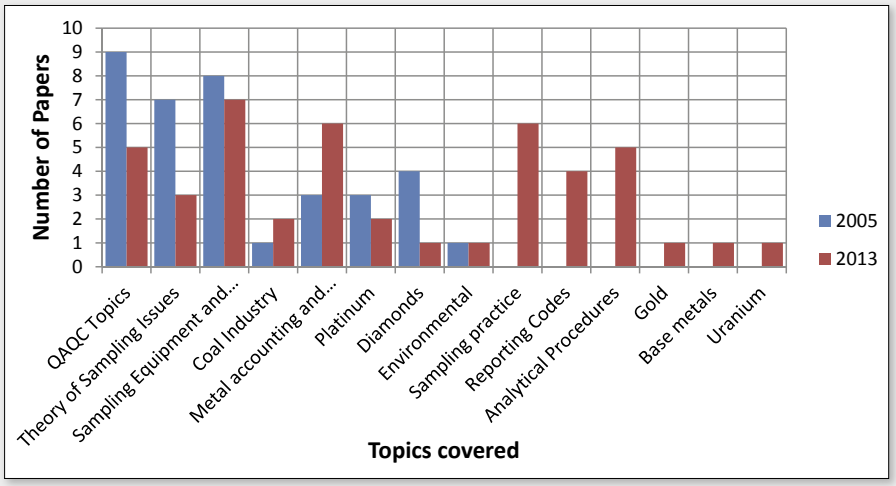

Figure 1. A histogram of the number of papers and the range of topics covered in the 2005 (blue) and 2013 (red) sampling conferences held in South Africa.

different from the 2005 conference to the one held in 2013, the numbers of papers and the topics presented being shown in Figure 1. This diagram is interesting in that QA/QC related topics (nine papers) were highest in 2005 with approximately half the number of papers on this topic in 2013 (five papers). Other issues that ranked high in 2005 were around the Theory of Sampling (seven papers) and sampling equipment and related software (eight papers). In 2013 sampling equipment topics were represented by the highest number of papers (seven), with metal accounting and sampling practice being covered by six papers each. Topics relating to QA/QC and analytical procedures were covered in five papers each, followed by issues around reporting codes (four papers) and the Theory of Sampling (three papers).

It is also interesting to note that commodity-specific papers on different sampling topics began to emerge in the 2013 conference, something that tended to be missing in the 2005 conference. In addition the topics on sampling practice, reporting codes and analytical procedures, not seen in the 2005 conference, were strongly represented in the 2013 gathering.

It should be noted that it was never the intention of the South African sampling conferences to become misaligned with what is happening globally through the WCSB and Australian conferences in trying to promote good sampling practice. Some unfortunately saw the South African conference as an attempt to upstage the WCSB conferences and the efforts being promoted in Australia. This was never the case. Instead we as organisers recognised that a lot of

excellent work was being done in South Africa, but nowhere was there a forum for this cohort of sampling practitioners to express and showcase their sampling best practice. It was also felt that many South Africans were standing aside to look on as the show took place elsewhere in the world.

The very positive and ready response from the South African sampling fraternity and the strong support from sampling equipment manufacturers for the latest conference indicate that a vibrant community interested in promoting best sampling and analytical practice is alive and well in South Africa.

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The Biota Guard marine oil leak monitoring system—novel sampling application of bivalve PAT biosensors

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The Norwegian high-tech company Biota Guard has developed a unique marine oil detection and monitoring system based on biosensors. The system uses marine *in situ* biosystems as novel sampling sensors in a Process Analytical Technology context which are documented to have a detection sensitivity vastly outperforming traditional physico-chemical sensors. The sampling element in the Biota Guard system receives special attention here.

Background

Environmental impact statements often contain elements related to water quality and water availability. These are issues which represent an increasing obligation for many industry players, governmental bodies and the public in general. Today environmental management is a part of the framework conditions for many industries, and often an important strategic factor. For oil and gas and mining companies, compliance with water quality regulations is instrumental for their "license to operate". In the offshore oil and gas sector, real-time marine environmental monitoring poses particular complications as there is a wealth of operational information (the "cause") but significantly less data related to the well-being of the recipient biota in open water masses (the "effect"). Throwing traditional Process Analytical Technology sensors at the problem has not been sufficiently successful.

The Biota Guard marine monitoring system (BGMMS) is developed to address these and other challenges, based on a novel sampling sensor system. This combined oil leak detection and environmental effect monitoring system is capable of detecting environmental stress at very low levels in sea water. The winner in this game is the system that can detect ambient condition deviations at the absolutely earliest occasion, with fully documented reliable efficiency.

The Biota Guard marine monitoring system has been in development since 2006, and has received a resounding interest in the offshore oil and gas industry. The company has received numerous awards and prices for its novel technological business concept, e.g. ONS innovation award for SMEs 2012, and has completed three successful joint industry projects backed by six oil operator companies. The first

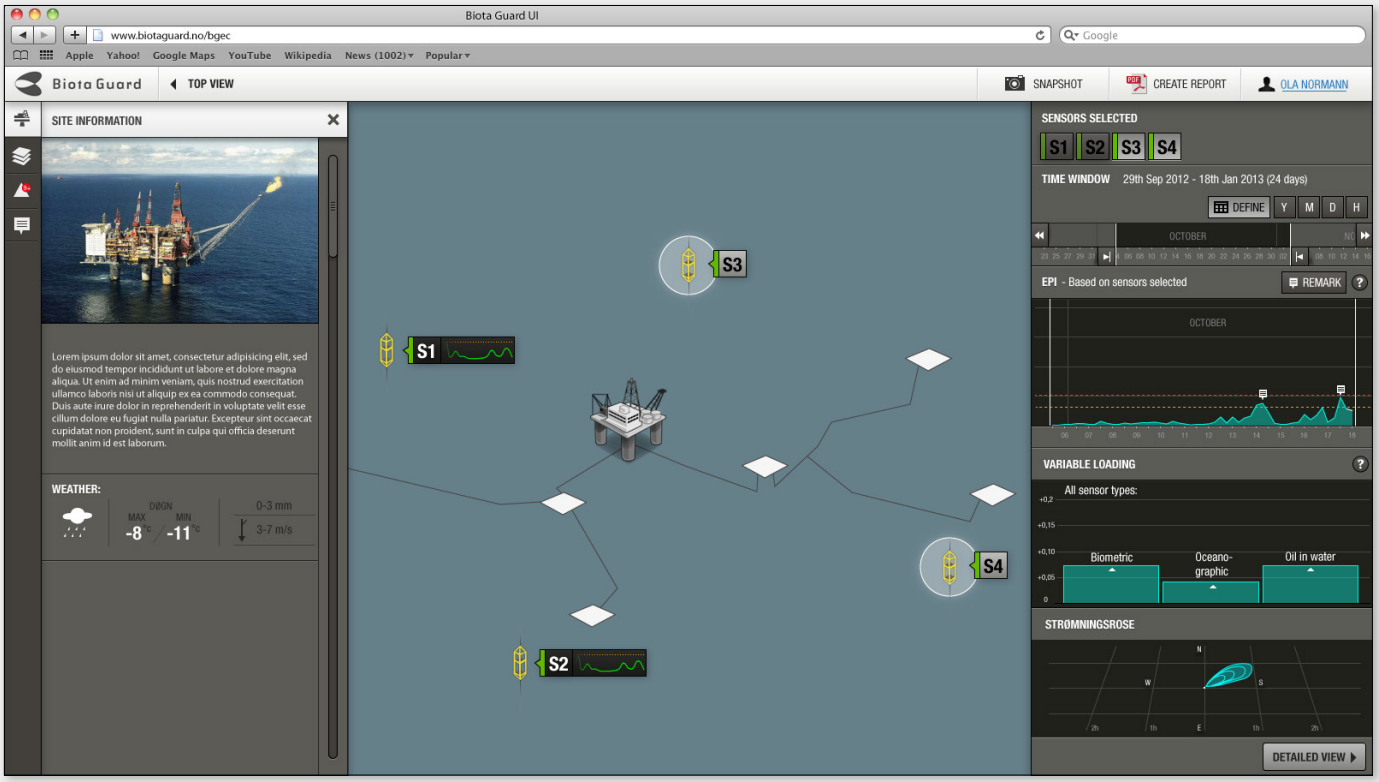

Figure 1. Overview of Biota Guard Marine Monitoring System (BGMMS) user interface. Subsea stations (S1–S4) are here deployed at strategic locations in the vicinity of a North Sea oil producing platform.

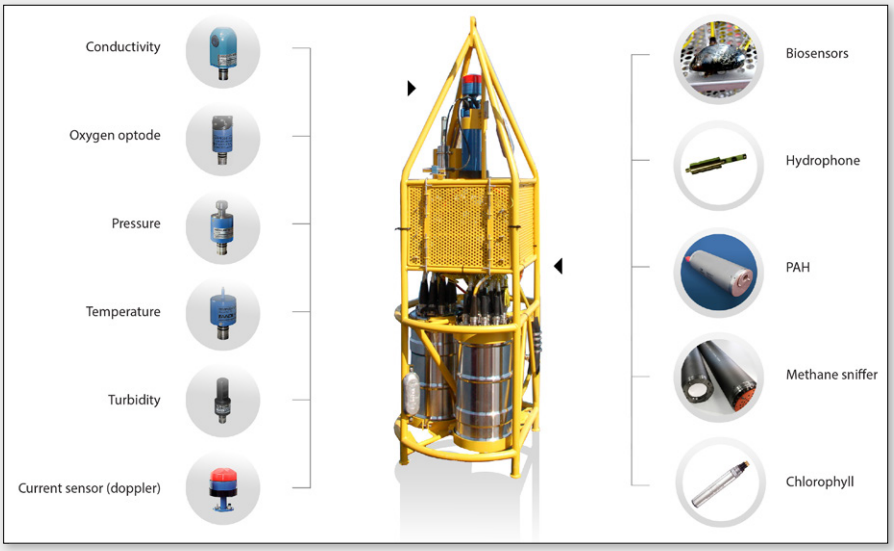

Figure 2. Biota Guard Marine Monitoring System station. The full complement of conventional oceanographic, PAT and the novel biosensors are shown in the side panels. All sensors are integrated in the subsea station (centre). The biosensors are located in the yellow cage (see further in Figure 3).

commercial contracts for to tailor environmental campaigns to assets specifics have been signed.

The general setting of a specific deployment of BGMMS stations is illustrated in Figure 1.

The BGMMS operates as a Process Analytical Technology (PAT) system, e.g. Bakeev (2010), but with a critical new sensor concept added. The system provides an Environmental Performance Index (EPI) by deploying *instrumented live organisms* in addition to conventional oceanographic PAT sensors. The EPI records the effects from chemical changes in the water based on specific biosensor responses. Specifically, ecologically representative bivalves, which typically live in the open water masses of the monitoring object, will show changes in their heart rate activity and other behavioural patterns (e.g. valve opening cyclicity) as a function of both acute and chronic exposure to unique and/or mixed contaminants. The resulting sensor spectra are consequently a reflection of the *total* water quality stressor situation and can be reported in real time. The resulting multi-sensor signals are clearly complex in nature, and critically dependent on the ability to decompose the sum-spectra reliably with respect to the full set of parameters calibrated. There is a huge amount of sensor, and process, technology involved at the front end of the BGMMS as well as chemometric data modelling (multivariate calibration) at the centralised monitoring software systems, before the operator displays emerge, Figure 1. A key issue is that the biosensors act as *sampling sensors*, in the form of "inverted" in-line sensor systems, inverted because the process system is led to the sensor, instead of the sensor being inserted in the process conduit. After this novel twist, however, conventional PAT principles will cover the needs of the full system.

Figure 2 illustrates the full array of physico–chemical oceanographic as well as the novel biosensor complement as employed in standard BGMMS stations.

Sampling sensors: bivalves

The Biota Guard sensor array employs a complement of 32 individual biosensors in addition to a wide array of potential chemical and physical sensors, not all of which are necessarily deployed in each specific situation. The combined sensor complement enables the proprietary Biota Guard software monitoring system to extract *latent* information from the specific suite of multiple sensors, resulting in an unprecedented, game-changing sensitivity with respect to oil concentration. Detection sensitivity in laboratory tests (e.g. trials at SINTEF Sealab in February 2013 over a 24-hour period) has been shown to be three orders of magnitude lower than traditional physico-chemical sensors that need to interact with the leaking medium. The sensitivity has also been tested and verified in extensive exposure studies at the International Research Institute of Stavanger – Environment (IRIS) carried out in Joint Industry projects, 2007–2013.

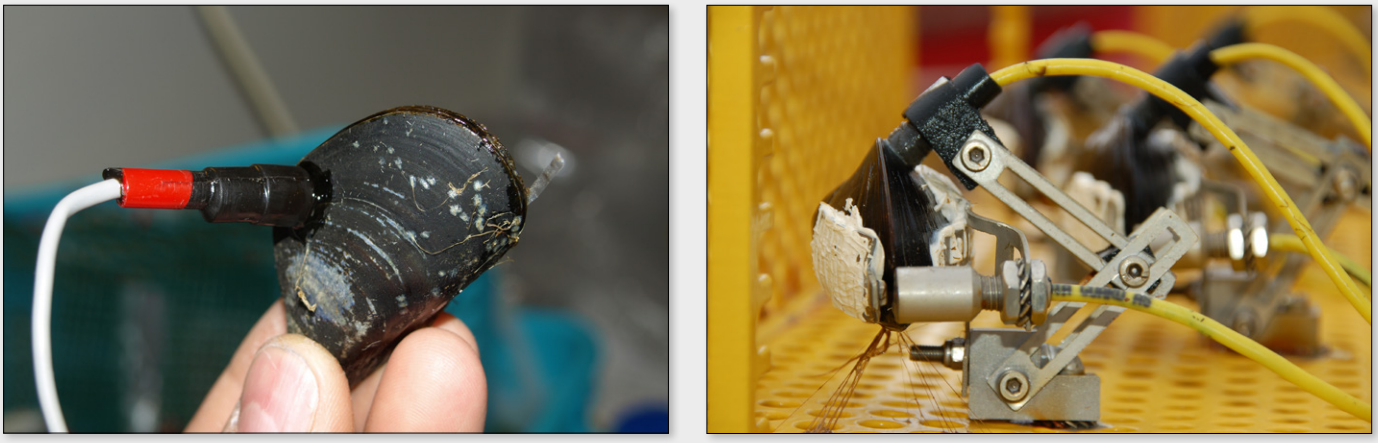

Figure 3. Instrumented bivalves fitted with an infrared sensor for heart rate determination (left), and with added calipers for recording valve gape (opening–closing) characteristics as well (right).

Figure 4. Training a "school" of bivalves in Biota Guard's water exposure tank. Signal acquisition is otherwise reminiscent of PAT and is further processed by chemometric methods. Training can be simple employing only one parameter at a time, or more realistically, targeted on several interacting parameters in order to reach full compliance with the natural open sea characteristics at a target location.

The core of the system is comprised of a general patented bivalve sensor concept, while the specific bivalve species selection is dependent upon the oceanographic conditions at the target location. Details of sensor instrumentation and acquisition system, digital signal transfer, signal processing and conditioning, data analysis and operator presentation principles and methods are only indicated in the selected illustrations. A key insight which can be disclosed, however, is that the information processing system is based on a core of advanced Theory of Sampling (TOS) elements as well as chemometric data modelling features (PLS regression).

The most interesting part of the system for readers of *TOS forum* is no doubt the *sampling biosensors* which are described in more detail below within the proprietary concept context (Figures 3 and 4).

The EPI reflects both acute chemical changes in water over short time spans, as well as accumulated effects over longer durations, all of which are reflected in minute changes in the characteristic biosensor spectral responses. A leak detection event is triggered when the EPI crosses a predefined threshold. The EPI threshold needs to balance sensitivity and specificity, in order to provide a reliable, robust detection with well documented zero false leak detection events. This is where a significant amount of chemometric data pre-treatment and data modelling is involved.

A critical success factor is proper *calibration* of the sensor system(s), i.e. multivariate calibration in the chemometric parlance. Figure 4 shows bivalve sensors in a predeployment holding tank in Biota Guard's laboratories, where training and calibration first takes place. Note that extensive sensor redundancy is needed to counteract the inherent biological variability between individual sensor elements. There is a certain analogy with electro-chemical "Electronic Tongue" arrays,[2–4] where the individual sensor dose-response differences are admittedly much larger, but also here only brought under full control by multivariate calibration and judicious validation.[5] In the somewhat simpler bivalve-stressor context, the experience is for excellent averaging results over 32 bivalves.

Calibration of the system follows experimental design principles, but not necessarily standard DOE layouts. From the number of stressor parameters involved in natural systems and the number of concentration levels needed, the potential total number of experimental runs will very easily reach impossible levels—one of the still proprietary elements in the BGMMS development plans is directly aimed at the means needed to circumvent this formidable obstacle.

Figure 4 shows a "class" of bivalves in the exposure tank about to graduate from such full and comprehensive schooling at the training academy to be installed in an active subsea station. It is not all finally deployed bivalves that need to be trained prior to live operation, however. Laboratory work gathers important input–output data during exposure study that increases our understanding and improves real-time models for ocean deployment.

Test campaigns

Two specific oil leak feasibility detection tests have been devised (in collaboration with SINTEF, Trondheim) in order to demonstrate the system's sensitivity to oil stress. Two leak scenarios were defined with specific oil exposure profiles. The objective was to determine the effective detection limit of the subsea sensor array under fully realistic deployment conditions. Table 1 gives an overview of the most important test parameters and their performance.

The BGMMS detected both types of leakage in these scenarios. The oil concentration at the point of detection was 1.2 mg L^{-1} and 0.5 mg L^{-1}, respectively. A key system sensitivity feature in comparison to other types of sensors concerns transition from ideal lab tests and calibration to operations in oceanic open water masses. BGMMS is more tolerant of varying oceanographic conditions, such as turbidity, luminous sources etc. To date this is a substantial challenge for other leak detection sensors based on optical principles.

SINTEF also performed a 3-D spatial simulation based on a given leak scenario with a leak rate of 1 m^3 per day. This simulation provided Biota Guard with concentration fields in the water column at various distances from the leak. Table 2 gives an overview of the distance from leaks required in order to *trigger* a leak detection event.

Test results from the full OSCAR simulation experiment, Table 2, allowed determination of an operative EPI threshold, which was set to ±3 std, which is the level used in the system illustrated in Figure 1.

Discussion

Continued monitoring of the marine environment and especially early warning oil leak detection is a challenging and complex endeavour. A range of different technologies are currently in use, based either on

Table 1. Leak detection results (SINTEF).

Scenario	Oil type	Exposure range	Leak duration	Leak detected	Concentration at point of detection	EPI threshold	Modelling mode
Minor leak	Statfjord	0–3 mg L^{-1}	10 days	Yes	1.2 mg L^{-1}	3 std	Batch
Acute spill	Statfjord	0–5 mg L^{-1}	1 day	Yes	0.5 mg L^{-1}	3 std	Batch

Table 2. Overview of leak detection ranges of the BGMMS, based on concentration fields generated by SINTEF's OSCAR (Oil Spill Contingency and Response) simulation.

Oil leak rate	Subsea sensor array distance from leak	Gradient concentrations	EPI threshold	In detection range
1 m^3 per day	100 m	2.75 mg L^{-1}	3 std	Yes
1 m^3 per day	200 m	2.5 mg L^{-1}	3 std	Yes
1 m^3 per day	500 m	0.180 mg L^{-1}	3 std	Yes
1 m^3 per day	1000 m	0.07 mg L^{-1}	3 std	No
1 m^3 per day	2000 m	0.045 mg L^{-1}	3 std	No

physico–chemical interaction with the leaking medium, on active or passive acoustics or on optical spectral detector principles (NIR in particular) or "fly-by" inspection enabled by ROVs. The comprehensive BGMMS sensor array represents a group of leak detector systems that is based on direct interaction with the leaking medium utilising several advantages. Because of the very low concentrations needed to be quantified, the sensitivities of traditional sensors has to date called for some sort of physical collection, *physical sampling*, in order to accumulate and amplify the oil concentration to detectable levels, requiring various analytical system additions and complexities.

Judicious use of novel instrumented biosensor systems, acting as direct integrating sampling agents and delivering direct digital multi-spectral signals, has allowed Biota Guard to develop a unique monitoring and detecting system with a very promising application potential in the oil and gas offshore industry, but also beyond (environmental and mine waste water monitoring in rivers and lakes etc.). The results listed in Table 1 testify to a very high sensitivity compared to other competing leak detectors that also interact directly with the leaking medium. As per the test results reflected above, this advantage is estimated to be up to ~1400 times more sensitive in these realistic scenarios.

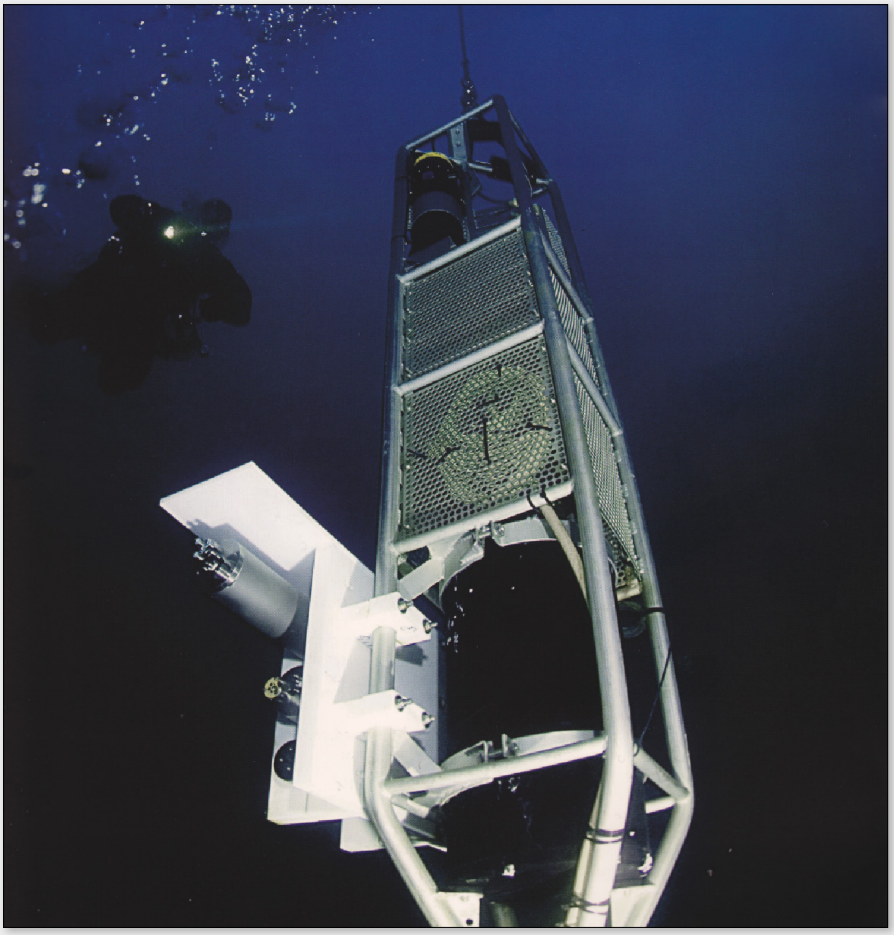

Figure 5. Fully calibrated bivalves are located in Biota Guard's subsea station (upper cage). The station shown here was deployed in a fjord in the Norwegian North Sea during one of Biota Guards full-scale testing campaigns. Credit: Vidar Skålevik.

Conclusions

The Biota Guard Marine Monitoring System (BGMMS) employs novel *sampling biosensors* which are representative of the deployment target site. The critical success factor of this system is intimately bound up with the use of novel instrumented biosensor systems, acting as passive, integrating sampling agents, delivering digital multi-spectral signals. Through chemometric data analysis principles (PAT) and dedicated design of experiment training, these signals are decomposable allowing a highly relevant Environmental Performance Index, EPI, to be developed and displayed on operator displays, increasing the reliability of decision-making.

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DS 3077 Horizontal—a new standard for representative sampling. Design, history and acknowledgements

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July 2013 saw the conclusion of a five-year project, design, development and quality assurance of a new generic sampling standard: DS 3077 Horizontal. DS 3077 Horizontal is published by the Danish Standardisation Authority (DS). Development of this standard was carried out by task force DS F-205. This contribution summarises the history of this endeavour, focuses on a few salient highlights and pays tribute to the taskforce and to a group of external collaborators responsible for initial proof-of-concept and the final practical quality assurance. DS 3077 describes the minimum Theory of Sampling (TOS) competence basis upon which any sampler must rely in that sampling can be documentable as representative, both with respect to accuracy and reproducibility. It represents a consensus based on industry, academe, official regulatory bodies, professionals, students and other interested individuals.

Introduction

The primary objective behind DS 3077[1,2] was to develop a fully comprehensive, yet short, easy-to-understand introduction to the minimum principles necessary for sampling all types of materials and lots, at all scales. The overarching goal was to be able to reach absolutely all sampling novices or persons who perhaps earlier had been overwhelmed by the oft-quoted (but wrongly so) impression that the Theory of Sampling is "difficult". This undertaking was ambitious—it took an accumulated 12 core participants in the task force a total of five years to reach a consensus and a product acceptable to all parties (industry, academe, regulatory bodies, students and professionals). Part of this work necessitated development of partially new didactic approaches, some of which are illustrated below. This contribution is only allowed to quote a few salient highlights for copyright reasons, but this is enough for an appreciation of the result achieved. The standard has benefitted significantly by valuable input from a large group of external reviewers, assessors, standard writers, sampling consultants and "users" from science, technology and industry, most of whom are thanked explicitly.

Ever since WCSB1, it has dawned upon the international sampling community that there is a serious lacuna in the arsenal with which we try to reach out to *new* communities in science, technology and industry regarding a simple, short, easy-to-understand sampling standard. Many attempts have been made but to date a truly universal standard has not yet seen the light—while very valuable achievements are on record regarding sampling standards with a restricted target, e.g. commodities, major raw materials, manufactured goods etc. These are highly significant such achievements, all of which have also served as inspiration for the present work regarding DS 3077. Setting the scene can best be done with a few selected quotes (indicated by the blue text), brought here with permission from the Danish Standardisation Authority, the publisher of DS 3077.

DS 3077 foreword

DS 3077 outlines a practical, self-controlling approach for representative sampling with minimal complexity, based on the Theory of Sampling (TOS). The generic sampling process described and all elements involved are necessary and sufficient for the stated objective, in order to be able to document sampling representativity under the conditions specified. It is always necessary to consider the full pathway from primary sampling to analytical results in order to be able to guarantee a reliable and valid analytical outcome. This standard, including normative and related references, annexes and further, optional references constitute a complete competence basis for this purpose. The present approach will ensure appropriate levels of accuracy and precision for both primary sampling as well as for all sub-sampling procedures and mass-reduction systems at the subsequent laboratory stages before analysis.

A sampling process needs to be structurally correct in order for the essential accuracy requirement to be fulfilled, with no exceptions allowed. For the process also to be sufficiently precise it is often necessary to proceed through iterative stages, until the effective sampling variance has been brought below an *a priori* given threshold; this is also known as 'fit-for-purpose'. In this endeavour the key feature is the heterogeneity of the target lot, which shall be identified and quantified. Heterogeneity characterisation forms one key element of the present standard. Only when both the accuracy and precision demands have been met properly, can all types of solid lots and two-phase (solid–liquid) materials be sampled representatively (gasses are excluded from the present standard), and the derived quality assurance of the sampling process is hereby subject to open public inspection. Without informed commitment to such an empirical heterogeneity characterization, all prospects of being able to document representativity will remain out of reach.

This standard outlines a systematic scientific basis for improving sampling procedures, which will lead to increased reliability for decision-making based on measurement results. Not all existing standards are in compliance with the appropriate TOS requirements, although partial elements can be found in many places (2.1 and Bibliography). Relationships to other standards, guidelines, good practices as well as regulatory and legal requirements shall be handled with insight. Where found in opposition to other, less TOS-compliant stipulations, it will be necessary to start a process of revision or updating of the relevant standards or norm-giving documents

which may be a lengthy process. While this is taking place, or when dictated by documented sampling variances that are too high (a key issue in the present standard), it is always an option to employ more stringent quality criteria from a TOS-based approach, than what may be presently codified. As there are serious economic and societal consequences of non-representative sampling, these are appropriately described and illustrated in this standard, which also outlines impacts caused by inferior analytical results and related non-reliable decision making.

DS 3077 has the overall objective to establish a comprehensive motivation and competence for taking the stand relying only on fully TOS-compliant sampling procedures and equipment irrespective of the theoretical, practical, technological, industrial or societal context under the law.

Scope

DS 3077 is based exclusively on the Theory of Sampling (TOS).

DS 3077 is a matrix-independent standard for representative sampling. Compliance with the principles herein ensures that a specific sampling method (procedure) is representative.

DS 3077 sets out a minimum competence basis for reliable planning, performance and assessment of existing, or new sampling procedures with respect to representativity.

DS 3077 invalidates grab sampling and other incorrect sampling operations, by requiring conformance with a universal set of seven governing principles and unit operations.

DS 3077 specifies two simple quality assurance measures regarding:

- Sampling of stationary lots, the Relative Sampling Variability test (RSV)
- Sampling of dynamic lots, Variographic Analysis (VA), also known as variographic characterisation, with an analogous $RSV_{1\text{-dim}}$. [DS 3077 contains a variographic software program (freeware) making simple variographic characterisation available to all readers]

DS 3077 stipulates maximum threshold levels for both these quality assurance measures.

DS 3077 enforces professional self-control by stipulating mandatory disclosure of one of two comprehensive quality assurance approaches as produced by RSV or variographic characterisation to all parties involved.

DS 3077 specifies documentation and reporting of sampling representativity and efficiency for each analyte in combination with a specific class of materials respectively. Any deviation from this standard's quality objectives (QO) shall be justified and reported.

DS 3077 employs a dual acceptance approach: items not mentioned are not acceptable as modifications in any sampling procedure or sampling plan, unless specifically tested and assessed by the QO's described herein—while all modifications successfully passing this test requirement are acceptable.

We can only bring you a small quotation from clause 3 "definitions and terms"; it will suffice here to concentrate on the didactic presentation which has been developed in order to comply with the aspirations re. a "short, simple, easy-to-understand ..." standard.

3.11 grab sample

increment resulting from a single sampling operation (literally "grabbing"), almost always emphasizing alleged efficiency, inexpensiveness, effort-minimizing desirability. (Figure 1).

Note: Grab sampling can result in representative samples only in the rarest of instances. If a grab sampling procedure is contemplated, it is mandatory to test and document it by one of the two heterogeneity characterization methods in DS 3077, RSV or variographic characterization.

Grab sampling constitutes the world's most misused sampling operation. All single-sample approaches for heterogeneous materials are in conflict with the Fundamental Sampling Principle (FSP) and militate against the necessary heterogeneity counteraction.

Note: Grab sampling is applicable at all sampling scales, from the field, in the industrial plant to the analytical laboratory, but fails totally to comply with the fundamental sampling principle. DS 3077 mandates composite sampling for all situations in which grab sampling has not been approved by a pertinent validation, either RSV or by variographic analysis."

3.6 composite sample

sample made up of a number, Q, of increments (Figure 2)

Note 1: The ISO equivalent of a composite sample is the bulk sample. There is full conceptual consistency between the definition of composite (TOS) and bulk sample (ISO), but a composite sample shall either be representative or not, according

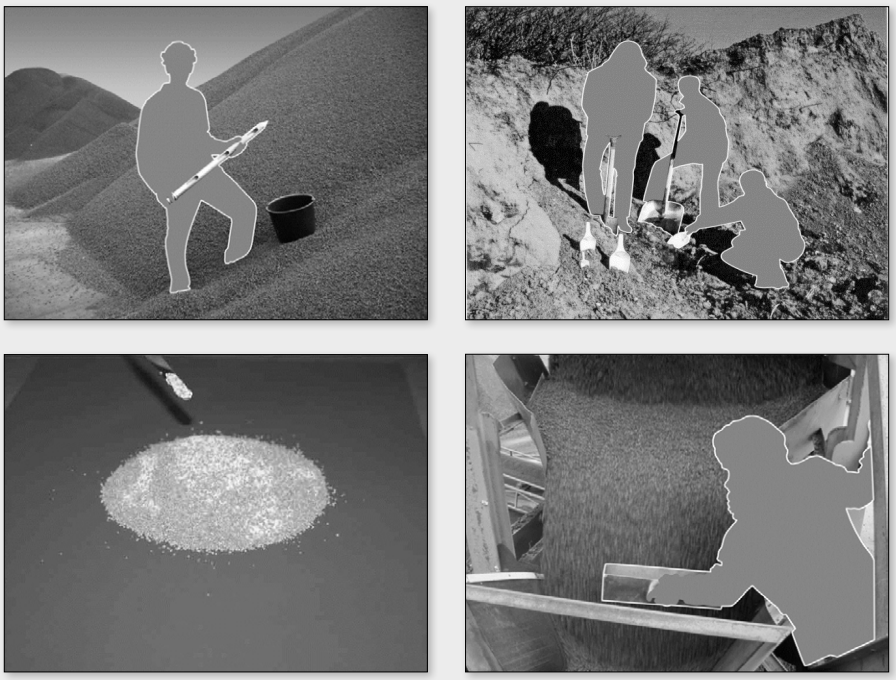

Figure 1. Grab sampling illustration across all scales of interest (from macroscopic stacks to powder piles) for both stationary and dynamic lots. The possibility for any single-increment extraction operation to achieve representativity is virtually zero since the lot cannot be covered with respect to its intrinsic spatial heterogeneity (DH).

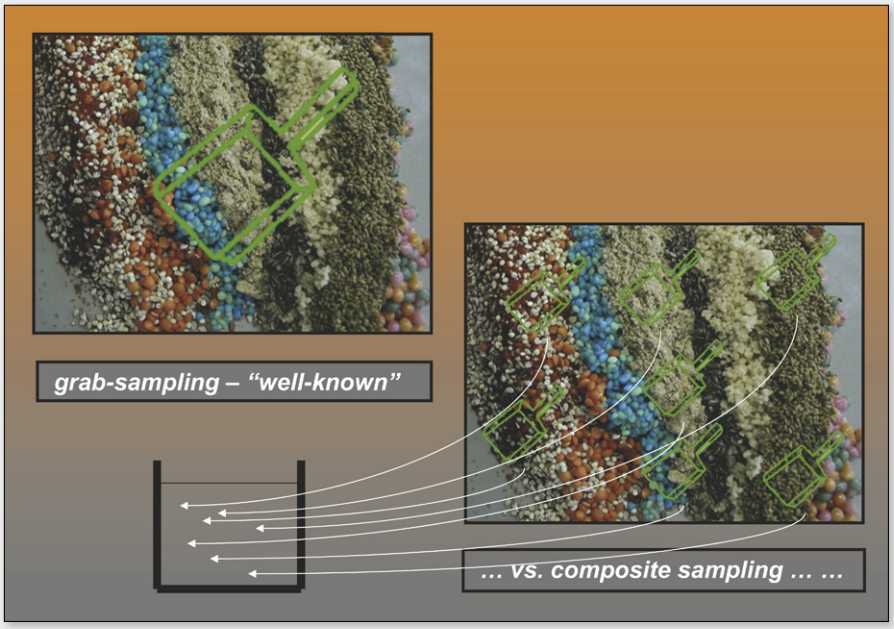

Figure 2. Composite sampling of significantly heterogeneous material. Irrespective of scale, a composite sample (Q increments) is able to "cover" the spatial material/lot heterogeneity far better than a sample originating from a single extraction operation (grab sampling).

to the characteristics of how its increments were extracted, a distinction only made in TOS.

Note 2: The primary purpose of composite sampling is to cover spatial and/or compositional heterogeneity of the lot as best possible subject to given logistical and practical conditions and a specific sampling procedure. The same sampling tool (e.g. scoop) can be used significantly better as a provider of a composite sample than when used for grab sampling (single sample operation). In principle, and in practice, informed and competent use of composite sampling will result in a considerably reduced sampling variance (TSE) compared to grab sampling; the average will in general also lie closer to the true lot composition for composite sampling.

Note 3: Composite sampling can also be used for more local purposes, i.e. for minimizing the effect of local heterogeneity (segregation or otherwise) of a single localized sample - for example when expressing or modeling concentration changes in 1-D, 2-D or 3-D geometrical contexts, e.g. trend surface analysis."

3.40 theory of sampling, TOS

a body of theoretical work starting in 1950 by the French scientist Pierre Gy, who over a period of 25 years developed a complete theory of heterogeneity, sampling procedures and sampling equipment assessment (design principles, operation and maintenance requirements). TOS was subsequently further elaborated into a coherent didactic framework in the next 25 years by Gy, as well as also added to by newer generations especially in the last two decades. Gy's personal account of TOS and its development history can be found in the note reference immediately below.

NOTE Pierre Gy has published c. 275 papers and seven books on sampling, in later years joined by several other international sampling experts (Pitard, Bongarcon, Minkkinen, Holmes, Lymann, Smith, Carrasco). A tribute to Pierre Gy's scientific *oeuvre* can be found in the reference below.[3]

TOS, synoptic overview

The figure below (Figure 3) shows a didactic flow path of relationships between sampling stages, sampling errors, four practical sampling unit operations (SUO) and three Governing Principles (GP).

Empirical heterogeneity testing, RSV (heterogeneity characterisation) is universally applicable, both for the total sampling process as well as for specific sampling stages. Process sampling relies on variographic analysis (VA) for heterogeneity characterization, sample mass (composite sampling, Q) and sampling rate optimization. There are two additional sampling errors especially related to process sampling (trend process sampling error; cyclic process sampling error), which can be brought under control relatively easily. Within the framework of this standard, sampling from either stationary or dynamic lots, covers a necessary basis with which to address very nearly all sampling issues...

Freeware; Variogram

DS 3077 Horizontal contains an appendix which is comprised by a stand-alone software package, designed to be able to perform basic variographic data analysis for an entry of up to 100 measurements. This software calculates a relative variogram on the basis of user input (two spreadsheet columns: concentration, increment weight—if no weight is assigned, the software assumes identical weights for all increments arbitrarily set to 1.00). Variogram calculation is the only option, indeed the only task included. This freeware is in no way

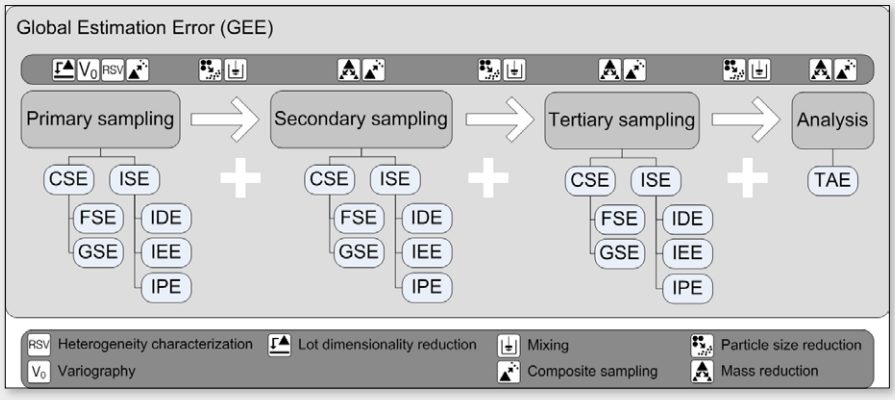

Figure 3. A minimum sampling competence encompasses FSP, TOS' paradigm of sampling correctness, five sampling errors (CSE/ISE) and four Sampling Unit Operations (SUO).

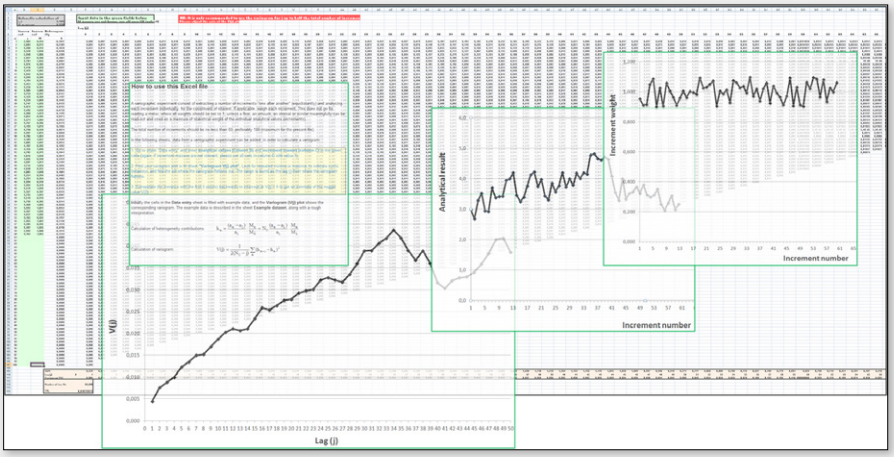

Figure 4. DS software VARIOGRAM (Appendix): Brief program manual, input spreadsheet, plotting routines for concentration and weight values and the resulting variogram (bottom). This software is designed for an input of up to 100 entries.

intended as a competitor to existing professional and commercial variographic software programs or packages on the market, all of which perform several more essential functions for in-depth usage, e.g. decomposition of variance components originating from periodicity and trends, estimation of TSE. The role of the freeware appendix is solely to allow standard readers an initial familiarisation with variographic modelling.

The VARIOGRAM freeware (Figure 4) was programmed by the second author of the present report (LPJ).

Discussion and conclusion

DS 3077 Representative Sampling—Horizontal has been discussed at innumerable occasions in the period since its gestation (which covers all the 10 first years of the existence of the WCSB conferences), where it was unanimously concluded that there is a serious need for such a standard. There is no doubt that the present ver. 1.0 is but the beginning on a new journey. As any other international standard it will be subject to regular revision in agreement with the pertinent stipulations (CEN/ISO). It is hoped that many will feel compelled to contribute towards its continuing development and improvement. DS 3077 Representative Sampling—Horizontal represents an intense five-year taskforce project, solely guided by the prospect of being able to contribute towards better teaching and dissemination of the Theory of Sampling (TOS). It represents a consensus based on industry, academe, official regulatory bodies, professionals, students and other interested individuals.

Attribution

The core taskforce behind DS 3077 (DS F-205) consisted of the following members: KHE (chairman), LPJ, Hans S. Møller, Christian Riber, Anders Larsen, Martin Thau, Jette Bjerre Hansen, Lars K. Gram, Jørgen G. Hansen and Bodil Mose Pedersen. Merete Westergaard Bennick and Lone Skjerning served as able secretaries. DS 3077 benefitted significantly by valuable corrective and additional input from a large group of external reviewers, assessors, standard writers, sampling consultants and "users" from science, technology and industry. The following individuals are gratefully acknowledged for their major contributions in this work—but are in no way responsible for perceived errors, omissions or declarative issues in the standard: Francis Pitard, Ralph Holmes, Pentti Minkkinen, Claudia Paoletti, Anna de Juan, Kaj Heydorn, Ulla Oxenboll Lund, Loren Mark, Melissa Gouws, Claas Wagner, Peter Thy, Peter C. Toft, Anders Larsen, Henri Sans and Mark O'Dwyer. In addition to this attribute, the first author would like to express his sincere gratitude to a core group of colleagues: **Hans S. Møller, Francis Pitard, Christian Riber, Pentti Minkkinen and Claudia Paoletti** for their steadfast personal support in this endeavour from the very beginning. It is equally pleasing to acknowledge PhD fellow **Claas Wagner** for extraordinary inspiration during the last three years of this work.

THANK YOU PROFOUNDLY ALL for contributing to the ever-increasing dissemination of TOS.

Acknowledgements

Tracing illustrations in Figure 1 are included with permission from the future publisher Wiley-VCH, to appear in Esbensen & Minkkinen: *Representative Sampling—In Science, Technology and Industry* (publication expected in 2014). Quotes from DS 3077 are reproduced with permission of Danish Standards.

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Historical snapshot from the inaugural meeting of taskforce F-205 (Danish Standards), 2008. From the right: Christian Riber, Merete Westergaard Bennick, Lars Petersen Julius, Jan Hinnerskov Jensen, Martin Thau, Lars K. Gram, Jette Bjerre Hansen, Kirsten Jebjerg Andersen. Photo: chairman KHE.

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Allen Graham ("Bon") Royle

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Allen Graham ("Bon") Royle died in Moreton-in-Marsh on 16 August 2013 aged 89. By any measure, he was a remarkable man with a remarkable life story, some of which, relating to WWII, has only recently come to light in its full detail.

As Bon told it, in his inimitable style, according to his birth certificate he was born on 1 March 1924, whereas according to his father he was born on 29 February but his father was "not having any of that leap-year nonsense".

Bon was born in Manchester in modest circumstances, even for those times. He attended Gorse Park Secondary School before winning a scholarship to attend Stretford Grammar School in 1935. He matriculated but the family could not afford the further cost for him to enter the sixth form and, just after war broke out, he left school at sixteen. Throughout his secondary schooling Bon's main academic interest had been Chemistry and he determined to make it his career. However, his parents had other ideas and he was sent to Loreburn College to be trained for a career in commerce. Financial constraints intervened and he left the College to take employment in the Sales Department of Turner's Asbestos Company in Trafford Park, Manchester. Deliverance from commerce finally arrived in the form of a job from Courtaulds Ltd as a laboratory assistant.

The chemical manufacturing plant at Courtaulds turned Bon's interest to a career in Chemical Engineering. In the autumn of 1940, to further his intended career, he enrolled at Manchester College of Technology to begin evening classes in mathematics, physics and chemistry. In the meantime, France had fallen, the Battle of Britain had been won and the nightly air raids had started.

In 1942, at the age of 18, Bon enlisted in the Royal Marines. In November of the same year, he was one of six newly recruited Royal Marines selected to join Ian Fleming's 30 Commando Intelligence Assault Unit. The legendary exploits of this unit were the inspiration for the James Bond novels and their story, including Bon's role, was published in Nicholas Rankin's 2011 book *Ian Fleming's Commandos* (Faber and Faber). A reviewer of the book noted that "as well as being intrepid fighters it seemed as much a requisite of joining 30AU that the soldiers possessed strong, not to say eccentric, personalities". Whilst perhaps not quite eccentric, Bon was certainly unique and characterised by wit, warm-hearted humour, and the generosity and graciousness of someone completely at ease with himself.

The role of the unit was essentially to steal German intelligence and its notable successes are widely credited with significant contributions to code-breaking and, as a consequence, of shortening the war. As a member of the unit, Bon took part in the landings in North Africa, Sicily and Normandy and in the liberation of Paris and thereafter in Yugoslavia, Belgium, Netherlands, Denmark and Germany.

Demobbed on 8 May 1946, Bon took advantage of a Further Education Training Scheme grant to enrol in Mining Engineering at the University of Leeds. In May 1948 Bon married Margaret Taylor whom he had known since childhood in Stretford and who had also recently been demobbed from the Women's Royal Naval Service. He graduated in 1950 with a First Class Honours degree in Mining Engineering.

Immediately after graduation Bon joined the Colonial Development Corporation (CDC) for a position at Macalder Nyasa Mines Ltd in Kenya. Thus began a 12-year sojourn in Africa, interrupted only by one year in Canada. His three-year appointment with CDC included 14 months in charge of a gold prospect in the Msoma district of Tanganyika and two months in charge of sulphur investigations in British Somaliland.

Following a less than satisfying year at Falconbridge Nickel Mines in Sudbury, Canada, Bon and Margaret returned to Africa in October 1954 where, until February 1958, Bon was Inspector of Mines for the Government of Tanganyika. His final appointment in Africa was from 1958 to 1962 as

Bon Royle

Assistant Chief Inspector of Mines for the Government of Sierra Leone.

Africa was obviously a source of inspiration for Bon. The many stories he told of his time in Africa are reminiscent of those of Alexander McCall Smith's novels of Botswana, and Bon told them with the same humour and affection for the people of those countries. Africa was also where Bon developed his interest in mineral resource and reserve estimation and in the theory and practice of sampling, which were later to become his primary research and teaching interests as an academic.

By 1962 with two very young children (Graham and Nicholas) it was time to return to the UK. The family moved to Lichfield and from 1963 to 1969 Bon was a Lecturer in Mathematics and Physics at Tamworth College of Further Education. In 1970 he was appointed Lecturer in the Department of Mining at the University of Leeds and this gave him the opportunity to formalise the practical aspects of mineral resource estimation and sampling and to begin his significant contribution to their academic development.

After attending the 1970 summer school in the newly emerging discipline of Geostatistics at the Ecole Nationale Supérieure des Mines de Paris in Fontainebleau he set up his own summer school in Geostatistics at

Bon in Cherbourg, France, in 1994.

Leeds, which ran for many years at Leeds and at the Mackey School of Mines in Reno, Nevada. In 1977 he established the MSc in Geostatistics at Leeds, which was offered continuously until 2003 and was the first such programme offered anywhere in English.

Bon was instrumental in the dissemination of Geostatistics in the English-speaking world and in translating it into a practical and meaningful language that contributed significantly to its understanding and implementation both in academe and in industry. His approach to the theory and practice of sampling followed the same path. Among his many achievements in this field Bon translated into English the entire French manuscript of Gy's book, *Sampling for Analytical Purposes* (1996). This was the deciding achievement in the selection of Bon as the first recipient of the Pierre Gy Sampling Gold Medal at the first World Conference on Sampling and Blending in 2003. The award is made for "distinguished service in disseminating the Theory of Sampling" and, on this first occasion, it was made on the insistence of the theory's founding father, in recognition of what Gy considered to be vital help at a crucial time in the development of the sampling theory.

Following retirement in 1989, Bon remained active in teaching and research as an Honorary Lecturer at the University of Leeds. He also completed a PhD on the *Sampling and evaluation of gold deposits*, awarded in 1995, and which stands as a major contribution to the field. He was still publishing papers and writing his own software for sampling up until a few months before he died.

Bon is survived by two sons, Graham and Nicholas, and their families. His wife, Margaret, died in 2006.

(No-one knows the origin of the nickname "Bon" and, if Bon knew, he never told anyone, including his family. He was, however, universally known as Bon.)

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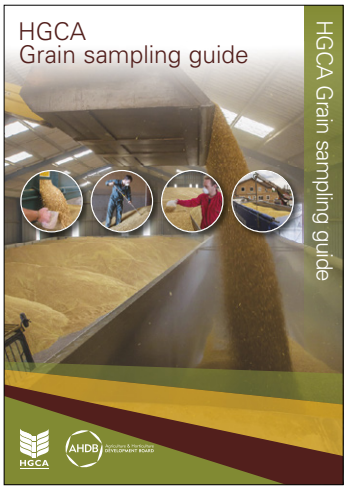
continued from page 2

The AgriQuant B8 uses Agritubes as the sampling container. The 60 mm diameter glass tube is filled with sample and inserted into the AgriQuant B8. The AgriTube is spun and moved forward during the analysis, providing a 375 cm^2 scanning area of the sample in less than 90 s. Agritubes are inexpensive, easy to fill, empty, clean and re-use, keeping the cost per analysis very low. The AgriQuant solution allows reference labs to rethink their work-flow. Previous technologies often worked with a single golden cuvette, however, the AgriQuant B8 concept allows many tubes to be filled prior to scanning in batches.

The AgriQuant B8 can be seen in action on the Q-Interline YouTube channel: www.youtube.com/user/qinterline

Grain sampling

HGCA have published their *Grain Sampling Guide 2013*. Understanding the quality and condition of grain is crucial. Accurate sampling at each stage of the grain chain is required to develop that understanding. It should help to reduce waste and minimise charges, claims and rejections. This guide brings together the key requirements for effective grain sampling for everyone involved, from growing to purchasing. It seeks to minimise duplication of effort, maximising efficiency. In this guide, sampling refers to the collection of physical grain and also sampling for moisture, temperature, pests and moulds. A PDF version can be downloaded from http://bit.ly/1f3MJNl. The HGCA guide will be evaluated from the perspective of TOS in the next issue of *TOS forum*.



DIARY

2014

11 February, Johannesburg, South Africa. **Domain Analysis in Isatis.** www.geovariances.com/en/mining-domain-analysis-in-isatis-co945

29–30 July, Perth, Western Australia. **Sampling 2014.** www.ausimm.com.au/sampling2014/, esanneman@ausimm.com.au

CONFERENCE ORGANISERS

Remember to let us know of any conferences or other events that you would like listed in the *TOS forum* Diary. Just e-mail the details to ian@impublications.com.

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Sampling errors undermine valid genetically modified organism (GMO) analysis

Kim H. Esbensen, Francis Pitard and Claudia Paoletti

Esbensen, Paoletti and Pitard. While the first is trying to get a sampling issue across, the latter two take a much more relaxed boat ride on Lake Como (2008).

This letter was written to the Joint Research Center, European Commision, some time ago, but the authors were asked not to publish it because "appropriate measures" were about to be undertaken. However, five years later, nothing has happened and the letter is therefore very much still relevant today. The authors are pleased that *TOS forum* has offered it an airing; the issue is serious.

The First Global Conference on GMO Analysis, 24–27 June, 2008, held in Cernobbio, Italy, was a scientific success, and very well organised. Its many purposes were all achieved: a broad and comprehensive scientific overview of all relevant issues related to genetically modified organism (GMO) detection and quantification was offered to an audience which represented just about every country, academic institution, industrial company and regulatory body involved, on a truly global scale (more than 70 countries were represented). In the matter of GMO policy enforcement, the entire world looks to Europe, with good reason. The European Commission has charged the Joint Research Centre, Ispra, with the responsibility of developing and supervising application of appropriate methods for GMO detection and quantification. We congratulate the organising and scientific committees for the substantial breakthrough of providing all stakeholders with an opportunity to see the entire width of the GMO playing field: detection, analysis, documentation, accreditation and harmonisation.

However, we want to point out and to express our grave concern about one salient matter that in our view was decidedly under-achieved at this conference, indeed in the GMO field ever since.

This timely conference also highlighted a dramatic weak point which threatens to undermine the legitimacy of GMO detection and quantititation in particular, viz. the issue concerning *sample representativity.* Primary samples, which form the input to all GMO laboratories and their subsequent quantitation constitute the singular critical factor concerning whether an analytical result will be reliable for decision making; or not. Although there is an alarming need for a unifying standard, it has not been possible to reach agreement between the relevant CEN and ISO parties on even the basics of this issue; amongst other reasons this is a matter of a marked transatlantic disparity regarding perceived GMO risk with derived different policies in Europe and the US. As a result, primary sampling issues today have no unifying common basis but standardisation is predominantly carried out on a case-to-case basis with a plethora of sub-optimal attempts to formulate principles and rules—alas with very disappointing efficiency, indeed none realising representative sampling. The issue can be stated with clarity: if a sample arrives at any GMO laboratory without proper provenance documentation (without documentation of being representative), the entire detection/analysis/validation/documentation chain is without merit, reliability or value. All non-representative samples are in reality not worth analysing, since the analytical result will only relate to the minute amount of material analysed (typically of the order of 50 mg). Failure to provide scientific and legal *proof* of a fully representative sampling and sub-sampling process disqualifies such "samples", because the analytical result cannot be reliably attributed to the original lot, which is the whole objective of analytical characterisation. This goes both for detection and quantitation.

However, a complete framework for representative sampling does exist, called the Theory of Sampling (TOS), which has been in existence for more than 50 years.

Sampling for trace concentrations (the legislative EU GMO threshold for adventitious occurrence of GMO is 0.9%) suffers from highly significant Total Sampling Errors (TSE) typically of a magnitude of 20–100× the analytical error. It therefore makes little, or no, sense to continue to focus overwhelmingly on analytical precision, if primary sample representativity cannot be reliably documented, i.e. if the accuracy of the analytical result is left unknown: accuracy concerns trueness (representativeness) with respect to the original lot from where the primary sample was taken (shipload, truckload, field etc.).

The Theory of Sampling constitutes the world's only complete scientific framework for all aspects of representative sampling, it covers all types of lots and materials, at all scales, including "from farm to fork". It especially also holds all principles for representative mass reduction in the analytical laboratory, where one typically finds appreciable representativity violations, GMO laboratories not excluded, as was indeed also demonstrated at the conference. Instead of continuing the tradition of one standard for each analyte, TOS forms an overarching framework, in fact constituting a much needed unifying standard for representative sampling. Full documentation has been available in the literature for more than 25 years.

At the conference there was a conspicuous lack of appreciation of the value (economic, societal, public safety) of the imperative of documentation that every primary sample can be documented to be representative. Very few presentations (lectures, posters) presented anything akin to compliance with the Theory of Sampling (TOS). In its place there was a widely felt complacency in referencing to the only current CEN technical specification dealing with this issue [CEN TS 15568: 2007: *Foodstuffs—Methods of analysis for the detection of genetically modified organisms and derived products—Sampling strategies*]. Unfortunately this

document comprises only a small first step towards harmonisation with TOS, and most emphatically cannot serve as the needed guarantee. There were scores of important presentations covering every conceivable aspect of laboratory estimation of GMO *measurement uncertainties* (MU) which in the case of GMO is considerable, a survey of the many contributions dealing with TAE alone reached a consensus of some 15–20% (rel). It is highly significant that this metrological term (MU) hardly includes any type of sampling error (only one of out seven sampling errors at best)! There were but a few contributions related to field sampling, but exactly **zero** empirical contributions concerned with uncertainty estimation from the primary sampling stage. Due to the foresight and diligence of the scientific organising committee, there were, however, three invited introductory contributions outlining all essential principles and procedures in the Theory of Sampling, including the pivotal fact that sampling errors are typically 20–50× larger than the total analytical error itself, TAE. This fact was uncontested at the conference, yet there was very little evidence of anything but lip service to the mandate of doing something about this.

The consequences of non-compliance with TOS are several: scientific, economic, authority. Non-representative sampling will perforce give rise to a significant, inconstant sampling bias (always present, but varying in magnitude with every new sampling operation), a bias which is not estimable and therefore not amenable to the classical bias correction we know from conventional statistics. The consequences of not focusing on reducing the Total Sampling Errors (TSE) as much as possible will necessarily also have economic and decision-making consequences—maybe severe—at least there are potential consequences regarding public health concerning non-authorised GMO.

The Joint Research Centre serves the European community and its citizens by providing scientific and technical support to European policy makers as a reference centre. Based on the success of the Global GMO conference, we here call upon the JRC to build on its unequalled success in establishing the ENGL network of harmonised and standardised national GMO laboratories, which covers all aspects of GMO detection and quantitation other than sampling, also to take up the critical success factor of introducing authoritative representative sampling criteria. We have also taken other appropriate scientific actions in the present context,[1–3] the above issues are here offered in the interest of optimal follow-through of the conference.[4] The political aspects of this task are best left with the JRC, but the scientific imperative is very clear:

"Statistical considerations include the accuracy of the analytical estimation with respect to a pre-selected level of tolerable 'risk' or 'uncertainty': It is understood that the lower the tolerable uncertainty, the more laborious the sampling will have to be (the more costly, perhaps somewhat more 'impractical' than today's procedures, which do not originate from in-depth understanding of heterogeneity or representative sampling). It is here essential to be able to distinguish between a sampling bias (which can be reduced/eliminated following TOS, but which is often neglected due to 'practical and economical reasons') and the remaining sampling variance (these two aspects are clearly discriminated in TOS' definition of 'representativity'). Within TOS' framework it is indeed possible to derive complete objective, reliable estimates of the Total Sampling Errors (TSE) accompanying existing or suggested sampling plans and how to decide on the most appropriate sampling procedures."

"Non-statistical considerations include such factors as financial, labor efforts and time constraints. Unfortunately these often dominate or downright rule current sampling protocols design (ISO vs CEN approaches), with the consequence that more approximate sampling protocols with large risks and uncertainties are routinely used—ostensibly 'to save time and money'. While it is not responsibility of science to define the acceptable risk threshold (clearly a political responsibility), science would be remiss if it did not elucidate the very serious consequences of a irresponsible, voluntary, slack acceptance of only these non-statistical issues."[1–3]

We call upon JRC to take the appropriate initiatives without hesitation. We are naturally at your disposition in this endeavour.

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doi: 10.1255/tosf.10

Non-representative sampling versus data reliability—Improving monitoring reliability of fuel combustion processes in large-scale coal and biomass-fired power plants

Name of candidate: Claas Wagner
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Defense: 2 December 2013
Supervisors: Professor Kim H. Esbensen, Hans S. Møller, Vattenfall, DK and Horst Faust, Pfaff/FLSchmidt

The impact of non-representative sampling on data reliability constitutes a critical factor for the validity of Process Analytical Technology (PAT) applications for industrial quality monitoring and control. The Theory of Sampling (TOS) is the only guarantee that ensures such reliability, as the only framework for complete understanding of heterogeneity and representative sampling. The primary application realm in this PhD concerns reliable process monitoring in coal and biomass-fired power plants, where combustion efficiency and atmospheric emission characterisation are of high priority. A fundamental requirement is reliable knowledge of fuel composition and its physical characteristics at all stages during unloading, grinding, mixing, pneumatic transportation and combustion. Where a sufficient alternative biomass fuel resource platform is available, conversion of coal-fired power plants is high on the agenda, in Denmark, in Europe and (to a lesser degree) globally. The present focus in Denmark is on wood pellet-fired power plants. In order to accurately control fuel quality, combustion and grinding processes, representative samples need to be extracted at all critical stages in the processing flow path.

The main practical goal of the PhD project has been to develop a new sampling device, termed the "EF-sampler" (Figures 1 and 2), allowing extraction of representative samples from pulverised particulate material streams transported in pressurised pipes, specifically in the section between mill and burners. This is a critical process location since characteristics such as particle size distribution and moisture content have direct impact on combustion efficiency and thus must be known with the best available validity. Pipe sections used for pneumatic transportation of pulverised material streams are mostly set up horizontally, however, causing a risk for severe segregation during sampling. Currently no reliable sampling device exists on the market that can perform representative sampling for pulverised particulate material streams in a horizontal flow, hence development of the EF-sampler. The present R&D also contributes to monitoring optimisation by means of acoustic chemometrics as a possible PAT application for biomass size distribution characterisation, in which reference sample representativity is critical for prediction model validation. Overall the PhD stresses the need for further integration of the TOS in current international standards as well as contributes to a call for reconciliation between the metrological measurement uncertainty (MU) concept and TOS.

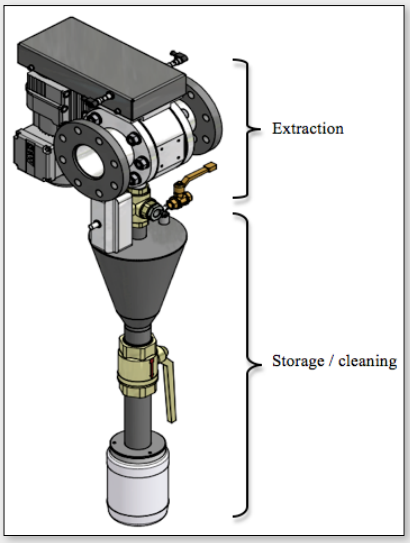

Figure 1. Schematic overview of the EF-sampler. Upper part shows the extraction mechanism including electric power supply and extraction mechanism with enclosed sampling arm. Lower part represents the storage/cleaning section including compositing cylinder, pressure valve, storage valve and storage container.

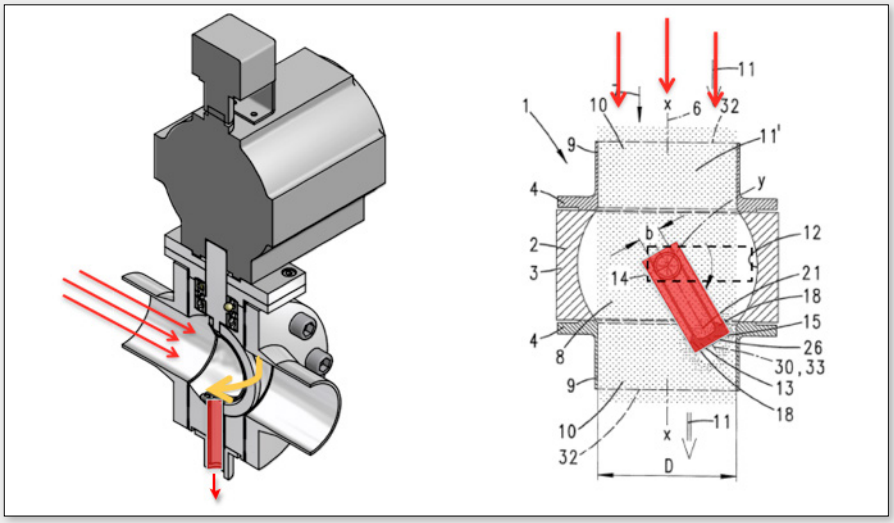

Figure 2. Schematic overview of the EF-sampler. Left figure showing side view, illustrating material flow direction, rotational movement of cutter arm and recovery of extracted material through outlet chute. Right figure shows top view of sampler, highlighting the rotational movement of the sampling arm, ducted material flow direction (top arrows) and parking position of sampling arm (dashed line).

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"Critique of Gy's Sampling Theory": Misplaced expectations of Wikipedia's democratic intentions

Geoffrey J. Lyman and Kim H. Esbensen

In today's age of the internet and the cloud's many "blessings", Wikipedia is widely hailed as the pre-eminent internet source of readily available information. Wikipedia has especially been acclaimed for its apparent *democratic* attitude towards building a free, open encyclopaedia of the time. Indeed Wikipedia carries a plethora of truly informative entries, and there are but few who have not had reason to sample information from this source. But there is also a darker side to all this enthusiasm—in that *anybody* can enter *any* new entry where none exists on a given topic, or edit any existing article. In fact, upon reflection, it dawns upon users that this democratic openness is not necessarily a blessing. Thus this institution has aptly been described by the following depressing characterisation: "Wikipedia is the medium in which your worst enemy can get to write your epitaph". This statement can act also as a clear pointer to our errand here regarding a contribution to Wikipedia in which a number of faults and accusations levelled at the Theory of Sampling (TOS) and its proponents unfortunately can be found. We find it incumbent upon us to draw public attention to this criticism of the entire life-time's achievement of Pierre Gy and the Theory of Sampling (TOS).

TOS critique in Wikipedia

We recently were directed to the fact that an entry is included in Wikipedia under the title "Gy's Sampling Theory",[1] in which a number of faults in the theory are implied. The Wikipedia text also provides a reference to an open access viXra.org (http://www.vixra.org/abs/1203.0081) document authored by Dihalu and Geelhoed. These two contributions are critical of Gy's work, and a full assessment of all scientific aspects with which the present authors, indeed most of the TOS community, will take issue will be presented elsewhere.

Suffice here to point out that Geelhoed has previously presented a paper that sought to question the matter of quantifying sampling variance in the presence of non-independent particle selection probabilities. This issue is at the root of Geelhoed's criticisms, and has also been published in several other fora. Geelhoed's work, as reported at the Third World Sampling and Blending Conference (WCSB3), Porto Alegre, is based on a new mathematical simulation approach to predicting sampling variance but provided no experimental results. This work harks back to his paper to the sampling community, presented at WCSB2, Brisbane, which did contain some experimental results and where the math behind the proposed new approach was first put forward. However, the experimental work was only directed at extremely simplistic two-component systems of particles with slightly different sizes (but identical composition and hence density), from which sweeping conclusions were attempted that claimed to represent inherent deficiencies in the foundation of Pierre Gy's Theory of Sampling. These claims, and especially their foundation, have been criticised on several occasions by several of the leading members of the sampling community.

First and foremost, it must be understood that the entire critique exclusively only addresses issues related to estimating the Fundamental Sampling Error (FSE) and that all Geelhoed's work only relates to Pierre Gy's 1979 work,[2] but nowhere refers to the three most fundamental works in the context, viz. Gy papers in 1967 and 1971,[3–5] which rank among the most central works specifically describing the issues surrounding the genesis of FSE—and the realisation of strict limits for the realistic application of the equation for its estimation. It has been pointed out to both Geelhoed and Dihalu on various occasions in several fora, that several empirical results and experiences from extensive experimental campaigns led Pierre Gy himself to conclude that the possibilities for the simple, first order "Gy's formula"[a] are more limited than many practitioners would like to accept, limited except for rather simple systems. Pierre Gy concluded that a second (of the so-called "correct sampling errors") was needed, the Grouping and Segregation Error (GSE), if one was ever to get a realistic grasp of the full complexity of the phenomena of heterogeneity. It is fair to state that this insight has been pointed out to Geolhoed *et al.*, but to no apparent avail, and this is especially germane to the entry in Wikipedia. With this background, we here focus on a few salient issues in the "critique".

It appears that the critical focus point in Geelhoed's assertions is that the random selection of a particle of one type to fall into an increment (a sample) may *influence* the selection probability for the following particle (a physical neighbour particle). That is, it is proposed that the selection probability for the second particle is not independent of the selection of the previous particle. This then might be the case where a "type 2" particle tends to associate with a "type 1" particle. This situation is well known from TOS as the case of "spatial coherence" or "grouping" if occurring in a broadly isotropic material, and as "segregation" in the case where such a tendency to coherence is primarily brought about by gravitation. In fact these relationships were discussed extensively in the (1967, 1971) fundamental Gy literature.[3–5] These issues are of course also present in any-and-all of Gy's later

[a]Gy himself loathed that this equation has been accorded this personal accolade—by others, who are not necessarily initiated to the full complexity of heterogeneity and how to counteract this in sampling. Gy has in fact always been highly dissatisfied and worried that his name should be associated with "just a first attempt, and a simplistic and highly approximate equation at that— trying to encapsulate something much more complex" (pers. com. 2008). This personal insight is key to understanding much of our vehement rejection of the Wikipedia "critique".

publications; a complete bibliography of Pierre Gy can be found in the proceedings WCSB1.[6]

Being not unskilled in statistical matters, and having reviewed Geelhoed's WCSB2 paper, one of us (GL) was hard pressed to understand the manner in which Geelhoed arrived at his final equations and conclusions. In response, he examined the problem of non-independent particle selection probabilities using a similar Markov process approach as Geelhoed and concluded, quite opposite to Geelhoed, that the non-uniform selection probability had only little impact on the sampling variance. This counter paper was also presented at WCSB3, Porto Alegre. It is fair to say that the scientific opposition that ensued here did not lead to substantial changes in either position.

It is a fact that Gy's work has sought only to identify first order effects on sampling variance, indeed Gy himself was adamant in pointing this out. Much of his early work was directed at elucidating the theoretical relationship associated with what became known as the Fundamental Sampling Error only (expressed both in theory and in practise as a variance). In analysing a given sampling circumstance, all experienced samplers, experts and consultants in the field have to work with *approximate data*, not with perfect statistical distributions. In all realistic situations in the field, in the plant or in the laboratory, in general one does not have access to full knowledge such as the distribution of particles' grades with respect to the critical analyte on a size by size basis, which is at the root of dealing theoretically with FSE, and which is the necessary foundation for simulating a sampling process. Nor does one possess full knowledge of the covariance function for grade in the process stream being analysed for example, another characteristic that needs to be known in order that realistic simulations can even begin to be contemplated. And finally, crucially, no one has the necessary means, short of prohibitively expensive experimentation, of assessing, for example, the extent of lateral particle segregation by grade on a conveyor belt from which a sample (or an increment) is to be drawn. It is absolutely critical to understand, and acknowledge, that such extra-FSE heterogeneity *per force* will change from second to second, minute to minute, hour to hour, day to day in the course of events of realistic sampling of real-world lots and materials—such is the nature of significantly heterogeneous materials. Instead one works with summary information obtained from preliminary, pilot study *heterogeneity tests* on material that has been collected with the specific objective of being representative of the general material class to be sampled, now **and** in the future, over some time-span of the task or project at hand. In this work, one relies, for example, on variograms estimated from survey samples collected from a process stream under conditions that are carefully characterised and which must be representative of the future sampling process. Above all one strives to the utmost to make the sampling process(es) "correct", i.e. unbiased, the conditions for which forms the most important part of TOS and which must be included in all types of evaluations of a realistic sampling process. To take one example, the efficiency of a sampling process is based on analysis of samples that span the full relevant range of compositional variations to be encountered in future applications of the same sampling process, either to a similar class of material and/or to similar material in the future. Armed with this type of empirical data relevant for the materials and processes at hand, one *may* now evaluate with some reliability the likely magnitude of the sampling variance that will be encountered. Based upon this kind of knowledge, one may venture further to design sampling systems that will then achieve, on average, a level of precision that is deemed to be economically important to the operation—after the accuracy issue (the bias) has been first eliminated by designing, and implementing "correct" sampling procedures. Here one seeks to provide a mechanically correct sampling system to ensure that the total remaining sampling uncertainties are controlled to an acceptable level. If one can deliver this, then and only then, the professional sampling job has been done.

All the above is a far cry from the conditions that underlie the simulations reported by the works referred to in the Wikipedia entry—indeed the simulations covered by these references can only be characterised as extremely simplistic—without any realistic relevance except for a simplistic case of an ideal two-component system. Geelhoed has been carefully informed of the extreme deviation between this situation and real-world heterogeneity on many occasions (KHE).

Pierre Gy himself, after extensive experimental work carried out to test the realism of FSE estimates, realised and publically acknowledged the existence and significance of such extra-FSE heterogeneity in the overwhelming majority of materials. For this reason he conceptualised and coined the second of the so-called correct sampling errors, the Grouping and Segregation Error (GSE), aimed at representing the sampling variance effects stemming from this irregular meso- to macro-scale heterogeneity characterising the lot geometry realm *beyond* the scale of one particle and its retinue of surrounding secondary particles. In this Gy was very much aware that the simple statistical apparatus he had used to start analysing the relationships regarding FSE would only be able to further a first order approximation. This is a demonstrable fact in several key publications from 1967 onwards (referred to in Reference 7). So, Gy was very well aware that in the realm to which he assigned the GSE, matters could not be subjected to any then-known statistical treatment. He would, however, undoubtedly, have welcomed any such professional attempt, as should all subsequent sampling theoreticians and practitioners for that matter. And this is precisely the realm to which Geelhoed and Dihalu direct their attention, indeed the PhD thesis of Dihalu bears the intriguing title: "The *Terra Incognito* of Sampling: Grouping and Segregation".[8] However, the Wikipedia entry and the open access document referenced contain severe misunderstandings of the nature of TOS, and, in our view unacceptably disrespectful comments are levelled at the intentions of its originator. We can only take up the most blatant such issue here.

"Fudge factors"

First, the criticism of the two parameters introduced in TOS to achieve a more detailed description of heterogeneity, the grouping- and the segregation parameters. These are directly called "fudge factors" (also in a few places in Dihalu's PhD thesis).

In attempting to estimate the influence of segregation in the body of a mineral mixture, we are essentially blind without

truly exhaustive sampling work, which is generally unjustified and anyway quite prohibitive in everyday sampling. Francis Pitard has said of the influence of segregation that: "If quantified today, it will differ tomorrow". This is a truism that has not been recognised by the authors of the critique. Central to our rejection hereof, and again an issue repeatedly presented to Geelhoed (KHE): Pierre Gy's grouping and segregation parameters are of a **totally different nature** in TOS: these are presented in the theoretical analysis of the complex concept of heterogeneity as "phenomenological parameters", intended to represent the influence from grouping ("groups-of-particles, clumpiness") and segregation in the formal mathematical–statistical apparatus developed by Gy for this purpose. This simply could not be further away from the postulated nature of "fudge factors" stated by Geelhoed and Dihalu, e.g. documented by a direct quote from their open access document: "The use of fudge factors to tweak the predicted values with the experimental values is a major point of concern in Gy's theory". TOS' phenomenological factors were never intended to be estimated and used to bridge the gap between the formula-based (FSE only) and empirical estimates (FSE + GSE). This is a fatal misunderstanding. For want of space, we refer the reader to the scholarly treatment of these issues in much more theoretical and practical depth (which indeed also is a direct response to the TOS criticism delivered by Geelhoed at three WCSB conferences) given by Pitard & Bongarcon.[7] The denigration of Gy's theoretical work as depending on fudge factors is an insult to all serious scientific dealings with the Theory of Sampling.

Overview of contrasting positions

To claim that Gy's theory needs rectification, on the basis of data collected under the particular circumstances of simplistic mixing is a red herring cast across the path of the use of Gy's work. The present authors have both been using Gy's results and methods since 1982 (GL) and 2000 (KHE), the former as a consultant with extensive experience from many industry sectors and application fields, the latter heavily involved in teaching and dissemination of TOS (also including many industrial sectors, corporate and regulatory bodies), and we have found no fault with the theory and application at all. If Geelhoed and Dihalu wish to construct a revised theory of sampling, this is a fully legitimate objective, and indeed one that would only meet with approval by all parties. But (the absolutely central issue), anybody undertaking such an endeavour **must** per force provide cogent descriptions of the alternative theory and back it up with solid, very careful and extensive experimentation. Most of all, it is incumbent upon any such contenders to provide **evidence** (theory and experiment) that the new theory provides results that make a **significant** difference to Gy's results. If the differences are only small, if the issues only address FSE, and if all issues related to the bias-generating incorrect sampling errors are totally **ignored**, all of which pertain to the Wikipedia "critique", one need absolutely not abandon Gy's work. Geelhoed should rather find means and ways to provide sound and full theoretical coverage as well as realistic experimental evidence, that Gy's work is in significant error before continuing to denigrate this work. In our experience, TOS has, throughout all of its 60 years' of existence, firmly defended all tests of theoretical riguour and practicality, over and over. There is an overwhelming published, peer-reviewed literature to back this up.

Conclusion

It is not wrong to (try to) level criticism at the Theory of Sampling (TOS). TOS is no sacred object. TOS is a comprehensive, indeed claimed to be a complete, theory of heterogeneity, sampling and the derived principles for design of representative sampling procedures and equipment. Nobody in the TOS community would object to the continued testing of theoretical concepts, or to assessment and evaluation of the practical correspondence with reality of TOS. Indeed this takes place all the time, as can be followed in full public detail in the continuing series of WCSB proceedings.

What is wrong, and what has lead to our strong consternation and rejection of the Wikipedia "Critique of TOS" section, is the superficiality in the levelled critique which represents a total lack of respect for the entire life's work, the formidable *oeuvre* of Pierre Gy. This will simply not stand.

Appropriate measures to have the current entry removed from Wikipedia and replaced with a more fitting, scientifically sound and more respectful entry is under way.

The reader is encouraged to make her/himself acquainted with the Wikipedia entries and to form their own opinion. Readers are invited to join in this endeavour, either by voicing their dissatisfaction with the current entry, or by presenting their reasons for supporting the Geelhoed & Dihalu claims. *TOS forum* is open to all reactions to the issues raised above.

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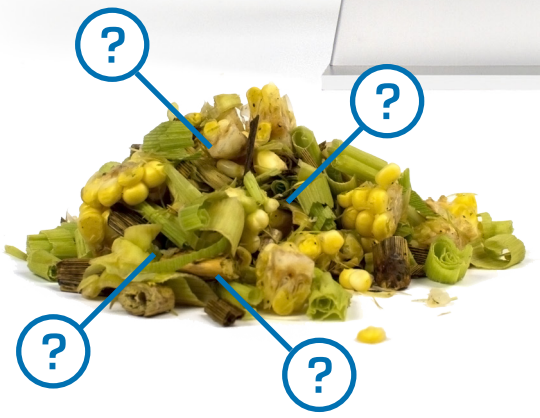

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