TOS forum

Issue 10 **2020**
ISSN: 2053-969X

Contents

WCSB10
in-person conference postponed to 2022

Ian Devereux 1940–2020

FORUM FOR THEORY AND PRACTICE OF REPRESENTATIVE SAMPLING (TOS)

Introduction to Theory and Practice of Sampling
page 16

Theory of Sampling and Sampling Practice
page 17

Theory and Practice of Particulate Sampling
page 18

editorial

doi: 10.1255/tosf.113

After more than a year, we are delighted to present *TOS Forum* to you again. One of the important missions of this issue is to provide the latest information on the 10th World Conference on Sampling and Blending (WCSB10). In these times of coronavirus, will the International Pierre Gy Sampling Association be able to continue the format of biennial *in-person* conferences, or not? IPGSA have made plans for conducting WCSB10 as planned ever since WCSB9 (Plan A), as well as being prepared for a Plan B—a simple one-year postponement. With the latter now having been decided upon, presenting the WCSB10 conference in detail is still the objective of the first feature in this issue.

We also answer the question “Exactly *how* did the World Conference of Sampling and Blending originate?” With WCSB 10 approaching, “three fellows” decided to do something about this. It turned out to be quite a detective story spanning 20+ years, three continents, many obsolete PC platforms and searching through several thousands of old e-mails. The story, as told here by Messieurs Francois-Bongarcon, Vann and Esbensen, is a tour-de-force of the pre- and very early history of the WCSB institution. I am sure many will enjoy this piece!

Next, a comprehensive *In Memoriam* for one of our most influential and respected members, Ian Devereaux (1940–2020). Scott Technology, who acquired Ian’s lifetime achievement company Rocklabs in 2008, have prepared an obituary over Ian’s remarkable life, together with a thorough scientific, technological and business history, which *TOS Forum* is honoured to bring here: RIP Ian Devereaux.

Next up is an absolute highlight in the life of IPGSA, a feature the editor has had in his sights since 2017, when at WCSB8 (Perth) it became clear that there were no less than three textbooks in preparation within the field of Theory and Practice of Sampling! This more than 20 years after the last such one was published, Pierre Gy’s own: *Sampling for Analytical Purposes* (1998). The editor has asked the authors of these books to present their works in parallel here. This comparison reveals three books with the most different scopes, contents, layouts and writing styles imaginable while pursuing the *same goal*. The editor also asked all three authors to supply a “companion piece”, indicating that it might be useful if these pieces had at least some relation to the topics treated in the books… What ensued were three even more different pieces, truly reflecting the individual interests and drives of each author.

The reader will next find a frontline R&D report introducing advanced on-line monitoring of automated sample preparation processes based on accelerometer sensors for Process Analytical Technology (PAT) application. This offers a glimpse of the future in industrial process technology. This is followed by a piece which has been under way a very long time, introducing “TOS principles for gas sampling”.

The last feature takes us to a place very far away from the down-to-Earth problems of practical sampling. It introduces the new version of Francis Pitard’s earlier book: *The Theory of Vacuoles and Low-energy Nuclear Reactions: A Correct System of Dimensions and Units*. This book represents a monumental attempt “to look behind the veil of standard physics”, which should be of interest to most who have ever contemplated the innermost nature—of Nature. The following snippet should bring you out of your armchair: “The mass of the electron is an established physical constant, as is the mass of the proton. The ratio m_p/m_e is about 1836. No one has so far been able to *explain* this ratio… In Chapter 7, this new book provides a clear answer! The electron shell that surrounds the central vacuole, or vacuoles, is mostly *outside* our three-dimensional universe. Only that fraction of the electron that lies *inside* our universe affects our mass measuring devices. The electron has the same mass as the proton, but is inside our universe for only 1/1836 of the time”. You will have to pay your respect to the entire book, but then you will *understand* this argument!

Et voila—the editor has fulfilled his duty trying to raise the interest of the potential reader for the entire 10th issue of *TOS Forum*. Enjoy your reading!

Kristiansand, Norway, will be the venue for WCSB10.

Issue Sponsor

We are most grateful to Scott Automation (https://www.scottautomation.com) for their sponsorship of this issue.

EDITOR
Kim H. Esbensen Owner, chief consultant, independent researcher at KHE Consulting, Denmark, khe.consult@gmail.com; guest-, associate-, visiting professor (Denmark, Norway, Puerto Rico, Quebec).

PUBLISHER
Ian Michael (ian@impopen.com)

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

IMPublicationsOpen

TOS forum is the communication forum for the theory and practice of representative sampling (TOS). Visit impopen.com/tosf for details.

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

doi: 10.1255/tosf.114

10th World Conference on Sampling and Blending (WCSB10)

Introduction

The WCSB10 conference will cover the latest research and application of the Theory of Sampling (TOS) and Blending in many important technology and industry sectors: mining, exploration, minerals processing, metals refinement, cement, food and feed, agri- and aquaculture, pharmaceutical production etc.

WCSB10 specifically has a broader societal, industrial and environmental emphasis with a special focus on sustainable science, technology and industry.

COVID-19

Due to the global impact of the coronavirus pandemic, it is impossible to know the scope and the precise conditions for international scientific conferences in the foreseeable future. The organising and scientific committees have, therefore, decided to prepare for several scenarios. Right up until the publication date of *TOS Forum*, planning for WCSB10 was in the hope that the conference could take place as an in-person conference as usual. However, it has now been decided that an in-person conference in June 2021 will not be safe—see bottom of p. 4. Therefore, WCSB10 will be postponed to June 2022. The committees will, of course, minimise possible economic consequences for the hosting party, for the conference sponsors and for already registered participants.

All developments affecting WCSB10 will be reported regularly on the conference website.

Historical backdrop: WCSB1–9

WCSB10 represents the continuation of the activities carried out over two decades by the global sampling community. The first nine conferences bear witness to steadily increasing scientific and social results, and a well-documented series of high-quality proceedings. The number of attendees to the inaugural WCSB1 in 2003 (Esbjerg, Denmark) was 117, which has grown at succeeding conferences with an average level of *ca* 150–175, and culminating in the unique 556 delegates to WCSB9 in Beijing, China (2019), where the proceedings reached 810 pages, out-pacing any previous conference. This two-decade development is, needless to say, highly satisfactory for the global sampling community, which has, since 2017, been organised as the International Pierre Gy Sampling Association (IPGSA).

WCSB10: a sustainable scientific conference

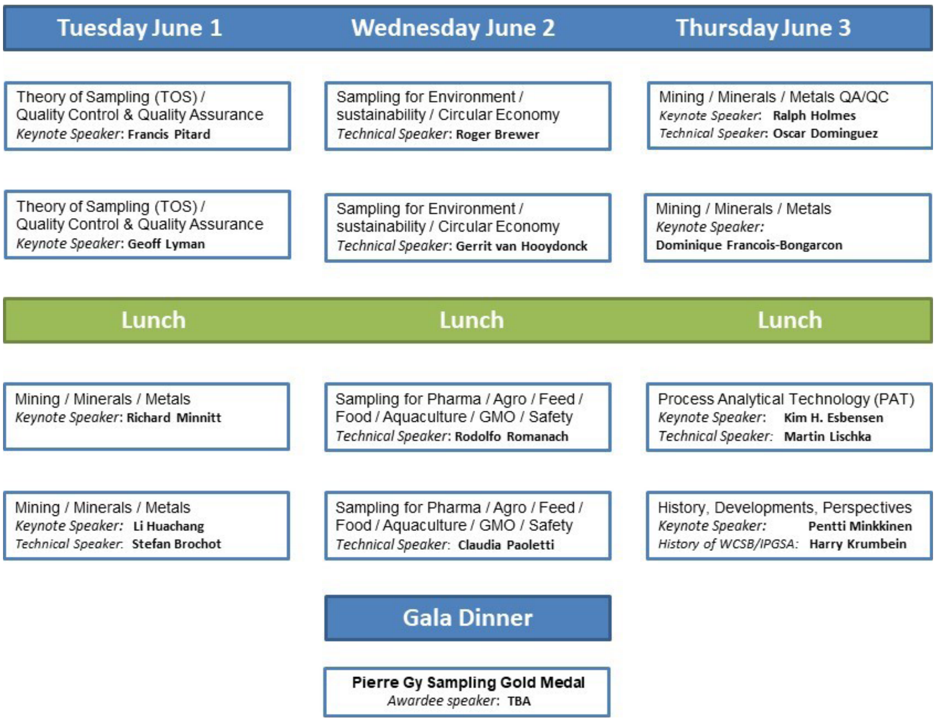
WCSB10 will likely continue the qualitative growth from previous conferences, but not necessarily in terms of quantitative numbers. The organisation committee and the EYDE Industrial Cluster would like to introduce a new sustainable direction for this conference, and future conferences as well. WCSB10 will be targeting the UN world development goals Nos 9 and 12, which address sustainable industry, innovation and infrastructure, and responsible production and consumption, respectively. It is hoped that the sampling community is interested and willing to contribute towards fulfilling the aspirations embedded in these goals. To facilitate this, some new items on the conference agenda are being introduced for WCSB10:

- The environment and sustainability is included as a new, separate session in the programme. All conference speakers are encouraged to reflect on if, and how, their work can contribute to more sustainable industry.
- Conference target numbers are deliberately scaled back. The committees wish to welcome you to a conference that is high in scientific quality and with pleasant social experiences. But WCSB10 does not need to match, far less surpass the unique scale and numbers achieved by the previous conference. This aim is also a reflection of the parallel activity of organising semi-regular Australian, South African and South American sampling conferences in the intervening years between the bi-annual WCSB.
- The amount of printed material and giveaways will be scaled down, as it is believed that the digital format is convenient and readily available worldwide.
- The organisation committee is working on offering a streaming option from WCSB10. If you cannot travel to Norway, this option will allow you not to miss out on the key scientific sessions at the conference. With this option you will also get a digital copy of the conference proceedings.

Scientific programme

An exciting programme of high-quality presentations is being developed. The following themes will form the core of the conference programme:

SUSTAINABLE DEVELOPMENT GOALS



Tuesday June 1	Wednesday June 2	Thursday June 3
Theory of Sampling (TOS) / Quality Control & Quality Assurance *Keynote Speaker*: **Francis Pitard**	Sampling for Environment / sustainability / Circular Economy *Technical Speaker*: **Roger Brewer**	Mining / Minerals / Metals QA/QC *Keynote Speaker*: **Ralph Holmes** *Technical Speaker*: **Oscar Dominguez**
Theory of Sampling (TOS) / Quality Control & Quality Assurance *Keynote Speaker*: **Geoff Lyman**	Sampling for Environment / sustainability / Circular Economy *Technical Speaker*: **Gerrit van Hooydonck**	Mining / Minerals / Metals *Keynote Speaker*: **Dominique Francois-Bongarcon**
Lunch	Lunch	Lunch
Mining / Minerals / Metals *Keynote Speaker*: **Richard Minnitt**	Sampling for Pharma / Agro / Feed / Food / Aquaculture / GMO / Safety *Technical Speaker*: **Rodolfo Romanach**	Process Analytical Technology (PAT) *Keynote Speaker*: **Kim H. Esbensen** *Technical Speaker*: **Martin Lischka**
Mining / Minerals / Metals *Keynote Speaker*: **Li Huachang** *Technical Speaker*: **Stefan Brochot**	Sampling for Pharma / Agro / Feed / Food / Aquaculture / GMO / Safety *Technical Speaker*: **Claudia Paoletti**	History, Developments, Perspectives *Keynote Speaker*: **Pentti Minkkinen** *History of WCSB/IPGSA*: **Harry Krumbein**
	Gala Dinner	
	Pierre Gy Sampling Gold Medal *Awardee speaker*: **TBA**	

- Theory of Sampling (TOS)
- Quality Assurance/Quality Control (QA/QC)
- Mining and Process Industry
- Minerals and Metals
- Environmental Sampling, Sustainability and Circular Economy
- Agri-, Food, Feed and Aquaculture Sampling
- Pharmaceutical Sampling
- Process Analytical Technology (PAT)
- New Developments and Equipment in Sampling

Keynote and technical speakers have already been invited for all sessions.

Details on how to submit your presentation can be found at https://wcsb10.com/contact/ The Scientific Committee will determine if an oral or poster presentation is appropriate.

Short courses

Prior to the official programme, short courses will be held, arranged by experts in the field of sampling, which will give participants an opportunity to strengthen their expertise.

One-day short courses

Introduction to the Theory and Practice of Sampling (TOS)—a New Didactic for Science, Technology, Industry, Commerce and Society

Course provider: Kim H. Esbensen (KHE Consulting, Denmark)

Grade Control in Underground Gold Operations

Course provider: Dr Simon Dominy

Process Analytical Technology (PAT) and TOS-Compliant Sampling in Pharmaceutical Production and Monitoring—the Rules of the Game!

Course providers: Brad Swarbrick, Rodolfo Romañach and Kim H. Esbensen

Two-day short courses

Variograms and their Analysis for Improved Process Knowledge

Course provider: Dr Geoffrey Lyman (Principal, Materials Sampling & Consulting, Southport, Australia)

Sampling Theory and Practice, their Economic Impact (Day 1) and Analysis of Sampling Correctness and the Futility of Bias Tests (Day 2)

Course providers: D. Francois-Bongarcon (AGORATEK International Consultants Inc., Canada) and Francis F. Pitard (Francis Pitard Sampling Consultants, LLC).

Detail of each short course can be found at https://wcsb10.com/program/workshop-and-shortcourses/

Proceedings

The Proceedings of WCSB10 will be published by IM Publications Open in both print and online versions. The online edition will be available as a special

WCSB10 in-person conference off for 2021, postponed to 2022

Due to global coronavirus developments as of mid-October 2020, the organising committee together with the hosting EYDE Industrial Cluster has had to conclude that it will not be safe to conduct WCSB10 as an in-person conference in 2021. The WCSB10 conference will be postponed to 2022, still in the in-person format, venue and timing likely unchanged: June 2022.

Further information will be made public on the WCSB10 website as soon as possible. Please keep checking wcsb10.com.

However, rather than just waiting out the pandemic for the 18 next months, the WCSB committees and EYDE Cluster are developing plans for a complementary event at the time of the postponed conference in 2021. This will be a digital event in the form of a one-day symposium.

The theme and topics of the symposium are being discussed and will be announced on the WCSB10 website. In any case, the topics will be guided by a natural focus on the two UN World Goals, "Sustainable production" and "Environmental stewardship" of the in-person conference in 2022 (see wcsb10.com).

All 2021 presentations will qualify for peer review on an equal basis with the 2022 WCSB10 conference presentations. The full WCSB10 Proceedings (2022) will thus include all successfully reviewed and accepted papers from this 2021 event.

Further information will be made public on the WCSB10 website as soon as possible.

PLEASE FOLLOW DEVELOPMENTS CLOSELY AT WCSB10.COM


Kristiansand waterfront by night. The conference hotel is to the left. Photo: Gorm Helge Grønli Rudschinat

issue of *TOS Forum* via the conference website, IM Publications Open and the IPGSA internet portal. In-person conference participants will receive a print copy at the conference.

Open access

The online edition will be an Open Access publication: freely available without any need for registration or other access requirements. This helps provide the widest dissemination for your work and allows all interested parties to read the latest research on the Theory of Sampling.

Authors' rights

Authors retain all rights in their paper, including copyright, and can choose a Creative Commons licence to publish under. This just makes it easy for authors. There is no need to worry whether you need permission to reuse your own work in future. You are free to submit to other publications; of course, their particular reviewing policy would apply.

Submission details

More information can be found at https://wcsb10.com/proceedings/.

Venue

The conference venue is Kristiansand, southern Norway. Kristiansand is popular with summer visitors who love to bask in the sun along *Fiskebrygga* (harbour area), stroll along the picturesque streets of *Posebyen* (the old town) or take a short hike in *Ravnedalen*. This beautiful city by the sea, with endless summer nights, offers many cultural and culinary opportunities for you to explore.

Conference hotel

The conference hotel is the Radisson Blu Caledonien Hotel, Kristiansand. Its city centre location right beside the sea provides a perfect base for enjoying the city. You will be staying within walking distance of the bus, ferry and railway stations and just 20 minutes from Kjevik Airport.

Committees

The Scientific and Organising Committees are crucial to a successful conference.

Organising Committee

The current members are:

- Head of Committee: Dr Elke Thisted (Glencore Nikkelverk)
- Proceedings Editor: Prof. Kim Esbensen (KHE Consulting)
- Conference Secretary: Kristine Fuller-Gee (Eyde Cluster)
- Commitee member: Ellen Nordgård-Hansen (NORCE)

Scientific Committee

- Head of Committee: Kim H. Esbensen (KHE Consulting, Copenhagen, Denmark)
- Roger Brewer (Hawai'i Department of Health, Oahu, USA)
- Stefan Brochot (CASPEO, France)
- Philippe Davin (Iteca Socadei, France)
- Simon Dominy (NOVO Resources Corp, Australia)
- Oscar Dominquez (BHP, Technical Centre of Excellence & Legacy Assets, Australia)
- Dominique François-Bongarçon (AGORATEK International Consultants Inc., British Columbia, Canada)
- Ralph Holmes (Mineral Resources, CSIRO, Australia)
- Li Huachang (B. Grimm, Beijing, China)
- Martin Lischka (HERZOG Maschinenfabrik, Germany)
- Geoff Lyman (Materials Sampling & Consulting, Brisbane, Australia)
- Pentti Minkkinen (Lappeenranta Lahti University of Technology, Finland)
- Richard Minnitt (School of Mining Engineering Witwatersrand University, Johannesburg, South Africa)
- Claudia Paoletti (European Food Safety Authority, Parma, Italy)
- Francis Pitard (Francis Pitard Sampling Consultants LLC, Broomfield, CO, USA)
- Rodolfo Romanach (University of Puerto Rico at Mayagüez, USA)
- Gerrit Van Hooydonck (Umicore Precious Metal Refining Hoboken, Belgium)

www.wcsb10.com

doi: 10.1255/tosf.115

Greetings from China, WCSB9

Li Huachang
BGRIMM MTC

On 7–9 May 2019, 555 delegates from 23 countries gathered in Beijing for the 9th World Conference on Sampling and Blending. WCSB9 took place in the Beijing International Conference Center and had the highest attendance of any previous conference, the highest number of accepted papers in the Proceedings and the highest number of exhibitors as well. This event marked a welcome culmination of the first 20 years of organised activities for the International Pierre Gy Sampling Association. WCSB9 was hosted by BGRIMM Technology Group and jointly organised by BGRIMM MTC Technology Co., Ltd and Unismart Events Ltd, with support from China Mining Association, China Association for Instrumental Analysis and The Chinese Society for Metals. A full report on WCSB9 can be found at http://bit.ly/WCSB9Report

The inaugural CSTM Material Sampling and Blending Technical Committee, which includes three international members.

The Pierre Gy Sampling Gold Medal committee awarding the WCSB9 (2019) Medal to Dr Geoff Lyman.

Prospects in China

As an important world economy and a major goods manufacturer, China has realised that there is a critical need for proper sampling and blending technologies to assist in global trade, product quality control and environmental protection. As well as carrying on the well-established scientific objectives of the WCSB series, the 9th conference also had a national aim, to contribute more to promoting further development and communication of sampling and blending technologies. The organisers spared no efforts in order to facilitate a constructive synergy between all these goals.

WCSB9 promoted the International Pierre Gy Sampling Association and the Theory of Sampling for the first time in China. More important was the establishment of China's first academic organisation for sampling—the CSTM Material Sampling and Blending Technical Committee, which will pave the way for Chinese professionals in the sampling field to connect with the international sampling community.

In addition to the traditions of previous WCSB, WCSB9 had a new event, a focus discussion on the "Differences between China and Other Countries in Sampling and Blending Theories and Practices for Bulk Commodity Trading", which aimed to enhance the understanding among the parties involved in sampling for international commodity trading.

The WCSB10 conference will take place in Kristiansand, Norway, in June 2021 (depending on the status of the coronavirus pandemic). China will continue to send representatives to the world conference series, and will in particular present an invited contribution: "The state of organised sampling work in China since WCSB9" at WCSB10. China wishes that WCSB continues to have a bright future, and hopes WCSB10 will be successful. We are looking forward to seeing you again next year in Norway.

TOS forum is a free publication for the sampling community, providing a

continued on page 10

doi: 10.1255/tosf.116

Origin of the World Conferences on Sampling and Blending (WCSB)

Dominique Francois-Bongarcon,[a] John Vann[b] and Kim H. Esbensen[c]
[a]**AGORATEK International Consultants Inc., Canada**
[b]**Group Head, Group Discovery & Geosciences.** john.vann@angloamerican.com
[c]**KHE Consult, Denmark.** kheconsult@gmail.com

The year 2021 is fast approaching when the World Conference of Sampling and Blending will see its anniversary 10th edition. Recently, some of the younger members of our community have been asking: "how did the WCSB series originate in the first place?" When pondering this, even those intimately involved had to admit to a substantial degree of memory uncertainty, and decided to set the record straight before everything has receded too much into a fog. The authors of this article have, with great difficulty, dug into their memories (not entirely successful) and their PC backlogs (much more helpful and successful). Recollections were coordinated, e-mails and other documentary material, some from more than 20 years ago, were exhumed (more or less easily from severely outdated physical hardware and software – the reader may, or may not, have a realistic idea of what 20 years represents in the form of how many generations of PC hardware and software have passed), and a concerted co-authorship action spanning Australia, Canada and Denmark was undertaken. It turned out that this visit down memory lane was in fact a lot of fun, besides a truly "last minute" rescue operation. We are delighted to present this historical nugget to the readers of *TOS Forum*.

How it all began I

"In a small city, in a small country, in a time far, far away…." The event was in late 1998, 20 December to be precise. The historical catalyst of what was to become the first WCSB (and much more), was a PhD defence for a student of Professor Pentti Minkkinen of the Institute of Chemistry, University of Lappeenranta, Finland. PhD student Riitta Heikka was to defend her thesis: "Sampling and Calibration in Process Analytical Chemistry", for which Minkkinen had decided to call upon opponents from two "very disparate disciplines", The Theory of Sampling (TOS) and Chemometrics. In reality, at this time only Professor Pentti Minkkinen had worked seriously to bind these disciplines closer together, and had in fact tried to get one of the present authors over a period of several years to join him in this endeavour, but "with only *sluggish results*" (Minkkinen's own words). This historical backdrop is well described in Minkkinen's contribution to issue 8 of *TOS Forum*, "Pierre Gy—in memoriam".[1]

As a consequence, he decided on one last try and called upon Pierre Gy *lui meme* (readers need not guess which discipline this first opponent was supposed to deal with) and KHE (at that time representing ~20 years of work within the discipline of *chemometrics*). And so it came to be that a French–Danish professional, and soon personal, friendship started, a development to last until 2015 when Pierre Gy passed away.

The immediate consequences of this meeting in Lappeenranta was that the chemometrics professor on the spot decided to make a 90° clean break with his then scientific career path, and start to delve much more into TOS and its applications to many technological and industrial sectors "because this was much more challenging than simply continuing to coast along a chemometric trajectory". This could not have come at a more appropriate time, as in August 2001 KHE was appointed Professor (in "Data Analysis and Process Technology") at Aalborg University, Esbjerg, Denmark. Thus, in the very early 2000s there had just

Figure 1. 20 December 1998, Lappeenranta University of Technology (LUT). Left: PhD defence for Riitta Heikka in the company of a proud supervisor Prof. Pentti Minkkinen and two international opponents, Dr Pierre Gy and Professor Kim H. Esbensen, respectively. Right: As far as chemometrics and TOS go, after the academic duties were respectfully discharged (to everybody's satisfaction, not least for Mrs Heikka), this was love at first sight.

Figure 2. Rydges Hotel on Hay Street, Perth, Australia.

started a small, but steadily growing, activity on the interface between sampling (TOS), chemometrics and process technology—in another, equally small city, in another equally small country, also far, far away…

How it all *really* began II

The year was 2000, February in Perth, Australia and the venue is the terrace of the erstwhile Rydges Hotel on Hay Street (Figure 2). That autumn afternoon, two fellows working in mining and geostatistics discussed "world matters" over a drink, *maybe* more... Their beers were pleasantly cool with which to take in that beautiful weather, business was booming and TOS was more appreciated than ever before in the mining industry. But even so, though life was good on Hay Street, there was this terribly frustrating issue, it was soon agreed, that in other circles scientific recognition of Pierre Gy's Theory of Sampling had been lagging for (far) too long…

As hardline followers of Pierre Gy, these gentlemen felt they **had** pulled all the strings they could think of, calling for public attention outside their own communities to Gy's magnificent scientific contribution to the industry at large. They felt that they had been trying very hard with professional institutions and academic organisations to obtain a mere gesture of recognition, perhaps a medal or an honorary degree of some kind for Gy, here, there, in Canada, in the USA, elsewhere—but in vain. Very, very frustrating!

After a few more beers, they then remembered how George Matheron, the father of Geostatistics, had indeed been honoured in various ways, and how he, and subsequently many of his students, were regular key persons at many a Geostatistical Conference, and how such ongoing events had, in effect, built a perpetual memorial to him.

It is true that the great Pierre Gy never indulged much into publicity or proselytism and had made only modest efforts to teach or convince others. Pierre felt that his scientific work should be judged on its own merit; he did not have much regard for "pushy self-marketing" and the like (quite a few academics a.o. in this world could learn a thing, or twenty, from Pierre Gy here). To be honest, quite conscious of the paramount importance of his work, this proficient mountain climber had single handedly, and painstakingly, built a full theory from scratch, complete with rigorous mathematical-statistical demonstrations and practical implementation rules, and he had done all this alone, with no exterior help and no other motivation than his own purely scientific quest.

However, the world *must* get to know more about this, our frustrated beer-drinking and reflecting gentlemen thought. It appeared clear that such a powerful theory, which had changed the face of the mining and related industries, did not need to be **proven** any longer, the successes were far too many and spectacular: but why then was his name still awaiting recognition outside this industrial sector? More efforts had to be marshalled!—but how? (more beers were ordered).

Then, the experiences from several geostatistical conferences finally did strike a chord that day in Perth, and John and Dominique saw that **this** was indeed a way they had missed all that trying time!

What then transpired?

As a consequence of the pre-history backdrop related in the introduction above, Pierre had at some intervening time, actually just a few weeks before this Australian encounter (November 2000), put Dominique and Kim in mutual e-mail contact, and they had agreed that the only opportunity to meet for two such busy entities would be *between* two of Dominique's incessant flights to and from all over the world. So, Copenhagen airport was chosen, since it at that time often served as a hub for many further flights for Dom, and it was (finally some luck) not a problem for Kim, who was based only 300 km away. So, by March 2001 the idea of a sampling conference (*somehow*, *somewhere*) and also a Pierre Gy medal (*if the one, then also the other …*) had been briefly introduced between the three present authors.

After finding and introducing one-another at Kastrup airport, beer was again on the menu (proper Danish beer of course) and soon the case about their common friend and Sampling Grand Master was front and centre of the agenda. The big thing of the day was that Kim, a relatively newly minted full university professor, had decided that he was now in possession of the logistics, the resources, the will, the energy and the motivation to get a first international sampling conference organised in the Kingdom of Denmark. The day was 6 April 2001.

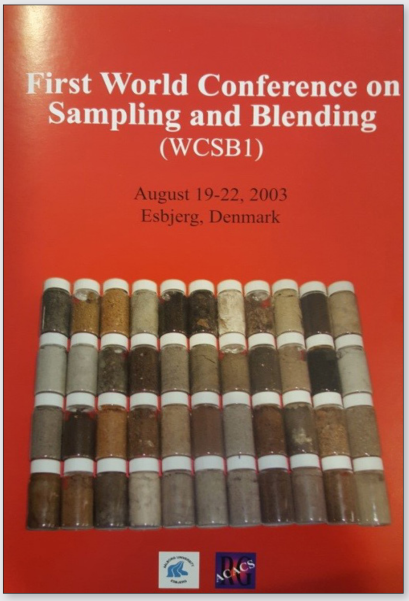
Fast forward: WCSB1

Fast forward to 19 August 2003, under the auspices of Alborg University, campus Esbjerg. A crowd is filling the conference room at Hotel Brittania, the venue selected for WCSB1. Pierre is sitting in the front row, and the atmosphere is one of great excitation. Indeed, even though maybe not everyone present realised it, history was in the making, starting a journey for decades to come... Finally, it was time to bestow the appropriate honours on Pierre.

Figures 4–6 are a few mementos from the first three years of the millennium.

Indeed, Esbensen had had to use rather strong words fighting off a group of fellow-professors (in the German vernacular such are known as "BesserWissers"), who accused him of "abusing his students". Well what fools were they—history had a very

Figure 3. Nobody was more happy along with Pierre Gy as the three originators (left-to-right: John, Dominique, Kim). The origins story had finally come to a successful closure, and organised scientific encounters and proper interaction could begin—which became the World Conference on Sampling and Blending (WCSB) forum.



First World Conference on Sampling and Blending
(WCSB1)

August 19-22, 2003
Esbjerg, Denmark

Figure 4. First Call (ever) to a World Conference on Sampling and Blending.

Figure 5. Praise where praise is due: those who realised the dream *in practice*. Most everything has a humble origin, so also WCSB. The WCSB1 organisational committee had absolutely no idea what would be the follow-through of this initiative. In fact, besides the conference chairman and secretary, there were no other professionals involved, but, indeed as it turned out, so much for the better, in the form of an untiring, highly energised crew of Prof. Esbensen MSc and PhD students (left-to-right) Lotte, Anette, Lars P., Casper, Ellen Karlsen (Conference Secretary) KHE (Conference Chairman), Julie and Hans-Henrik.

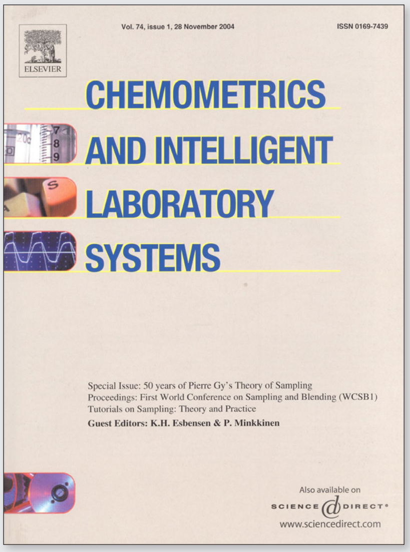
different judgement, witness the publication of the Proceedings of the First World Conference on Sampling and Blending.

Hereafter the institution of WCSB developed pretty much by itself through a series of intrepid colleagues who were willing to take on the hard work of organising international conferences. The crucial next step came in the form of swift midwife action by Ralph Holmes who "on the spot" offered to organise the 2nd WCSB, venue to be located in Brisbane. After that, in a wonderfully uncoordinated fashion, a next chairman always simply showed up (at time literally out of blue, thin air) intent on furthering this development. It must be kept in mind that it was not until 2017 that the International Pierre Gy Sampling Association (IPGSA) was inaugurated, at WCSB8 (Perth). Until then, some chairmen came close to "mortgaging their houses" to get a guarantee for financial backing and sometimes only backed by rather *ad hoc* organisational and scientific committees. Our community can indeed count itself lucky that chairmen and committee members all rose to the occasion with flying colours more and more now joining forces with relevant scientific, organisational or commercial entities AusIMM, SAIMM, GECAMIN). Indeed, most conferences were able to pass forward a small, but important economic surplus to its successors. The subsequent historical development of the WCSC series is described in Reference 1.

…and **that** is how it all came to be….

References

1. "History of WCSB" https://intsamp.org/wp-content/uploads/2019/03/History_of_WCSB_KHE_WCSB6_proceedings.pdf



Vol. 74, issue 1, 28 November 2004 ISSN 0169-7439

ELSEVIER

CHEMOMETRICS AND INTELLIGENT LABORATORY SYSTEMS

Special Issue: 50 years of Pierre Gy's Theory of Sampling
Proceedings: First World Conference on Sampling and Blending (WCSB1)
Tutorials on Sampling: Theory and Practice
Guest Editors: K.H. Esbensen & P. Minkkinen

Also available on SCIENCE DIRECT
www.sciencedirect.com

Figure 6. The emerging community of professional samplers owe a great debt of gratitude to Elsevier Publishers for taking on the first ever proceedings from an unknown, at that time rather obscure, motley crowd meeting in an even more obscure small city in the remote Kingdom of Denmark! However, these proceedings are today priceless evidence of the beginning of a new entity in the history of organised science. If you don't already have it, you can get your own copy at: https://www.sciencedirect.com/journal/chemometrics-and-intelligent-laboratory-systems/vol/74/issue/1

2. International Pierre Gy Sampling Association (IPGSA) https://intsamp.org/
3. K.H. Esbensen, P. Minkkinen (Eds), "Special issue: 50 years of Pierre GY's Theory of Sampling & Proceedings of the First World Conference on Sampling and Blending (WCSB1)", *Chemometr. Intell. Lab. Syst.* **74(1),** 1–236 (2004). https://www.sciencedirect.com/journal/chemometrics-and-intelligent-laboratory-systems/vol/74/issue/1

Appendix: IPGSA archives

Please view this historical note as an *invitation* to submit whatever historical documentation is in your possession to the IPGSA homepages. We are in the enviable situation that we already have built up a complete historical record of how the organised work surrounding the Theory of Sampling came to be.[1] Now it is time to do the same regarding the WCSB *historical institution*. It is the intention to establish a historical archive, which can only succeed because of contributions from **you**. A vast volume of photographs exists a.o. from the entire WCSB series out there, but most of it resides in your personal archives only – and what's the wider effect of that? The IPGSA Council has appointed KHE as historical curator. *Any-and-all relevant entries* from 2000 on are of the greatest common interest.

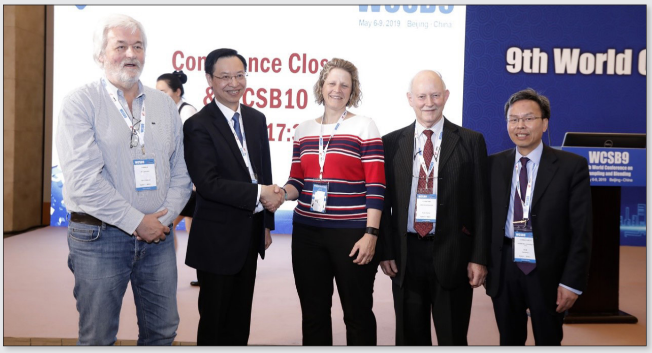
Please submit material to: khe.consult@gmail.com

[Curatorial note: please include copious text descriptions of venues, persons-in-view, anecdotes etc. History need not at all be *dull* …]

---

continued from page 6

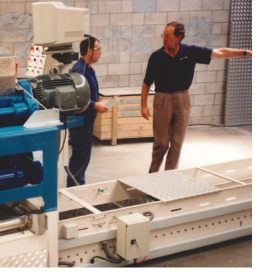
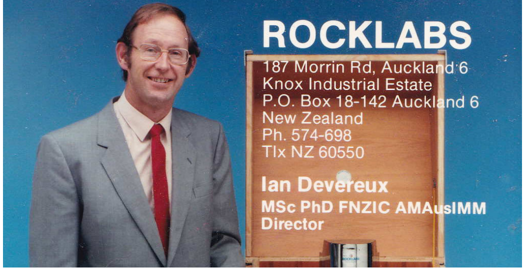
The forum focusing on "Differences between China and other countries in sampling and blending".



Hand over from WCSB9 conference chairman Dr Han Long to WCSB10 Conference Chairperson Mrs Elke Thisted. At opposite ends, the chairmen of two scientific committees (right: Dr Li, WCSB9, left: Dr Kim H. Esbensen, WCSB10)—presided over by IPGSA President Dr Ralph Holmes.

communications platform for all interested in the theory and practice of representative sampling and blending. We hope this publication will help more and more Chinese academicians, technicians and managers to understand sampling theory and to appreciate representative sampling procedures and equipment from all over the world. Equally, we hope that international readers can draw lessons from the development in sampling approaches and technology in China.

Ian Devereux
1940–2020





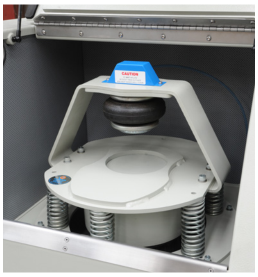













doi: 10.1255/tosf.117

Tributes to Ian Devereux, 1940–2020

“So sad to hear of Ian Devereux’s passing. He made an exceptional contribution to sampling and sample preparation in the mineral industry and will be sadly missed. I have fond memories of discussions with Ian at the various sampling conference that I have organised, many of which Ian sponsored.”

“I remember well the early development days of the Boyd and looked forward to the visits from Ian and Ross as we solved many of the world’s problems over some fine wines. The world and our industry has lost a great man.”

“I arrived in the sampling community only as late as the year 2000, but did have occasion to meet Ian, and with his family at home, a number of times in the period 2005–2008 + a series of WCSB conferences. Always a happy man, professionally as well as regards outlook to life, Ian was quite a soul mate, also to me. He showed me around at Rocklabs and his pride in its achievements were a joy to share with him.”

“Ian was one of the true gentlemen of business with a huge personality. Ian was an inspiration to me and a mentor not only with respect to Rocklabs and sample preparation but also in business. Very fond memories for which I thank Ian and his family. He will be missed.”

“Ian was a top man with contagious vision and passion who achieved a significant legacy! We will miss you Ian!”

“I was so fortunate to have been able to call Ian a friend. I’ve met few people who had the natural curiosity, intelligence, drive and practical smarts and pure inventive talent that Ian was gifted with. All of that plus one of the most soft spoken, caring and gentlemanly men I’ve ever met. So many firsts. He revolutionised sample preparation practices and equipment, and set the standard that so many other companies tried to emulate. Finally, as if he had not done enough for the industry he loved he set out to revolutionise and create lab CRMs that were excellent of quality, but cheap in price so that they could be used at an insertion rate far higher than ever practical before.

I got to see him one last time in Auckland in 2018 with the Scott team and although he was frail and slower of speech his passion for the Geochem lab industry and the team and company that he built shone through. I will miss the talks and friendly arguments we had over how and what type of CRMs to use, prep equipment, procedures and philosophy. He touched and mentored so many, a true legacy second to none. RIP my friend, I’m sure the sample prep lab in heaven needs some mechanical tweaks and a strong pair of hands!”

“I learned from him several things that I have used in my life and work, I heard a lot of histories from him that taught me how to see the life in other way and enjoy his parsimony. I hope to have the chance to talk again with him over there where you are now waiting for all of us... and I will tell him, how I did it.”

“The entire family and staff send their sincere condolences on the passing of this great legacy of a man who has been such an inspirational, knowledgeable revolutionist. He created an amazing legacy that provided employment and added value to so many people across the globe! May he rest in peace.”

“Ian was a remarkable, genius and unforgettable man. He achieved so much in his lifetime. We believe he is dancing in heaven! It was a pleasure and honour to know him.”

“Our sincere condolences from your cousins in the ‘South’. My mother shared very fond memories of Ian with me and how when she stayed on the farm at ‘Moa Flat’, Ian and the sisters would always greet her with warmth. She always admired how the family would ‘Play together, sing together and learn together’. She said Ian was the ‘perfect brother’ and the family was very fortunate to have him. Our love is with you at this time.”

“I grieve for a friend and teacher. I worked with Ian for many years and always admired his extraordinary knowledge, attitude and sense of humour. My family is very grateful for the participation that Ian took in our lives. We grieve and remember his unique smile.”

“Ian was an amazing Man so bright and intelligent, but above that, such a sensitive, caring and sharing Person. Never one to indulge himself with worldly trappings he quietly supported so many individuals and organisations.

From our perspective we will always remember how, when our son was diagnosed with Leukemia, Ian came into the hospital and shared that he just didn’t know what he could do so he went and gave blood. We had many trips and adventures with Rosy and Ian on overseas travels and NZ bike rides. There is still a very vivid vision of him riding his Travel Scoot through the aisles of Selfridges Jewellery department right alongside million dollar watches in display counters, and also riding it into the rear compartment of a London Taxi.

And then there were of course those ice-creams, and the international sausage roll survey. So long Friend and Mate. Go well, have another ice-cream or two and don’t forget the sausage roll survey.

You will be so missed by the family and friends you have left behind.”

“It is with great sadness that I write these few words to acknowledge the warmth and friendship I have had the pleasure to enjoy for many years. Ian was like a father to me and I was proud to represent Rocklabs in Australia during this time. He was always full of enthusiasm and new ideas which he shared with the audiences at conferences and seminars. He was never shy to take on a new challenge. Our first dishwasher (F&P) was earned as a result of this. Above all he was a proud Kiwi with an admiration for all that was good in the world. He was a great man that will be missed by many. Goodbye my friend. Travel in peace.”

doi: 10.1255/tosf.118

Ian Devereux and the story of Rocklabs

Rocklabs has a rich and unique history. Originally established as a commercial laboratory specialising in geochemical analysis and fire assaying, Rocklabs became a world leader in the manufacture and supply of sample preparation equipment. Now part of the global automation and robotics company Scott, Rocklabs began as an Auckland-based operation, but the story of what led founder Ian Devereux to build such a game changing company starts at the bottom of the South Island of New Zealand. In 1956 Devereux, who was born and raised in Central Otago, finished high school and decided to study a science degree at the University of Otago the following year.

“When I came to Otago University I didn't know what I wanted to do but I had a general interest in science and took a science degree with a lot of different subjects. I thought I might end up in the agricultural world. I studied chemistry, physics, maths, geology and botany thinking somewhere among those would be a career. I liked chemistry and geology and did a masters in chemistry. With an interest in geology, for my master's degree, I did a thesis in the geology department.”

“I heard a lecture given by a scientist from the DSIR about the work going on at a place called the institute of Nuclear Sciences, a geochemistry research laboratory in Lower Hutt. I went to work there in 1961 and in 1964 went to Auckland. Mind you, this was all to do with a woman who wanted me to come to Auckland! I couldn't get a job at the time, but by then I had a PhD from Victoria University. While I was working for the DSIR I studied for the PhD and the institute worked very closely with the university, so I was fortunate to be a full time student at the university while I was a full time scientist at the DSIR.”

“In Auckland there were tough times as people wouldn't hire me because with the PhD they said I was overqualified. I met up with Dr Jim Sprott who was a forensic and industrial chemist. In 1969 we formed Rocklabs, specialising in geochemical analysis and fire assaying. Jim Sprott was involved in lots of things, most famously the Arthur Allan Thomas trials after the Crewe murders. In those trials he provided evidence about the planting of a cartridge while I gave evidence about the wire that was used to tie the bodies. That was an interesting part of my career.”

“Apart from the drama of the forensic analysis, work in the laboratory involved analysing rocks and solids which had been crushed and pulverised using various sorts of preparation equipment. Geologists used to arrive with batches of up to 500 samples. I saw a future in establishing a laboratory which would cater just for this mineral exploration and so Rocklabs began. The samples were mainly for copper as gold was at a very low price. To get the raw material ready for analysis crushing and pulverising machines were needed, but there were long delays in getting them from Germany. It was decided to make them locally, at first just for Rocklabs use, but later to sell to others.”

Ian Devereux heard of a one-man band engineering company called Gilco Products Ltd, run by Ian Gillies and showed him some equipment which had been imported by Auckland University. “Ian Gillies decided he could make a version of the pulverising machine, which was a new type, and a crushing machine for our laboratory. People came to the Rocklabs laboratory and asked for a pulveriser of the same type and Ian Gillies would make them.” Between 1970 and 1975, Rocklabs ran the laboratory but also began to sell more equipment. Equipment was sold to visitors from places like Australia and Canada, so the company began exporting instead of just selling in New Zealand. All this was unplanned, originally done as favours to customers, but just six years later, under the success of the exports it had had since 1970, Rocklabs began making sample preparation equipment on a commercial basis.

Laboratory work was not growing, but there seemed to be a future in the equipment side of the business. There was not a market in New Zealand where there was virtually no mining, but Ian Devereux was confident that having sold some equipment without even trying then some real marketing work would bring success. His task was to convince the bank manager that there was a future in exporting. Faced with proof of the orders from overseas and that Rocklabs was the first company to be a specialist in this type of equipment, the bank approved a $5000 loan and a $5000 overdraft. Ian Gillies agreed to make the equipment and Ian Devereux undertook the selling. Three machines were made in the first batch. The plan was to sell ten machines in a year which would keep the business afloat, while the maximum might be twenty if the year went well.

In 1975 Rocklabs was going well, with orders approaching the maximum of 20 machines. The business was succeeding, in part because their competition was too slow. If a customer's machine broke down they wanted another one immediately, not in a year's time, as was standard with Rocklabs competitors, so Rocklabs kept a few machines in stock, always ready to send. The machine being made by Rocklabs prepared a sample for analysis but did no actual analysis. Sample preparation usually involved three steps. A sample was first dried in an oven at 100 °C then crushed using a rock crusher. Then a portion was pulverised into a powder and a sample of that was taken for the analysis.

The crushing was done with a normal jaw crusher made by Ian Gillies, a machine that has two jaws with a fixed and moving plate. However, in the early 1990s engineer Philip Boyd invented a new type of crusher and this was licensed to Rocklabs. Rocklabs called the crusher a Boyd crusher and it became the preferred crusher worldwide and the number one machine in Rocklabs catalogue.

“The pulverising machine was called a ring mill and consisted of a steel pot with concentric rings inside and a lid. The crushed rock was put in the pot with the rings and the lid was put on. This was called a head which went on a machine that had a sort of hula hoop motion with an out of balance weight and this hula hooping motion set up all the rings inside which pulverised the rock. It was very fast and very noisy but would pulverise very uniformly and very finely. This machine, which was very new in our early days has taken over almost every lab in the world for pulverising. Rocklabs still sells a ring mill but it's much different to what it looked like in the past. It used to stand on the floor, now it is in a soundproof cabinet with either mechanical or pneumatic clamps. We've broadened the range and now we sell mills, crushers and splitters. Then we developed those products into mechanised processes and automated

Ian Devereux with the pulverising machine.

processes. When we started one of those mills in a box was $500—now we've had orders up to $US3 million from one lab to automate a sample preparation procedure in a big gold mine. So our company has grown vertically and horizontally.”

Rocklabs tried to keep things simpler than their competitors because the equipment was going into remote areas like 5000 m up the Andes in South America. Instead of robots, Rocklabs made mechanical devices like small conveyor belts with a small bin containing a sample. A container would be packed with the components and then the system would be installed once the container reached the customer. The container could be taken into very rough country and orders were delivered to Russia, Canada, the United States, Chile and many other countries. Distance has not been a problem for Rocklabs, but initially it made customers wary, as Ian Devereux recalls:

“Customers felt we were a long way away and they did not see New Zealand as a mining country. The distance was much more important to the customer when they thought of things breaking down, so we had to have a really good service. We'd get an order in the morning and within 24 hours it was on a plane. We built up a reputation around the world, people would say, ‘Gosh, you can get stuff to our mine faster than we could get it from the hardware shop down the road’. When we started off most of our competitors came from Germany and a few in the United States, but the latter just seemed to fade away. They weren't developing new products and the mining industry was decreasing in the United States because of environmental issues. The lack of interest by the Germans was mainly from companies who made a whole range of products at that time. If you were starting up a mine you would go to one of these places and they could design you a whole mine, mainly coal mines, but they could do anything. So, you would buy diggers and processing equipment and ball mills right down to a laboratory. From their perspective, the lab equipment was very small and didn't cost much and no one was really interested in it. They would wait until they got ten or twenty orders and then they'd make a batch. The customer might wait a year and that was one of the reasons I thought we'd succeed because we were very small, specialised, flexible and energetic. We'd be on a plane and off to see someone right away and so we were in an ideal position to take over a lot of this business. It didn't take too long to do a job because we had machines in stock, we made that decision early on so we had it there when it was needed and spare parts stock as well in case something broke down and someone needed it in a hurry.”

After a successful 30 plus years growing Rocklabs, Ian Devereux had begun thinking about retirement and wanted to sell the business to ensure Rocklabs would continue to grow and be successful on the global stage. He was looking to sell to a New Zealand company when he came across a newspaper article stating that Scott were looking to acquire companies. The background was suitable—engineering, automation and exporting. Nor was Scott Technology too big. Rocklabs had about 40 staff and Scott Technology about 160. The sale was soon accomplished:

“I decided after visiting lots of companies overseas to ring up Scott Technology and offer them the business. Chris Hopkins will remember the day because he was about to go out to lunch and Mary Aberhart at reception said, ‘There's someone on the phone from Auckland who's got a business for sale. Could he please speak to someone?’ He said, ‘Oh, ok, I'll speak to him before I go to lunch’, thinking it might have been some kind of lunatic. I gave him a quick rundown of the company and told him I'd decided to sell because I was getting stressed and didn't have any family members interested in the business. The business was growing rapidly and needed a different type of owner. I'd built the business up from sales of $10,000 in the first year to $20 million in my last year and wanted the very successful company to stay in New Zealand. Chris said, ‘When can I see you? I'll be up in a couple of days to see.’ I decided to sell to Scott Technology in 2008 and I stayed on for a couple of years as manager until I retired finally at Christmas 2011, roughly 40 years since I started.”

Since its founding in 1969, Rocklabs has seen significant technological advancements and has had to adapt, growing and changing to meet their clients' needs in the timely and customised nature that their reputation is built upon. Rocklabs products have evolved from simple bench top equipment to complex end-to-end automated systems. The game changing Boyd double acting jaw crusher is featured in many of these advanced automated systems, however, an ongoing commitment remains for the supply and support of stand-alone sample preparation equipment to commercial labs, academic institutes and mining operators alike.

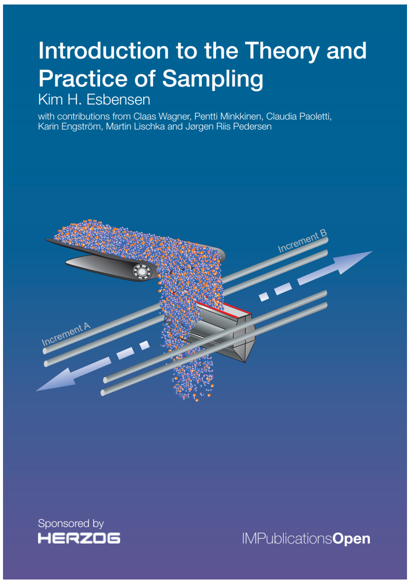
With such a successful 50 years under their belt, the future for Rocklabs looks bright. Rocklabs will continue to bring new and innovative disruptive technologies into the future with ongoing advances in safety, productivity and quality, as the world leaders in sample preparation.

In 2017 an excellent retelling of Ian Devereux's journey was published. *To Cut a Long Story Short* by Karen Jarvis is a vivid account of an inventor who followed his passion and believed in himself. From bullied farm boy to PhD scholar, to family man and founder of the highly successful, internationally acclaimed company, Rocklabs, Ian Devereux has lived a full and fascinating life.

Devereux gives a gripping account of his work as a forensic scientist on the Arthur Allan Thomas case. Anecdotes from business trips to politically unstable countries, including near death experiences, will engross readers. His unorthodox approach and willingness to take huge financial risks gave rise to a niche marketing business model that was revered by economists of the day.

Shining through this biography is Devereux's generous and trusting nature, formidable intellect and contagious sense of humour. Karen Jarvis's lively narrative will keep the reader engrossed to the end.

To order *To Cut a Long Story Short*, e-mail maria@lifestories.co.nz.



Introduction to the Theory and Practice of Sampling

by K.H. Esbensen

IMP Open, Chichester, UK (2020)

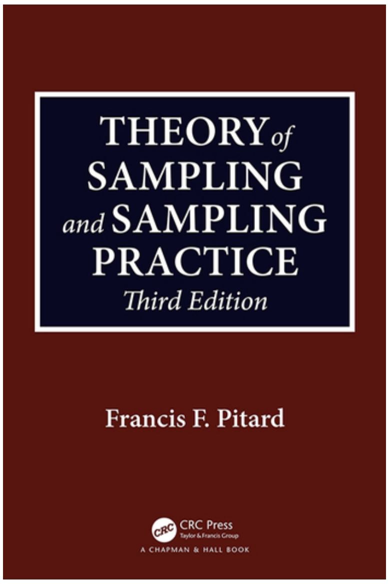
ISBN: 978-1-906715-29-8

DOI: 10.1255/978-1-906715-29-8

Price: £69.00

https://store.impopen.com/introduction-to-the-theory-and-practice-of-sampling.html

---



Theory of Sampling and Sampling Practice, 3rd Edn

by F.F. Pitard

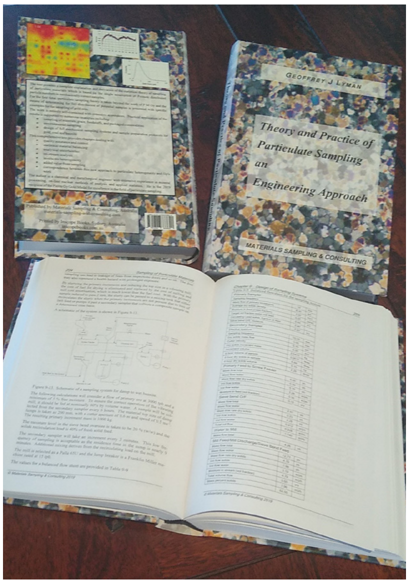
CRC Press, Taylor & Francis Group (2019)

ISBN: 978-1-138-47648-6

DOI: 10.1201/9781351105934

Price: U$260.00

https://www.amazon.com/Theory-Sampling-Practice-Third/dp/113847648X



Theory and Practice of Particulate Sampling: an Engineering Approach

by Geoffrey J. Lyman

Materials Sampling & Consulting (2019)

ISBN: 978-164633382-0

Price: AUD 405.00

https://materials-sampling-and-consulting.com/Textbook

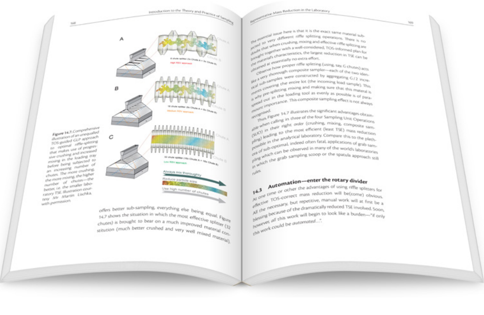
doi: 10.1255/tosf.119

Introduction to the Theory and Practice of Sampling

Kim H. Esbensen, kheconsult.com

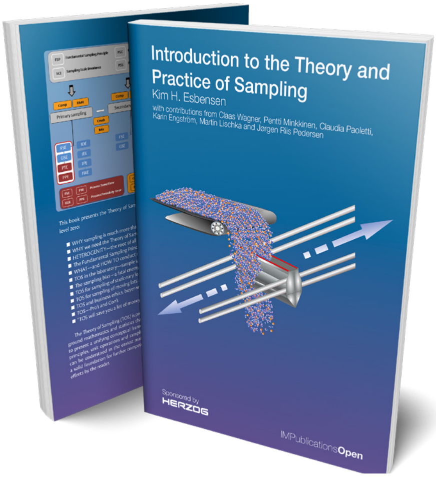
"Sampling is not gambling". Analytical results forming the basis for decision making in science, technology, industry and society must be relevant, valid and reliable. However, analytical results cannot be detached from the specific conditions under which they originated. Sampling comes to the fore as a critical success factor before analysis, which should only be made on documented representative samples. There is a very long and complex pathway from heterogeneous materials in "lots" such as satchels, bags, drums, vessels, truck loads, railroad cars, shiploads, stockpiles (in the kg–ton range) to the miniscule laboratory aliquot (in the g–µg range), which is what is actually analysed. Exactly how to acquire a documented, representative analytical result across mass-reduction of up to six orders of magnitude of heterogeneous materials is far from a simple materials handling issue. There are specific principles and rules behind representativity. The TOS to the fore!

This book presents the Theory and Practice of Sampling (TOS) starting from level zero in a novel didactic framework without excessive mathematics and statistics. It represents 20 years of teaching experience which has developed into a unique conceptual framework with which the TOS' six principles and four unit operations can be understood in a unifying manner, enabling the reader to start sampling in a correct fashion right away. The book covers sampling from stationary lots, from moving, dynamic lots (process sampling) and has a vital focus on sampling in the analytical laboratory. It contains a wealth of complementing cases, examples and references (most of which are accessible on-line) meant to inspire and motivate the reader to individual skills-building and further self-study. The book has been assessed and reviewed extensively, see below.



The book will teach you:

- WHY sampling is much more than materials handling
- WHY we need the Theory of Sampling (TOS)
- HETEROGENEITY—the root of all evil
- The Fundamental Sampling Principle—which must never be broken
- WHAT—and HOW TO conduct representative sampling
- The TOS in the laboratory—sample splitting without errors
- The sampling bias—a fatal enemy that can be avoided
- The TOS for sampling of stationary lots and materials
- The TOS for sampling of moving lots and materials—process sampling
- The TOS and business ethics, buyer–seller relationships, vendors' obligations, societal needs
- The TOS—Pro's and Con's
- "The TOS will save you a lot of money"



K.H. Esbensen, *Introduction to the Theory and Practice of Sampling*. IMP Open, Chichester, UK (2020). ISBN: 978-1-906715-29-8. https://store.impopen.com/introduction-to-the-theory-and-practice-of-sampling.html

Personal consultation

Buyers of the book can choose to add a personal virtual consultation with the author for just £69 at the time of purchase. Find out more about this unique opportunity at http://bit.ly/tosconsult.

"...the TOS is presented in an easy, comprehensible style that is accessible to everyone..."

"I recommend this book to all newcomers to TOS, but especially also to those who want to go beyond the TOS basics and further explore its numerous literature sidebars and background references. For in depth coverage of the quantitative nature of sampling theory and practice, this is the place to start."

"For a reader like me, a newcomer to the field, this new book gives the reader a well-crafted overview of how to get your sampling right from the start—and what it will cost you if you don't."

"From the start, the author delivers a book written in a somewhat unorthodox fashion that makes it very easy to read, complete with many detailed examples and case histories. This book may well end up being the standard introduction sourcebook for representative sampling."

"...it demonstrates the often large quantitative influences on the final uncertainty of the tiny analytical samples that ultimately are delivered to the laboratory."

"One of the book's major advantages is the lavish use of carefully designed didactic diagrams which help the reader to form his/her own understanding of what turns out not to be so "complex" subject-matter as many claim."

"...one of the book's strongpoints is that is shows the common nature of proper sampling."

"...this book should be compulsory in educating not only geology students at universities, but also scientists and technicians in a number of other disciplines, not least analytical chemistry (there is a whole world outside the four walls of the laboratory). All will benefit fundamentally from addressing this book."

doi: 10.1255/tosf.120

Theory of Sampling and Sampling Practice, Third Edition

Francis F. Pitard

Using this third edition, teach yourself everything there is to know about the Theory of Sampling and become an expert.

The first edition of this book (1988) was devised as an adequate but simplified condensation of Dr Pierre M. Gy's work, suitable as a two-volume manual for the teaching of a short-course. The first edition was a success and well-received by engineers around the world.

The second edition (1993) stayed consistent with this spirit; however, collaboration with practicing mathematicians, statisticians and research scientists helped me to prepare a much better, more complete version. It was an overwhelming success and became a classic around the world for more than 25 years. Here is the credo of the second edition:

> “There are no such things as reliable feasibility studies, unbiased ore grade control, accurate environment assessments, effective process control, if you cannot identify and minimize the eight major sources of sampling variability and know them by name.”

The third edition could have been highly technical, treating Sampling and Statistical Process Control, but it would have missed its primary objective, which is to successfully explain why each of us, in the mining industry and other industries, at any given place of a process, is a customer of, and/or a supplier to, somebody else. Therefore, it is imperative for this third edition both to provide high-level theoretical background, but also pragmatic solutions to the many problems samplers are facing every day. Because of the author's background, the reader may complain about an over emphasis on the mining industry. However, TOS is universal and applies to many other industries as well, such as the food industry, the chemical industry, the oil and gas industry, the pharmaceutical industry and many more.

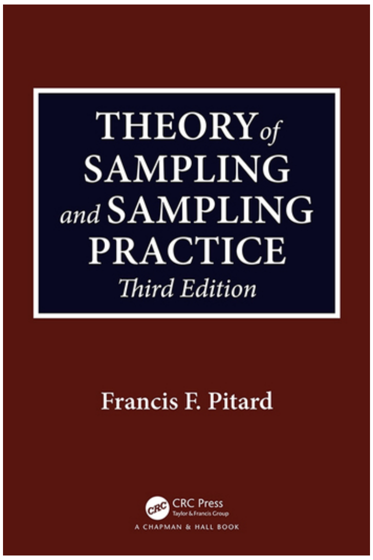
The third edition of this textbook could have been a highly philosophical guideline about the many subtleties of Total Quality Management, but it would again have missed its primary objective, which is to successfully explain why each of us, in all these industries, at any given place of a process, is the mean by which objectives are met on target, within specifications and within acceptable cost.

Therefore, what is special about the third edition of this book has been to find an equilibrium between how far someone must go through the theoretical and technical aspects of a given task to better understand, predict, control and improve conditions leading at the end of the day to a successful job. The theoretical aspect of our problems is an essential means for penetration and greater insight. The technical aspect of our problems is a necessary implementing process. The pragmatic aspect of our problems is a necessary product of our creativity, and we are paid to be pragmatic without giving up too much on theoretical and technical necessities; this is how one becomes a successful professional. If we learn how to do this, we may never lose the scope of our story: every time we leave work, we shall feel happy and proud of making the job of somebody else easier, better and more effective.

This third edition of the textbook is also different because a special effort has been made to present sampling and laboratory problems in their inescapable, economic context. The main reason for the Theory of Sampling (TOS) having been much neglected in the past is due to the failure to place it in its economical context. As a result, many important executives around the world saw the TOS as an academic achievement with no obvious practical value. To correct this unfortunate situation, this third edition is now a proper blend from several important worlds:

1) The Management Approach by W. Edwards Deming
2) The Sampling Theory of Dr. Pierre M. Gy
3) The undeniable touch from geostatistics with variography leading to chronostatistics
4) The extraordinary competence of a famous analytical chemist and sampling expert, C.O. Ingamells
5) The works of J. Visman
6) The modern philosophies of Statistical Process Control and Six Sigma

Blending these different worlds, especially the works of C.O. Ingamells and J. Visman who definitely deserve a special place in TOS, was a daring endeavour on my part. I hope the result will make sense to many of my clients.[a] This edition of the book should help set priorities to optimise operations, eliminate costly and incorrect practices accumulated through the years by tradition, mistaken beliefs, shortcomings from naïve common sense and wrongdoings from practitioners and manufacturers with conflicts of interest.



F.F. Pitard, *Theory of Sampling and Sampling Practice*, 3rd Edn. CRC Press, Taylor & Francis Group (2019). ISBN 978-1-138-47648-6, Price: U$260.00. https://www.amazon.com/Theory-Sampling-Practice-Third/dp/113847648X

The third edition of the book is, therefore, the basic, essential tool to make sure that due diligence in many modern applications is friendly enough when applied.

---

[a] The importance of the contribution of C.O. Ingamell's and J. Visman's seminal works makes it a mandatory addition to the TOS. These two historic contributors, and also admirers of Gy's work, unfortunately passed away before the WCSB forum was created. This is the deep reason behind chapters 14, 15 and 16 in the third edition of this book. Let's be very clear: the TOS would incomplete without this valuable addition.

doi: 10.1255/tosf.121

Theory and Practice of Particulate Sampling: an Engineering Approach

Geoffrey J. Lyman BEng, MEng, PhD
Materials Sampling & Consulting Pty Ltd. materials-sampling-and-consulting.com

A full development of particulate sampling theory on a sound mathematical basis that goes beyond the work of Gy and others
This is a text for people who are serious about sampling system design and quality control of these systems

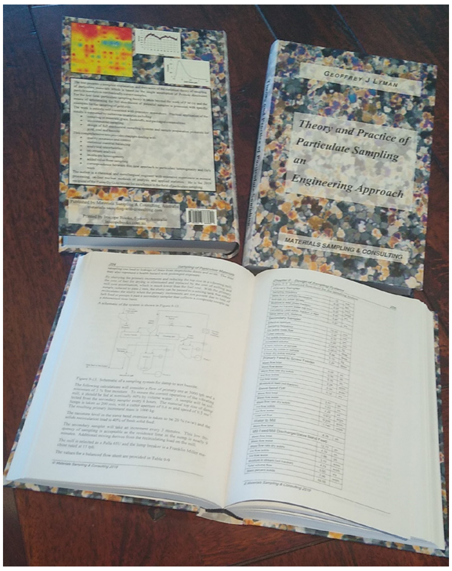
The Theory of Sampling (TOS) as put forward by Pierre Gy forms a foundation for the sampling of particulate materials and has been in use now for many years, especially in the mineral industries. It is only recently that interest and appreciation of sampling theory has found its way into some corners of the mineral industry, such as industrial minerals, other industries and the power of the theory has been recognised and harnessed.

One aspect of the statistical theory of sampling that has been lacking is the ability to calculate the entire sampling distribution. The result of a sampling procedure or protocol is a numerical result. This is a statistical quantity because it is subject to uncertainty; statisticians call this a random variable. To know everything about a statistical quantity, it is necessary to know its distribution, which is quantified by its probability density function or distribution function. Until the author’s developments, statistical sampling theory provided only the variance or “spread” of the distribution of the sampling uncertainty. When dealing with sampling of low and trace level components of a mixture, such as precious metals, mycotoxins and valuable mineral contents of process streams such as tailings or waste streams, the distribution of the concentration of the target constituent is usually skewed (asymmetric). This is almost always the case with gold bearing materials, and there has been great difficulty in the correct and successful application of sampling theory to gold ores.

To overcome this restriction, the author has developed the whole of particulate sampling theory from the premise that the numbers of particles, or grains of mineral of any one type in a mixture, follow Poisson distributions. This assumption alone permits all of the mathematical results of sampling theory to be derived in a completely coherent manner. The resulting theory encompasses all previous correct presentations of sampling theory and takes the theory to the point where the entire sampling distribution can be calculated. This novel accomplishment is of particular value to the gold industry where the impact of coarse gold on sampling uncertainties can be profound and have serious economic impact.

With the publication of this text, statistical sampling theory for particulate materials has been brought to a full conclusion and end point. If a source for the teaching of statistical sampling theory is required, this text provides all that is required. So-called intrinsic or constitutional heterogeneity is completely dealt with. The text provides means of quantifying the heterogeneity of particulate material either through laboratory work or the use of the scanning electron microscope. The text also deals fully with sampling variance due to time- or tonnage-wise grade variation, which is known as distributional heterogeneity.

The text is fully self-contained. Even though there is a good deal of mathematical and statistical detail in the book, a comprehensive Appendix dealing with all aspects of statistics in the book is provided so that the reader can rapidly come up to speed with the material required to fully understand and utilise all material.



Go to materials-sampling-and-consulting.com to order the book and see the Table of Contents

The text includes a chapter dealing with the design of sampling systems for a gold run of mine ore, a raw coal sampling system and for a hard to handle damp bauxite ore. The engineering details of the system deigns are considered with quantitative calculations of sampling uncertainties and material flows. Practicing mineral process engineers will find these examples of particular value.

Apart from the uncertainties introduced by the particulate nature of minerals and other material when sampling, it is also vital to understand the uncertainties that stem from the variation of material grade with time or tonnage. The uncertainties involved in sampling in process settings such as in mineral processing plants are almost always dominated by the uncertainties due to these variations (distributional heterogeneity) and are analysed mathematically by the methods used by geostatisticians when dealing with spatial grade variations in ore bodies. The basis of such analyses is the theory of random functions and the principal tool used is the variogram or covariance function which characterises the time-wise or tonnage-wise variation in a process stream. Gy developed his work at a time that geostatistics as a discipline was just appearing. Gy’s inclusion of variogram methods was very much simplified as a result and with the further development of geostatistics and computing power, we can do much better today.

The text treats variograms in great detail and provides a variety of variogram models that can be fitted to data by both conventional methods and the improved method of maximum likelihood. A comprehensive

Appendix deals with variograms and includes methods of simulation of random functions which is vital for anyone wanting to build a total simulation of a sampling system.

A major chapter deals with the types of mechanically correct sampling equipment available for the plant and the preparation of samples down to the aliquot level. Methods of modern on-line analysis are also treated with the inclusion of methods of determination of the precision of such analysers with examples.

The text does not forget that sampling of processes leads to laboratory analysis of the samples with the concomitant issues of quality control which is dealt with in a separate chapter and shows how modern cumulative sum techniques can be used to improve upon the standard approach of statistical quality control with Shewhart charts. A chapter deals with analytical uncertainties in laboratories.

A chapter is also devoted to methods of statistical material balancing (metallurgical accounting) where the author has wide experience.

For the reader from outside the mineral processing field, a chapter deals with the sampling of foodstuffs, including the difficult sampling of grain for mycotoxins, the sampling of packaged material and environmental sampling for site contaminants. This material is not found elsewhere.

A number of other issues are dealt with in the text that will be helpful to the reader dealing with sampling systems on a routine basis. The topics of mixing and blending, bias testing and the method of maximum likelihood, which is perhaps the most powerful statistical analysis tool ever invented, are presented.

It seems that many people express an interest in sampling theory and its practical implementation and take courses on the subject either at conferences or through in-house training by a sampling authority. However, in the author's experience, few actually get to the point where they can take on a sampling problem in full. Part of the problem stems from the fact that statistics is a "nasty" subject and soon (gratefully) forgotten from university studies.

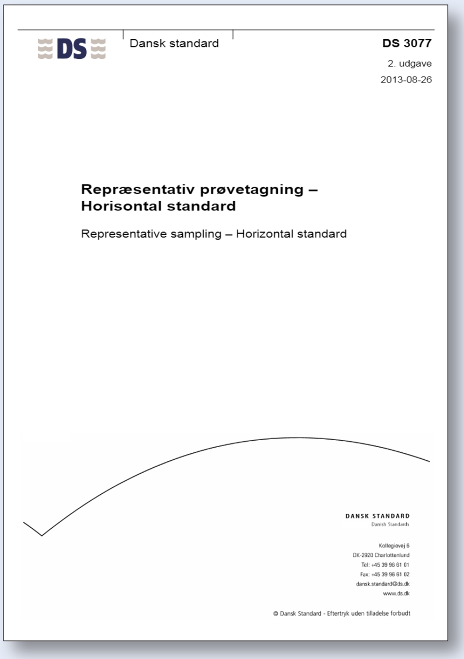
The author is a widely experienced chemical and mineral processing engineer who has had a research career solving problems through the application of mathematics and statistics. The title of the text suggests that the book will appeal to engineers; it was written with the intent that it could be used by engineers to create systems that achieved "representative" sampling and analysis. The word "representative" really means that the results from the sampling scheme are "fit for purpose". The result delivered is accurate (unbiased) and sufficiently precise that use of the result does not expose the user to unacceptable financial risk. The text will permit you to achieve this goal.

The text is available through the author's website. The website will also provide the opportunity to access software implementing methods of analysis described in the text. The MSC Toolbox consists of applications that permit rapid calculation of variograms from detrended data as well as fitting of a wide variety of variogram models to data. You will be accessing the tools that have been developed over nearly 40 years of expediting the solution of problems for clients.

The author has stepped away from the viewpoint on sampling theory first put forward by Pierre Gy and has derived and extended sampling theory by taking a rigorous approach using mathematical statistics. This results in a simplification of the notation and presentation of the theory. The new approach permits the extension of the theory to the point where the exact sampling distribution as well as all the moments of the sampling distribution, not just the variance, can be calculated. An appendix of background statistical information has been included to assist readers in understanding the mathematical procedures used throughout the text. The practical aspects of sampling are well covered with examples of the design of sampling systems for gold, bauxite and coal. The text also covers the sampling of foodstuffs such as bulk grains and packaged foods. Sampling in these circumstances involves random distribution of contaminants throughout a lot and requires special statistical models outside of current sampling theory to deal with this type of distributional heterogeneity. Certain cases of environmental sampling are also included. This text will be of use to engineers, food scientists and regulators in understanding sampling of particulate and packaged materials and can form a complete text for the teaching of sampling theory for commodities.

Contents

Preface
1 Introduction
2 Motivation for Accurate Sampling
3 Mechanically Correct Sampling
4 Intrinsic Heterogeneity
5 Distributional Heterogeneity
6 Gy's Simplified Formulation of Sampling Variance due to Intrinsic Heterogeneity
7 Analytical Uncertainties
8 The Total Sampling Distribution
9 Design of Sampling Systems
10 Quality Control and Assurance
11 Statistical Material Balances
12 Added Value from Sampling and QA/QC
13 On-Line Analysis
14 Sampling of Foodstuffs and the Environment
15 Mixing and Blending
16 Bias Testing and Standards
17 *In Situ* Heterogeneity and Sampling of Drill Core
18 Precision of Sampling Systems by Interleaved Sampling
Appendix 1 Notation
Appendix 2 Topics in Statistics
Appendix 3 CUSUM Theory and Tools
Appendix 4 Random Functions, Variograms and Covariance Functions
Appendix 5 Errors in Variables Regression
Appendix 6 Locally Weighted Regression
Appendix 7 Materials Handling Issues
Appendix 8 Maximum Likelihood Methods
Appendix 9 The MSC Toolbox Index



Dansk standard

DS 3077
2. udgave
2013-08-26

Repræsentativ prøvetagning –
Horisontal standard

Representative sampling – Horizontal standard

DANSK STANDARD
Danish Standards

Kollegievej 6
DK-2920 Charlottenlund
Tel: +45 39 96 61 01
Fax: +45 39 96 61 02
dansk.standard@ds.dk
www.ds.dk

Representative sampling—horizontal standard

Publication details:
https://webshop.ds.dk/en-gb/standard/ds-30772013-2
Number of pages: 44
Contains: Didactic stand-alone macro for variographic analysis (100 entries)
Published: 16 September 2013
Date of approval: 26 August 2013
Publication price: EURO 96.56

Scope

- DS 3077 is a matrix-independent standard outlining the principles of 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 and new sampling procedures with respect to representativity.
- DS 3077 specifies two quality assurance measures (Quality Objectives, QO) regarding:
  - 1) sampling of stationary lots, Relative Sampling Variability test (RSV).
  - 2) sampling of dynamic lots, Variographic Characterisation (VC).
- DS 3077 contains a stand-alone variographic software program (freeware).
- DS 3077 recommends maximum threshold levels for both quality measures (QO).
- DS 3077 is based on the Theory of Sampling (TOS), and contains a comprehensive initiation literature background, complemented with additional references (Bibliography).
- DS 3077 enforces professional self-control and full transparency by stipulating mandatory disclosure of quality assurance as produced by RSV or variographic characterisation.
- DS 3077 specifies documentation and reporting of sampling representativity and efficiency for each analyte for the specific class of materials targeted. Any deviation from this standard's QO shall be justified and reported.
- DS 3077 is fully described in a previous article in *TOS Forum* (https://doi.org/10.1255/tosf.7)

doi: 10.1255/tosf.122

TOS reflections: is there a third way? (to promote the Theory of Sampling)

Kim H. Esbensen
KHE Consulting, kheconsult.com

A standing discussion topic within the sampling community is: "*What is the best way to promote the TOS—not only as a theory, but also as a tool to help customers?*" The latter objective casts the question into a rather more direct format: "*How to sell TOS-compliant equipment, sampling system solutions, consulting and audit services to customers with only little or no familiarity with the need for proper sampling?*" These reflections address the two most dominant answers: i) the economic argument "*You'll lose a lot of money if you don't…*"; or ii) the technical argument: "*You need to understand these critical aspects of the TOS, or else …*". However, this is usually but a futile debate; obviously one should be able to wield a flexible tactics which best matches a specific marketing or application need with one, or both, of these approaches. But a recent event has tickled the imagination—is there possibly also a third way?

Introduction

Recently KHE Consulting was asked to contribute to a one-day professional meeting within the context of environmental soil sampling: "*Delighted to, no problem—but give me a day or two to find out the precise scope that will be most appropriate…*". However, this issue was thrown into a different context by the title of the contribution in the immediately preceding programme slot: "*Which technical uncertainties can a lawyer live with?*" That indeed got this author thinking…

Could there actually be a third way to promote interest in the TOS—a compelling third way?

Historical background

Traditionally, there are two schools-of-thought regarding how best to promote the TOS and its application:

The **economic argument**: presenting easy-to-understand, compelling examples and case histories focusing on the adverse economic consequences of not invoking proper TOS, of the type (rather in-your-face): "*This is how much money you lose by neglecting proper sampling in this particular situation*". This approach, it is claimed, will lead to a clearer understanding of *hidden causes* for loss of profit. After this argument has caught the attention of the stakeholder, the door is opened, it is hoped, to be allowed to present also the technical arguments—and the race is off.

Or, vice versa:

The **technical argument**: focus is here on making the stakeholder *understand* the concepts, principles, sampling errors etc. in the TOS. Specifically, this approach aims at bringing about a full understanding of the devastating effects of *sampling bias*, if not properly eliminated. This approach is designed to lead to recognition of *understandable causes* for loss of profit. It is, however, (with very good experience) the dominant opinion that this approach is (much) more difficult for the stakeholders in question, e.g. company and corporation CEOs and other top management, who, while experts in business, will not necessarily also be experts in this subtle aspect of the TOS.

Where- and whenever two or more sampling practitioners and sampling experts have met in person, there has been no end to this evergreen debate. Understandably, this interaction has been exponentially expanded with the start and development of the WCSB fora…. While there would not appear to be a *clear* winner, it is fair to state that the overwhelming opinion is that it is the economic argument that works best—"*It's the economy, stupid!*"

A personal aside: the present author has never been comfortable presenting the economic argument to members of top management in companies, corporations and/or organisations: "*You stand to lose a lot of money, if you don't listen to me about the TOS*". I cannot escape the feeling that this flies directly in the face of highly competent and experienced stakeholders. To put it bluntly, they do not like to be *told* about the business perspective of their work! To me this approach can easily appear a bit rude or lacking proper respect… But I may be wrong.

So, while there is only one way to sample—the TOS way—is there a third type of argument?

Figure 1. "There is only one way to sample—the TOS way!". Messieurs Pitard, Esbensen and Francois-Bongarcon at the 1st International Conference on Mineral Sampling, Lima, 2018.

The third way

The **third approach**. Focus is here not on the potential economic loss, nor on the more complex issues surrounding sampling errors and sampling bias, the third way takes its point of departure on interactions in which sampling plays the *crucial* role—i.e. trade agreements aiming at fairness and benefits for all parties, method transparency etc. This approach will require us to stray a bit outside the strictly scientific, technical and economic issues; in fact we shall call in the *lawyers*, with the legal point of view as concerns contractual obligations.

A compelling case for the TOS in trade and commerce

Case example: *raw materials or commodity trading; transport, e.g. via ship, train or truck; strong contractual emphasis on each party's right to independent control (loading, transport, off-loading, sampling, analysis). The material specifics in this example are not important—trade interaction is the focal issue, and sampling is the crucial success factor involved.*

According to international trade traditions, contractual agreements and codes, disputes between buyer and seller are to be pre-empted by duplication (or triplication) of primary samples, of which one is analysed by the buyer, the other by the seller and a third sample is often archived to be used if disputes can only be resolved in a court of law. Sometimes, a third technical party is called for, which then analyses the archival sample or (although much less frequently) is asked to perform a completely new primary sampling + analysis.

Usually, however, only the two analytical results from the buyer and seller are available and compared. These should ideally fall *within* a commonly agreed upon uncertainty interval, which is specified in the contract; the simple average value is then often used for the pertinent business purposes.

The interesting case is, of course, when analytical differences *exceed* this acceptance interval, in which case trade codes most often mandate that the archival sample is forwarded to, and analysed by, a third *independent party*, whose analytical result is sometimes used directly *by fiat*. But if this is not acceptable to one or both parties, the dispute goes to arbitration in a court of law. The court will then, in most cases, dictate to use the average between the two *nearest* of the three analytical values, upon which to conduct the salient business transaction. This arbitration approach appears eminently logical and is easy to follow—and is never questioned further, likely because there is always a guaranteed *resolution* that appears intuitively fair to both parties.

However, there is a hidden elephant in the room—a very big elephant!

There are very rarely sufficient stipulations in the relevant contractual framework on **how** primary samples are to be extracted! Most often there is only a stony silence on this topic. When pointed out, the response most likely is: "Well, this is obviously a *technical issue* that will be taken care of by the relevant experts—this is not a legal matter". The crucial issue is that it is not recognised that the sampling method plays any role—the subsequent analysis is all that matters. This focus is overwhelmingly on the magnitude and the quality of the final analytical results' Total Analytical Error (TAE), which is the basis for establishing the acceptance interval in the first place. The Total Sampling Error (TSE), which unfortunately *dominates* the total uncertainty budget,[1–4] simply does not exist within the traditional legal framework from which trade contract traditions originate. The distinction between TAE and TSE is acknowledged, for example, in *metrology*,[5] but constitutes a fundamental lacuna within the legal area.

It is thus acceptable that the seller and the buyer perform sampling independently, typically the seller samples at the production site, or at the port of loading of a ship's cargo, while the buyer samples the same cargo but at the receiving port upon arrival. This is because every pair, or every triplicate set, of primary samples is tacitly *assumed* to be identically fully *representative* of the cargo in question; otherwise the above arbitration rules will fall apart and be invalid.

Thus, the crucial issue is that the dominating sampling error effects are *invisible* in the gamut of contractual stipulations—where it is all about the numerical values of the analytical results and about the *quality* of the analytical determinations involved, the TAE. The focus is only on TAE, instead of TSE + TAE.

Sampling procedures for which the TOS demands elimination of all bias-generating errors (Incorrect Sampling Errors, ISE)[1–4] are not heeded, which unavoidably leads to *biased sampling*. This leaves everybody without control of the magnitude of the influence from the material heterogeneity. This will unavoidably lead to a significant *inflation* of the practical sampling variability, the more so with increasing lot heterogeneity [larger vertical bars (black) in Figure 2]. Biased sampling, whether recognised or not, is the prime reason behind inaccurate (non-representative) sampling, with the unavoidable consequence that the analytical results (even when under impeccable analytical control, i.e. with a minimum TAE) will also be non-representative—and by an unknown factor.[1–4] And it gets worse—there is no way non-representative samples, and ditto analytical results, can be corrected! (See References 1–4 and further references within.)

When the critical primary sampling procedures are but a free-for-all, optional, unregulated matter, i.e. when one, or both, parties in an analytical dispute are not in compliance with the prerequisites for representative sampling, the empirical sampling variability is highly likely to be much larger

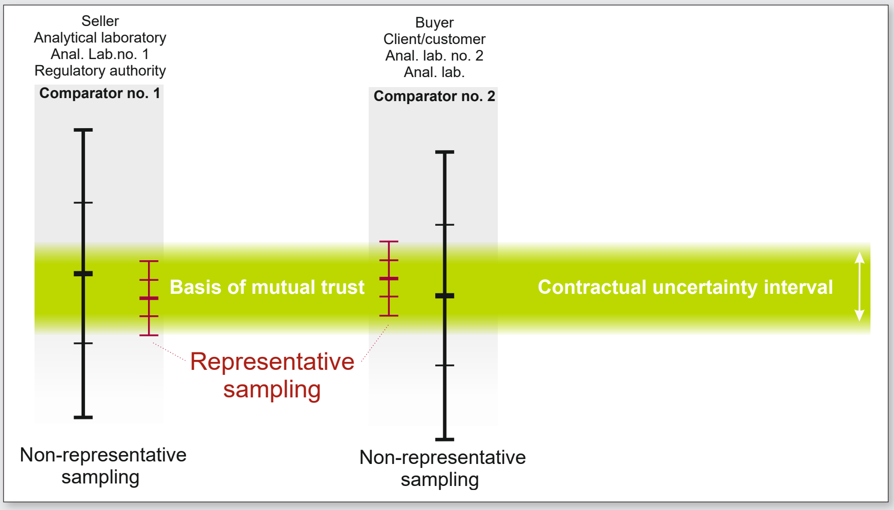


Figure 2. The consequences of non-representative sampling are identical for buyer and seller—an inflated sampling variability (black, denoted "non-representative sampling") making it very difficult to be able to satisfy the contractual uncertainty interval (green). Vertical bars show simplified distribution characteristics of repeated [sampling + analysis], a central average result with ±2 standard deviation variability. Resolution of an analytical comparison impasse is only possible when all parties agree only to use representative sampling procedures (red, denoted as "Representative sampling", see also text below and Chapter 20 in Reference 1. Reproduced from Reference 1; ©2020 IM Publications Open.

than the commonly agreed upon contractual uncertainty interval, Figure 2. This translates directly into a high probability that the analytical results from both parties cannot be resolved within the traditional legal framework, but will have to go to arbitration. This is the *status quo* for very many current international trade agreements, codes and contracts. The degree to which this scheme results in the need for arbitration is directly proportional to the inherent heterogeneity of the material involved, and to the degree of procedural deviation from the principles in the TOS that guarantee representative sampling. Lots and materials with low heterogeneity will only rarely experience a need for arbitration, but if/as heterogeneity goes up, so will the number of cases in which efforts to resolve different analytical results are structurally impossible.

The key feature here is that it is the degree of heterogeneity of the lot or material, as sampled by a specific procedure in use (representative or not), that is the *real determinant* w.r.t. the magnitude of the difference between analytical results—and most emphatically not the aptitude of the analytical laboratories involved as is invariably implied when TAE alone is the basis in the trade contract.

This is unfortunately all the more disingenuous since very nearly always analytical errors are very well under control (minimum TAE)—indeed these are often practically negligibly small compared to the dominant total sampling error effects (TSE). This all means that within this traditional context there will never be a bona fide *common basis* upon which to evaluate the magnitude and the significance of the difference between any two or three analytical results, no matter what resolution effort. As long as there is no agreement or contractual stipulation that legally *demands* representative sampling, there will never be an objective basis nor a rational treatment of “analytical disputes”. There will never be a rational understanding of the reason behind the, completely unnecessary, inflated sampling variability, Figure 2.

TOS is a missing element in the legal contract arena. It is imperative that legal competence includes a full understanding of the distinction between TAE and [TSE+TAE].

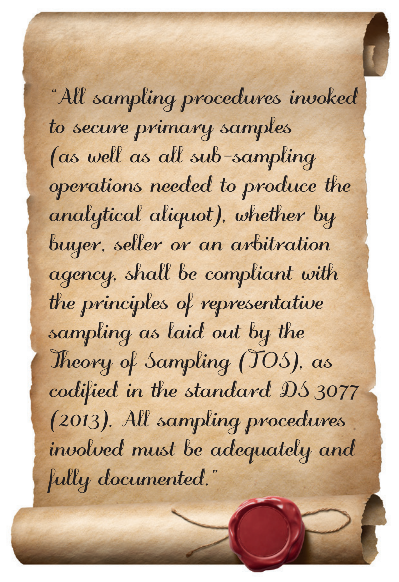
Only representative procedures are able to deliver the effective minimum sampling-and-analysis [TSE+TAE] uncertainty that is the only relevant basis for the contractual uncertainty interval. Things get really out of control if/when buyer and seller, and/or an arbitration agency, can freely choose their own sampling procedure.

The mind boggles when it is realised that a single paragraph is able to rectify the fatal quagmire outlined above, a paragraph that needs to be included in all contracts forthwith for cases that demonstrably involves sampling *before* analysis…

The credo of contractually stipulated representative sampling

Imagine a world in which the following credo was universally accepted, and willingly complied with (Figure 3):

> “All sampling procedures involved to secure primary samples (as well as all sampling operations needed to produce the analytical aliquot), whether by buyer, seller or an arbitration agency, shall be compliant with the principles of representative sampling as laid out by the Theory of Sampling (TOS) as codified in the standard *DS 3077* (2013). All sampling procedures shall be adequately and fully documented.”



“All sampling procedures invoked
to secure primary samples
(as well as all sub-sampling
operations needed to produce the
analytical aliquot), whether by
buyer, seller or an arbitration
agency, shall be compliant with
the principles of representative
sampling as laid out by the
Theory of Sampling (TOS), as
codified in the standard DS 3077
(2013). All sampling procedures
involved must be adequately and
fully documented.”

Figure 3. The sampling credo SCROLL. Reproduced from Reference 1, © 2020 IM Publications Open, scroll image: Shutterstock/Andrey_Kuzmin.

In the words of Louis Armstrong: “What a wonderful world it would be”.

First and last: the economy vs TOS competence

So, which is the best way to promote TOS: economic, technical or legal?

It stands to immediate reason that the current situation shown in Figure 2 will result in significant losses of profitability due to exacerbated dangers of making decisions relying on *hidden, unnecessarily* inflated sampling + analysis uncertainty, see, for example, Chapters 20–25 in Reference 1. This point of view *combines* the technical and the economic arguments.

Because of the need for universal acceptance of the sampling credo, there is here a compelling reason to make sure that sufficient TOS competence is available for all parties involved, either in-house (already existing or by training), or via external sampling expert consulting. It is, therefore, *necessary* that a minimum of TOS competence be inducted not only in technical departments but at legal, administrative and executive levels as well.

Thus, there are indeed three avenues to application of TOS, each arguable on their own merit: for technical reasons, for economic reasons **and** for legal reasons.

References

1. K.H. Esbensen, *Introduction to the Theory and Practice of Sampling*. IM Publications Open (2020). https://doi.org/10.1255/978-1-906715-29-8
2. F.F. Pitard, *Theory of Sampling and Sampling Practice*, 3rd Edn. CRC Press, Taylor & Francis Group (2019). https://doi.org/10.1201/9781351105934
3. G.J. Lyman, *Theory and Practice of Particulate Sampling: An Engineering Approach*. Materials Sampling & Consulting (2020).
4. *DS3077, Representative sampling—Horizontal Standard*. Danish Standards (2013). http://www.ds.dk
5. K. Heydorn and K. Esbensen, “Sampling and metrology”, *Accredit. Qual. Assur.* **9(7),** 391–396 (2004). https://doi.org/10.1007/s00769-004-0808-z

doi: 10.1255/tosf.123

The legacy of Charles Oliver Ingamells (1916–1994)

Francis F. Pitard

Charles Oliver Ingamells passed away in April 1994 at age 77. Ingamells received his BA at the University of Western Ontario and his MS at the University of Minnesota. During his later years in his retirement home in Florida he was a faithful representative of a group of well-known world experts in Sampling Theory, such as Pierre M. Gy, Francis F. Pitard, Jan Visman, Paul Switzer at Stanford University and J.C. Engels at the US Geological Survey and the Linus Pauling Institute in Menlo Park, California. His association with Francis F. Pitard during several years at Amax Extractive Research & Development in Colorado has added to a unique combination of different experiences in the field of geochemical analysis. His pioneering work in the field of geological sampling led to collaboration with the above experts.

Charles Oliver Ingamells, CIE, BASc, MS, MM, ILI, RPCV

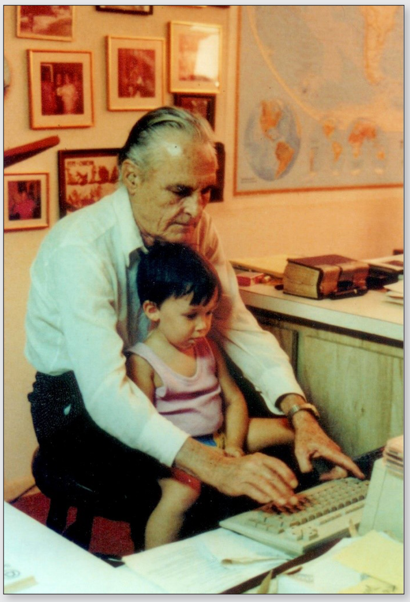
Passing away much too young from brain cancer, Oliver Ingamells was one of the most brilliant intellectuals I ever met. He would have loved the concept of the WCSB and would have been, with no possible doubt, an amazing addition to the TOS community. As early as 1967, he was an admirer of Dr Pierre M. Gy's work.

During his life, Oliver was never short of straight-to-the-point remarks when he would reach a point where patience was running short. As his daughter, Margaret I. Resnick said it so well, "My father was an Einstein; and it is a shame that he was not more recognised. His genteel, selfless and aggressive desire to learn what's out there made him a valuable asset to the scientists who want to further mankind's sense of awareness." For many personal reasons, I fully agree with these words. But, as a man of great vision, he had no patience for people who are prisoners of short-sighted paradigms. Another point I fully agree with Margaret Resnick is when she said: "My father was scientifically superior but diplomatically inferior!" It was easy to feel the accuracy of that statement when working every day with Oliver.

The legacy of Ingamells for TOS

Ingamells's knowledge on sampling[1–8] has its roots with J. Visman, who he personally knew very well. It would be futile to compare Ingamells's work with Gy's achievements. Rather, it is important to emphasise the work that may be beneficial and provide relevant, harmonious additions in some areas of TOS, and indeed there are many possibilities. Such additions may enhance our capabilities to predict sampling difficulties by using a stronger strategy and to design better sampling experiments that would allow us to further understand the heterogeneity of minor and trace constituents.

Amounts of minor and trace constituents are the key issues in many industries where their accurate determination is of paramount importance. The Theory of Sampling would be incomplete without an understanding of what we can do when *Poisson processes* are almost inevitable, or when people are unaware of such possibilities, or when people are in denial that they are indeed a possible event. There are numerous examples, such as quantifying trace amounts of constituents in pharmaceutical products, in high purity materials, in the environment, in genetically modified organisms, in precious metals exploration etc. This is where the work of Ingamells is priceless; his entire work is based on Visman's work and Poisson statistics. It is of paramount importance to make the emphasis very clear: *without a good understanding of Poisson processes there is no possible in-depth understanding of the TOS* because too many subtleties become elusive, and this has escaped the attention of most sampling practitioners around the world and it needs to be corrected.



Oliver Ingamells showing the subtleties of a 1993 PC world to his grandson Sender.

The logical evolution of Ingamells's ways of thinking

The best way to follow the evolution of Ingamell's ways of thinking for sampling issues is to read the first chapter of *Applied Geochemical Analysis*, a textbook written by Ingamells and Pitard in 1986.[9] This article presents an overview of some of the most important of Ingamells' work, which can be summarised as follows:

"If you wish to sample the ocean for its salt content, several cups of seawater taken in several of the world's seas would probably yield a useful distribution of *assay values* and a useful average value. But, if you wish to sample the ocean for its herring content, a million cups would very likely yield a false distribution of assay values and thus an erroneous average. No one would blame the person who counts the number of herrings in the nets for potentially poor estimate of the herring content of the ocean; yet geologists have sometimes been led into the habit of collecting minuscule samples of *mountains* (literally) containing large chunks (nuggets) of ore sparsely distributed analytes and attributing anomalous assay values to deficiencies in the analytical techniques."

All his life, Oliver Ingamells was concerned on how a 1-g analytical subsample can fairly represent "an entire mountain" (this caricature is intended quite deliberately). In his own words:

"Traditionally, the geochemical analyst receives a *small* sample in a bag or bottle, further removes, again, a small portion hereof (sometimes as little as a few milligrams), and compares this with a small portion of another material of *known* composition, using an instrument of some sort, such as a burette, a set of weights and a balance, a spectrometer, a colorimeter etc. He then uses a measured ratio to obtain one or more numbers, which he reports. The submitter of the original sample uses the data so obtained to make important geological, geochemical decisions or other judgements.

For this process to be successful, several essential requirements **must** be met:

1) The sample submitted to the analyst must have the same composition, within acceptable limits, as the material from which it was taken.
2) The small analytical subsample must have the same composition, within acceptable limits, as the submitted sample.
3) The material used as a *reference* (the balance weights, the salt to prepare a standard solution etc.) must be *known* with acceptable certainty.
4) Small analytical subsamples of the *known* must have the same composition, within acceptable limits, as the bulk reference material. This requirement is important when analysed *standards* are used to calibrate an instrumental method (e.g., X-ray fluorescence spectrometry).
5) The process of comparison and ratioing is essentially unaffected by differences in composition between *known* and *unknown*.
6) Interfering factors are insignificant or under adequate control.
7) The measurement precision is adequate.
8) The sampling weight baseline is preserved throughout.

In each analytical exercise, these essential requirements assume different degrees of consequence, but they should all be kept in mind. Failure to meet any one of them will lead to the generation of poor or meaningless data."

A summary of C.O. Ingamells and F.F. Pitard: *Applied Geochemical Analysis* (1986)

This unique textbook about primary analytical methods used to prepare geostandards starts with a long chapter on *sampling* presenting Ingamells' views on sampling issues.

Ingamells' perception of Gy's Sampling Theory

Oliver had a hard time with the concept of the Liberation Factor. I recall the many times we discussed that subject. To him, the size of particles of the constituent of interest was the only relevant factor, and it did not make any difference if the constituent of interest was liberated or not. What was missing in his ways of thinking is the fact that no matter what, the sample must represent all size fractions, gangue (side rock) and constituent of interest, since it is very likely the grade of the constituent of interest would change between coarse and fine size fractions. Ultimately, he fully agreed with that concept.

Elaboration of Ingamells' and Switzer's constant K

The constant K is a way to measure the sample ability of a well-mixed granular material defined as the weight w necessary to achieve a 1 % uncertainty.

A summary of Visman's Sampling Theory

This part is an introduction to the concept of the Fundamental Sampling Error (FSE), or its Visman equivalent, and to small scale segregation.

Relationships among the Sampling Theories

Ingamells makes an attempt to show similarities between Gy's and Visman's theories, a concept I vastly expand in my Doctoral Thesis and in the third edition of the textbook *Theory of Sampling and Sampling Practice* published in 2019.

Comments on Geostatistics

Ingamells emphasises the fact that the geostatistician must assume that irrelevant variance due to subsampling and analytical errors are low. If not, calculations are likely to show a false nugget effect that generate incorrect assessments.

The laboratory sample

Emphasis is also made that a stringent guideline must be provided to the laboratory to prevent unfortunate difficulties during the subsampling process when starting with the field sample that may weigh 5–10 kg and end up with a representative 0.5-g analytical subsample.

Calibration standards

Rapid instrumental methods require calibration; calibration is most satisfactory if a few of the actual samples analysed by primary methods are used to develop working calibration curves.

Samples and subsamples

A warning is stated about the economic consequences of introducing unacceptable subsampling errors at the laboratory.

Weight proportions and volume proportions

In a mixture of two minerals, or an ore mineral and a gangue, the weight proportions of the two components are the same as their volume proportions *only* if the densities of all minerals in the mixture are the same. Most often, analytical or assay values are reported in terms of weight proportions (e.g., percent, part per million, ounces per ton and so on). Sampling characteristics of the mixture are, however, more dependent on volume proportions: it is, therefore, necessary to relate these two ways of measuring concentrations.

Size and number of particles in a mixture

Introduction is made of a uniform hypothetical mineral mixture making a simulation of a real mixture of the same minerals.

Contribution of a single grain

This section is an introduction to create a Poisson model that would be accurate enough to give early warning to the fact that sometimes the subsample mass that has been selected is totally inappropriate. Approximations made in this model are good enough to make such an assessment of paramount importance.

Histograms

Histograms should be constructed using a rational interval. Use of a completely arbitrary interval may lead to a false impression of a distribution.

Standard deviation and estimated standard deviation

The standard deviation is an index used to measure the dispersion of a number of measurements about their arithmetic mean. In dealing with analytical or assay values, there are almost always too few of them to permit an exact measure of their dispersion, and only an estimate can be made. The standard deviation, σ, is a theoretical quantity; the estimated standard deviation, s, is an experimental approximation of σ. Nevertheless, the estimate s is often referred to as *the* standard deviation, without mention of the fact that it is an estimate only with all its inherent limitations.

Gaussian, or Normal, distribution

At one time in history, scientists became convinced that the Gaussian distribution was universally applicable, and an overwhelming majority of applications of statistical theory are based on this distribution. In this context, a common error has been to reject *outliers* that cannot be made to fit the Gaussian model or some modification hereof, e.g. the popular log-normal model. Failure to recognise that the real distribution of the grade *may not* be Gaussian is one of the biggest mistakes made in sampling practice.

Poisson statistics

A sample is too often only a miniature amount of material and within such small scale an observed feature, such as why this particle is there rather than here, or why is it bigger than the other one, is a property of statistical independence; and yes, in practice this assumption of independence is satisfied only approximately. The Poisson model is only the simplest and most random possible model to describe a phenomenon where the collected sample is obviously one or several orders of magnitude *too small* to contain a sufficient, statistically significant number of particles of the constituent of interest, the analyte. If the drill-core sample shown in the Figure 2 weighs, say, 10,000 g, and contains only a limited number of gold particles that cannot comminute, we may well wonder what will happen for the analytical subsample weighing only, say, 30 g?

Relative deviation

The subtle distinction between the terms *relative deviation* and *coefficient of variation* is addressed; the former is a theoretical quantity while the latter is an estimate obtained by empirical investigation, an experiment.

Homogeneity

An effort is made to demonstrate that completely homogeneous materials are so rare that they may be considered non-existent.

Reduction of samples to laboratory subsamples

Given an original sample of weight W that must be reduced to weight w, to find the subsample weight demanded by an analytical method for determining the constituent of interest X with a certain reliability, one may follow a number of procedures. Such procedures must be rationally designed.

Gy's sampling slide rule

At one time Ingamells was very proud to show Pierre Gy that he was using his slide rule to optimise subsampling protocols. Then, Pierre Gy's remark was "I use it myself to draw lines!"

Determination of Visman constants A and B

Ingamells describes the logic behind Visman's *Homogeneity Constant* A and the *Segregation Constant* B.

Determination of gangue (side rock) concentration *L*

The low background content L that is easy to sample can be a parameter of great interest. It is a variable of its own in a mineral deposit, or in a high purity product, or in the environment. Such variability should be the object of more research as it can have significant geometallurgical and economic implications. For example, if a deposit is difficult to sample for its gold content, it would be critically important to find out *what proportion* of the gold is difficult to sample.

Sampling diagrams

Ingamells' sampling diagrams are very different from Pierre Gy's nomographs which we are accustomed to. They are more complex and contain far more information. Figure 3 illustrates the concepts of Low Background Content L (i.e., portion of the constituent of interest easy to sample) and the Most Probable Result (i.e., the *mode* of a Poisson process) as a function of sample mass shown by the dashed line.

Figure 4 illustrates the evolution of the standard deviation of the Fundamental Sampling Error (Visman's homogeneity concept).

Sampling diagrams for segregated mixtures

With segregated mixtures (i.e., mixtures in which all particles are *not* randomly distributed), it is necessary to estimate not only a *homogeneity constant*, A, but also a *segregation constant*, B. It must be understood that B is a constant only at certain sampling stage, since segregation is a transient phenomenon that can change rapidly. Nevertheless, we need to have an idea

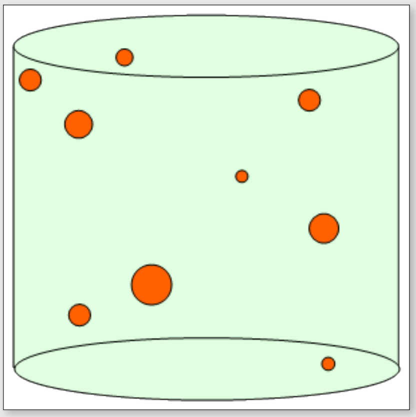


Figure 2. Illustration of a possible Poisson process for gold assaying.

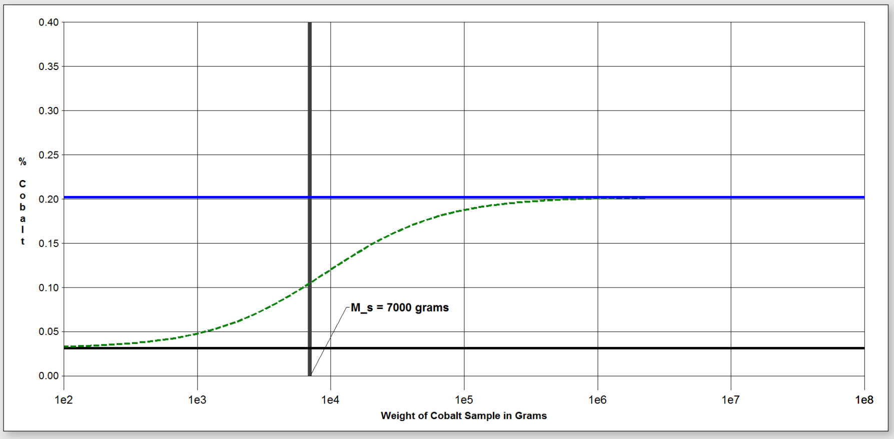


Figure 3. True content (Blue line), Low background content (horizontal black line), and most probable assay value (green dashed line) as a function of sample mass.

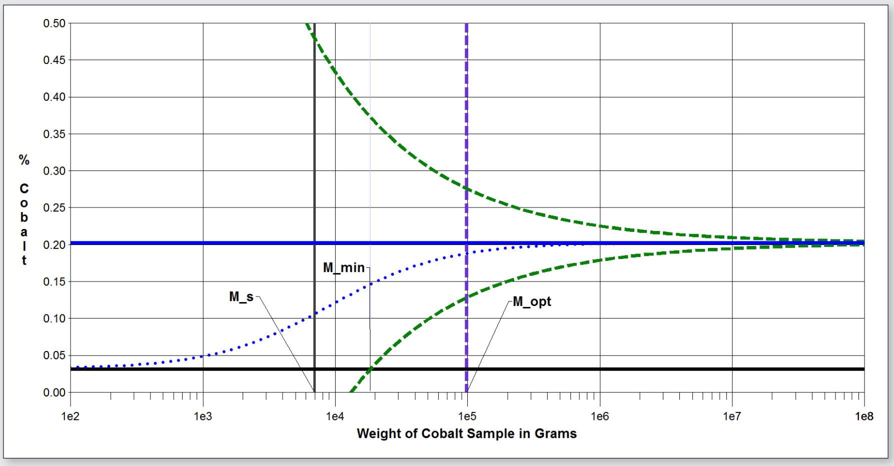


Figure 4. Adding the standard deviation of the Fundamental Sampling Error as a function of sample mass (green dashed line).

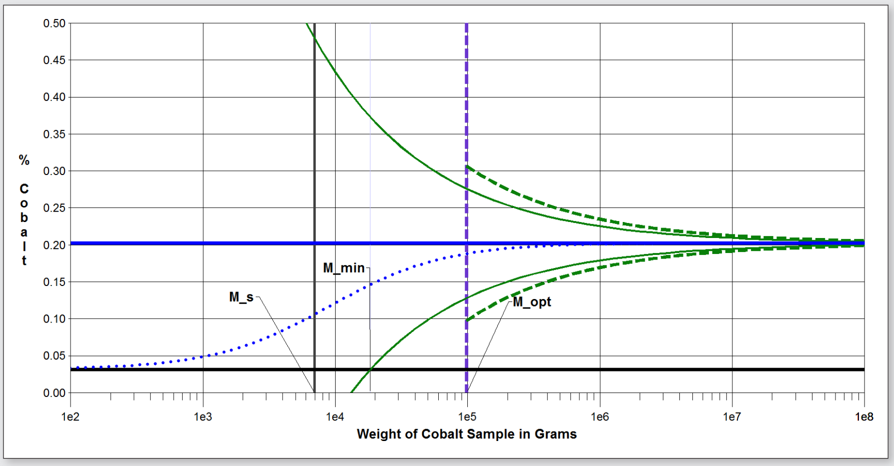


Figure 5. Adding the concept of optimum sample weight = A/B.

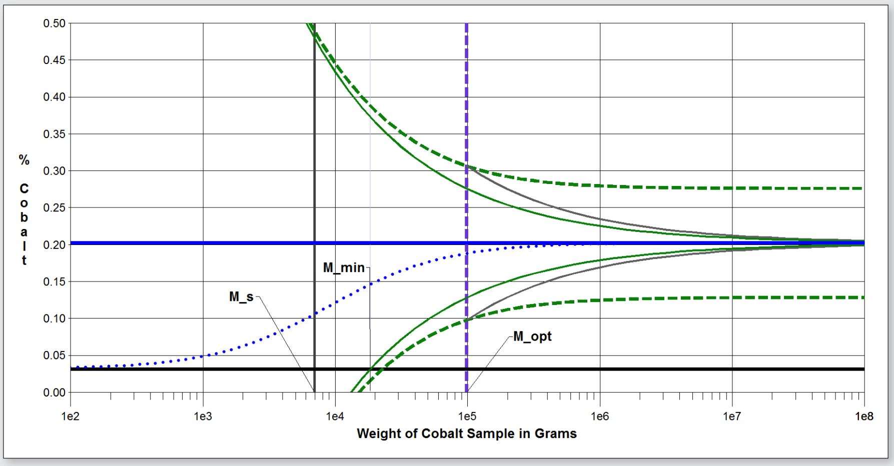


Figure 6. Illustration of the complete sampling diagram.

about its order of magnitude and its likely occurrence. Figure 5 illustrates the additional curve (dashed green line) showing the combination of FSE and the contribution of possible segregation *if* a sample were of an optimum sample weight defined as the ratio of Visman's sampling constants A and B (i.e., A/B). By following the convergence of that line toward the true content one may easily calculate how many samples of optimum weight should be collected over the field of observation to reach a certain preselected overall precision.

Construction of sampling and subsampling diagrams

Ingamells shows that to construct a valid sampling diagram, it is desirable to calculate the Visman sampling Constants A and B by the method of repetitive determination using two series of samples of different individual weight or by another avenue.

Figure 6 illustrates (dashed green line) what would be the overall uncertainty if only one sample was collected over the lot. You may notice that regardless of sample mass, the error due to segregation cannot be minimised as it, to a large extent, is a non-random variable.

Usefulness of sampling and subsampling diagrams

Once a sampling diagram has been prepared, one can tell at a glance how large a sample or subsample should be to achieve the desired sampling precision. For segregated materials, the total weight of a sample does not establish sampling precision; the number of samples taken is equally important. All samples may be assayed, or only considered as increments to prepare a representative large composite sample.

Planning a sampling campaign for exploration

Procedures for sampling and analysis of unknown masses of material such as ore bodies, shipments, mountains, rock piles, slag dumps and so on, should of course be designed to minimise costs, using available sampling theory to avoid misdirected effort and applying analytical techniques in the most efficient manner. Any evaluation of the unknown mass must take place in several iterative stages or steps:

1) Design a pattern for sample collection
2) Sample collection
3) Reduce samples to analytical subsamples
4) Assay for the elements of interest

5) Analyse and interpret data
6) Loop back to 1
7) Continue until information is as adequate as cost permits.

This chain of steps is no stronger than its weakest link.

Effect of variable sample or subsample weight: weighted average

Ingamells warns that it often happens that available data are derived from samples or subsamples that are not all of the same weight. Such data make the estimation of sampling constants difficult, especially when there is appreciable segregation.

Minimising exploration costs

Any system of data evaluation assumes *a priori* that the data points are sufficiently accurate to warrant evaluation. It is assumed that the assay value developed from a field sample reflects to a reasonable degree the composition of the ore surrounding the place from which the field sample was taken. It is also assumed that the assay value is, within acceptable limits, representative of the composition of the field sample itself. Ingamells shows that for these assumptions to be true, the field sample must be:

1) Large enough to represent the surrounding ore, and
2) Reduced to an analytical subsample in such a way that the 1-g, or so, weighed out for assaying has the same composition as the whole field sample.

There must be a cost-effective balance between field sample mass and the number of field samples collected to minimise risk and reach the point of diminishing returns.

Evaluation of preliminary data

Ingamells raises a red flag when the standard deviation of preliminary data is *larger* than the mean. This may occur for one or two or more reasons:

1) The ore body may be badly segregated on a large scale, then geostatistics takes over.
2) The field sample may be too small. Or
3) Errors in reduction or assaying may have been committed.

It is of paramount importance to be able to make a difference between three cases.

Manipulation of skewed data

Exploration data are often highly skewed. It is important to discover the underlying causes of skewness in any particular case. If it is due to segregation on a large scale, field samples should be *small* and *numerous*, and Matheron's geostatistics should be employed in data evaluation that are often log-normally distributed. If on the other hand, the skewness is due to coarse-grained ore, or randomly distributed pockets of ore, larger field samples should be taken because a Poisson process has taken place, and the use of geostatistics is counter-indicated, at least until the Poisson process has been reasonably minimised. Ingamells suggests an interesting data manipulation to eliminate the skewness if it is proven that the field sample mass was indeed too small.

Data from segregated ore bodies

Ingamells invites caution in applying his suggested manipulation if the variance due to large scale segregation is misinterpreted.

Double Poisson distribution

When samples taken from a geological formation of interest (Ingamells' proverbial "mountain"), or other accumulations of material that contain the constituent of interest in discrete grains, are subsampled in such a way that the subsamples also contain discrete grains of reduced size, a double Poisson distribution of the assay values is likely. This is a worse-case scenario during sampling in connection with exploration, grade control, environmental assessments, high purity materials and pharmaceutical products and their trace constituents content assessments. The general analysis of such cases by Ingamells is profound and extremely useful.

Fitting statistical models

Ingamells emphasises that in data sets derived from ore bodies and in trace elements data, the Gaussian approximation is seldom valid; its uninformed application is likely to lead to erroneous conclusions.

Purposes of sampling

Ingamells shows that sampling may have other purposes than the determination of the gross composition of materials. In geochronology, for example, whole-rock rubidium-strontium or potassium-argon ages depend more on the character of the portions taken for analysis than they do on the sample being chemically representative of the whole-rock mass. On the other hand, age determination on specific minerals depends more on the rejection of altered material and on clean mineral separation from geological masses and rocks, than they do on gross sampling procedure.

Field sampling methods

Geologists and mining engineers are often unaware of the difference between a rapid and a primary analysis and must be informed when they ask for one but need the other.

Sampling for potassium-argon dating

Ingamells did considerable work of great importance for K-Ar dating of low-potassium minerals when these minerals are cogenetic with high-potassium minerals that have suffered diffusional or other loss of either potassium or of radiogenic argon.

Mixing and blending

Most of the attempts towards a complete sampling theory as outlined by many authors is based on the *assumption* that during reduction the material being sampled is *well mixed*. That is **all** mineral grains are randomly distributed among themselves. However, it is not easy, in practice, to maintain thorough mixing throughout the reduction process. Ingamells stresses that various widely employed mixing devices should be regarded with *suspicion*; some of them actually segregate minerals of different particle shape and density, and the V-blender is a good example of such a problem.

Contamination

It is **impossible** to collect, reduce, grind, screen and mix rock or mineral samples without introducing some (significant, but typically low level) contamination from the equipment and the environment. The best that can be done is to make sure that critical contaminants are excluded. Which contaminants can be tolerated and which cannot depends on the purpose at hand. Ingamells provides a list of common problems.

Preparation of the laboratory sample for analysis

When a mass of material has been efficiently sampled, mineral separations have been completed, unavoidable contamination have been measured and the analyst has received a small vial containing the results of all these efforts, he or she must decide on the preliminary steps to be taken prior to analysis for the constituents of interest.

The first step should usually be a microscopic examination. This will often give much useful information in a very short time. Under a binocular microscope, the presence of a relatively few grains of a minor mineral rich in the constituent of interest will effectively warn of subsampling difficulties. A judgement of the need for further grinding, screening or purification can be made.

Basically, the amount of information and extremely pertinent questions is massive, even today on the eve of WCSB10.

The unique contribution of Ingamells about Poisson processes in sampling

To this day, nobody has analysed Poisson processes in sampling as far in depth as Ingamells and this valuable work is on display in the list of references provided in this tribute. This is the reason why the author included Part V, Chapters 14–16, in the third edition of his sampling book *Theory of Sampling and Sampling Practice*—to make sure this valuable knowledge does not get lost. The lengthy summary of major issues above is a call for action!

Outliers—which are not outliers

A common error clearly pointed out by Ingamells concerns the ease and willingness to reject data points as *outliers* if they cannot be made to fit the universal Gaussian model. This inclination, used by some geostatisticians, is tantamount to *make the data fit a preconceived model instead of searching for a model that fits the data*.

Table 1 shows a case where an entire NQ-diameter core sample was assayed for gold to extinction, in other words until no material was left. What should be food for thought to the reader is the undeniable fact that the few bolded assays shown in red **are not outliers, but they illustrate a Poisson process where all values are real values and none of them should be** tampered **with!** This example illustrates where Ingamells was a maestro.

Today, it is now apparent that *outliers* are often the *most important data points* in a given data set, and a good understanding of Poisson processes is not only a convenient tool to use, but a mandatory one! Is this a universal understanding in 2020, however? Sadly **not**, there is still much work to do.

Other scientific breakthroughs from C.O. Ingamells

The classic rock or mineral analysis

This subject matter is where C.O. Ingamells also was a historic master. The term *classical analysis* has become something of a misnomer. In Ingamells' work it is used to signify not the way things were done in ancient times, but the hard core of well-tried methods of maximum accuracy. Those who talk of the *superiority* of new methods are missing the point. Whenever a primary method is developed and is proven more accurate than the old, it is incorporated in the *classical* scheme. Thus, by definition, the classical analysis is more accurate than any other. The fact is that the classical procedures often require more skill and more knowledge and ability than those that involve little more than putting the sample in a machine and reading a signal.

A common error is to confuse accuracy, which cannot be objectively measured, with precision, which can. There are numerous examples of highly precise methods from which systematic error can be eliminated only by means too tedious to warrant the effort. Those who promote such methods on the basis of their precision alone anarchise the art and science of geochemical analysis.

Besides drawing the distinction between *precision* and *accuracy*, it is necessary to observe the differences between *analysis* and *determinations*. Analysis is the opposite of synthesis; it is the separation, partial or complete, of a material into its constituents. How these constituents are determined, after their separation, is an entirely different matter.

Many instrumental methods reduce the amount to analyse almost to zero prior to determination of one or another constituent; probably this is a cause of the common failure to distinguish the two concepts.

The classical analysis, skillfully performed, provides high accuracy, but without consideration of time and cost. Instrumentation is used to the extent that it can provide greater accuracy. There is no dependence on samples analysed by someone else. The work of paramount importance of Ingamells in this domain is well documented in *Applied Geochemical Analysis*.[9] Unfortunately, this knowledge is slowly getting lost today in the name of efficiency and cost effectiveness.

Table 1. Replicate 30-g fire assays from a single 1-m NQ core sample. Results expressed as g t^{-1} gold. Red values are not outliers, but they illustrate a Poisson process where all values are real values. What is shown here is but an example of extreme material heterogeneity.

0.524	1.722	0.436	0.664	0.611	0.546	0.490	**53.826**
0.574	0.528	0.557	0.557	0.527	0.529	0.490	0.519
9.739	1.052	**6.852**	0.668	1.052	0.677	0.468	0.831
0.948	0.742	0.588	0.555	0.744	0.188	1.600	0.725
1.591	0.800	1.400	0.677	0.670	0.749	1.817	0.846
1.200	0.640	0.587	1.078	0.769	**22.000**	0.983	2.383
2.609	1.235	2.017	0.857	1.765	0.833	0.913	3.583
0.703	0.664	0.688	1.417	1.591	0.715	**7.235**	0.734
0.505	0.492	1.278	0.698	0.669	1.261	0.527	0.794
3.017	0.685	0.674	0.655	1.296	2.765	0.983	0.785
1.374	1.191	1.27	0.549	0.672	0.587	2.122	1.374
0.693	0.570	0.896	1.052	0.609	1.339	0.592	0.541
0.668	0.568	0.584	2.852	0.681	0.652	0.360	0.948
1.339	0.597	0.670	0.589	0.703	0.597	0.530	0.590
0.538	0.503	1.278	**16.696**	0.522	2.417	0.704	0.666
0.739	0.636	0.638	0.641	1.113	**63.043**	1.722	2.174

X-ray matrix corrections

Energy-dispersive X-ray analysers have poor resolution. Ingamells suggested a method for deconvoluting two, three or more overlapping peaks that is entirely based on Poisson statistics. The method is unique and unparalleled by anyone else.

A better system of dimensions and units for nuclear physics

Ingamells showed, beyond any possible doubt, that our current system of dimensions and units, metric or not, is not an appropriate tool for advanced nuclear physics; it is unnecessarily complex with foundations that are more emotional than scientific, probably due to the fact that some areas of physics were established by people who were reluctant to communicate with other branches of physics. The system is acceptable for our day-to-day lives, when we cook for the family or work for the mining industry as we both did, but totally unacceptable when we explore the nature of the Universe. Ingamells suggests a simpler system that makes it easier to penetrate the subtle environment of which we are all part.

He proved that time, mass, permeability and permittivity do not need units of their own. In the suggested new system, all values for the "fundamental" physical constants are absolute, with the exception of the so-called "time-thickness constant". This alone eliminates unnecessary ambiguity and greatly simplifies our search for the ultimate truth.

The amazing achievement of his essay is proving beyond any possible doubt that the electric charge of electrons, protons etc… **are a surface area**, which is by itself a scientific achievement of paramount importance, and still unrecognised and never addressed by the "Establishment" today.

The theory of vacuoles

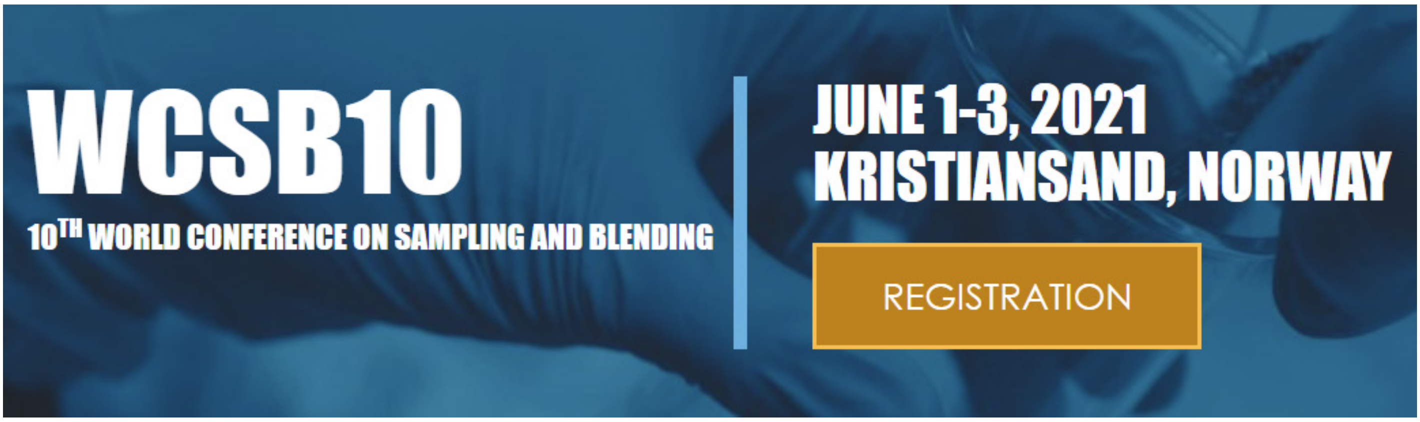
The direct by-product of this new, far more powerful system of dimensions and units, and greatly enforced by the fact that the electric charge of electrons, protons etc… is a surface area, is the new possibility that our existing model of particles is *flawed*, or at the very least very *naïve*. Based on this, following many years of investigation, Ingamells suggested the *vacuole hypothesis*, which was a completely new view of the Bohr atom. The long-term implications of this work are still unclear, but most certainly carry profound possibilities.[10]

Conclusions

Overall, and this is what is most fascinating, for every subject where Charles Oliver Ingamells found some interest to make a participation, he left his footprint as a challenge for many people and many years to come. It definitely takes a superior mind to be able to do this and this is the deep reason for his due place also within TOS.

Ingamells' work related to sampling

1. J.C. Engels and C.O. Ingamells, "Effect of sample inhomogeneity in K-Ar dating", *Geochem. Cosmochim Acta* **34,** 1007 (1970). https://doi.org/10.1016/0016-7037(70)90082-7
2. C.O. Ingamells, J.C. Engels and P. Switzer, "Effect of laboratory sampling error in geochemistry and geochronology", *Proc. 24th IGC*, sect. 10, 405 (1972).
3. C.O. Ingamells and P. Switzer, "A proposed sampling constant for use in geochemical analysis", *Talanta* **20,** 547 (1973). https://doi.org/10.1016/0039-9140(73)80135-3
4. P.K. Samland and C.O. Ingamells, "New approaches to geostatistical evaluations", *Proc. 12th Comp. Appl. Conf.*, Vol. 2, Colorado School of Mines, Denver, F 108 (1973).
5. C.O. Ingamells, "New approaches to geochemical analysis and sampling", *Talanta* **21,** 141 (1974). https://doi.org/10.1016/0039-9140(74)80036-6
6. C.O. Ingamells, "Control of geochemical error through sampling and subsampling diagrams", *Geochem. Cosmochim. Acta* **38,** 1225 (1974). https://doi.org/10.1016/0016-7037(74)90118-5
7. C.O. Ingamells, "Derivation of the sampling constant equation", *Talanta* **21,** 263 (1976). https://doi.org/10.1016/0039-9140(76)80188-9
8. C.O. Ingamells, "Evaluation of skewed exploration data—the nugget effect", *Geochim. Cosmochim. Acta* **45,** 1209 (1981). https://doi.org/10.1016/0016-7037(81)90144-7
9. C.O. Ingamells and F.F. Pitard, *Applied Geochemical Analysis*. Wiley-Interscience, New York (1986).
10. F.F. Pitard, *The Theory of Vacuoles and Low Energy Nuclear Reactions*. mediahead.ca/Francis_Pitard_LENR/files/assets/common/downloads/publication.pdf



doi: 10.1255/tosf.124

Material intrinsic heterogeneity: statistical derivation

Geoff Lyman
Principal, Materials Sampling & Consulting, materials-sampling-and-consulting.com

The value of a fully statistical sampling theory is that it is possible to quantify a measure of material intrinsic heterogeneity and, on this basis, provide the entire distribution of the analyte content of potential samples to be extracted from the lot. The analyte content of a sample of a given mass is a random quantity as samples of nominally equal masses taken from a lot in a given state of comminution will not have exactly the sample analyte content. The analyte content of a sample is correctly described as a random variable and to characterise a random variable completely it is necessary to know either the probability density function or distribution function for the random variable, or all of the moments of the random variable (mean, variance and all the higher moments). The following discussion derives the fundamental sampling variance from a purely mathematical statistics basis, relying on the *assumption* that the number of particles of any one type (size and analyte content) that fall into a sample taken in a mechanically correct manner (following the principle of equiprobable sampling) follows a Poisson distribution. In addition, the Poisson distributions of particle numbers are statistically independent. A more fully argued substantiation of this fundamental assumption, partial experimental evidence and standard statistical introduction to the definition and properties of the Poisson distribution, and reasons for its use, can be found at the end of this article.

Material heterogeneity

The intrinsic heterogeneity (IH) of a particulate material with respect to a particular analyte or component of the material reflects the extent to which the size and compositions of the particles differ. A jar of identical white marbles (same size, mass and chemical composition) possesses zero IH. A jar containing both black and white marbles of the same size possesses some positive IH (IH cannot be negative as it is a variance). Similarly, a sack of wheat will possess some intrinsic heterogeneity, but this will differ depending on what aspect of the wheat is under scrutiny. There will be one level for the IH with respect to nitrogen, another due to concentration of mycotoxins and another with respect to the content of small mineral or stone particles of the sack of grain. Likewise, a sample of a broken base metal ore will have different IH measures with respect to Cu, Ag, Au, Fe, Zn, Pb and S. IH is essentially a measure of the variability of a material with respect to the mass of an analyte carried within a particle. If all particles are the same, as the case of white marbles, the IH is zero.

Derivation

In a general mixture of particles there will be a range of particle sizes and, within each size fraction, there will be a range of particle compositions with respect to a target analyte. The material can be conceptually broken down into particle classes within which all particles are assumed to have the same nominal volume v_k. Then within each volume class, particles can be put into composition classes of average analyte content a_{kp} and average density ρ_{kp}. The k^{th} volume class represents a mass fraction x_k within the mixture and the p^{th} composition class represents a mass fraction y_{kp} within the k^{th} size class. Table 1 summarises the notation for this model of the particles. The model can be made arbitrarily accurate by expanding the number of volume and composition classes. For fine particles (<5 mm), it is possible to collect information on individual particle sections using an automated scanning electron microscope (Qemscan or MLA or other machine) from which this information can be calculated directly.

This form of a material model can be adapted to most particulate mixtures, but low grade gold ores are a possible exception, especially when the gold is present as relatively large grains within particles (in general, the term "grain" can be used to refer to a contiguous volume of a phase within a larger "particle" which is a single contiguous and distinct volume of a material). In such a case it is the size distribution of the gold

Table 1. Descriptors of a particulate material—the material model.

Symbol	Description	Units	Convenient unit
N_s	Number of size classes into which the material is divided	—	—
N_c	Number of composition (analyte content) classes into which the material is divided	—	—
x_k	Mass fraction of the total lot or sample falling in the k^{th} size class	—	—
y_{kp}	Mass fraction of the p^{th} composition class within the k^{th} size class	—	—
v_k	Volume of the average fragment within the k^{th} size class	L^3	cm^3
ρ_{kp}	Density of the average fragment in the p^{th} composition and k^{th} size class	$\text{m}\,\text{L}^{-3}$	$\text{g}\,\text{cm}^{-3}$
a_{kp}	Average concentration of the analyte in the p^{th} composition and k^{th} size class—may be a mass fraction or other (w/w) concentration unit such as ppm	—	—

grains that is of primary importance. Special methods have to be adopted to determine the size distribution of the gold.

The usual definition of the volume of the average fragment in the k^{th} size class is

$$v_k = f\,\frac{d_{k-1}^3 + d_k^3}{2} \tag{1}$$

where d_{k-1} and d_k are the square screen apertures defining the size fraction and f is a shape factor usually taken to be 0.5. Other definitions may be taken such as the geometric mean size which is the square root of the product of the defining sieve apertures with the inclusion of a shape factor.

Note that sorting particles into density classes is not the same as sorting into composition classes. A density class can have a substantial range of compositions with respect to a particular analyte if there are more than two mineral phases in the particle mixture. Similarly, a composition class with respect to a particular analyte can contain particles of a range of densities in a multiphase mineral mixture.

The general equation for the composition of a sample, based on conservation of mass, can be written as

$$A_S = \frac{\sum_{k=1}^{N_S}\sum_{p=1}^{N_C} a_{kp} m_{kp} N_{kp}}{\sum_{k=1}^{N_S}\sum_{p=1}^{N_C} m_{kp} N_{kp}} \tag{2}$$

where the N_{kp} are the numbers of particles and the m_{kp} are the masses from each size-composition class appearing in the sample. The numbers, N_{kp} are taken to be independent Poisson random variables. A_s is a random variable as it is a function of other random variables.

The variance of the sample composition can be derived by the well-known rules of propagation of variance by which the composition is expanded in a Taylor series about the expected value of the number of particles. The derivatives are

$$\left.\frac{\partial A_S}{\partial N_{kp}}\right|_{\tilde{\mathbf{N}}} = \frac{a_{kp} m_{kp}}{\sum_{k=1}^{N_S}\sum_{p=1}^{N_C} m_{kp}\tilde{N}_{kp}} - \frac{\sum_{k=1}^{N_S}\sum_{p=1}^{N_C} a_{kp} m_{kp}\tilde{N}_{kp}}{\left(\sum_{i=1}^{N_S}\sum_{j=1}^{N_C} m_{kp}\tilde{N}_{kp}\right)^2} m_{kp} \tag{3}$$

and are evaluated at the expected number of particles in the sample. Expected values of a quantity are denoted by a tilde, for example, $\tilde{N}_{kp}$.

The expected sample mass is identified as

$$\tilde{M}_S = \sum_{k=1}^{N_S}\sum_{p=1}^{N_C} m_{kp}\tilde{N}_{kp} \tag{4}$$

and the expected sample analyte content is

$$\tilde{A}_S = \frac{\sum_{k=1}^{N_S}\sum_{p=1}^{N_C} a_{kp} m_{kp}\tilde{N}_{kp}}{\sum_{k=1}^{N_S}\sum_{p=1}^{N_C} m_{kp}\tilde{N}_{kp}} \tag{5}$$

so the derivatives can be simplified as

$$\left.\frac{\partial A_S}{\partial N_{kp}}\right|_{\tilde{\mathbf{N}}} = \frac{a_{kp} m_{kp}}{\tilde{M}_S} - \frac{\tilde{A}_S}{\tilde{M}_S} m_{kp} = \frac{m_{kp}}{\tilde{M}_S}\left(a_{kp} - \tilde{A}_S\right) \tag{6}$$

Using only the first term in the expansion, the variance is by definition

$$\begin{aligned} \operatorname{var}\left\{A_S\right\} &= \sum_{k=1}^{N_S}\sum_{p=1}^{N_C}\left(\left.\frac{\partial A_S}{\partial N_{kp}}\right|_{\tilde{\mathbf{N}}}\right)^2 \operatorname{var}\left\{N_{kp}\right\} \\ &= \sum_{k=1}^{N_S}\sum_{p=1}^{N_C}\left(\frac{m_{kp}}{\tilde{M}_S}\left(a_{kp} - \tilde{A}_S\right)\right)^2 \operatorname{var}\left\{N_{kp}\right\} \end{aligned} \tag{7}$$

Since the particle numbers are Poisson random variables for which their variance is equal to their expected value,

$$\operatorname{var}\left\{N_{kp}\right\} = \tilde{N}_{kp} \tag{8}$$

so

$$\begin{aligned} \operatorname{var}\left\{A_S\right\} &= \sum_{k=1}^{N_S}\sum_{p=1}^{N_C}\left(\frac{m_{kp}}{\tilde{M}_S}\left(a_{kp} - \tilde{A}_S\right)\right)^2 \tilde{N}_{kp} \\ &= \frac{1}{\tilde{M}_S}\sum_{k=1}^{N_S}\sum_{p=1}^{N_C}\frac{m_{kp}\tilde{N}_{kp}}{\tilde{M}_S} m_{kp}\left(a_{kp} - \tilde{A}_S\right)^2 \end{aligned} \tag{9}$$

The usual variables in the model of the material can be identified as follows

$$\begin{aligned} x_k y_{kp} &= \frac{m_{kp}\tilde{N}_{kp}}{\tilde{M}_S} \\ m_{kp} &= v_k \rho_{kp} \end{aligned} \tag{10}$$

Then

$$\operatorname{var}\left\{A_S\right\} = \frac{1}{\tilde{M}_S}\sum_{k=1}^{N_S} x_k v_k \sum_{p=1}^{N_C} y_{kp}\rho_{kp}\left(a_{kp} - \tilde{A}_S\right)^2 \tag{11}$$

or

$$\frac{\operatorname{var}\left\{A_S\right\}}{\tilde{A}_S^2} = \frac{1}{\tilde{M}_S}\sum_{k=1}^{N_S} x_k v_k \sum_{p=1}^{N_C} y_{kp}\rho_{kp}\left(\frac{a_{kp} - \tilde{A}_S}{\tilde{A}_S}\right)^2 \tag{12}$$

The result of the derivation is the following expression for the sampling constant

$$K_S = \sum_{i=1}^{N_S} x_i v_i \sum_{j=1}^{N_C} y_{ij}\rho_{ij}\left(\frac{\tilde{A}_S - a_{ij}}{\tilde{A}_S}\right)^2 \tag{13}$$

The sampling constant is an intrinsic property of the material; hence the term "Intrinsic Heterogeneity". An intrinsic property of a material is one that does not depend on the mass or amount of the material present. In his work, Pierre Gy refers to a quantity he calls the "Constitution Heterogeneity" (CH). There is a difference between these two quantities, as Gy's CH is a dimensionless measure. Pitard makes the same definition of the intrinsic heterogeneity as above.

The IH is more appropriate and in line with the naming of properties in thermodynamics and the engineering literature. It is a direct measure of the heterogeneity of the material with respect to a given analyte in a given state of comminution. It has the units of mass.

The relative variance of the sample analyte content when taking a sample of nominal mass $\tilde{M}_S$ is

$$\frac{\operatorname{var}\left\{A_S\right\}}{\tilde{A}_S^2} = \frac{K_S}{\tilde{M}_S} \tag{14}$$

This expression can also be written in terms of particle numbers and masses but Equation 13 is the most convenient.

This expression for the sampling constant is entirely consistent with Gy's work. It is also consistent with an expansion of the denominator in the expression for the sample assay, which provides another means of making the derivation.

It must be stressed that the sampling constant will differ for each chemical element of interest in the mixture unless the elements of interest all occur only in a single mineral phase. The sampling constant may also be calculated to apply to a mineral phase in the mixture. If an element is carried by only one phase in the mineral mixture, then the sampling constant for the element will be equal to the sampling constant for the phase.

It is convenient to define a heterogeneity for a size fraction as

$$IH_k = \sum_{p=1}^{N_C} y_{kp}\rho_{kp}\left(\frac{a_{kp} - \tilde{A}_S}{\tilde{A}_S}\right)^2 \tag{15}$$

Note that this quantity has units of density rather than mass.

This quantity is a mass-weighted second moment of the particle composition about the sample analyte content (not the analyte content of the size fraction itself) and generally (but not always) increases as one moves from one size fraction to a finer one.

For a distribution of particle composition, as shown in Figure 1, the quantities involved in the summation, except for the density term, are shown on the Figure.

With the above definition, the sampling constant can be written as

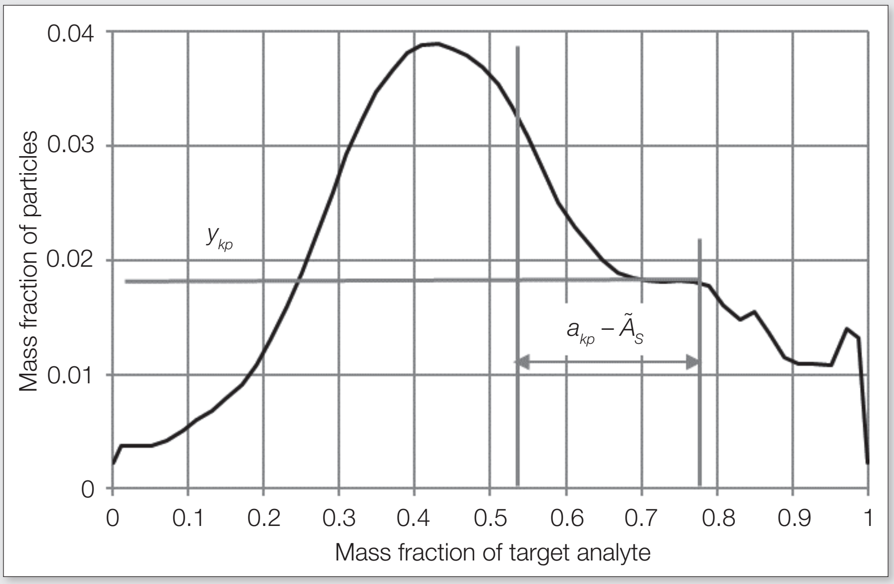


Figure 1. Illustration of terms involved in calculation of the IH value for a size fraction.

$$K_S = \sum_{i=1}^{N_S} x_i v_i IH_i \tag{16}$$

This form of the equation emphasises that the sampling constant is a weighted sum of the IH values for the size fractions where the weighting factor is the product of the mass fraction of the i^{th} size fraction in the material and the nominal volume of the particles in that size fraction. Even if the IH values for the size fractions increase modestly as finer particles are considered, the volume weighting tends to be a dominant factor, so it is the IH values for the coarser size fractions that dominate the value of K_s. The exception to this is nuggetty gold ores and diamonds.

This derivation demonstrates that it is possible to derive the expression for the constitutional heterogeneity, or the intrinsic heterogeneity, which is an important component of the fundamental sampling variance (error), from a purely statistical basis without reliance on a concept of material heterogeneity.

The derivation is based on Poisson distributions of particles numbers that fall into "correctly extracted" samples. This basis of Poisson distributions of particle numbers can also be used to derive the full sampling distribution using the method of characteristic functions. When the analyte content of the sample defined in Equation (2), is expanded as a Taylor series in particle numbers, it becomes a weighted sum of independent Poisson random variables for which the characteristic function can be written explicitly. Inversion of this function then provides the probability density function for the analyte content of potential samples from a lot. Knowing the form of the characteristic function also permits calculation of all the moments of the sampling distribution of which the sampling variance is simply the second central moment. These expressions are explicit and require no inversion calculation.

The Poisson Distribution: brief tutorial

When events occur at random but with a particular average rate, λ, the number of events occurring in a defined period of time follows a Poisson distribution. If the period of time or the width of an interval is denoted as t, the expected number of events in t is $n = \lambda t$. The probability that J events will take place in this interval is

$$p(J \mid n) = \frac{n^J e^{-n}}{J!} \tag{17}$$

The expected value of the number of events and the variance of the number of events are equal, so

$$\mathrm{E}\{J\} = \mathrm{var}\{J\} = n \tag{18}$$

The characteristic function of the Poisson density is

$$\varphi(u) = \exp\left[n\left(e^{iu} - 1\right)\right] \tag{19}$$

The time or distance between consecutive events in a Poisson process is exponentially distributed.

The probability density function is illustrated in Figure 2. The function is substantially skewed for low expected values, but becomes more symmetrical as the expected value increases.

Why is the assumption of Poisson distributed particle numbers a sound and reasonable one? There are several arguments that can be marshalled to support the use of the Poisson distribution for particle numbers in correctly taken samples.

First, from a mathematical viewpoint, the rules of propagation of variance used to arrive at the results in Equations (11) or (12) are known to be a correct methodology. If the variance of the number of particles were not taken to be equal to the expected value of the number of particles, Gy's result for the sampling variance would not result from the present analysis. The sample variance would be either smaller or larger. The assumption of the property of the Poisson distribution is the only one that leads to Gy's result, because there is no other discrete distribution having a variance equal to the expected value.

Second, there is experimental evidence. It is possible to take a batch of small (about 2.5 mm) coloured plastic particles, combined in known proportions, and pass a sample of this material through a small rotary sample divider to create a number of subsamples. The particles in each of the subsamples can then be counted and the variance of the numbers over the subsamples can be compared with the average or the expected number. In courses given by the author, participants and students have carried out this exercise with results that are statistically compatible with the Poisson assumption.

Third, from the point of view of ways of describing randomness, picture a set of particles laid out along a line in the most random possible manner, in such a way that there is some average number of particles per unit length when a long line segment is considered. If particles are placed at positions along the line in the most random manner possible, it is natural to think that the probability of finding a particle in any one short line segment "dx" is constant; no part of the line is favoured. This uniform distribution of the particles along the line leads to the mathematical conclusion that the number of particles in any finite line

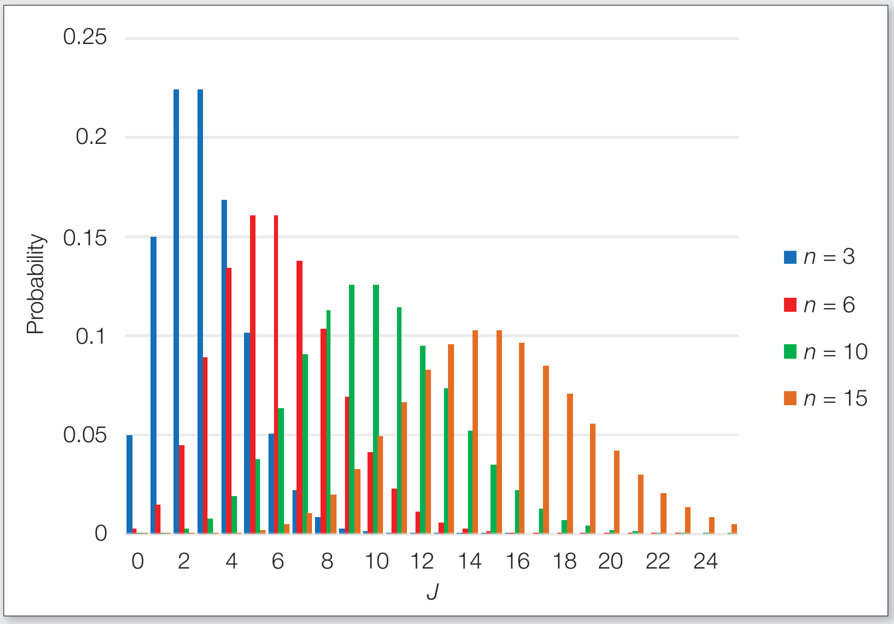


Figure 2. Examples of the Poisson distribution for various expected values.

segment of length L will follow a Poisson distribution. The nature of placement of the particles is known to statistical mathematicians as a Poisson point process. So, if one were to take a "stopped belt" sample over a particular length of the line, the number of particles in that sample would follow a Poisson distribution with an expected value proportional to the particular length considered. The Poisson point process for distributing particles in space is the most random and statistically uniform of all point processes and is, therefore, the most reasonable assumption to make regarding the distribution of the numbers of particles falling into a correctly taken sample.

Finally, a fourth argument can be made on the basis of equiprobable sampling. If particles are selected from a lot one by one and at random and the entire set is accessible for selection (correct sampling), the number of particles of any one type that are selected will follow a hypergeometric distribution (drawing elements at random from a finite set without replacement). However, if the size of the set is large compared to the number of particles selected, the hypergeometric distribution converges to a binomial distribution. And, when the size of the set is very large, the binomial distribution can be represented by a Poisson distribution. These limiting cases are well-known in the statistical literature.

doi: 10.1255/tosf.125

High-resolution PAT monitoring of sample preparation grinding by accelerometer sensors: the key to ensuring accuracy and long-term consistency

Martin Lischka

André Mehling

Martin Lischka and André Mehling
HERZOG Maschinenfabrik GmbH & Co. KG, Germany

Industrial operations are often based on critical quality measures obtained for technical process control and/or to determine the value of raw materials and product streams. Process Analytical Technology (PAT) monitoring is applied to characterise, for example, raw materials, semi-finished as well as finished products. There is an active interest in approaches for "smart" online, real-time industrial sensor applications, especially where industrial operations involve high sample throughput and/or may involve hazardous substances demanding *automation*. State-of-the-art sample preparation procedures and equipment can deliver key performances indicators, often supplemented by sensor data that are used as *proxy* quality measures which helps to ensure measurement representativity and optimal process/product control. We here illustrate this industrial front-line arena by an example in which PAT accelerometer data are used for real-time monitoring of the efficiency of the automated grinding sample preprocessing process.

Introduction

Process Analytical Technologies (PAT) has seen an enormous application rush in the last 20 years, starting out in pharma and chemical industries, and has recently seen many creative applications also in industrial sectors well beyond this origin.[1] Various PAT sensor methods and approaches have been developed for specific purposes within the industrial automation realm, e.g. to monitor torque in spear sampling systems, to ensure constant material feeds and also for monitoring milling machines that treat metal samples. Here parameters representing the physical phenomena *vibration* and *torque* are used to monitor the condition of cutting tips of active milling heads. For example, if tool cutting tips are not in the right condition, correct removal of sample surface layers cannot be assured with subsequent adverse analytical results.[2]

Background

Mineral raw materials are often pressed as fine powder (typically less than 75 µm) into steel rings and analysed with X-ray fluorescence (XRF). The calibration of the analytical device is linked to a certain target particle size distribution as manifested by the calibration standards used. For optimal analytical quality this particle size distribution needs to be in compliance for all subsequent routine samples in the longest possible post-calibration period of routine application. However, there is often a lack of methods to monitor compliance for long enough periods in order to ensure the necessary analytical accuracy and constancy.

Disc mills are used in the automated laboratory to comminute granular sample material by grinding, typically reducing the grain size from 1–5 mm down to 150 µm, and below. The eccentric movement of grinding vessels puts the internal grinding set (puck and ring) into circular motion. The sample particles are ground due to shearing, impacting and compression of the material between the grinding set elements and the wall of the vessel. In many instances, the ground material is subsequently pelletised and analysed, e.g. by XRF. The grain size distribution following grinding has a significant impact on the quality of the XRF results. The so-called *particle size effect* may cause variances in elemental analysis of more than 30 % only due to different particle size distribution and

Figure 1. Examples of sample preparation equipment for pressed pellet preparation used in automated XRF analysis. A: Various grinding and pressing accessories for manual sample preparation setup. B: Grinding vessel with sample material. C: Finished pressed pellet suitable for XRF analysis. D: Mill and press combination (HP-MP) used in automatic sample preparation for XRF analysis.

not to compositional differences between samples.[2] It is, therefore, critical to minimise the variability of grain size distribution after grinding in order to decrease this sample preparation bias of the analytical results.

For many materials, the reproducibility of grain size distribution after grinding is very high. This is especially true because of the use of automatic pulverising mills compared to equipment with more manual sub-process stages involved. For other materials and applications, post-grinding grain size distributions may exhibit a higher (to distinctly high) degree of variability due to variation in material constitution. In the automated laboratory realm, it is practically impossible to determine particle size distribution *after* each grinding run. It would consequently be of great help if the grinding efficiency could be monitored in real time *during* the grinding process.

Here, we show that the start and duration of the grinding process can be easily identified from simple acceleration monitoring data. We first provide insights that acceleration signals correlate well with grinding efficiency and with grain size distribution. Based on comparative results from initial experiments we are able to elucidate the underlying mechanism for diagnostic changes in acceleration-monitored milling signals. Routine monitoring based on acceleration data functions as satisfactory proxies for the contemporary grain size distribution, allowing significantly better process monitoring and control.

Comparative study

All tests reported here were carried out on i) a manually loaded grinding vessel [HSM 100P, tungsten carbide (TC)], ii) semi-automatic chrome steel vessel (HP-M 500) or iii) a fully automatic disc mill (model HP-MP, TC vessel). In each case, an acceleration sensor was mounted on the lower half of the swinging aggregate and connected to the programmable logic controller of the grinding mill for data acquisition. For analysis of the grinding vessel motion, the acceleration in both x- and y-directions was assessed. For evaluation of grinding efficiency, the root mean squares (RMS) of the x- and y-accelerations were calculated as previously described,[3,4] allowing RMS levels to be plotted over time for graphic evaluation. We also calculate the standard deviation (SD) of the individual RMS values to determine the ensemble RMS variability.

In some instances, we also analysed the grain size distribution of the ground material using a vibratory sieve shaker.

Results

Acceleration signals representing an empty grinding vessel: efficient and inefficient grinding

For this initial test series, we used the HSM 100P disc mill. First, we assessed acceleration during motion of an empty grinding vessel without sample material (only puck and ring) at a rotation speed of 1000 rpm. Second, we performed a grinding run with 50 g of pure silica sand at a grinding speed of 1000 rpm, resulting in a significant grain size reduction (efficient grinding), and, third, 50 g of the same material was ground at a lower speed of 600 rpm leading to only minor grain size reduction (inefficient grinding). The duration of each grinding run was identical, 30 s.

The empty grinding vessel (Figure 2A) is characterised by a very uniform signal without fluctuations over time. The mean RMS was 30.1 m s^{-2}, the mean SD of the ensemble RMS was low at 1.4. During efficient grinding (Figure 2B), the initial acceleration signal was relatively constant with a low variability (RMS 29.9 ± 2.8 m s^{-2}). After 8.5 s, however, (red arrow in Figure 2B), there was a significant change in the signal pattern with a constant increase of the variability (RMS 31.3 ± 5.1 m s^{-2}). During inefficient grinding (Figure 2C), the acceleration signal remained unchanged with little variability throughout the entire grinding period (RMS 11.8 ± 1.2 m s^{-2}).

Influence of the sample weight on the acceleration signal

In this second test series, we assessed the influence of the sample weight on the acceleration patterns during grinding of silica sand or iron ore. For each of these materials, we carried out five tests, increasing the sample load from 50 g to 90 g in steps of 10 g. Each run was carried out under identical conditions using the HSM 100P with a grinding time of 30 s and a rotation speed of 1200 rpm.

For silica sand, we found a characteristic change in the acceleration signal over time. In each run, the signal showed an initial uniform acceleration pattern without major fluctuations followed by an abrupt change to a pattern displaying an increasing fluctuation concomitant with a lowering of the absolute RMS values (Figure 3). The time of the signal change depended clearly on the sample weight, being systematically delayed with each increased sample load. Thus for 50 g, the signal change appeared at 9 s. For 60, 70, 80 and 90 g the change took place later at 15 s, 26 s, 28 s and 31 s, respectively (red arrows in Figure 3). The initial RMS values were similar between trials. In the run with 60 g of silica sand, the mean RMS before the signal change was 49.4 ± 1.8 m s^{-2}, thereafter 32.5 ± 8.5 m s^{-2}.

For iron ore, we observed a similar signal behaviour as for silica sand

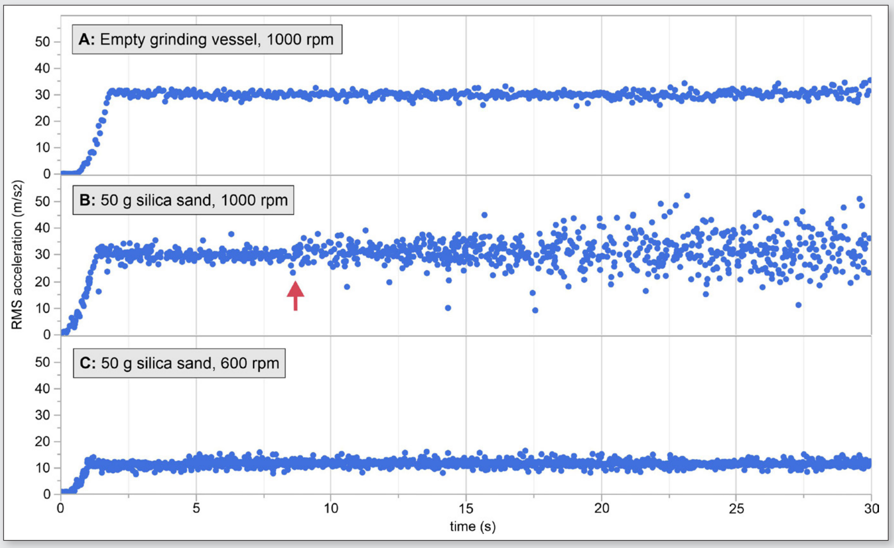


Figure 2. Monitoring RMS acceleration signals of an empty grinding vessel (A) and during efficient grinding (B) vs inefficient grinding (C) of pure silica sand.

(Figure 4). The time point of the signal change depended on the sample weight and increased from 12.5 s (50 g) to 25 s (90 g). However, the signal changes were smaller than for silica sand. For 60 g of iron ore, the mean RMS before the signal change was 50.1 ± 2.6 $m\,s^{-2}$, thereafter 46.6 ± 3.4 $m\,s^{-2}$.

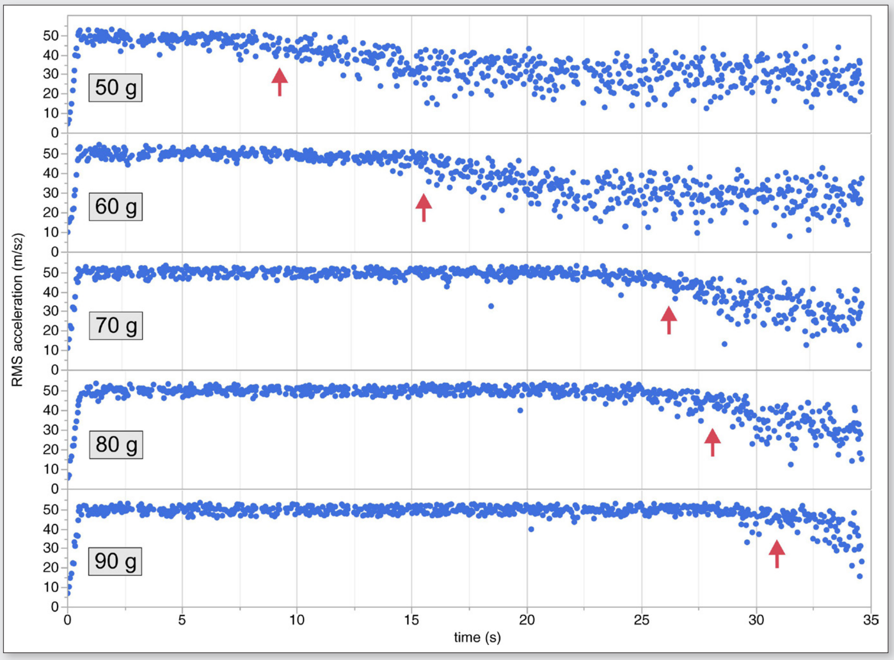


Figure 3. RMS acceleration signal assessed during grinding of different loads of silica sand in the manual disc mill of the type HSM 100P. The onset of the efficient grinding phase is characterised by an increase of the RMS variability (red arrow). The point of time when the signal changes depends on the sample weight.

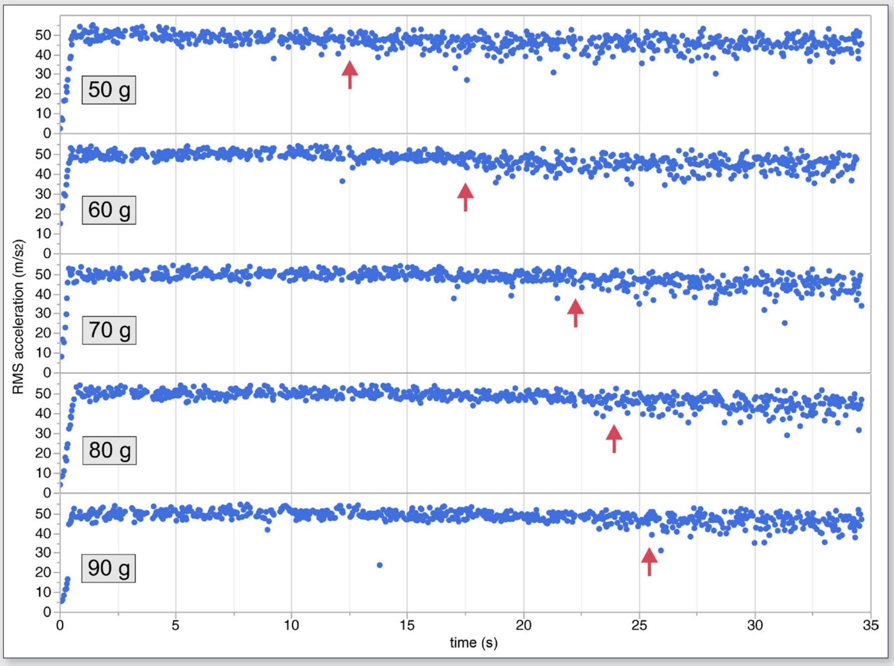


Figure 4. RMS acceleration signal assessed during grinding of different loads of iron ore in the manual disc mill (HSM 100P). Similar to results for silica sand, the onset of the efficient grinding phase is characterised by an increase of the RMS variability (red arrow). Also, here, the onset of the signal changes depends on the sample weight, but compared to silica sand, the iron RMS changes are less pronounced.

Influence of the rotation speed on acceleration signal and grain size distribution

In this test series, we examined the influence of different rotation speeds on the acceleration signal. The test runs were carried out on the semi-automatic HP-M 500 during grinding of 200 g of iron ore for 60 s. The rotation speed was different in each run (900, 1000, 1100 rpm). After each run, we determined the grain size distribution of the ground material using a vibratory sieve shaker.

For 900 rpm, the signal change occurred very late during the grinding process, at 57 s. For 1000 and 1100 rpm, the signal change was earlier, at 50 s and 38 s, respectively (Figure 5).

For the grain size analyses, we found an increase of the fraction < 45 µm from 41.2 % at 900 rpm to 51.0 % at 1000 rpm and 59.6 % at 1100 rpm. At the same time, the fraction > 150 µm decreased from 31.2 % to 17.3 % and 6.4 %, respectively (Figure 6).

Oscillation analysis

In order to evaluate the underlying cause for the change of the acceleration signal during grinding we performed an oscillation analysis. We examined the RMS signal during grinding of iron ore in an automatic mill (HP-MP) at a rotation speed of 1000 rpm. For all the tests above we initially observed a uniform signal with little fluctuation which then changed to a signal with larger fluctuations (Figure 7). In order to try to understand more, we performed an oscillation analysis *before* the signal change (red box at 10 s, Figure 7) and later (red box at 15 s, Figure 7).

For this purpose, the acceleration values in the x- and y-direction on an ideal sinusoidal oscillation were projected on a graph (Figure 8). When set in motion, the grinding vessel describes a circular path around its centre. Therefore, the acceleration in the x- and y-direction shows a phase lag of 90 ° in Figure 8.

At 10 s the values for x- and y-acceleration are located on the ideal reference sinusoidal curves (Figure 8A). Also, the phase lag of x- and y-acceleration was quite constant at 90 °. Accordingly, the resulting RMS values of x- and y- direction plot in a relatively straight line with very little deviation. This corresponds to a situation when the grinding vessel can move relatively undisturbed along its ideal circular path. After 15 s we found that some of the x- and y-acceleration values were lower than

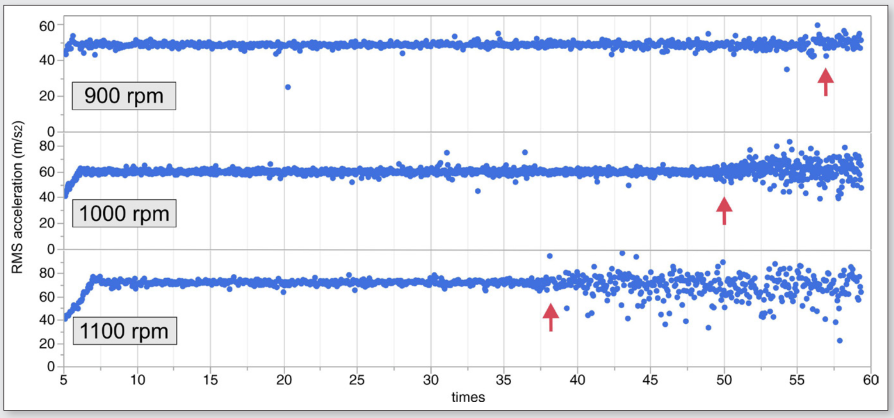


Figure 5. RMS acceleration signal representing grinding of 200 g iron within the HP-M 500. The rotation speed varied from 900 rpm to 1000 rpm. The grinding time in all trials was 60 s. The onset of the signal change (red arrow) depend on the rotation speed with earlier starts at higher rpm values.

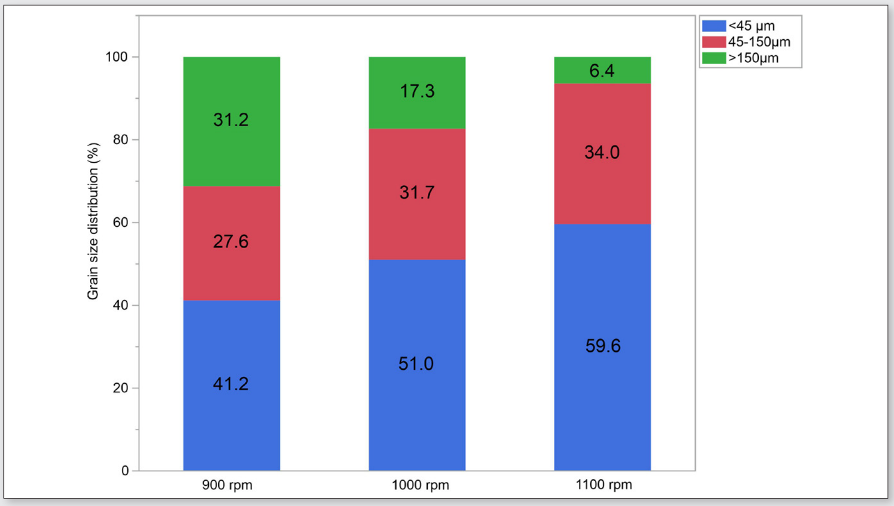


Figure 6. Empirical grain size distribution after grinding of 200 g iron ore in the HP-M 500 at different rotation speeds for 60 s.

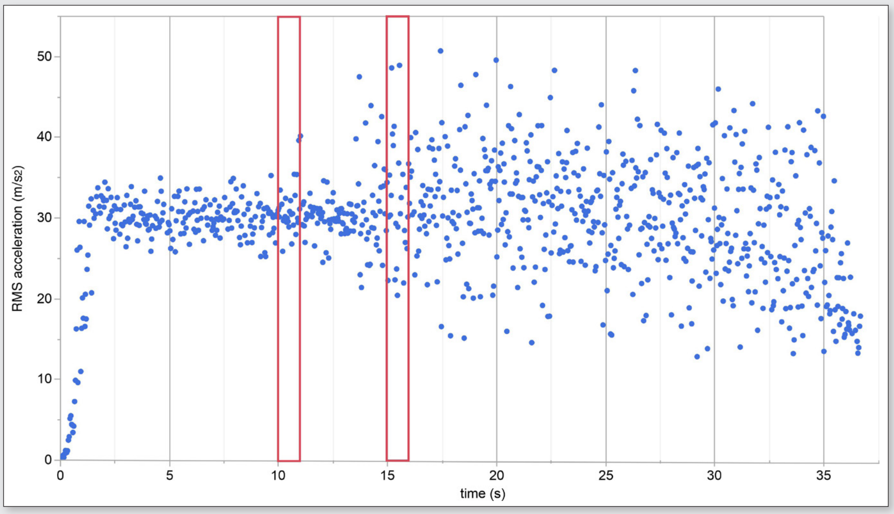


Figure 7. RMS acceleration signal during grinding of 60 g iron ore in an automatic mill (combined mill and press of the type HP-MP). The recording was used to guide an oscillation analysis at two different times each covering 1 s (red boxes). The first oscillation analysis was carried out before increase of the acceleration variability (at 10 s), and the second analysis after the transition to efficient grinding had occurred (at 15 s).

predicted by the ideal sinusoidal curve (Figure 7B). These temporary decelerations are interpreted to be the cause of the increased variability of the RMS signals in this test.

Discussion

In this study, we introduce a new method for real-time monitoring of the grinding efficiency in disc mills. We demonstrate that the increase in acceleration variability, and the concomitant decrease of acceleration magnitude, is a suitable *proxy marker* for efficient grinding. This finding is corroborated by the following observations: 1) Motion of an empty grinding vessel produced only a uniform acceleration signal with low variability. 2) Inefficient grinding due to slow rotation speeds, or high sample load, is characterised by absence, or late onset of the characteristic increased acceleration variability. 3) By contrast, efficient grinding is correlated with an early and swift increase in acceleration variability. At the same time the mean acceleration magnitude is decreased.

The described signal patterns were observable in all disc mill types used in this study, including manual and automatic mills with a 100 cm^3 tungsten carbide grinding vessel as well as a semi-automatic mill with a 500 cm^3 chrome steel vessel. This shows that the signal pattern is a *general phenomenon* that likely can be utilised for a wide range of different discs mills and applications.

The underlying reason for the characteristic signal pattern change is not yet fully understood. The first oscillation analysis showed that increased variability is attributable to brief *decelerations* of the grinding vessel in the x- or y-directions. We believe that these acceleration interruptions are due to short blockages of the motion of the grinding set (puck and ring). The impeded motion of the grinding set likely leads to momentary decelerations of the entire grinding vessel which can be measured by the acceleration sensor.

What is the reason for increased motion blockage of the grinding set within the vessel during efficient grinding? The flowability and "effective viscosity" of powders strongly depends on the particle size and shape.[5,6] At small average particle sizes and, therefore, high inter-particular forces, stable bridges are formed between particles. Moreover, these bridges are not only stable but also reform quickly. At the beginning of the grinding process, the average particle size is large and hardly any inter-particular bridges are built. This means that flowability

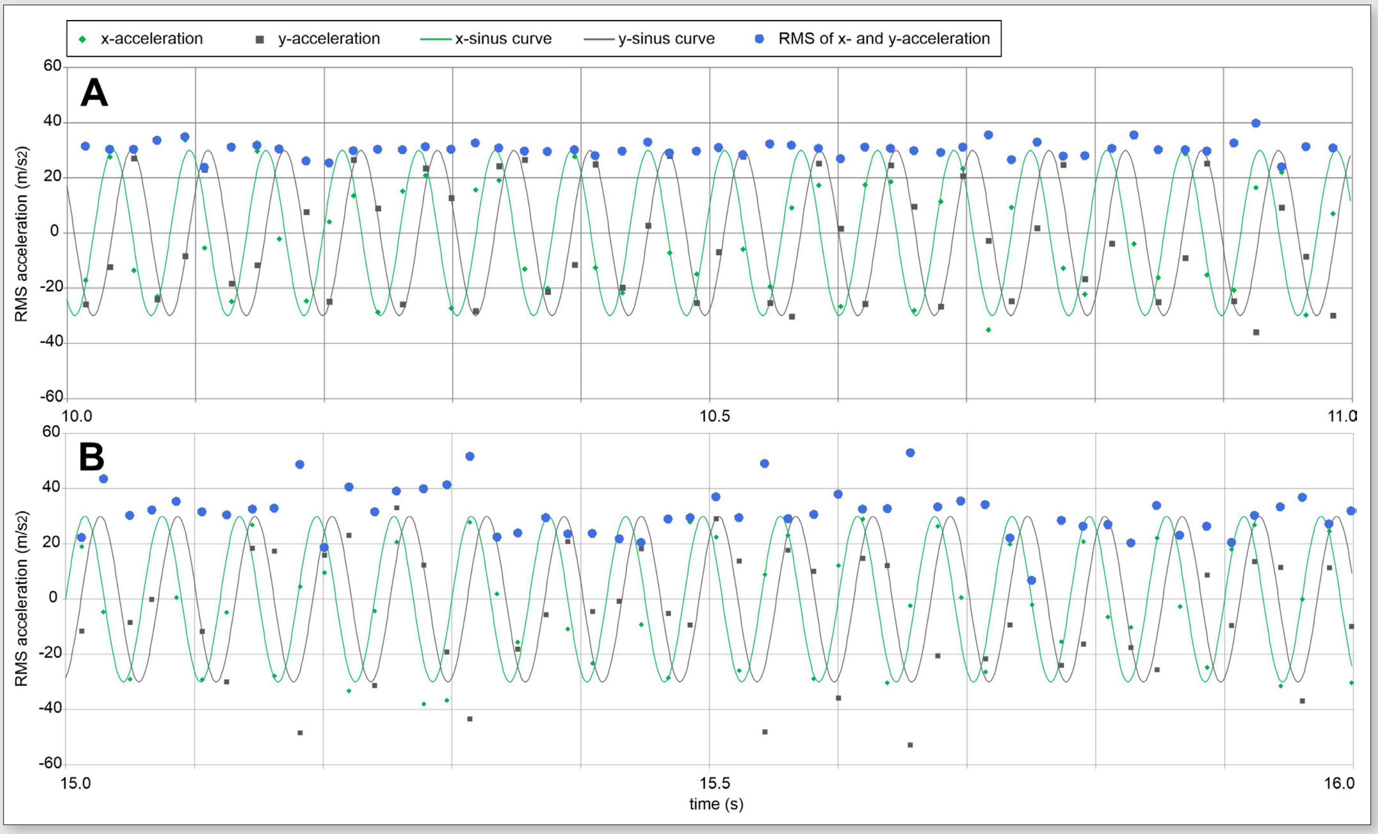


Figure 8. Oscillation analysis of the grinding run shown in Figure 6 for two different time points—*before* onset of variability increase at 10 s (A) and *after* increase at 15 s (B). If the grinding vessel shows a completely undisturbed circular motion, the x- and y-accelerations can be described as sinusoidal curves with a phase lag of 90° (green and black curves). (A) Before onset of efficient grinding the measured x- and y-acceleration values plot along these curves resulting in constant RMS values. (B) After onset of efficient grinding, x- and y-values show significant decelerations with deviations from the ideal curve, resulting in a higher sum-total variability of RMS values.

of the sample is high and, vice versa, viscosity is low. Therefore, the grinding set can move relatively unhindered through the powder within the grinding vessel.

However, as efficient grinding begins to take place, gradually the average particle size decreases. This leads to a build-up of inter-particular bridges resulting in lower flowability and higher viscosity. This in turn causes increasing blockage of the grinding set as measured by the increased acceleration variability.

What is the reason for decreased acceleration amplitude during efficient grinding? The increased variability during efficient grinding is accompanied by a general decrease of the total acceleration magnitude. This phenomenon *may* be due to transfer of the rotationally inducted kinetic energy into energy used for comminution of the sample material.

Conclusion

The accelerometer PAT monitoring approach opens up numerous opportunities for easy, real-time monitoring of the general grinding process. This is a smart-industry solution offering significant benefits in application development and condition monitoring of routine processes and samples. Basic models linking particle size distribution and sensory data from the grinding process can be used to define a Statistical Process Control (SPC) setup for automated sample preparation processes. Biasing factors, e.g. changes in material composition or preparation equipment wear, can be detected and appropriate counter-measures can be invoked.

Figure 9 shows a principal example of how such proxy observations can be used to develop calibration models for specific sample types. In Figure 9A a typical three-phase particle breakage evolution of multiple samples is captured, which can be linked to a certain Particle Size Distribution (PSD). This could be, for example, the calibration standards for an XRF instrument. The particle evolution itself is characterised by an initial phase where most of the bigger brittle particles are reduced in size (blue bar), followed by a second phase with a decreased size reduction efficiency (yellow bar). The third phase (red bar) is characterised by analytical precision disturbing agglomeration effects of the material.

In this example, a PSD of 80.7 % (±1.2 %) below 45 µm is expected for a reference or calibration sample after grinding. Therefore, this model can be used to evaluate the match of routine samples and gives an illustration of how a particular sample matches the expected procedural outcome. Thus, Figure 9B illustrates a sample plot within the calibrated model boundaries, while the sample shown in Figure 9C is clearly out of model range. Depending on the overall application scenario, this can, for example, indicate offsets in the preparation procedure, changes in raw material feed or in sample composition (e.g. mineral composition).The present experimental results show that high-resolution accelerometer sensor data would appear to be suitable to monitor automated processes in various ways. Here we are focusing on accelerometer sensor

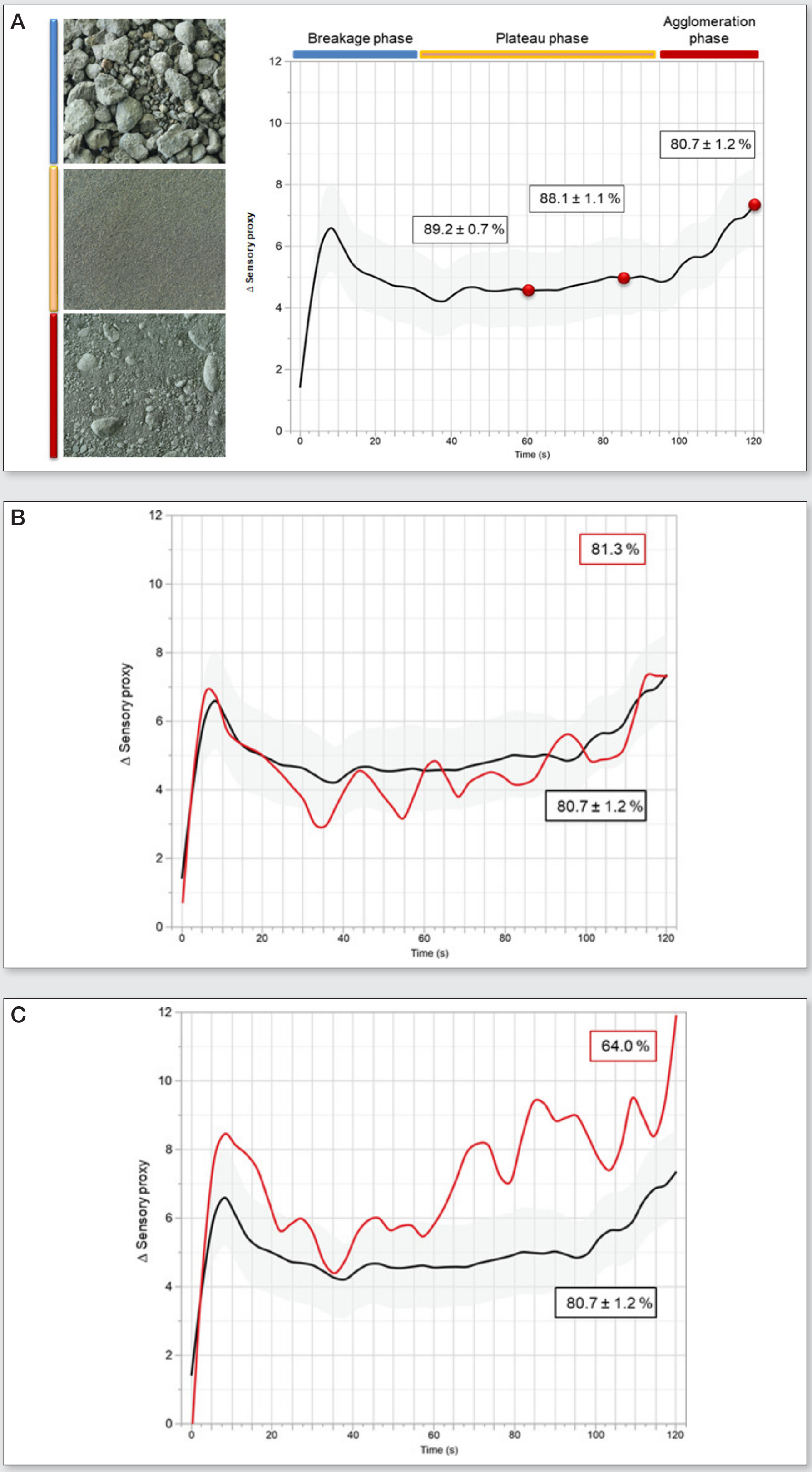


Figure 9. Schematic model for SPC of the grinding process in an automatic pulverising mill used to identify biasing changes in the measurement system caused by particle size effects. The bar far left shows a microscopic picture of the sample appearance according their comminution phase (see colour bar legend in A). A: Average sensor data model with specific PSDs to be expected (rel. values in boxes). The black line displays the mean of a set of calibration samples. Average particle size 80.7 % (±1.2 %) less than 45 µm. B: Routine sample with an acceptable range of expected PSD with 81.3 % less than 45 µm. C: Routine sample displaying an out of range PSD with 64.0 % less than 45 µm. Values in boxes: Relative content of particles below 45 µm.

types used for grinding sample preprocessing purposes. This type of approach also opens up the potential for powerful tool condition monitoring, analytical result validation and prediction of material changes in processes, all subject to further investigations on the nature and information content of observable PAT sensor data.

It is sometimes possible to augment the monitoring potential by also using complementary sensor types. This option, of course, strongly depends on the specific process a.o.[1]

References

1. K.A. Bakeev (Ed.), *Process Analytical Technology*, 2nd Edn. Wiley (2010). https://doi.org/10.1002/9780470689592
2. *Tool Condition Monitoring for Precise Evaluation of Milling Efficacy*. HERZOG Application note 19/2018. https://www.herzog-maschinenfabrik.de/medien/downloads/application-notes/?tx_news_pi1%5Bnews%5D=165&tx_news_pi1%5Bcontroller%5D=News&tx_news_pi1%5Baction%5D=detail&cHash=74499b1b32f353b36dbb98332744dd5d
3. Z. Mzyk, I. Baranowska and J. Mzyk, "Research on grain size effect in XRF analysis of pelletized samples", *X-Ray Spectrom.* **31,** 39–46 (2002). https://doi.org/10.1002/xrs.534
4. *Tool Condition Monitoring of Disc Mills—Monitoring of the Proper Swing Aggregate Function*. HERZOG Application note 25/2019. https://www.herzog-maschinenfabrik.de/medien/downloads/application-notes/?tx_news_pi1%5Bnews%5D=585&tx_news_pi1%5Bcontroller%5D=News&tx_news_pi1%5Baction%5D=detail&cHash=fbedf76ffe19e44b1f03a5aa58201ff2
5. *Tool Condition Monitoring of Disc Mills—Online Monitoring of the Wear of the Grinding Set*. HERZOG Application note 26/2019. https://www.herzog-maschinenfabrik.de/medien/downloads/application-notes/?tx_news_pi1%5Bnews%5D=588&tx_news_pi1%5Bcontroller%5D=News&tx_news_pi1%5Baction%5D=detail&cHash=be5ab495493b53b0c77222ebb7643610
6. J. Weigand, "Viscosity measurement on powders with a new viscometer", *Appl. Rheol.* **9(5),** 204–211 (1999). https://doi.org/10.1515/arh-2009-0014
7. T. Hao, "Analogous viscosity equations of granular powders based on Eyring's rate process theory and free volume concept", *RSC Advances* **5(115),** 95318–95333 (2015). https://doi.org/10.1039/C5RA16706J

doi: 10.1255/tosf.126

Principles of gas sampling: TOS with critical challenges

Anders Larsen[a] and Kim H. Esbensen[b]
[a]**CTO Q-Interline, Denmark. www.q-interline.com**
[b]**Professor, owner KHE Consulting, Denmark. https://kheconsult.com**

Introduction

Sampling and analysis of materials in the gas phase is not covered in general sampling standards and guides, due to the complex nature of the subject matter. Most gas-phase materials exist in the region from ambient temperatures (~300 K) to combustion temperatures typically around ~1200 K. Common to both temperature range margins, though predominantly for hot gases, is the fact that continuous reactions often take place in material that is moving at high speeds, presenting less than trivial challenges to conventional Theory of Sampling (TOS). The purposes of representative gas sampling are many, but three standard cases are presented, covering the most dominating scenarios met with in science, technology and industry.

Volume sampling

Sampling of a nominal gas volume, contained in a bespoke container, suitable with respect to processing and analysis at a different location and/or or at a different time.

In situ sampling

This case has the aim of monitoring a specific gas component under a set of fixed conditions (usually specified by a set of physical parameters). This sampling modus is relevant for gas components or gas-phase phenomena, which are changing or unstable over time, i.e. gas processes that will change, oxidise, adsorb, react or shift balance due to irreversible chemical reactions.

On-line gas analysis

This involves, for instance, securing a representative gas sample in a gas cell, cuvette, chamber or other analytical device, ensuring a representative basis for process monitoring and control.

It will be clear that gas sampling to a very large degree must be addressed on a case-by-case basis. Very often gas samplers must be designed and implemented as built-in sampling valves/fixed piping, often with considerable sample conditioning hardware. Still the TOS must rule supreme.

Classical gas sampling cases

Most gas sampling can be classified as either a "hot" or a "cold" case, which distinction refers to the need to keep the gas temperature above a certain threshold to *avoid condensation*, primarily of water vapour, but other species may also add significantly to the complex dew point issue. Another argument to keep temperature high is the fact that various components only exist above an elevated temperature—a good example being SO_3, which will dissociate an oxygen atom, thus becoming SO_2, below a few hundred degrees Celsius. Thus, the analytical temperature may quickly become a critical issue depending on the gas mix composition.

The most often met with cases of gas sampling are for the following analysis purposes:

- Outdoor air quality (cold)
- Indoor air quality (cold)
- Stack emission monitoring (hot)
- Process gas characterisation or monitoring (hot and cold)
- Combustion gas characterisation or monitoring (hot, very hot)

In the descriptions below annotations in [square brackets] refer to the complement of the TOS sampling errors [SE] vs the total analytical error [TAE]. Focus will naturally be on the so-called "Incorrect Sampling Errors" [ISE], which cause a significant, sometimes fatal *sampling bias.*

There are four [ISE], viz. the Incorrect Delineation Error [IDE], the Incorrect Extraction Error [IEE], the Incorrect Preparation Error [IPE] and the Incorrect Weighing Error [IWE]. The TOS describes how [ISE] that have not been eliminated will give rise to a *sampling bias* which is inconstant, and which, therefore, cannot be corrected for (however desirable). Occasionally there *may* also be sampling challenges caused by the two so-called Correct Sampling Errors [CSE]. These are a function of material heterogeneity and thus [Fundamental Sampling Error (FSE) and Grouping and Segregation Error (GSE)] *may* also influence the total sampling error [TSE], although it is generally assumed (with good reason) that gas mixtures are universally *well mixed*. A special case very far removed from the well-mixed gas paradigm is analysis near a burner in a furnace, in which case pockets of high concentration can be present in semi-stable scenarios presenting a [GSE] challenge when placing a sampling point near such burners.

Delineation of specific gas *analytical errors* is also contained in the text below.

Physical manifestation of gas mixtures

A gas mixture, a gas matrix, consists of several types of chemical species, all under the influence of a set of physical parameters that need special attention to overcome unwanted effects and non-representative sampling [ISE, CSE]. A gas mixture is always comprised by one or more components of the classes below:

- Major gas components (usually present at % levels)
- Trace element gas components (necessarily present at ppm, or ppb, levels)
- Mechanical dust, of three types:
  - Organic dust (bio effluents, pollen, *unburned* organic matter)
  - Inorganic dust (ash, salt, sand)
  - Metal particles
- Aerosols (sub-µm droplets); a case made highly relevant in the era of the coronavirus pandemic.

Typical major gas components would be "classical species", e.g. Nitrogen, Oxygen, Carbon dioxide, Argon, water vapour. The class of major components can be subdivided into *active* and *passive* components. Whereas Nitrogen and Argon, in almost all cases, will act passively, species like oxygen and water vapour may affect, and sometimes react readily with, other major or trace gas components. If this takes place after sampling, significant [IPE] effects will be unavoidable.

Trace components gases are typically present from a maximum of 10,000 ppm (1 %) to as low as ppb (or even ppt) levels. While the list of major components is fairly quickly exhausted, the list of variously interesting trace components is in the hundreds or higher. Trace components can further be subdivided into the subclasses of inorganic and organic species.

Mechanical dust is present in almost all gas mixtures from ng Nm^{-3} to higher levels in the g Nm^{-3} range and may give rise to severe challenges. Besides the purely mechanical effects of blocking, clogging, wear and tear of the sampling tool [IDE, IEE], sub-µm particles may function as "seeds" for forming aerosols/droplets, e.g. causing catalytic effects, thereby *changing* the composition of the gas mixture, both physically as well as chemically [IPE]. Most extractive systems try to avoid the different dust species by *filtering* the gas mixture prior to extraction, i.e. a problem-specific fractionation, which may work well, but careful consideration should be given to a range of potential unwanted effects in the filter (selection and manufacturing of the filter material) as this may cause changes to the sample as well [IEE, IPE].

Aerosols exist in more or less all gas mixtures when a matrix is in a state *below* a complex dew point temperature regimen (actually a series of dew point temperatures), which must be calculated specifically *for each case and specific hardware configuration*. This is especially true when sub-µm dust particles form a seeding basis for aerosol formation. Aerosols may consist of relatively harmless matter, e.g. water, but since many trace components are soluble in water, the aerosols may also easily take on roles much different from harmless [IDE, IEE, IPE] and will then generally be of an acidic nature, causing damages to pipelining, sampling equipment and optics if spectroscopic analytical devices are used.

In general, therefore, a gas matrix is characterised by (at least) the following important features:

- Temperature
- Dew point(s)
- Matrix effects

Passive vs active components

Passive compounds

A gas component that can be analysed *in situ* or extracted, *without* reacting with other gas components or parts of the extraction and analysis system (filter, pipe, cell, cover glass etc.). In practice, this means that the gas sampling and analysis system has been designed in a TOS-informed way, such that the quality criterion is that *no* [ISE, CSE] can occur.

Examples: Nitrogen; Argon (other inert gases)

Active components

A gas component that in general will have a non-neglectable *tendency* to react with *other* gas components to form new compounds [IEE, IPE]. The degree to which the sampling is compromised may vary, and will have to be evaluated by problem-specific consideration or by a pilot experiment (replication experiments or perhaps a variographic characterisation).[1–3]

Examples: Oxygen, various nitrous gases N_xO_y, water vapour, SO_2, SO_3

Aggressive components

A gas component that *always* displays a significant propensity to react with the sampling and analysis systems. This will always cause an *indirect* quantitative effect by reducing the activity of the analyte gas in the sample volume, thereby causing [IEE, IPE].

Examples: HCl, HF, NH_3

Three most common sampling strategies

In situ sampling

In situ sampling and analysis is conducted directly in the gas matrix, for example in a pipeline, in a gas chamber or in open air. *In situ* sensor sampling [for example in the Process Analytical Technologies (PAT) regimen] is based on transmission of a continuous beam of energy across the analytical volume with an illumination source power appropriate to achieve a representative spectroscopic response from the gas component(s) analysed for. Typical optical sources operate from the ultraviolet (UV) to the infrared (IR), i.e. wavelengths from 200 nm to several µm. The analysed gas volume is the volume of the *optical cone* formed by the geometry of the source and detection system. Over time, the risk of sampling volume changes *may* develop, e.g. by condensation, scaling or precipitation, which will cause [IDE, IEE]. Special attention should also be on the fact that it cannot be guaranteed that concentrations are constant at all positions in the "observation cone" giving rise to potential [GSE].

This heterogeneity issue may sometimes make quantitative calculations difficult, arising for two reasons:

i) Lambert–Beer's law states that the optical pathlength, as well as the specific molecular concentration, serve an equally important role with respect to the *total absorption* of the radiation emitted and detected.
ii) Energy absorption is almost always non-linearly related to the concentration, which in practice means that a localised high concentration "pocket" will not necessarily get weighted properly in the cumulative absorption signal recorded at the detector.

The inferred total concentration may then show up as being *lower* than in reality. Such effects are usually considered sufficiently countered by acquiring many (very many) signals over time, strongly relying on a beneficial mixing and averaging effect. N.B. this may, or *may not*, be justified in specific cases, however.

An upside regarding *in situ* sampling is the absence of typical mechanical effects, and abundant "real-time" opportunities. Once this type of sampling has been proved to function according to the desired specifications, the road is open to reliable, representative on-line (in-line) process monitoring and control (PAT). Here the use of variographic analysis will be especially relevant and welcome, see, for example, References 1–3.

Extractive sampling

The objective of extractive sampling is to facilitate removal of a representative sample that is reliably contained and ready for at-line analysis, or which can be transported for analysis in the laboratory or similar. Extractive analysis is widely used, and highly efficient empirical solutions for many sampling systems have been developed for many standard applications, but a series of complex effects must nevertheless still be carefully considered and counteracted where appropriate. Such effects are due to:

- gas physics
- oxidation
- catalysation

- adsorption
- substitution

The most important issue to address regarding extractive gas sampling and analysis systems is related to the governing gas physics, i.e. to the ideal gas equation:

$$P \times V = nRT$$

This famous equation links pressure (*P*), volume (*V*) and temperature (*T*) to the number of molecules (*n*) in a simple linear relationship, i.e. any one parameter cannot be changed without a *resulting* change in one of more of the others. To secure a representative sample in an extractive container for transport or analysis, the "*n*" signifies the number of molecules extracted. This should "obviously" be the same number in a volume of the original gas matrix equal to that of the sample container. This may seem trivial, but if, for example, the pressure drops in the gas matrix, without *concomitant* volume and temperature changes, the number of molecules will actually change as some molecules will drop out of the gas phase and become liquid (condensation) and in this way change the concentration of the analytical aliquot [IDE, IEE, IPE].

Other ways of "losing" molecules are oxidation of a species, NO becoming NO_2 (or reversibly). Such oxidation or oxygen-balance reactions may be catalysed along the walls of the sampling system, for which reason due attention should also be given to the choice of container material. Stainless steel tubes and PTFE hoses are predominantly used in most gas systems, both have distinct advantages and disadvantages, which must be known and considered in the design of a gas sampling and analysis systems.

Various gas components are keen to adsorb and thus form a monolayer on many surfaces [IDE, IEE, IPE]. A building up of immobilised molecules in the sampling system may then contribute to a gradual lowering of the analytical response time, adding a [TAE], and may in the long term even cause harm to the sampling system. Components like HCl, and especially ammonia, are known readily to form such monolayers, *unless* the sampling system is heated and a prescribed level of water vapour keeps the adsorbing species in the gas phase; note that these are active counter measures to ISE and TAE effects. For water vapour, significant hydrogen bonding capability and water molecule electro-negativity effects will typically result in adsorption to the sampling/analysis system walls, blocking out adsorption from other species characterised by less attraction force. If a monolayer of, for example, HCl is present in a sampling system and water vapour is introduced (unintentionally), very high levels of HCl can be released in very short time spans (seconds) giving rise to a large concentration spike, which is *not* a truthful signal pertaining to the matrix under analysis, however.

Finally, an important potential effect is *substitution* and *reaction* with the sampling system materials. At high concentrations, various gas species may *swap* molecules with those of the sampling system. Examples are high-level HCl flowing in PTFE (poly-tetrafluoroethylene) conduits in which Fluorine and Chlorine atoms can be substituted, leading to detectable levels of HF in the analytical system. HF is a very aggressive component and may thus be especially harmful to analytical gas cells made from various glass types and has even been reported to form complex new species with silica.

From the above it is clear that designing a gas sampling and analysis system can be fraught with a range of problem-specific difficulties, ranging from the easy to the extremely difficult, very often requiring considerable in-depth knowledge of gas and mixture physics and chemistry, as well as a professional command of the TOS.

The extraction system

The principal major elements involved in a gas extraction system are shown in Figure 1.

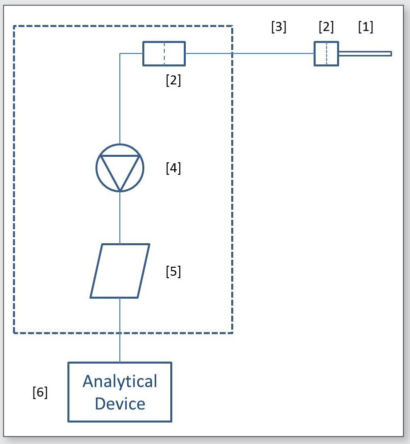


Figure 1. Schematic illustration of a generic gas sampling system. [1] Probe; [2] Filter(s); [3] Transportation lines; [4] Pump; [5] Conditioning system; [6] Analytical device (or storage container).

Probe

The extraction probe consists of a series of elements, not all of which are used in all cases. The main component is the probe head, which is typically placed outside the process containment. Inside the probe head, a filter can be placed if and when appropriate. The filter can be metallic, ceramic or made from other suitable materials, which must be considered from case to case to avoid in-probe reactions. To avoid condensation, the filter can be heated, which is needed for all above-ambient temperature sampling scenarios. To reach into the process, to be able to sample the process, a probe inlet pipe is connected to the head. The material and size/shape of the probe pipe is subject to identical problem-dependent considerations as outlined above. The probe head also works as the necessary link to gas sampling transportation lines. One needs to pay special attention to so-called *cold spots*, which constitute potential locations where unwanted condensation *may* occur [IDE, IEE, IPE]. A gas sampling probe may have the option of a "blow back" facility, for example by mean of a series of solenoid valves. Dust blow back creates a series of bursts of pressurised air with the intention to clean the filter. Another option is an arrangement of valves allowing introduction of a pilot and calibration gas(es) from certified reference gas cylinders with known gas concentration.

In many situations it is necessary to arrange for *iso-kinetic gas extraction* in order to avoid various *influx segregation* phenomena; this is especially critical for two-phase systems like gas–dust, gas mixture–dust, gas–droplets systems etc. This is a sampling aspect which is governed by "classical" TOS considerations, many of which are presented in Reference 2.

Filters (extra)

Wherever appropriate additional filters can, if necessary, be inserted before the analytical equipment. Considerations follow the same principles as outlined above.

Transportation lines

All gas sampling systems need suitable tubes and pipes connecting the probe head to the gas conditioning and the analytical equipment. The most important considerations concern allowing for appropriate temperature conditions and the choice of piping material; other issues concern the diameter and flow regimen necessary to eliminate the kind of [ISE] described above. In general, the best performance of a gas sampling system is achieved when the tube/pipeline diameters, and the gas flow, are kept *constant* throughout the entire transportation length, since a sudden diameter change with a fixed flow may generate unwanted pressure fluctuations, again with the potential of unwanted condensation.

Pump

The pump, or the device to facilitate a pumping effect in case of a venturi pipe, is a very important component in any gas sampling system. The process pressure is often different from standard atmospheric conditions; the pump must, therefore, be able overcome all over- and under-pressure issues, while being able to yield a steady flow through the analytical system before releasing the gas sample into ambient or back into the process. The pump can be inserted either before or after the analytical device, creating a small over or under pressure in the analytical device. Some analytical technologies will be sensitive to pressure changes, since it changes the number of molecules in a given volume.

Conditioning system

The gas conditioning system serves the critical role of setting up, or changing, the physical state parameters of the gas flow, or the gas volume intended for analysis, so that the gas aliquot corresponds with the stipulated requirements of the analytical method/analytical equipment. There may also be a need for conditioning gas samples before extensive transport and/or storage before analysis, as described above.

Analytical device, or gas container

When gas is collected for analysis (or processing) at another location, or time, one is obliged only to use appropriate gas sample containers, thoroughly pretested and validated with regard to the suitability of the materials, which must be chemically non-reactive.

Eventually, if, and if after, *all* the above issues regarding proper sampling, handling, transport, conditioning etc. have been properly dealt with, the representative gas sample arrives at the analytical device. The analytical technology must be *appropriate* for the gas quantification demands at hand. A large number of technologies are available.

Gas homogeneity in time and space

In order to be able to sample representatively in time and space, the fundamental issue is *how to* sample without the debilitating effects from the sampling process itself [ISE], i.e. the TOS' "sampling correctness" imperative, or effects due to the material heterogeneity [FSE, GSE]. There are simple rules that always must be observed even for relatively easy mixable multi-component gas systems.

In the full dynamic context of a combustion process, say, species like oxygen and carbon monoxide are far from evenly distributed in space and time, but will tend to form steady-state spatial *patterns* like that shown in Figure 2, in which is illustrated that fuel injection point(s) will cause a variable oxygen depletion in the core of the flame. Similarly, nitrous gases are also known to form at specific locations, but subsequently they will be reduced in concentration due to oxidation, an example of how the *sampling location* may critically determine the validity of the gas analysis. Likewise, for outdoor or indoor air quality monitoring, odour (or even poisonous bursts of gases from process doors opening and closing) may contribute to create a time-dynamic inhomogeneous gas matrix, inhomogeneous in both time and space.

"Temporal homogeneity" here means the ability to sample/detect *flash* or *spike* phenomena existing for only a short time, but which may well contribute to significant concentration variations with a high impact on hourly average values, for example. It is obvious that temporal homogeneity will be operatively dependent upon a pre-specified time-resolution threshold. When temporal heterogeneity is significant, fast, repeated sampling is needed to map out such variation with accuracy and precision in time. Variographic characterisation is particularly well advised for this type of time-dynamic systems. A variographic pilot experiment may be essential.

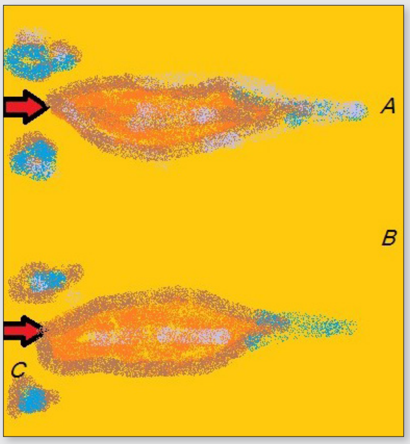


Figure 2. Illustration of alternative deployments of a gas sampling probe inlet. The analytical result from locations A, B or C will not be identical (even though it is commonly assumed that gases are always well mixed).

"Spatial homogeneity" means the ability to sample at one specific point location, or across a given cross-section, and be able to ascertain that such sampling reliably represents the point location intended or the entire cross-section of a gas stream with respect to the relevant components in the mix. Since this is not often the case, for example close to a combustion chamber, in a process reaction vessel or at a specific point location in a factory building, the sampler/analyst must often choose between *point analysis* (in both time and space) or make use of integrated *composite sampling* (which may also be in both time and space, although most often only in time). N.B. it is often *assumed*, quite often without sufficient justification, that gas systems are always "well mixed". Another way out of such heterogeneity problems may be to increase the distance to the source and rely on the inherent mixing in containers and/or pipelines etc. to provide for a less heterogeneous gas matrix. There are also

Gas conditioning system. Photo credit: Q-Interline often issues related to non-contained gas matrices or to specific outdoor situations—common for these contexts are the very real danger of *unwanted dilution*.

Analytical methods, criteria

Many analytical technologies exist for single gases, gas mixtures and for other components in gas matrices. Common to all of them is a set of attributes that must be taken into consideration in order to select an *appropriate* analytical method.

An analytical device is characterised, and should be validated by the following criteria:

- **Specific sensitivity**, i.e. is the analytical tool sensitive *only* to a specific component, or to a general group or type (e.g. hydrocarbons are often reported as total C_nH_m in Methane equivalents).
- **Cross-sensitivity**, normally specified in % of range, is the documented and validated analytical error introduced from *other*, specified gas components.
- **General sensitivity** is the ability to detect *small* changes in concentration.
- **Limit of detection (LOD)** is the smallest *detectable* concentration.
- **Limit of measurement (LOM)** is the smallest *measurable* concentration.
- **Response time T90** is the time for the analytical equipment to reach 90 % deflection when subjected to a high-gradient concentration change.
- **Linearity** is the specification within a concentration range, of how linear the dose–response relationship will be.

Some analysers are designed for single component analysis whereas others are multi-component systems, but the same set of validation criteria apply to all.

The most common quantitative gas analytical technologies are:

Mass spectrometry (MS) is based on the principle of fragmenting and ionising the gas components, after which the sample is introduced to the analytical chamber, in which different molecular fragment masses are accelerated towards the detector. A magnetic field induces differential deflection, resulting in a mass spectrum, allowing for interpretation and quantification. MS may suffer from cross-sensitivity, but can importantly be made sensitive to ppt levels.

Gas chromatography (GC) is based on a separation principle. Introducing a small volume of gas into a very thin pipe, constructed so that different gas components will travel with different velocities, thus coming through the terminal end of the fibre effectively separated from each other. Chromatographic separation may prove useful for complex mixtures of very similar components (e.g. hydrocarbons).

Spectrometry (Vis/UV/IR/FT-IR/Laser) are all technologies making use of the different absorption of energy/light by various molecules. The technologies may be single component non-dispersive infrared-based analysers or multi-component systems based on Fourier transform infrared spectroscopy.[5]

Several other gas analytical technologies exist; the list above is merely to indicate examples, and is in no way exhaustive. The general Process Analytical Technology introduction[4] also treats gas analysis for on-line and in-line purposes, but the full arsenal of potential analysis techniques for use in science, technology and industry is much larger.

N.B. A critical success factor for many gas analytical systems is the common challenge to able to deliver exactly the same volume to the inlet of the analytical device. This challenge has been met with a variety of specific solutions all focused on avoiding potentially debilitating [IWE] effects. Solutions are typically mechanical, or consist of data analytical normalisation, e.g. row-summing of multivariate spectral data in chromatography.

Theory of Sampling: governing principles

The dominating issue in gas sampling, based on the synoptic summary above, is to eliminate (or at least reduce the effects as much as possible) the so-called Incorrect Sampling Errors [ISE], i.e. IDE (Incorrect Delineation Error), IEE (Incorrect Extraction Error) and IPE (Incorrect Preparation Error). There may, or may not be, a fourth incorrect sampling error, IWE (Incorrect Weighing Error), which in the case of gas sampling is equivalent to an error committed when not being able to secure exactly the same gas volume for each sample. It is comparatively rare, however, that this is an important issue with modern gas sampling and analytical equipment. The governing principles for “correct sampling”, i.e. non-biased sampling, are described in the general TOS literature; see references below (and many additional references therein).[1–4]

Benchtop gas analytical setup: a modified IR instrument equipped with the necessary pre-analysis hardware. Photo credit: Q-Interline.

Variographic characterisation of a process gas sampling/analysis system

All gas sampling and analysis systems intended to contribute towards reliable process monitoring and control, must be evaluated and assessed by a *variographic analysis*, the essential features of which are described in References 2 and 3.

Conclusions

Gas sampling is an application field that to a very large degree must be attended to on a case-by-case basis. Very often gas samplers must be designed and implemented as fixed, *built-in* sampling valves/fixed piping, often with dedicated sample conditioning hardware as well. Thus, many of the complex gas sampling issues are very specific and would at first sight appear not to be part of the *standard* TOS curriculum. However, this overview has shown that the *sampling process* for gases, gas mixtures and two-phase systems (g,s) or (g, l) nevertheless always must be in strict compliance with the principles outlined in the TOS, lest several, quite typical sampling errors are equally unavoidable as for all other solid material heterogeneous systems, especially regarding IDE, IEE, IPE, IWE. No application area escapes the demands for representativeness, i.e. TOS will reign supreme also for gas sampling.

But, as has been shown above, there is quite an array of special issues within this field, which only have been introduced here. We would, therefore, like to guide you to the book: *Industrial Sampling Systems: Reliable Design & Maintenance for Process Analyzers* by Tony Waters[6] in which can

continued on page 47

doi: 10.1255/tosf.127

The Theory of Vacuoles and Low-energy Nuclear Reactions

Francis F. Pitard

A new version of Francis Pitard's book, *The Theory of Vacuoles and Low-energy Nuclear Reactions: A Correct System of Dimensions and Units* has just been announced, and is available from the author's website: http://www.fpscsampling.com/publicationsnewsletter/books/. *TOS Forum* is glad to make its readers aware of this publication which takes us all into a very interesting place *inside* elementary particles, which on closer contemplation are claimed not to exist. What in the world of Physics is going on?

Vacuoles

The Theory of Vacuoles was in its infancy until 2010. It was not received in a positive way by sceptical scientists, and with some justification. However, the Alain Aspect experiment performed in 1982 changed everything when it was demonstrated that photons travelling in opposite directions can still communicate at 10,000 times the speed of light. Obviously, we are missing something, and the Quantum Mechanics explanation is far from being satisfactory to many.

The Theory of Vacuoles offered an explanation in its claim that particles as we know them do not exist. Only vacuoles in the Universal Medium give the illusion of particles; there is a huge difference. It requires a complete change of paradigm, which is always a challenging proposal for many scientists.

In a nutshell, the Theory of Vacuoles says that there are no photons separated by long distance that can communicate at 10,000 times the speed of light. Instead, the two so-called photons are the same identity, the Universal Medium activated by waves and waves only, through Universal Entanglement. Basically, matter as we know it is an illusion and, frankly, a beautiful one.

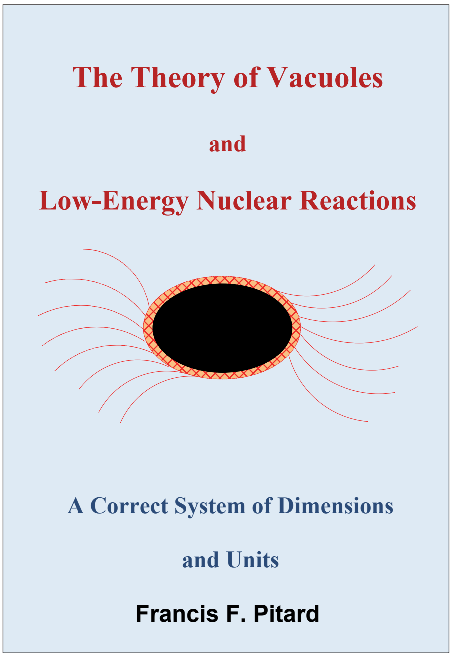
Charles Oliver Ingamells, a good friend of mine, who did most of the work on the Theory of Vacuoles quickly found out that our systems of units (SI) and dimensions is not appropriate for Nuclear Physics, and suggested a far simpler system in line with the thoughts of Sir Arthur Stanley Eddington. The problem was not because a system like SI was better than an older system such as CGS; frankly any system can do. It was more that the existing SI system is unnecessarily complicated. The SI system is based on facts that are acceptable. e.g. in relation to building a car, but unacceptable to visualise so-called particles. This undeniable fact has been hiding important properties about so-called particles that is interfering with effective scientific progress.

In the suggested new system (the topic of Chapter 3), all values for the "fundamental" physical constants are absolute, except the so-called *time-thickness constant*, *t*. This book demonstrates in an unambiguous way that Time, Mass, Permeability and Permittivity are relative concepts and do not need units of their own. It is also demonstrated in an unambiguous way that the electric charge is a surface area, and this alone is a big development for Physics. In the suggested new system, all physical constants can be expressed in terms of 1, 2, 3, ϖ and *t*. Coincidence? Most certainly not!

The mass of the electron is an established physical constant, as is the mass of the proton. The ratio m_P/m_e is about 1836. No one has been able to explain this ratio. Louis De Broglie, one of the brightest Physicists who ever lived, explored the problem and concluded that "The problem of mass is very difficult, and one cannot say when or how it will be solved".

In Chapter 7, the new book provides a clear answer!

The electron shell that surrounds the central vacuole, or vacuoles, is mostly outside our three-dimensional universe. Only that fraction of the electron that lies inside our universe affects our mass measuring devices. The electron has the same mass as the proton, but is inside our universe only 1/1836 of the time. However, the positron is the mirror image of the electron: think about it! Would it be conceivable that the positron and proton, which carry exactly the same charge, and, therefore, the same surface area (**coincidence?**) are actually exactly the same thing? That would change a lot of things in Physics, but these findings are undeniable. Perhaps, this fascinating coincidence is the key to better understand or predict Low Energy Nuclear Reactions?



The Theory of Vacuoles

and

Low-Energy Nuclear Reactions

A Correct System of Dimensions

and Units

Francis F. Pitard

Chapters 8 and 9 may appear more controversial at first glance, but the end product of this work is exposed in Chapter 10.

From this chapter, we can find a several very interesting observations that can be related to other observations made by many people around the world, such as:

- Possible Low Energy Nuclear Reactions taking place between hydrogen and some nickel isotopes
- Possible transmutations from Potassium to Calcium
- Explaining the awesome power of forest mycelium
- Speculating on a possible alliance between Carbon and Silicon networks
- The proportion of mercury isotopes used in CFL bulbs does not match the normal proportion of mercury isotopes found in nature

- Lithium batteries catching on fire for no apparent reason

This list could go on. The question is: why is it that all these suspicious observations actually match this new classification based on the natural stability of isotopes in a most remarkable way? Coincidence? Most certainly not! This analysis is far from perfect, however, all along, we must have done something right, worth far more work.

Finally, we all jump from our limited 3-dimensional universe to something far bigger, and perhaps, revive the old Sir Fred Hoyle works in astronomy that make far more sense when using the Theory of Vacuoles.

A word of wisdom: the message in this book should not be taken as a criticism of the Physics Establishment. This is most certainly not the case; the authors of this book respect immensely the wonderful works of many scientists around the world. We are only pointing at some details that may have escaped observation for too long. We are trying to help to *see*—in a humble way.

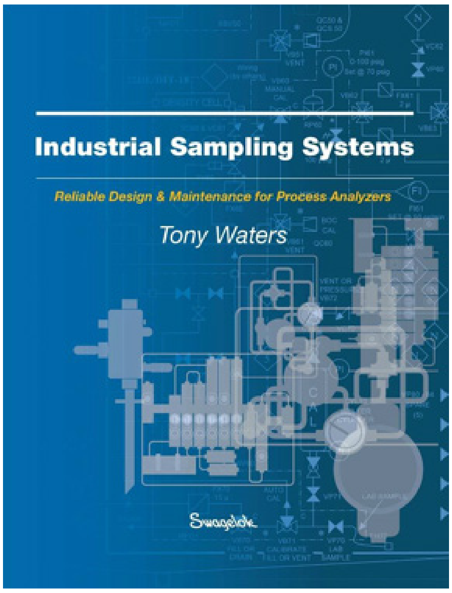
---

continued from page 45

be found a plethora of design, implementation, operational and other aspects also pertaining to gas sampling, substantiated by a vast catalogue of practical examples and experiences. We strongly recommend this book as a powerful complement to the full set of principles for representative sampling (TOS). An overview of the book can be found in Reference 7.

References

1. K.H. Esbensen, *Introduction to the Theory and Practice of Sampling*. IM Publications Open (2020). https://doi.org/10.1255/978-1-906715-29-8
2. K.H. Esbensen and P. Mortensen, "Process sampling (Theory of Sampling, TOS) – the missing link in Process Analytical Technology (PAT), in *Process Analytical Technology*, 2nd Edition, Ed by K.A. Bakeev. Wiley, pp. 37–80 (2010). https://doi.org/10.1002/9780470689592.ch3
3. R.C.A. Minnitt and K.H. Esbensen, "Pierre Gy's development of the Theory of Sampling: a retrospective summary with a didactic tutorial on quantitative sampling of one-dimensional lots", *TOS Forum* **7,** 7–19 (2017). https://doi.org/10.1255/tosf.96
4. K.A. Bakeev (Ed.), *Process Analytical Technology*, 2nd Edn. Wiley (2010). https://doi.org/10.1002/9780470689592
5. J. Bak and S. Clausen, "FTIR emission spectroscopy methods and procedures for real time quantitative gas analysis in industrial environments", *Meas. Sci. Technol.* **13(2),** 150–156 (2002). https://doi.org/10.1088/0957-0233/13/2/302
6. T. Waters, *Industrial Sampling Systems: Reliable Design & Maintenance for Process Analyzers*. Swagelock (2013). http://bit.ly/IndustrialSampling, ISBN: 978-0-615-73250-3
7. T. Waters, "Analytical sampling from industrial processes", in *Encyclopedia of Analytical Chemistry*, Ed by R.A. Meyers. Wiley (2017). https://doi.org/10.1002/9780470027318.a9618



Tony Waters and Swagelok have published *Industrial Sampling Systems*, a comprehensive book covering the engineering involved with designing and operating a sampling system for a process analyser. The book has 750+ pages of full-colour technical content in a hardbound cover, organised into twelve chapters with three detailed appendices and 1000+ photos, tables and drawings.

The book covers:

- Introduction to sampling
- The core principles of sample system design
- Evaluation and design of sample transport lines
- Location and design of process sampling taps
- Preconditioning the process sample
- Controlling sample flow
- Controlling sample pressure
- Sample temperature control
- Change of state
- Sample conditioning and disposal
- Sample isolation and switching systems
- The future of process sampling

This book focuses on important design characteristics of sampling systems for process analytical measurements. Design principles that are essential to the success of any process analyser installation are discussed in full, as are the consequences of neglecting those principles. The application of sampling principles to homogeneous and heterogeneous process streams is considered in detail, as are the calibration and validation procedures, the maintenance concerns and the necessary safety precautions.

50 YEARS OF SAMPLE PREPARATION EXCELLENCE

ROCKLABS

Rocklabs has been a world leader in sample preparation equipment since 1969, with our reliable products perfect for any lab - big or small.

Rocklabs was founded over 50 years ago and began exporting sample preparation equipment, with our range of crushers and pulverisers becoming industry favourites globally. We've since adapted to varying global challenges, moving with the times by cultivating new and innovative disruptive technologies to bring to the market. Rocklabs has grown from the simple bench top equipment of 1969 to large-scale fully automated systems as part of the Scott Technology group. Automated solutions from Scott are the key to quality, productive, flexible processes, with improved safety through smart design, and a continual focus on developing world leading technologies that meet the specific requirements of our customers. Scott will continue to develop, collaborate and add value to our clients with our high quality Rocklabs products, carrying on the legacy and vision of our founder, Ian Devereux.