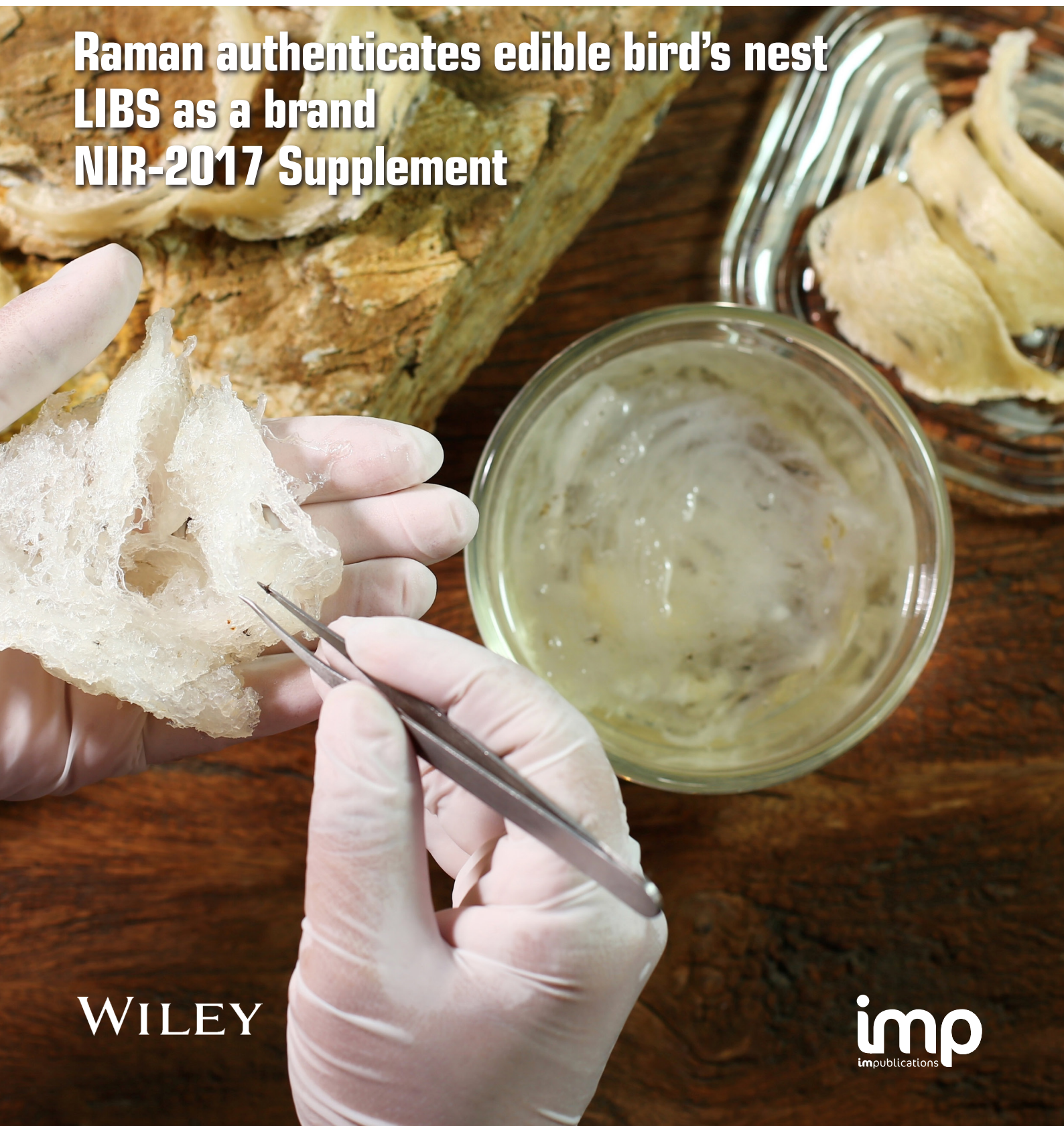


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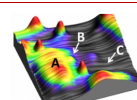
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I would like to start this issue by drawing your attention to the page opposite and the fact that *Spectroscopy Europe* has a new website hosted on a new, faster server. Please do take a look, and update your details. Whilst we have transferred your details to the new site, we have been unable to move your password from the old site due to security settings; sorry. So, if you have not done so already, you will need to follow the guidance opposite to retrieve/set a password. I know this is always a nuisance, so Option 2 is always there! We would also be delighted to hear comments/suggestions/problems that you would like to pass on; please feel free to e-mail me at ian@impublications.com.

The first article in this issue is by Vince Palleschi, who has taken a slightly different approach to reviewing the current state of laser-induced breakdown spectroscopy (LIBS) in "If laser-induced breakdown spectroscopy was a brand: some

market considerations". Vince puts the strengths and weaknesses of LIBS in context and gives some examples of industrial applications.

Eric Shim and Soo-Ying Lee describe "Raman microspectroscopy is a rapid technique to authenticate edible bird's nest—a glycoprotein". Whilst many readers may not be familiar with edible bird's nest (EBN), the article shows yet another way in which spectroscopy is used to detect adulteration of food and prevent fraud in a quick and cost-effective manner.

Tony Davies and Marcel Simons start the columns in this issue with "Day-to-day inorganic nuclear magnetic resonance spectroscopy". Tony is delighted to find out how much easier it is nowadays to measure inorganic nuclei with NMR spectroscopy.

In the Quality Matters column, Chris Burgess and John Hammond look at "Instrument qualification: a possible qual-

ity by design-based approach". Chris and John look back 40 years to the start of GLP regulations and consider how closely qualification processes are aligned to quality by design principles.

In the Sampling Column, Kim Esbensen and Claas Wagner are on the move with "Introduction to process sampling". Having developed a sound theoretical understanding of representative sampling and the Theory of Sampling, more practical applications are now considered.

There is also a Supplement for the NIR-2017 conference and exhibition in the centre pages, and information on our report on new products at Pittcon 2017, which you will find in its entirety on our new website.

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Edible bird's nest being cleaned. There are a number of ways adulterants that can be introduced for commercial gain, but Raman microspectroscopy can detect many of them. Find out more in the article starting on page 10.

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Vol. 29 No. 2
April/May 2017

ISSN 0966-0941

CONTENTS

3 Editorial

6 If laser-induced breakdown spectroscopy was a brand: some market considerations

Vincenzo Palleschi

10 Raman microspectroscopy is a rapid technique to authenticate edible bird's nest—a glycoprotein

Eric K.S. Shim and Soo-Y. Lee

14 Tony Davies Column: Day-to-day inorganic nuclear magnetic resonance spectroscopy

Antony N. Davies and Marcel Simons

18 NIR-2017 Supplement

Exhibition Guide and Programme

22 Quality Matters: Instrument qualification: a possible quality by design-based approach

C. Burgess and J.P. Hammond

26 Sampling Column: Introduction to process sampling

Kim H. Esbensen and Claas Wagner

31 Pittcon report 2017

Ian Michael

32 Product Focus on Atomic Spectroscopy

32 New Products

35 Diary

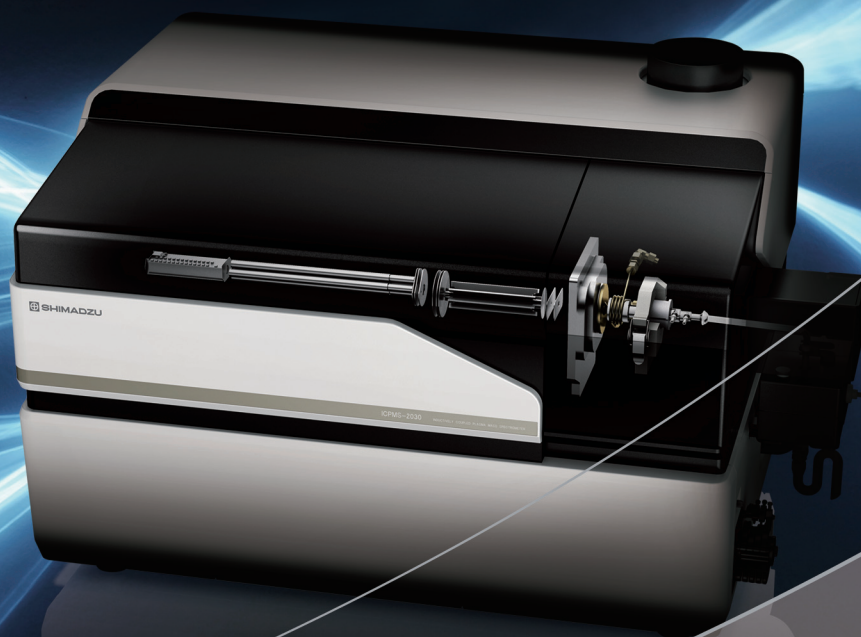
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If laser-induced breakdown spectroscopy was a brand: some market considerations

Vincenzo Palleschi

Applied and Laser Spectroscopy Laboratory at ICCOM-CNR, Pisa, Italy. E-mail: vincenzo.palleschi@cnr.it

I have worked in laser-induced breakdown spectroscopy (LIBS) for more than 30 years. In fact, I was one of the first in Europe to work with this “new” technique. I was also, in the year 2000, the founder of the LIBS international conference that was held last year for the ninth time in Chamonix, France, while in June, this year, I will be the chairman of the 9th Euro-Mediterranean Symposium on LIBS in Pisa, Italy.¹ I have published about 100 scientific papers on LIBS, had my experience with LIBS patents and used to collaborate with a small local firm for the development of LIBS instruments. All of these things would have probably granted me, if LIBS was a brand, a chair on the Board of Directors of the Company, and this makes me wonder what I would have done, in my new (fictional) position.

The first thing I would consider would be the opportunity of cashing in my shares and spending the rest of my life going fishing somewhere around Europe. However, as a matter of fact, I do not like fishing; moreover, the LIBS shares seem to have shown a constant growth trend over these last years, so I probably would keep my position, trying to maintain and hopefully increase my 30 year-long investment. Over these decades, however, I have experienced all the phases of the development of the LIBS brand: enthusiasm, disappointment, hope, in more or less regular cycles. How could I be sure that the powerful Bull of today would not turn, tomorrow, in a sad Bear?

In the business world, it is often repeated that brand managing is, basi-

cally, developing, realising and maintaining promises. In this sense, the LIBS brand promise was, since the beginning, very clear: LIBS is an elemental analytical technique that does not require any sample treatment, as inductively-coupled plasma–optical emission spectroscopy requires, can analyse non-conducting samples that Spark-OES cannot analyse and is not limited to the analysis of heavy elements, as X-ray fluorescence is. Moreover, LIBS can be used in standardless mode to obtain precise analytical results without the use of any reference sample; it can perform surface analysis with a spatial resolution of a few micrometres, and in-depth analysis with sub-micrometric resolution. These peculiar characteristics of the LIBS brand come from a brilliant (pardon the pun) idea: the pulse of a laser (usually in the range of a few nanoseconds) is focused on a small region of the sample (usually in the range of a few square micrometres) to realise AT THE SAME TIME the sampling of the material, through the process of laser ablation and its excitation, through the formation of a hot (although short lived) plasma which emits in the range of near ultraviolet/visible/near infrared. The plasma light is then collected and spectrally analysed using spectrometers similar to those used in ICP-OES or spark-OES (see Figure 1).

If LIBS was a brand, the Marketing Department of our fictional Company would often remind us on the Board that the features described above are unique to LIBS, making LIBS definitely more competitive than other analytical techniques in the field of elemen-

tal analysis. In fact, they launched a massive advertising campaign for LIBS after the LIBS 2000 Conference in Pisa. Unfortunately, the returns from this campaign were relatively small. Actually, after the initial enthusiasm, the market became increasingly hostile towards the LIBS brand, and our shares reached their historical minimum. Our brand probably suffered the consequences of the large imbalance between the advertising and the information given to our would-be customers. It seems as we forgot to tell LIBS potential users that all the definite advantages of LIBS are associated with definite drawbacks, too. A large part of the success of ICP-OES as an analytical technique, for example, is associated with the possibility of treating the sample for pre-concentrating, for example, a given analyte or for avoiding or limiting the matrix effect. The quantity of material analysed, in general, is large enough to guarantee a good representativeness of the analytical results, as well as a good signal-over-noise ratio in the spectra. On the other hand, the high spatial resolution of LIBS means that only a few nanograms of material are sampled, in a laser shot. This makes it extremely difficult to compare the results of LIBS analysis, which gives information about very small regions of the samples, with the established laboratory analytical techniques, operating on a much larger scale. An example of the danger of comparing the results of a micro-analytical technique, such as LIBS, with conventional macro-scale analysis is illustrated in Figure 2. The figure shows the distribution of lead (bright spots) in

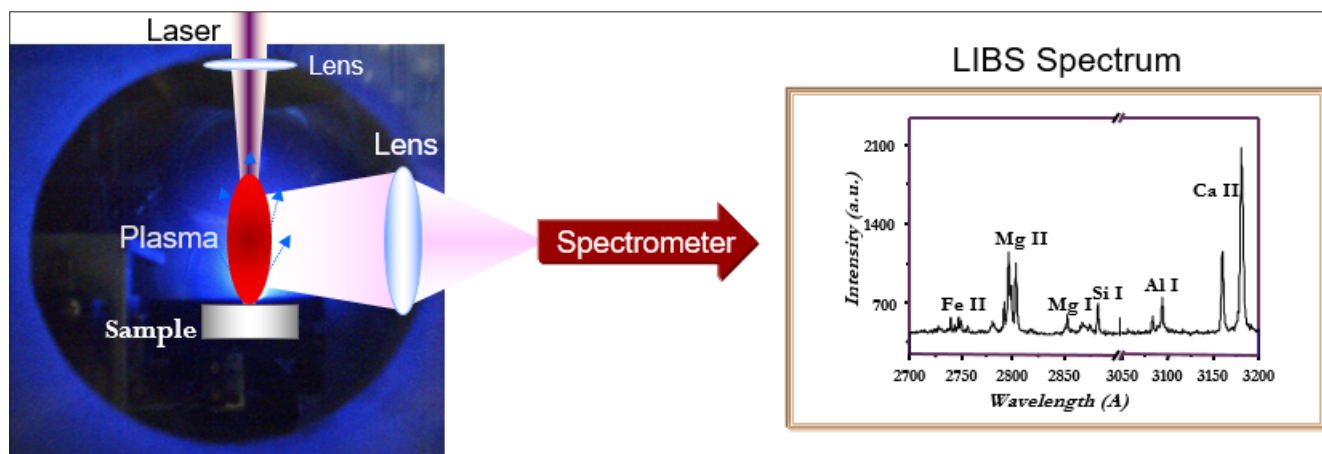


Figure 1. Schematics of a LIBS experiment.

a steel sample; the map (50×50 points on a 1 cm^2 surface, size of the LIBS crater = $20 \mu\text{m}$) shows the inhomogeneity of the sample. This feature of the sample cannot be detected with other more conventional macro-scale laboratory techniques, which would only give the average concentration of Pb in the sample. Nevertheless, in the analytical chemistry community the large variability of the LIBS signal would be probably attributed to an intrinsic “irreproducibility” of the LIBS technique and not to the physical characteristics of the sample.

The limited amount of matter ablated in a single laser shot is responsible for the other important drawback of the LIBS technique: its poor sensitivity. In

that respect, if LIBS was a brand, distinguished members of the Board would have probably already pointed out that the limits of detection (LOD) of LIBS are generally poor only when the concentrations are considered. In absolute terms, mass LODs of LIBS are exceptionally high; however, in most laboratory applications the amount of sample is, in general, relatively large. Therefore, the possible customers of the LIBS brand hardly accept the fact that only a minimal part of the available sample is actually used for the LIBS analysis, completely wasting the performance of the technique with respect to other more conventional laboratory techniques.

For laboratory use, it seems that the better positioning of our fictional LIBS brand would thus be in the niche of elemental micro-analysis and compositional imaging, where the limited mass ablated per laser shot is not a drawback, but on the contrary becomes a definite factor of merit. Other interesting approaches suggest the use of LIBS together with laser-ablation ICP mass spectrometry, for a better analytical determination of the light hard-to-ionise elements.² More recently, the use of surface-enhanced³ or nanoparticle-enhanced LIBS techniques has been proposed.⁴ It is probably too early to forecast the market’s reaction to these new proposals; the results reported seem very interesting, but the risk of radically changing the characteristics of the LIBS brand, going back on the fundamental promise of a technique that would not require any treatment of the samples, is very high.

Five years ago, interest in LIBS technology suddenly rocketed (excuse the pun, again) as a result of the NASA Curiosity Mars mission. The Curiosity rover, which landed on Mars in August 2012, hosts a LIBS remote spectrometer, which has been continuously sending LIBS spectra back to Earth since then. It is an interesting paradox that the Curiosity LIBS instrument produced a greater impact on Earth than on Mars. Using the same technology tested on Mars, a number of hand-held LIBS instruments were introduced to the market and the analytical

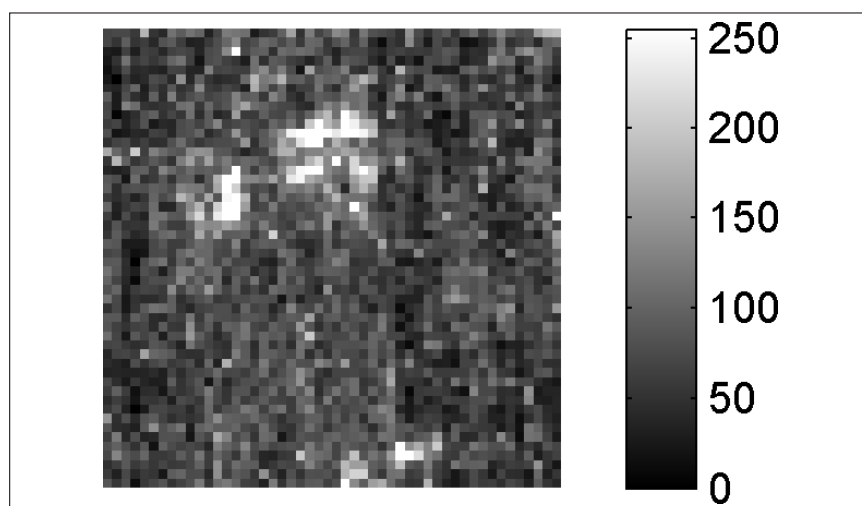


Figure 2. Compositional map of a steel sample. The bright points correspond to higher concentrations of Pb.

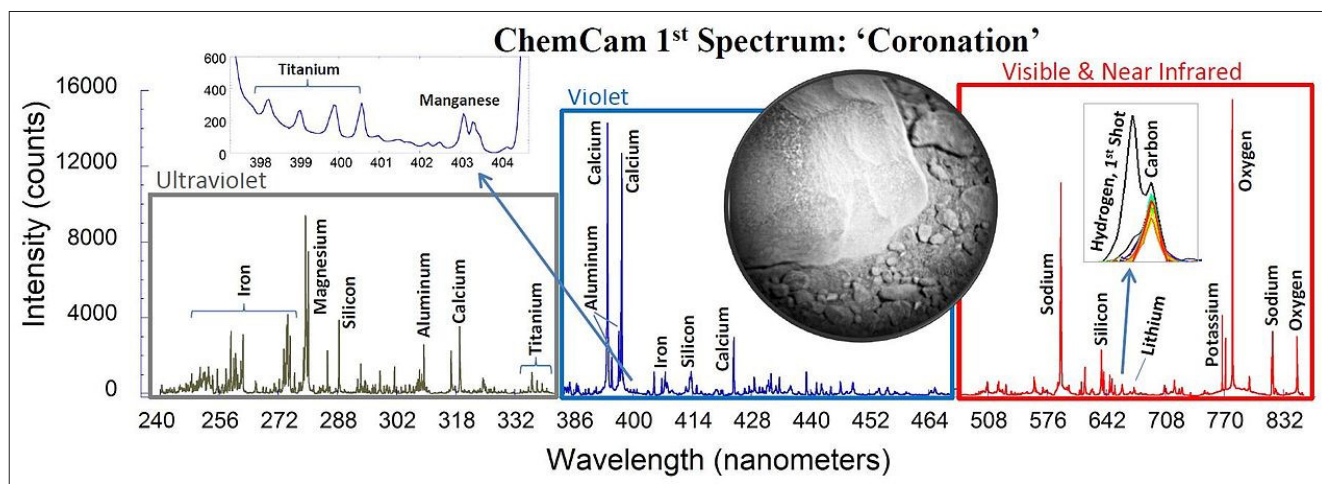


Figure 3. The first LIBS spectrum taken on Mars by the ChemCam instrument (NASA/JPL-Caltech/LANL/CNES/IRAP, © Public Domain).

community suddenly realised that other intrinsic characteristics of the LIBS technique (the possibility of performing very fast and remote analysis, for example) were not only appropriate for zapping Martian rocks, but also for analysing, among other things, the world outside the laboratory.

Industrial applications of LIBS

In fact, a number of application of LIBS to "real world" situations have been reported. In most cases, however, the results reported were just "proofs of principle", usually funded by public organisations in Europe or abroad, which lasted for the duration of the project and did not make a significant impact on the industrial sector. My feeling is that the situation is going to change quickly. Even considering the difficulties of introducing new control technologies in industry, it is undoubtable that the intrinsic capabilities of LIBS make this technique extremely interesting for real-time control of industrial processes. Even our people at the Marketing Department would suddenly realise that LIBS could be extremely competitive, in situations where no other competitor exists.

My group, the Applied and Laser Spectroscopy Laboratory of ICCOM-CNR, in Pisa, Italy, has recently been involved in three major projects for the on-line analysis of coal, steel and automotive scraps. The common features of these projects (one funded by a private

company, the other two supported by the European Commission) involved the need to determine the composition of objects moving on a conveyor belt, at a distance ranging from 1 m to 8 m. To the best of my knowledge, no other viable technology would allow the real-time analysis of such objects, at a distance and without sampling.

One of these projects seems to be particularly promising, because the use of LIBS did not just improve a previously established process, but allowed the realisation of what was previously impossible to realise. I am thinking of the SHREDDERSORT (Selective Recovery of non-Ferrous Metal Automotive Shredder by Combined Electromagnetic Tensor Spectroscopy and Laser-Induced Plasma Spectroscopy) project, funded by the European Commission in the 7th Framework, which was aimed at the development of a LIBS-based sorting procedure for recovering and recycling non-ferrous scraps from the automotive industry.⁵ The average European car produced in the sixties was heavy, about

80% of it was made of iron; aluminium was 2% of the total weight. The oil crisis and the environmental concerns of the seventies encouraged a reduction of car consumptions and emissions. One of the strategies to reach this goal was a decrease in the weight of the vehicles; in the mid-eighties an average European car was made of about 70% of iron and 4.5% of aluminium. In the year 2000, the percentage of aluminium increased

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Figure 4. Some aluminium scraps used for laboratory tests in the SHREDDERSORT project.

ficial neural network approach, which we have tested in factory conditions (uncleaned samples of irregular shape, moving at a speed of 2 m s^{-1}); a 90% accuracy in the classification of the samples was obtained. We believe that these results can lead the way to a new approach for the recovery and sorting of the non-ferrous fraction of automotive scraps. LIBS allowed to obtain this not just improving an existing technology, but creating a completely new way of analysing, sorting and recycling the automotive scraps. I am sure that the future of LIBS will show many other examples of new industrial processes built around the unprecedented capabilities of this technique.

So, even if LIBS is not actually a brand, and there are no LIBS stocks on the market, believe me, if it was, this would be the right time to buy!

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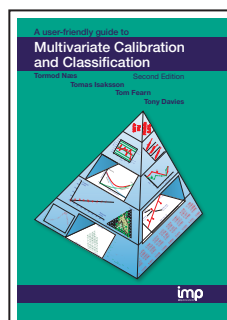
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to 8% of the total weight of the vehicles, while the content of ferrous materials decreased to around 65%. Considering a life-span of about 15 years, this should be considered as the average composition of the vehicles reaching their end of life nowadays.⁶ The amount of waste generated by the European automotive industry is estimated to have been around 14 million tons in 2015 and 8% of this shredder corresponds to non-ferrous metals. None of the existing sorting technologies is able to sort the light fraction of these metals (Al and Mg), which consequently must be down-graded to produce cast aluminium. In the next few years, the production of primary Al will increase by 25% unless new technologies can enable the recovery of aluminium in the form of wrought alloys. The SHREDDERSORT project has successfully demonstrated the possibility of sorting untreated scraps of irregular shape, moving at the speed of 2 m s^{-1} on a conveyor belt, using a LIBS system operating at a distance of 1 m.

One of the main difficulties of the SHREDDERSORT approach is related to the surface nature of the LIBS analysis. When analysing moving objects, the laser pulse always samples points on the surface. This is fine when analysing homogeneous objects, but becomes a

problem in the presence of surface dirt, or corrosion or, even worse, paint coatings (see Figure 4).

The same problem occurs in steel and coal analysis; it can only be overcome by using sophisticated experimental strategies and analytical approaches. In the SHREDDERSORT project, we faced the problem using a two-step approach; in the first step, the wrought aluminium fraction is quickly separated from the cast, based essentially on its silicon content (silicon content is typically higher than 5% in weight in cast aluminium). After that, a second round of multi-elemental analysis of the wrought fraction allows the kind of alloy (3xxx, 5xxx, 6xxx and 7xxx) of each scrap and the subsequent recycling strategy to be determined. The sorting of wrought aluminium scraps in the corresponding classes is achieved using a "fuzzy" arti-



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Raman microspectroscopy is a rapid technique to authenticate edible bird's nest—a glycoprotein

Eric K.S. Shim and Soo-Y. Lee*

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Introduction

Edible bird's nest (EBN)

Edible bird's nest (EBN) is one of the most costly food products of the Orient. EBN is especially valued by the Chinese as a quintessential food for its reputed health benefits, and has been documented in scientific publications since the last century.¹ Cleaned EBN, retailing for a few thousand US dollars per kg, has sometimes been referred to as the "Caviar of the East", but it has neither a relationship to, nor the appearance of fish eggs. The trade in EBN is estimated to be worth a few billion US dollars annually, with a large market, particularly in China. The swiftlet species that builds the EBN is native to South-East Asia, with Indonesia, Malaysia and Thailand the top three largest suppliers of EBN.

EBN is built strand by strand over a period of about a month using a viscous liquid secreted from a gland under the tongue of the swiftlet, primarily *Aerodramus fuciphagus*, during the breeding period. Unlike saliva, the secretion is for nest building and has no known digestive function. The bird interweaves feathers between the strands to form a strong composite material to hold the weight of a pair of nestlings and the parent birds. The nest is cleaned of feathers and other visible impurities before being sold in the market as cleaned EBN. Due to the high cost and driven

by a profit motive, producers are often tempted to introduce edible adulterants into the cleaned bird nest.

EBN has been shown by proximate analysis to be a glycoprotein containing around 63% protein, 26% carbohydrate, 8% moisture, 2% ash/mineral and 1% lipid.² The protein is made up of 17 types of amino acids: serine, valine, isoleucine, tyrosine, aspartic acid, asparagine, glutamic acid, glutamine, phenylalanine, arginine, glycine, threonine, alanine, lysine, histidine, leucine and methionine. The major carbohydrate saccharides are galactose, *N*-acetylneuraminic acid (Neu5Ac, a sialic acid), *N*-acetylgalactosamine (GalNAc), *N*-acetylglucosamine (GlcNAc), mannose and fucose.³

Adulteration of EBN

The common edible adulterants introduced into EBN can be classified into two types: Type I adulterants (e.g. tremella fungus, coralline seaweed, agar, fish bladder and pork rind) are water-insoluble with a similar external appearance to EBN and can be adhered to the surface of EBN strands; and Type II adulterants (e.g. sucrose, glucose, hydrolysed collagen and monosodium glutamate) are water soluble and can be absorbed within the EBN cement to form a uniform composite material on drying.⁴ The externally adhered Type I adulterants can be detected with a microscope and sepa-

rated out for analysis, but not the Type II adulterants that have been incorporated into the EBN cement since the final product looks exactly like the unadulterated EBN.

Some laboratory techniques such as metabolite mapping,⁵ gel electrophoresis (GE)⁶ or enzyme-linked immunosorbent assay (ELISA),⁷ allow us to check for the authenticity of EBN, but they are slow, destructive, require bulk sample sizes and may require specialised personnel to perform the analysis.

Raman microspectroscopy

Raman spectroscopy is a simple, rapid, direct, requiring no sample preparation and non-destructive method to provide molecular information on a sample with good sensitivity and specificity. It is a light scattering technique that gives a molecular vibrational "fingerprint" of the chemical bonds present and thus allowing us to identify and quantify the chemicals in a sample. The laser beam and optical microscope allow focusing on a microscopic sample area of a few μm in diameter. The ease of use and the fact that it is not affected by the presence of water in a sample makes Raman microspectroscopy an increasingly important tool for characterisation and quality control in the food industry. It is an ideal tool for the study of EBN where moisture is present in the sample.

Materials and methods

EBN and adulterants

Raw, white EBN samples were obtained from bird houses in widely separated geographical locations in South-East Asia—West Malaysia, East Malaysia and Indonesia. All adulterants were purchased from commercial sources. In the preparation of samples with Type II adulterants, EBN was soaked in 2% to 10%, (w/w) aqueous solutions of sucrose, glucose, hydrolysed marine collagen or monosodium glutamate (MSG) overnight and air-dried to constant weight.

Raman microspectroscopy

Raman spectra were collected with the Ramantouch microspectrometer (Nanophoton Inc., Japan) under the same collection conditions (785 nm laser, LU Plan Fluor 20X, 600 gr/mm, 140 mW, 60 s) at 24°C. Every sample was measured in triplicate over different spots and all the Raman spectra were baseline corrected with Origin Pro 8.0 (OriginLab Corp., USA).

Results and discussion

Unique Raman spectrum of EBN

EBN made by the same species of swiftlets (*Aerodramus fuciphagus*) from different geographical locations show a unique Raman spectrum (Figure 1), where the Raman spectra are overlapped, indicating that they were made of the same material.

As EBN is a glycoprotein, Raman bands attributed to protein and carbohydrate can be observed and were assigned using spectral data of other glycoproteins,⁸ *N*-acetylneuraminic acid,⁹ tyrosine¹⁰ and collagen¹¹ as reference. The strong Raman bands that can be attributed to the protein component are: 1671 cm⁻¹ (amide I), 1446 cm⁻¹ (CH deformation) and 1241–1262 cm⁻¹ (amide III). Various Raman bands of the saccharides, particularly sialic acid or *N*-acetylneuraminic acid (Neu5Ac), *N*-acetyl-glucosamine (GlcNAc) and *N*-acetyl-galactosamine (GalNAc) can be seen. Some of the bands for the saccharides overlap with those for the

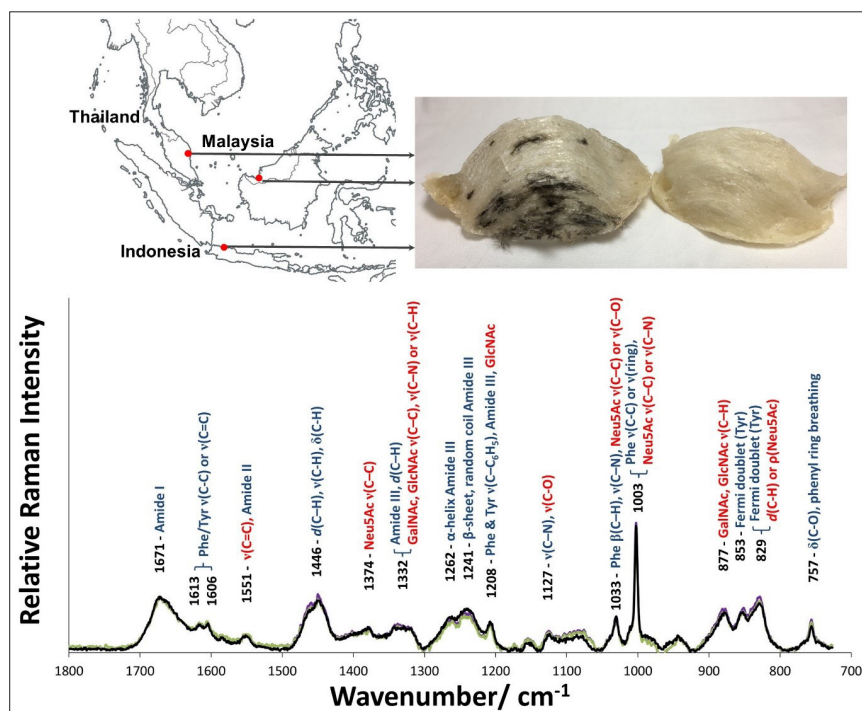


Figure 1. Top panel: Map of South-East Asia showing the geographical locations of Kuantan (West Malaysia), Kuching (East Malaysia) and Jakarta (Indonesia) where the EBN samples came from. Lower panel: the unique Raman spectra of EBN, shown overlapped, can be used as a standard for authentication. Peptides bands are shown in blue and saccharides in red, showing that EBN is a glycoprotein. (ν —stretching; α —out-of-plane bending; β —in-plane bending; δ —scissoring; ρ —rocking; d —deformation).

protein. In particular, the strong intensity of the 1003 cm⁻¹ Raman line, with relative peak intensity about 2.2 times that of the amide I band, has contributions from both the ring vibration of phenylalanine (Phe) and the C–C and C–O stretches of sialic acid. From the Raman spectra of pork rind, fish bladder and hydrolysed marine collagen, which lack sialic acid, we deduce that phenylalanine contributes about the same intensity as the peak of the amide I band, and so about 55% of the intensity of the 1003 cm⁻¹ Raman line in EBN is due to sialic acid. The unique Raman spectrum of EBN, using the band frequencies and the relative intensities of the bands, can be used as a standard for authentication.

Raman spectra of surface adhered Type I adulterants

Raman microspectroscopy allows measurements to be made over a microscopic area. Edible, surface adhered Type I adulterants (e.g. tremella fungus, agar,

coralline seaweed, pork rind and fish bladder) can be picked up by a microscope as there are significant differences in their microscopic images as compared to EBN which is characterised by translucent strands of 1–2 mm thickness. The microscopic images of the Type I adulterants and EBN are shown in the right panel of Figure 2.

The Raman spectra in the left panel of Figure 2 show that Raman spectroscopy can distinguish between the polysaccharides (e.g. tremella fungus, agar and coralline seaweed) which lack amide bands, the polypeptides (e.g. pork rind and fish bladder) with strong amide bands and EBN, a glycoprotein, with amide and saccharide bands. EBN has a particularly strong 1003 cm⁻¹ Raman line due to phenylalanine and sialic acid, and a strong 830 cm⁻¹ line due to sialic acid. Pork rind and fish bladder do not have sialic acid, and the weaker 1003 cm⁻¹ Raman line is due to phenylalanine only; they also do not have the 830 cm⁻¹ line. Instead, they show a medium intensity

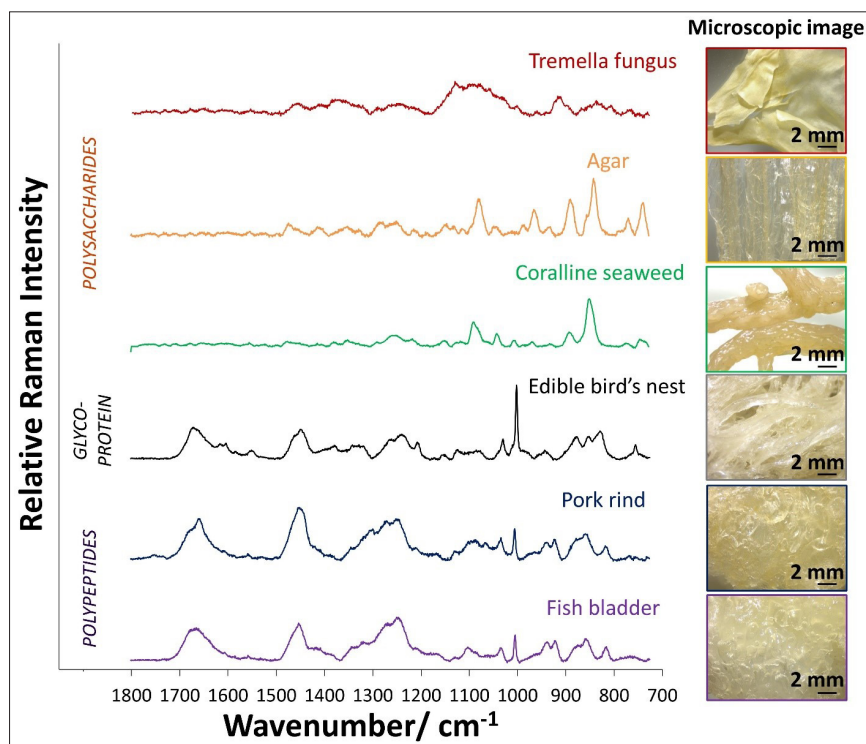


Figure 2. Left panel: Raman spectra of Type I adulterants, which may be polysaccharides or polypeptides, in comparison with EBN. Right panel: microscopic images of Type I adulterants and EBN.

line at 810 cm^{-1} which is due to C–O–C stretching from lipids.

Raman spectra of composites of EBN with Type II adulterants

EBN can soak up an aqueous solution of edible Type II adulterants [e.g. sucrose, glucose, (hydrolysed marine) collagen and MSG] which upon drying gives a composite material that looks like unadulterated EBN. Any substance that is water soluble, forming a clear solution, can be a Type II adulterant to form a composite with EBN. The uptake of adulterants in the dried composite EBN as a function of the concentration of adulterant solutions used are shown in Figure 3, and we have used a quadratic least square fit of the data, but the plots are almost linear. The uptake of Type II adulterants in the dried composite EBN can be considerable. At 10% w/w of adulterant solutions, the uptake was about 40% w/w of sucrose, about 34% w/w of glucose, about 29% w/w of collagen and about 20% w/w of MSG.

Raman microspectroscopy can detect the Type II adulteration of EBN. In Figure

4, we show the Raman spectra of the EBN composites with sucrose, glucose, collagen and MSG, which were prepared

by soaking in 5% w/w of adulterant solutions, in comparison with unadulterated EBN.

For sucrose, glucose and MSG which lack protein bands, the Raman spectra of the composites were normalised with respect to the amide I band of EBN, and the difference spectrum was calculated and compared with the corresponding Type II adulterant in each subplot in Figure 4 (A–C). For collagen which has Raman amide bands but no sialic acid, we have used the following information to scale the Raman intensity of the composite relative to EBN: (a) the composite has about 18% of collagen and about 82% of EBN as shown in Figure 3, (b) the intensity of the 1003 cm^{-1} Raman line is due to phenylalanine and sialic acid, with sialic acid coming solely from EBN, (c) the intensity of the 1003 cm^{-1} Raman line of the composite due to phenylalanine is the same as the peak intensity of the amide I band of the composite, and the rest of the intensity of the Raman line can be attributed to sialic acid. So, with EBN as the standard, we know the intensity of the sialic acid contribution at 100% EBN, and so we scale the Raman spectrum of the composite so that the intensity of

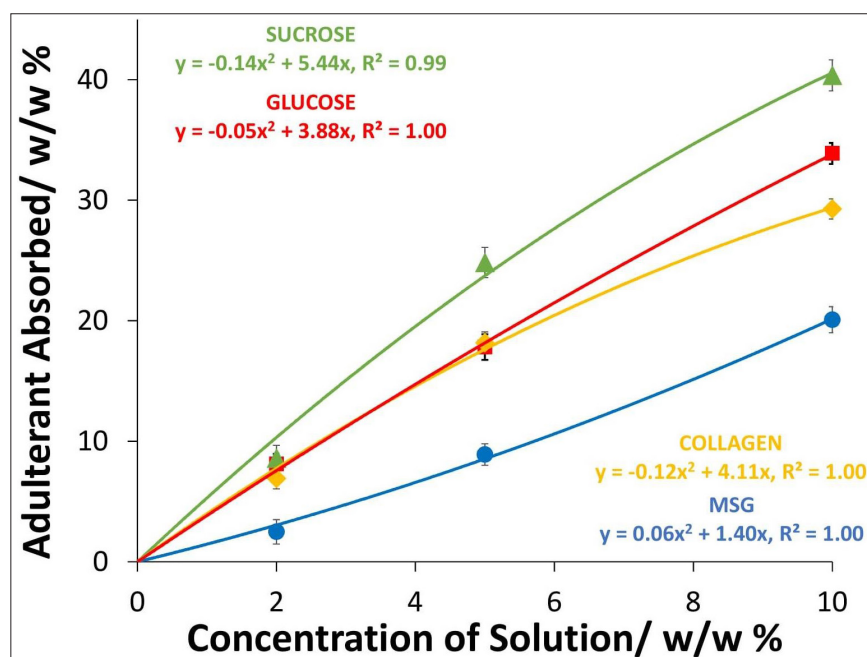


Figure 3. Graph of the uptake of the Type II adulterants by EBN when dried versus concentration of adulterant solutions used in soaking.

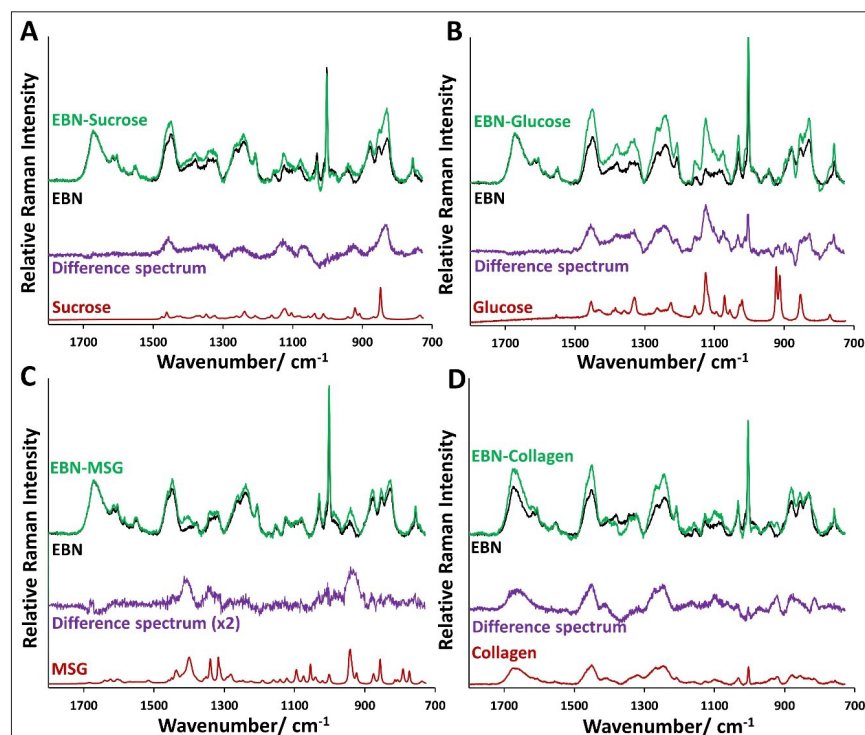


Figure 4. Comparison of normalised Raman spectrum of EBN composites with Type II adulterants (in green)—sucrose, glucose, (hydrolysed marine) collagen and MSG—prepared by soaking in 5% (w/w) solution of Type II adulterants with the Raman spectrum of unadulterated EBN (in black). The difference Raman spectra (in purple) resemble that of the adulterants (in red).

the sialic acid component is 82% of that. The results are shown in Figure 4(D), together with the difference Raman spectrum and the Raman spectrum of collagen. It can be seen in Figure 4 that the difference Raman spectra resemble those of the corresponding adulterants, but the Raman lines in the difference spectra are generally broader for sucrose, glucose and MSG. The reason is because the Raman spectra of these adulterants were taken in the pure crystalline form, whereas in the EBN composites these molecules are embedded in an amorphous EBN cement. Collagen, however, is already in an amorphous form and so the difference spectrum has broad lines similar to that for collagen.

Conclusions

The investigation showed that EBN has a unique Raman spectrum that can be used as a standard for authentication. Raman microspectroscopy can distin-

guish between polysaccharides (no amide bands), polypeptides (strong amide bands) and glycoproteins (both amide and saccharide bands), and so can be used to detect edible, water-insoluble Type I adulterants which are polysaccharides or polypeptides and can be adhered to the surface of EBN strands. Clear, edible, water-soluble Type II adulterants can be adsorbed by EBN to form a composite that looks like the unadulterated EBN under a microscope. However, the EBN composites with Type II adulterants give rise to Raman spectra that differ from the unique Raman spectrum of unadulterated EBN. Raman microspectroscopy thus offers a rapid, non-destructive technique, requiring very little sample and no prior treatment to authenticate EBN.

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Day-to-day inorganic nuclear magnetic resonance spectroscopy

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Many years ago, I was involved in a project where for a short while I dreamt of exploiting the capabilities of nuclear magnetic resonance (NMR) spectroscopy to look at differently bound silicon oxide environments. The complexities of finding an NMR expert who had the capability and the time, and the willingness to convert their instrument for

these measurements on nuclei with low abundances and often complex spin systems were enormous. The time-frame of the project meant that I had to give up on what looked a very quick and promising solution to my problem. Ever since that experience, I have generally avoided the ordeal of locking horns with NMR experts and confined myself

to the peaceful waters of familiar spin $\frac{1}{2}$ carbon-13 and proton NMR spectroscopy. I am pleased to say that I was recently shaken out of my comfort zone by an NMR expert not only carrying out measurements on these interesting nuclei but also happy to go out and preach about their usefulness. Marcel Simons enthusiastically presented how

Table 1. Some common isotopes useful for NMR analyses and their relative sensitivities assuming equal T_1 and T_2 relaxation times and temperatures.

Nucleus	Natural abundance (%)	Spin (I)	Magnetic moment μ (μ_Z/μ_N)	Gyromagnetic ratio (γ)	Molar sensitivity (rel. ^1H)	Receptivity natural ab. (rel. ^1H)
^1H	99.99%	0.5	2.793	26.7522	1.0000	100.000%
^7Li	92.41%	1.5	3.256	10.397704	0.2940	27.100%
^{11}B	80.10%	1.5	2.689	8.584707	0.1650	13.200%
^{13}C	1.07%	0.5	0.702	6.7283	0.0159	0.018%
^{23}Na	100.00%	1.5	2.218	7.0808516	0.0927	9.270%
^{25}Mg	10.00%	2.5	−0.855	−1.63884	0.0027	0.027%
^{27}Al	100.00%	2.5	3.642	6.976278	0.2070	20.700%
^{29}Si	4.69%	0.5	−0.555	−5.31903	0.0079	0.037%
^{35}Cl	75.76%	1.5	0.822	2.6241991	0.0047	0.358%
^{39}K	93.26%	1.5	0.392	1.2500612	0.0005	0.048%
^{79}Br	50.69%	1.5	2.106	6.725619	0.0795	4.030%
^{81}Br	49.31%	1.5	2.271	7.249779	0.0995	4.910%
^{135}Ba	6.59%	1.5	0.839	2.67769	0.0050	0.033%

developments in the available hardware, higher field instruments, better multinuclear probes including cryoprobe options, the spectrometer control systems and also desktop NMR data processing software had all combined to make the measurement of inorganic nuclei a potentially commonplace and very helpful, often complementary, technique to other spectroscopic analytical tools.

Sensitivity myth and legends

One of the biggest issues in the past has been the lack of sensitivity of NMR instrumentation to the "exotic" nuclei. For those unfamiliar with the technique, it is worth remembering that essentially only isotopes that contain an odd number of protons and/or neutrons have a magnetic moment and angular momentum to be detected by NMR spectroscopy. Other isotopes with even numbers of protons and/or neutrons have zero spin and cannot be detected. The basic sensitivity of any particular nuclei is a function of the relative abundance (natural concentration of the NMR active isotope) and the magnetic moment. Of course, for the analysis of nuclei whose measurable isotopes are only present in very low abundances it is always an option to select experiments which use isotopically enriched samples. However, this is generally an expensive option, not available to many except in very special cases, and not really a solution for day-to-day analysis.

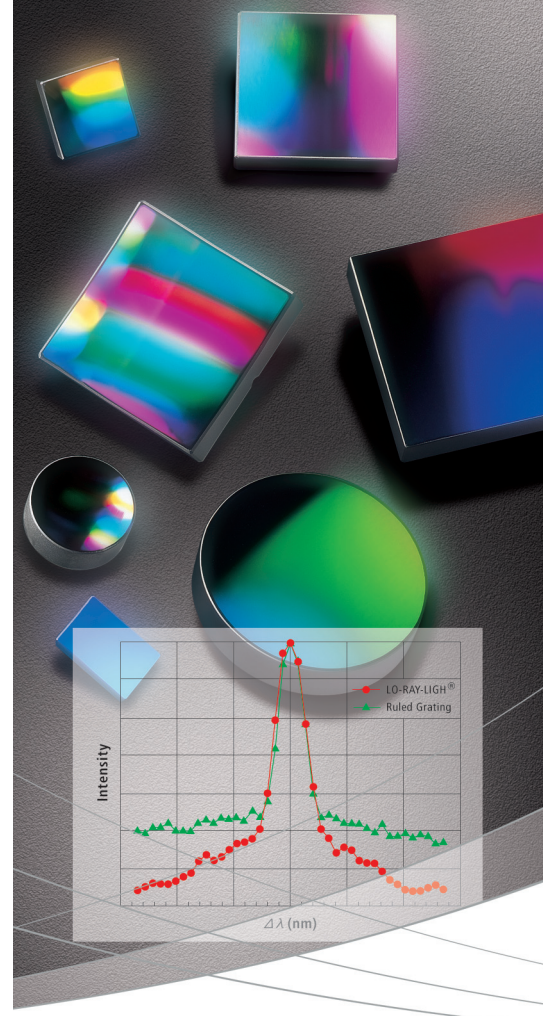
So, if you successfully persuaded your NMR experts to carry out these inorganic experiments it often used to mean tying down the instrument for long periods not only to convert to a different probe head but simply to acquire enough scans in order to deliver a good enough signal-to-noise ratio to allow meaningful interpretation of the data received. The basis for this can be easily seen in Table 1, where the natural abundance, spin state and magnetic moment for a few common NMR inorganic isotopes is given. The term relative receptivity is used as a more useful guide to nuclear response. It is the product of the rela-

tive sensitivity and the isotopic natural abundance compared to the proton. So, the myth of insensitivity of the inorganic isotope in NMR over organics can be debunked to a certain extent if we look at the receptivity of ^{13}C , where the relative receptivity compared with ^1H is $0.0159 \times 1.108 = 0.018\%$. All the common inorganics selected for Table 1 do better than ^{13}C ! Of course, the absolute concentration of carbon in the sample also plays a key role in the final signal-to-noise ratio of the measurement compared to proton NMR spectroscopy. So for scientists concentrating on organic or organometallic chemistry, this is something of a spurious comparison. But it is worth remembering that it is *not* the sensitivity of the inorganic isotopes themselves in NMR which are inhibiting factors in their own right.

Effect of field strength etc.

Stronger magnets have greatly helped deliver better signal-to-noise ratios. Doubling the field strength, say going from 300 MHz to 600 MHz instruments, whilst keeping everything else constant, doubles the population difference induced in the sample (Boltzmann distribution). Additionally, the current in the probe head doubles whilst only increasing the noise in the head by $\sqrt{2}$ (overall improvement effect in the probe head = $2/\sqrt{2} = 1.4142$) giving an overall beneficial increase in signal-to-noise from the doubling of $2 \times 1.4142 = 2.8284$, everything else being equal.

An additional beneficial effect is the narrowing of the linewidth achieved, as this can bring weak signals out of the noise in some cases. Table 2 summarises some of the factors discussed above and some additional considerations which will influence the applicability of inorganic NMR spectroscopy in the day-to-day operation of your spectroscopic laboratory. Some are influenced by the specific isotope to be analysed, some on the available instrumentation including probe types and bores available, where some effects are down to the molecular environment of the isotope being measured.



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Table 2. Some influences on the sensitivity of inorganic NMR of particular isotopes.

Sample/isotope factors

- Magnetic momentum
- Natural abundance
- Gyromagnetic ratio
- T_1 (Boltzmann)
- T_2 (FWHM)
- Nuclear Overhauser Effect (NOE) (can be positive but also negative)
- FWHM (peak area = $\sim$ FWHM $\times$ peak height)
- Atomic mass (C_6H_6 vs KBr)
- Spin–spin coupling (singlet, doublet, triplet, quartet, multiplet)
- Satellites
- Temperature (Boltzmann)

Instrumentation factors

- Magnetic field (400 MHz, 600 MHz...)
- Boltzmann
- Spectral resolution (FWHM)
- Number of scans (NS)
- Sensitivity probe head
 - ☐ BBO vs BBI
 - ☐ tube diameter 1 mm, 1.7 mm, 3 mm, 5 mm, 10 mm
 - ☐ room temperature vs cryo probe (nitrogen- vs helium-cooled)
 - ☐ flow probes with different cell volumes (30 μ L, 60 μ L)

Decoupling and multidimensional experiments, LOQs

As with the more widely used isotopes a range of revealing experiments are also available for the inorganic isotopes. Figures 1 and 2 show the beneficial effect of a proton decoupling experiment on a ^{119}Sn spectrum.

However, multidimensional spectroscopy experiments can also apply to inorganic isotopes, and Figure 3 is an example of a multidimensional NMR experiment which can give great insight into connectivity and arrangement of the inorganic moieties in complex structures. Here the longer-range couplings (2–4 bonds) are revealed in a heteronuclear

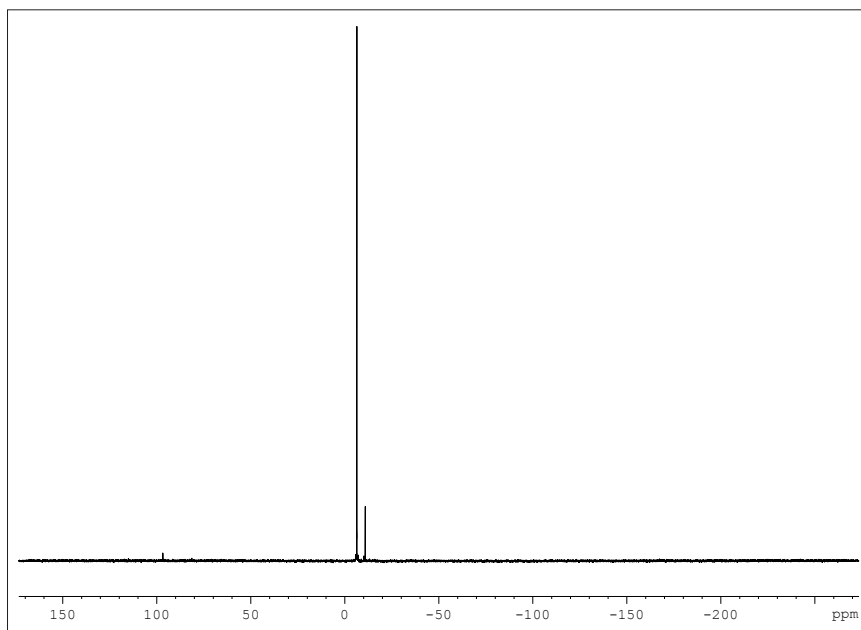


Figure 1. ^{119}Sn spectrum of 145 mg sample in 1.1 g CDCl_3 with 0.03% TMS standard.

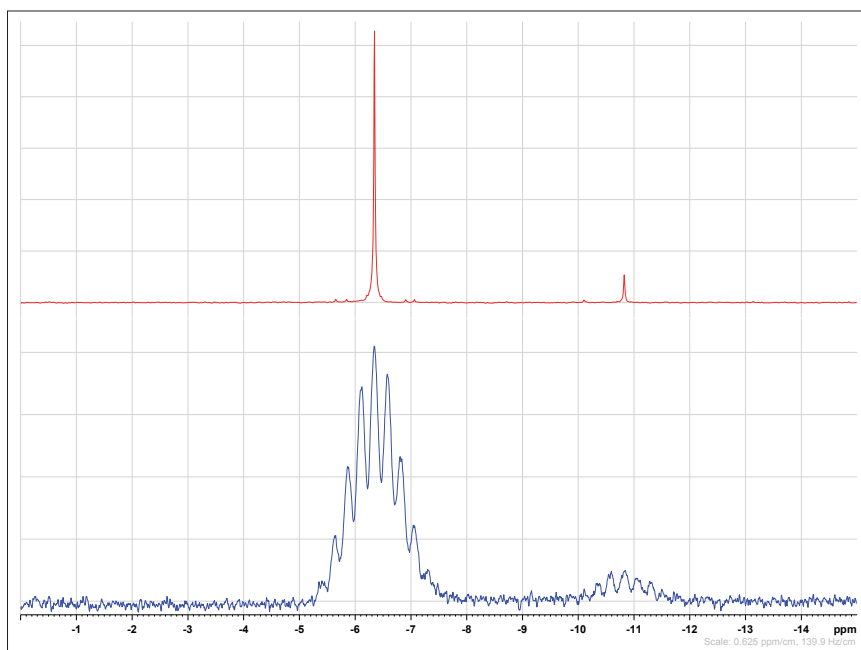


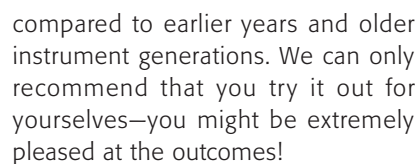
Figure 2. Detail of the same ^{119}Sn spectrum of 145 mg sample in 1.1 g CDCl_3 with 0.03% TMS standard showing (bottom) the original coupled measurement and (top) the beneficial effect of a proton decoupling experiment on the signal-to-noise ratio. All in all, for an average 1 h single-dimensional experiment limits of quantification based on 10 $\times$ signal-to-noise ratio are commonly around achievable in the 10s of mg kg^{-1} range.

multiple bond correlation (HMBC) experiment.^{1–3}

Conclusions

I have been surprised how easy it has become to execute inorganic

NMR experiments delivering good insights into samples in ways no other technique can deliver. Marcel has convinced me that we can get far more information out of our samples now, with comparatively little effort



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NIR-2017 SUPPLEMENT

Conference Programme

SUNDAY	16:30: Opening Ceremony 1 17:30: Karl Norris Award 18:15–20:00: Opening Ceremony 2								
MONDAY	8:30	09:15	9:45	10:00	10:15 BREAK	10:45	11:15	11:30	11:45
	Tomas Hirschfeld Award		Chemometrics I			Chemometrics I			
	Chair: Ana Garrido-Varo		Chair: Tom Fearn			Chair: Tom Fearn			
	Jim deHaseth Presentation of Tomas Hirschfeld Satoru Tsuchikawa Award address		Harald Martens Keynote: “NIRS in Big Data Cybernetics”			Jordane Lallemand Orthogonalisation Method for Robustness Improvement of Online NIR Applications	Jean-Michel Roger Drop-D : Dimension Reduction by Orthogonal Projection for Discrimination	Juan-Antonio Fernandez-Pierna New Strategies for Local Modelling for Untarget Analysis and Regression Using Near Infrared (NIR) Spectroscopic Data	Geir Rune Flåten Batch Modelling of NIR Data in Relative Time
TUESDAY	Pharma and Biotech				10:15 BREAK	Pharma and Biotech			ICNIRS
	Chair: Thomas Skov					Chair: Thomas Skov			
	Erik Skibsted Keynote: “Current and Future Applications of Near-infrared in Pharmaceutical and Biopharmaceutical Industry”	Francisca Folque Gouveia Lifecycle Management of Process Analytical Technologies in Pharma/Biopharma Industries: Integrating Analysis with Process Control	Yi-Chieh Chen Extracting and Monitoring Particle Size Distribution Information for Pharmaceutical Crystalisation Process using Spatially and Angularly Resolved Visible-NIR	Mathias Schilling Determination of Lactase Activity using Near-Infrared Spectroscopy		Hui Yan Identification of Fengdou Produced From Different Dendrobium Species by a Handheld NIR Spectrometer Based on DLP Technology and CARS-PLSDA Evaluation	Marie Pettersson Batch Modelling of NIR Data in Relative Time		Roger Meder Presentation of ICNIRS2019
	PAT					PAT			
WEDNESDAY	Chair: Thomas Skov				10:15 BREAK	Chair: Thomas Skov			
	Frans van den Berg Keynote: “NIRS in process control ... time is on my side”	Peter Skou Applying Extreme Value Theory on Near Infrared Spectroscopy Predictions of Moisture Content in Milk Powder	Remo Simonetti From Laboratory to the Continuous Manufacturing Line: Update of a NIR Calibration Model for Tablets' Content Uniformity Evaluation	Annelies Postelmans Particle Size Distribution Estimation of Suspensions Based on Bulk Scattering Properties		Tom Scherzer Monitoring of Lamination and Impregnation Procedures in Textile Processing by Near-Infrared Chemical Imaging	Marina Cocchi Fusing NIR and Process Sensors Data for Polymer Production Monitoring	Benze Kozma Model System Based Scalability Test and Comparison of NIR and Raman Spectroscopy by the On-Line Prediction of the Glucose Concentration of Cho Cell Cultivations	TBD TBD
	Theory and Instrumentation					Chemometrics II			
	Chair: TBD					Chair: TBD			
THURSDAY	Christian Huck Keynote: “Theoretical and Technical Advancements of NIRS and its Operational Impact in Industry”	Tine Ringsted Long Wavelength Near-Infrared Transmission Spectroscopy using a Supercontinuum Laser	Robbe Van Beers A Handheld Multispectral Sensor for the Separation of Scattering and Absorption Properties	Dilusha Silva Towards Imaging Micro-Spectrometers for Airborne Applications	10:15 BREAK	Nathalie Gorretta Setting Local Rank Constraints using Orthogonal Projections for Image Resolution Analysis: Application to the Determination of a Low Dose Pharmaceutical	Federico Marini In the Neighborhood: Advances in Local Modeling for Calibration and Classification	Tom Fearn Classification with NIR Spectra using Bayes Rule and Kernel Density Estimates	Sharon Nielsen Near Infrared Calibration with Linear Mixed Models

NIR-2017 SUPPLEMENT

NIR-2017, Copenhagen, Denmark, 11–15 June

12:00		13:30	14:15	14:45	15:00	15:15		15:45	16:15	16:30		
		Dairy and Food						Dairy and Food				
LUNCH POSTER SESSION A		Chair: Birthe Møller				Chair: Birthe Møller			18:00–20:00 Foss Event			
		Steve Holroyd Keynote: “The use of NIRS in the Dairy Industry: New Trends and Applications”	Carl Emil Eskildsen Visualising Model Dependencies By Projections—Predictions of Individual Fatty Acids in a Complex Food Matrix	Lola Perez-Marin Fine-Tuning and Cloning of a Fibre-Optic Probe for <i>in situ</i> Monitoring and Evaluation of Quality of Olive Oil Products	Stephen Walford NIRS– Rethinking the Analysis of Sugarcane Factory Streams	Ben Aernouts Evaluating and Increasing the Robustness of an NIR Sensor for Online Quality Analysis of Raw Milk	Laura Marinoni On Site Monitoring of Grana Padano PDO Cheese Production using Portable XNIR Spectrometers	Yasuhiro Uwadaira NIR and H-1 NMR Statistical Heterospectroscopy for Non-Destructive Quality Evaluation of Peaches				
		Water, Soil and Enviroment				Water, Soil and Enviroment						
LUNCH POSTER SESSION B		Chair: TBD				Chair: TBD			16:45 University of Copenhagen Honorary Award 17:15 ICNIRS Meeting 19:15–21:15 Bruker Event			
		Véronique Bellon-Maurel Keynote: “Could Near Infrared Spectroscopy be Useful to Digital Agriculture?”	Jessie Au Predicting Nutritional Quality for Koala Habitat Assessment using Near-Infrared Spectroscopy	Manuela Mancini Use of FT-NIR Spectroscopy for the Detection of Residues from Wood Processing Industry in the Pellet Sector	Alexia Gobrecht Potential of Polarised Light Spectroscopy To Predict Rheological Parameter of Sludges in Wastewater Treatment Plants	Jelena Muncan On Different Roles of Water in Soft Contact Lenses—Near Infrared and Aquaphotomics Study	Kasper Borg Damkjær Investigation of the Feasibility for using NIRS for Online Monitoring of the Mineral Content and Other Impurities in Reused Industrial Process Water	Tereza Pastore Comparison of Two Handheld NIR Spectrometers Applying PLS-DA and SIMCA Models for Determination of The Mahogany Wood Provenance				
		Agriculture				Agriculture						
LUNCH POSTER SESSION C		Chair: TBD				Chair: TBD			19:15–0:00 Gala Dinner			
		Daniel Cozzolino Keynote: “How to Stop Worrying About Calibrations and Embrace the Benefits of NIR”	Said Nawar Random Forest Approach for Modelling On-Line Vis-NIR Spectroscopy of Soil Total Nitrogen and Total Carbon for Different Scale Datasets	Umesh Acharya Classification of Citrus Fruit with Ensemble Techniques	María-Teresa Sánchez Application of Local Regression Methods To NIR Spectra Database of Citrus Fruits for the Assessment of Internal Quality	Vincent Baeten Performance Comparison of Bench-Top, Hyperspectral Imaging, Hand-Held and Pocket NIR Spectrometers: The Example of Protein Quantification in Wheat	Franklin Barton Calibrations for the Determination of Minor Fibre Components	Eloise Keeffe The Challenge of Analysing Fresh Raw Sugar with Near Infrared Spectroscopy				
		Hyperspectral Imaging				Hyperspectral Imaging						
LUNCH POSTER SESSION D		Chair: TBD				Chair: TBD			17:15 Closing Cermeony			
		Maria Angela Franceschini Keynote: “Clinical Neuro-Monitoring with Diffuse Correlation Spectroscopy”	Jens Petter Wold On-Line Detection of Wooden Breast Syndrome in Chicken Fillets by Hyperspectral NIR Imaging	Rosalba Calvini Data Dimensionality Reduction Strategies for Fast Exploration and Classification of Large Datasets of Hyperspectral Images	Nghia Nguyen Do Trong Cross-Polarised VNIR Hyperspectral Reflectance Imaging for Mapping Moisture Content and Texture of Banana Slices during Drying	Matthew Eady Bacteria Cell Classification with Hyperspectral Microscope Imaging and Multivariate Analysis	Erick Ramanaidou Hyperspectral Imaging of Lateritic Nickel Deposits in New Caledonia	Torbjørn Mehl Increased Sensitivity in NIR Hyperspectral Imaging by Enhanced Background Noise Subtraction				

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22

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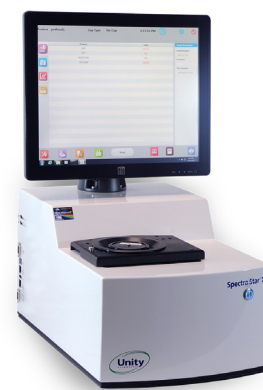
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Instrument qualification: a possible quality by design-based approach

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Background

Reviewing published documentation provides some interesting information as to how the requirement for the "calibration" of spectrometers has changed and evolved over approximately the last 40 years, and not least, the associated terminology of the science.

Why "40 years"? Because in 1976, the FDA promulgated a series of proposed GLP regulations, which were finalised under 21 Code of Federal Regulations (CFR) 58 in 1978 as well as the established cGMPs in 21 Code of Federal Regulations (CFR) 210 & 211. Purely by coincidence around this time, we began our own spectroscopic journeys performing measurements on old manual prism-based spectrometers such as the Beckman DU, Unicam SP 500 and Hilger Uvispek Mk IX. In those days, the focus was simply on technical performance characteristics.

By the late 1990s, in addition to the publication of guidance documents in key aspects of regulatory control, a defined qualification process was documented by various interested parties, including the current authors in several collaborative ventures.

These documents^{1,2} established the qualification framework as shown in Figure 1 and the recommended approach to UV/vis spectrometry.

At the same time that the 4Qs qualification protocol was being developed, the central role of this essential qualification

process was summarised by an instrument vendor, as shown in Figure 2.

The statement made at that time was that:

The value of the chemical measurement depends upon the degree of confidence that can be placed on the result

and thereby its "fitness for purpose". If you couple this statement with any of the internationally recognised Quality Standards, one irrefutable observation is that both have a common requirement—effective equipment performance verification, often simply referred to as

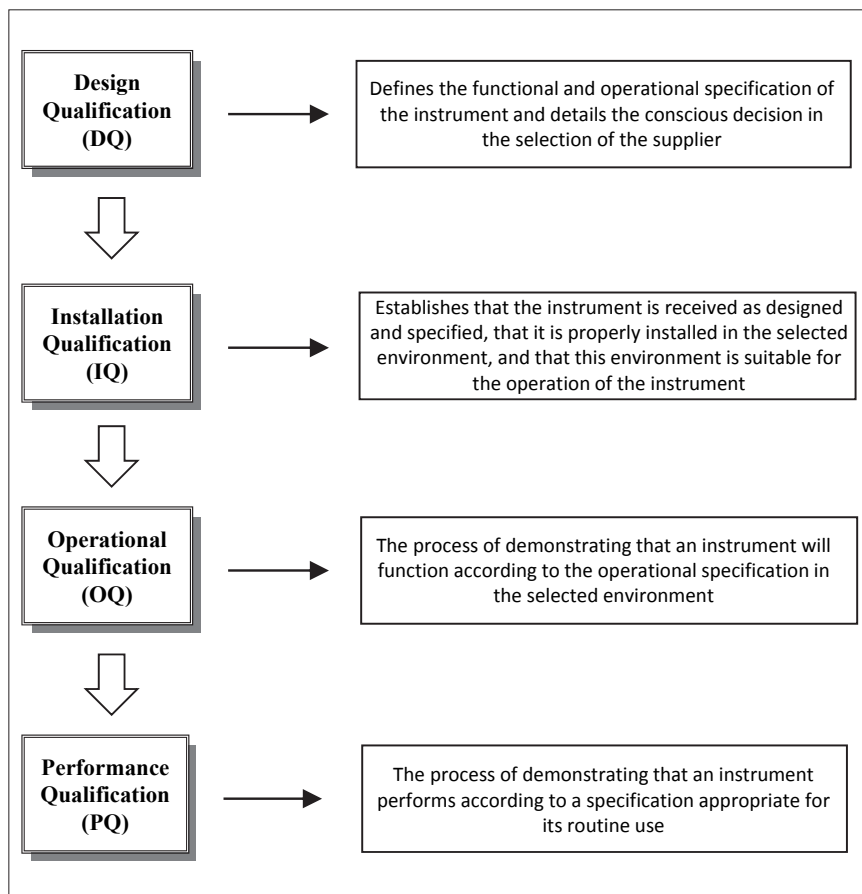


Figure 1. Qualification framework 1997–2000 Valid Analytical Measurement (VAM) Programme.

QUALITY MATTERS

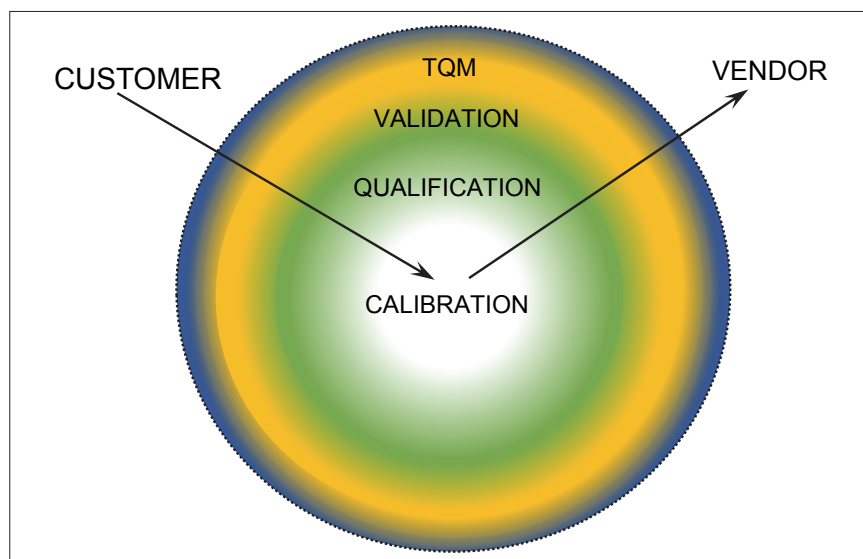


Figure 2. Vendor-derived validation/qualification and calibration (VQC) "Shells" circa 2000.

calibration. This requirement can be graphically shown as part of a series of concentric Validation/Qualification/Calibration (VQC) "shells".

This structure affects both user and vendor, and the sequential process shown in Figure 2 will depend upon one's initial starting position. As a user, the overall perspective is planned before specific tasks are undertaken. As an instrument manufacturer, clearly establishing calibration to specification is the first quality requirement of a newly produced instrument.

From the user's viewpoint in practical terms this meant:

- 1) Establishing total quality management (TQM) protocols.
- 2) Formulating a validation plan.
- 3) Qualifying the instrument or system.
- 4) Ensuring initial (and maintaining) calibration.

From the vendor's perspective this required:

- 1) Ensuring calibration to specification.
- 2) Assisting the end user in the qualification at the system location.
- 3) Assisting/advising on additional validation & calibration/TQM aspects.

At the same time, the Royal Society of Chemistry's Analytical Methods Committee, Instrumental Criteria Subcommittee published a detailed proposal on the selection of UV/vis/NIR systems.³

This concept is still valid today, some 20 years on, but as our title suggests—as always, there may be another and possibly better way.

Quality by design

At the same time as these fundamental validation, qualification and calibration principles were being defined and structured, in a parallel development, quality by design (QbD) as a concept was outlined by quality expert Joseph M. Juran in many publications, most notably *Juran on Quality by Design*.⁴

Designing for quality and innovation is one of the three universal processes of the Juran Trilogy, in which Juran describes what is required to achieve breakthroughs in new products, services and processes.⁵ Juran believed that quality could be planned, and that most quality crises and problems relate to the way in which quality was planned.

While QbD principles have been used to advance product and process quality in industry, and particularly the automotive industry, they have also been adopted by the pharmaceutical industry. As has been discussed many times in the column, international harmonisation is an on-going process, and QbD is no exception. In this case, regulators in the European Union (the European Medicines Agency), Japan and the

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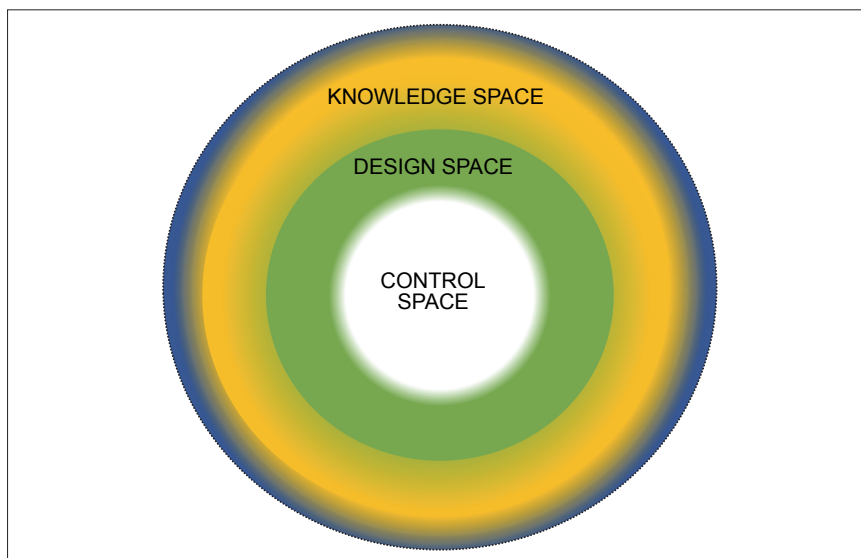


Figure 3. Qualification in a QbD environment.

US Food and Drug Administration (FDA) have furthered QbD objectives through the International Conference on Harmonisation of Technical Requirements for Registration of Pharmaceuticals for Human Use (ICH). ICH guidelines Q8 (on Pharmaceutical Development),⁶ Q9 (on Quality Risk Management)⁷ and Q10 (on Pharmaceutical Quality System)⁸ provide guidance for manufacturers to implement QbD into their own operations.

There is not the space within this article to expand further on this well-reviewed and discussed topic, but a simple search will reveal an extensive library devoted to this subject. However, the concept is introduced here because this guidance is being developed further into risk-based approaches to the management of quality, and are very much seen as the way forward in to the future.

Therefore, let us take a conscious decision to combine these two concepts and see what is produced. That is to say, if we bring this VQC shell structure up to date and apply a similar approach using QbD terminology, what is the result?

The result is shown in Figure 3.

If you compare Figure 2 and Figure 3 it is apparent that:

- Knowledge space and validation both form the outer shells.

- Design space links to qualification, and interestingly, both form the essential core framework on which the structure is built.

and

- Control space maps to calibration, the working centre of both structures.

If we now focus on Figure 3, this can be considered on the paper in two dimensions, i.e. a circle as a “space” in which you have:

- Knowledge space
- Design space
- Control space

But in practice, as discussed below, these spaces are in fact multi-dimensional surfaces encompassing the critical process parameters. Obviously, as with all concepts, these may be considered generic terms, and therefore may be defined as such, but such definitions are often difficult, as by design, they will reflect the environment for which they are intended, e.g. mathematical, pharmaceutical etc. Some basic definitions are given from a spectroscopic viewpoint below.

Knowledge space

The theory and science associated with UV/vis spectroscopy, which after 70 years as an instrumental technique, is not inconsiderable and its critical process parameters (CPPs) are well established. In addition, the desired metrological

outputs are specified as critical quality attributes (CQA).

Design space

A multivariate mathematical model relating the input CPPs and output CQAs to establish a region where at a level of probability the measurement process delivers “fitness for purpose” outcomes. Working within the design space is not considered as a change. Movement out of the design space is a change and would normally initiate a regulatory post approval change process. Design space is proposed by the applicant and is subject to regulatory assessment and approval.⁶

This is essentially the space in which a UV/vis spectrometer has been specified by the vendor and used for operational qualification (OQ).

Control space(s)

A more constrained region within the design space, sometimes called the “normal operating range”, is based on in-house specifications. This space covers the user-defined operational parameter range over which the instrument is going to be routinely used. For different applications, there may be different control spaces with the same overall design space. For example, the same spectrophotometric system may be used for one very specific application, over a defined wavelength and absorbance/transmittance range, or the system may be used for multiple applications, as shown in Figure 4.

A CPP from a spectroscopic viewpoint is a physical optical characteristic that should be within an appropriate limit, range or distribution to ensure the desired metrological qualities (CQAs), and therefore in the case of UV/vis spectrometry, such CPPs are likely to include:

- Operational ranges of absorbance and wavelength.
- Wavelength accuracy and precision over the operational ranges.
- Photometric accuracy and precision over the operational ranges.
- Stray light.
- Spectral bandwidth.

So in a practice sense, we would suggest that with respect to the requirements nothing has changed, there is

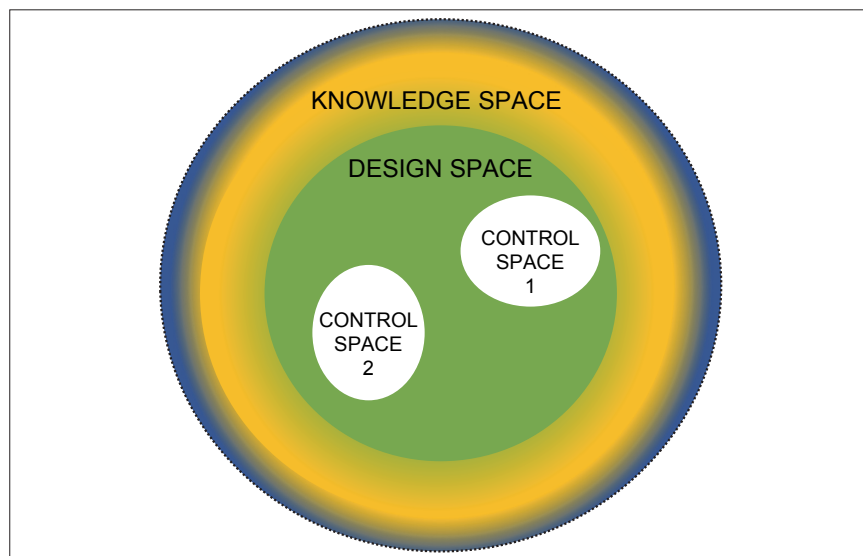


Figure 4. Multi application control spaces.

still the requirement to “calibrate” a spectro(photo)meter and it has always been there.

However, with these QbD concepts in place, the environment is more defined, is more structured and, once understood, easier to control. The next step is to introduce the “analysis of risk” into the process—but that is a topic for another day.

To bring the discussion “full circle”, also in 1975, Klaus Mielenz of NBS (now NIST) published a short paper on “The Nomenclature of Spectrometry”.⁹ Recent discussions have shown that it would appear we are no further forward in deciding whether the correct terminology for an instrument measuring transmittance across a defined wavelength range is an absorption spectrometer, or spec-

trophotometer; but again, this is probably a topic for another day?

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Introduction to process sampling

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Previous columns have been devoted to a comprehensive introduction to the basic principles, methods and equipment for sampling of **stationary materials and lots**, as part of a description of the systematics of the Theory of Sampling (TOS). The next instalment of columns will deal with **process sampling**, i.e. sampling from **moving streams of matter**. As will become clear there is a great deal of redundancy regarding how to sample both stationary and moving lots, but it is the specific issues pertaining to dynamic lots that will be highlighted.

Lot dimensionality: ease of practical sampling

The Theory of Sampling (TOS) has found it useful to classify lot geometry into four categories. The strict scientific definitions are not necessary at the introductory level in these columns, which will rather focus on lot dimensionality from the point of view of sampling efficiency (or sampling possibility, in difficult cases). A straightforward lot dimensionality classification is seen in Figure 1.

From a practical point of view, sampling needs to be concerned with the ease with which one is able to extract increments from a *randomly chosen* location in the lot (or selected according to a *sampling plan*). Thus it is relatively easy to extract slices of any lot which has one dimension which *dominates*, i.e. is vastly longer (the extension dimension) than any of the other two dimensions (width, height). From this sampling point of view, the lot is effectively only 1-dimensional because all material in an incremental slice “covers” completely the full width and height of the material. This is the reason for TOS’ classification of 1-dimen-

Lot Dimensionality (definition via *increments*)

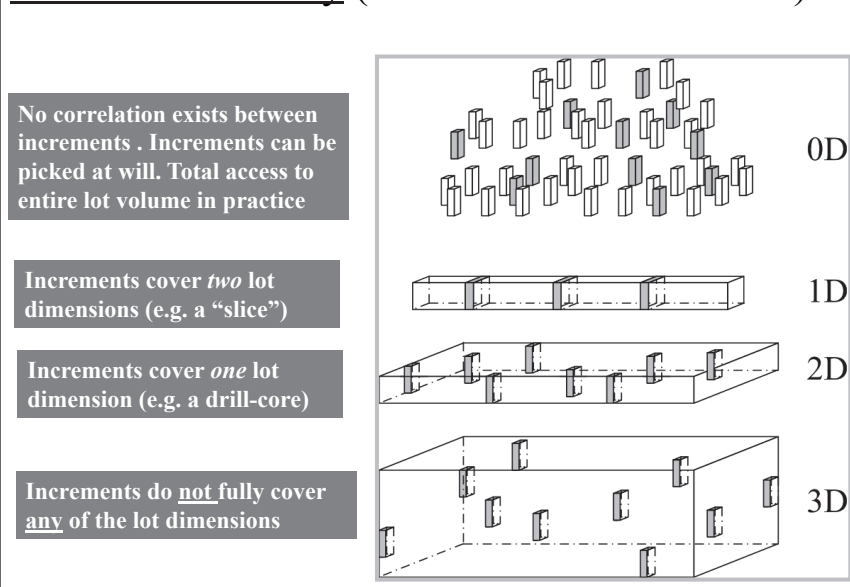


Figure 1. TOS’ practically oriented classification of lot dimensionality; the odd “0-dimensional lot” type is explained fully in the text. Illustration credit: Lars Petersen Julius (with permission).

sional lots, or 1-D bodies. 1-D lots have a special status in TOS, for various reasons (see further below). Observe that a 1-D lot can either be a stationary, very elongated body (stock, pile etc.) or it can be a dynamic 1-D lot, i.e. a moving or flowing stream of matter (the material being transported by a conveyor belt is an archetypal dynamic 1-D lot; likewise the moving matter confined to a pipeline). It is a very important issue that 1-D lot sampling increments have the form of a “slice”.

It is equally easy to define a 2-D body (see Figure 1). 2-dimensional lots are characterised by the fact that all increments will only “cover” one dimension. Very often 2-D lots are horizontal, with the remaining dimension vertical (think

of a drill core penetrating a geological formation, or a layer), but not necessarily in this orientation. The defining issue is that there is only one degree of freedom, namely where in the X–Y plane is the 1-dimensional increment to be located “where to sample in the X–Y plane?”. The operative increments in sampling 2-D lots are either “cylindrical increments” or box-like, see Figure 1.

The key feature for the sampler, or for the sampling equipment, is that there is full access to the entire lot in the case of 1-D and 2-D lots. This is an important empowerment because it allows the demands of the fundamental sampling principle (FSP) to be honoured: all potential increments from a lot **must** be accessible for physical extraction if/

SAMPLING COLUMN



Figure 2. There should always be an element of randomness in a good sampling procedure, here the locations along the extension dimension of a 1-D lot are selected in this fashion. All slices correspond to complete slices of the width–height dimensions of the lot. Illustration credit: KHE.

when selected. Indeed, this feature is scale-invariant, one can sample **all** 1,2-dimensional lots of any size under the FSP. Going on to 3-D lots leads to a perplexing revelation. It is very difficult to define a 3-D lot from the point of view of practical sampling, logically the operative increment *form* here should be a sphere. But in our 3-D world, extracting spherical increments is not exactly easy... .. Be this as it may, TOS has many alternatives to offer for 3-D sampling, but this is outside the present scope (see, for example, Reference 1).

WHAT then is a “0-dimensional lot”, the top illustration in Figure 1? This is another of TOS’ penetrating ways to focus on the underlying systematics of sampling. A 0-D lot is a lot that is “small” enough so that it is particularly easy **always**, under **all** circumstances, with **all kinds** of equipment to extract any size increment desired (increments of any form, so long as the increments are all *congruent*, i.e. of the exact same form and size). In other words, a 0-D lot is a particularly easy-to-sample lot. Obviously there is a grading demarcation between a 0-D lot and a 3-D lot, but in practice this discrimination has been found

immensely useful. It is *full accessibility* in sampling practice that is the key operative element in these definitions.

Thus, with respect to sampling practice, lots come in groups [0-, 3-D lots] vs [1-, 2-D lots] of which the latter are of overwhelming importance—because this allows practical sampling no longer to be concerned with the size, magnitude, volume, mass of the lot. All [1-, 2-D lots] can be sampled appropriately, and this is a very large first step towards universal representativity.

Lot dimensionality transformation

This is a most advantageous feature of 1-D lot configurations. Irrespective of whether a 1-D lot is stationary or moving, it is 100% guaranteed that the **entire** lot will be available for increment extraction. 1-D lots are **always** particularly easy to sample, irrespective of their *original* configuration—it could have been a 3-D, 2-D or a 0-D lot that was decided to be transformed into a 1-D configuration... much more of this aspect below. From the largest lot sizes involved, e.g. a very big ship’s cargo (100,000 tonnes for example) down to an elongated pile of

powder in the laboratory; when present in a 1-D configuration, slicing off the number of increments, Q , decided upon[†] constitutes the most effective sampling condition known from TOS’ analysis. This scenario is the most desirable of all sampling options.

This finding has led to one of the six governing principles in TOS, lot dimensionality transformation (LDT). Wherever, whenever possible, it is an absolute advantage to physically transform a lot (0-D, 2-D, 3-D) into the 1-D configuration. Figure 3 illustrates this governing principle.

Even if there will have to be *some* work involved (sometimes *a lot* of work) in moving, transporting (bit-by-bit) a lot, say a 3-D lot, and for example loading its content onto a conveyor belt, this is very often a welcome expenditure because of the enormous bonus(es) now available. There is no comparison because of the ease with which the gamut of sampling errors can be eliminated or reduced with the 1-D configuration. TOS’ literature is full of examples, demonstrations and case histories on this key issue, e.g. Reference 1 and literature cited herein.

The subsequent set of sampling columns will describe the full diversity of *process sampling*, but this is a first foray to give the reader a useful overview of what is to come.

Process sampling

Process sampling concerns 1-D lots where there is a distinct spatial (stationary lots) or temporal *order* between the lot units *along* this defining dimension. The units may appear either as an ordered series of discrete units (in time or space) or as a moving/flowing material stream. All such elongated or moving material bodies are, strictly speaking, three-dimensional objects, but by transformation into 1-D objects their sampling turns out to be *identical* in principle as well as in practice. The movement involved is *relative*: either the matter streams, or flows, past the

[†]How to set an appropriate number of increments, Q , is an integral part of sampling of 1-D lots, and will be explained in details in future columns.

SAMPLING COLUMN

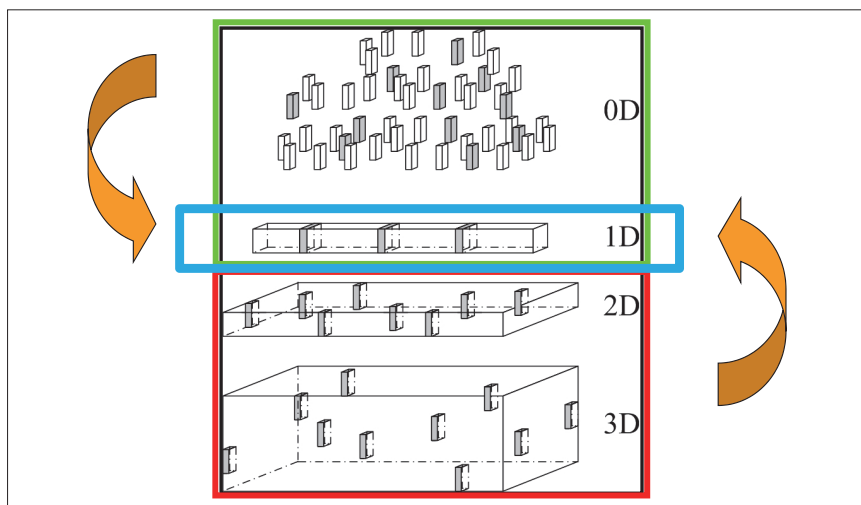


Figure 3. In practical sampling, TOS has shown the absolute desirability of transforming 3-D, 2-D and sometimes even 0-D lots into a 1-D configuration. Illustration credit: KHE.

sampler/sampling equipment, or the sampler “walks up and down” along the extended dimension of the lot. From a sampling point of view, these two situations are identical and will therefore both be covered even through the terminology most often speaks of *process sampling*.

It is now time to focus on the nature of the lot material to be sampled. In process sampling, the 1-D lot can be classified in three broad categories:

- A moving or stationary stream of *particulate material*. Examples: conveyor belts transporting aggregate materials, powders, slurries in ducts etc.
- A moving or stationary *fluid flow* (i.e. gasses, liquids). Examples: rivers or produced/manufactured fluids in pipelines.
- A moving or stationary stream made of *discrete units*. Examples: railroad cars, truck loads, or “units” (bags, drums, packages...) from a production or a manufacturing line.

Besides the distributional and constitutional heterogeneity (explained in earlier columns), there are further aspects that need to be considered to characterise the heterogeneity of 1-dimensional lots. This especially involves understanding the nature of the non-random heterogeneity fluctuations *along* the elongated lot. Interest is no longer so much in the heterogeneity *within* the units of obser-

vation (because the full slice will be extracted and its heterogeneity is therefore now only a matter for the subsequent mass-reduction step(s) which is easily managed under TOS), but specifically in the heterogeneity related to the differences *between* them. This is the lot heterogeneity *along* the entire length of the 1-D lot (which actually is the entire *volume* of the original lot).

Often “slicing” in such a case amounts to nothing more than appropriate *selection* of units viewed as a basis for a time series of analytical results. But the 1-D lot can also manifest itself as a more or less continuous body (1-, 2-, 3-phase continuum) along the length dimension, in which case it is the sampler/sampling equipment that forcefully “cuts” the stream to produce the extracted units. The location of where, and how, to cut the stream of matter is of critical importance in process sampling.

The heterogeneity contribution from an extracted unit (increment) is composed of three (four if including the total analytical error (TAE) parts in the case of 1-D processes:

- A random, discontinuous, short range fluctuation term. This term describes the constitutional heterogeneity *within* the increment.
- A non-random, continuous, long-range fluctuation that describes *trend* in the process/lot (between units) over time/distance.

- A non-random, continuous, cyclic term, describing cyclic or *periodic behaviour* of the process/lot.
- A random fluctuation term, taking into account all errors stemming from extraction, weighing, processing and analysis. This can be viewed as the *extended TAE*. Sometimes it is desired to keep the strict analytical errors isolated, as TAE proper. Either way, no confusion need arise and various cases will be illustrated in the following columns.

1-D lot heterogeneity

Characterisation of the heterogeneity of a 1-D lot must include information on the *chronological order* of the units extracted and their *in-between* correlations. Upon reflection, it is clear that it will be of interest to be able to characterise the intrinsic heterogeneity of the 1-D lot at *all scales* from the increment dimensions itself (there can be no *resolution* of the 1-D heterogeneity smaller than the physical dimension of the increment in the extension direction, which below is defined as the *lag*) ... up to, say half the length of the entire 1-D body (corresponding to the, in practice, unlikely case in which the lot was sampled as but two very large samples, each of the magnitude of half the lot; this scale is of no practical interest in the overwhelming number of meso- and macroscopic cases, but is occasionally brought to bear on exceptionally small lots). It is actually necessary to be able to express the 1-D lot heterogeneity at all these scales simultaneously. This may appear as a complex task, but TOS has developed an amazing, and amazingly easy to derive, facility for exactly this purpose—the *variogram*.

Variographic analysis: a first brief

In order to characterise the *autocorrelation* between units of the process/lot, the variogram is very powerful. It allows understanding the variation observed between extracted increments as a *function of the distance between them* (in time or space). The smallest equidistance between increments to be extracted is called the “lag”. This lag is determined by the sampler when setting

SAMPLING COLUMN

up the basis for a variographic characterisation (the variographic data analyst) if there has been made no variogram earlier. In certain cases valuable information from an earlier attempt will allow an optimal lag to be fixed; more on setting the critical parameter lag later. In addition, a variogram also yields information in the forms of the so-called “nugget effect”, the “sill” and the “range”, which are outlined below.

A variogram is based on the analytical results from a series of extracted increments, which are all mass-reduced and analysed in a proper TOS-correct manner—this is so as to suppress as much as possible sampling, mass-reduction and analytical errors, in complete agreement with the objectives regarding stationary lots. All extracted increments are in a sense treated as individual samples in the variographic context (but their status as *grab samples* is not a cause for worry, as shall be clear—because we have access to a lot of them covering the entire lot).

A variogram can be calculated based on a series of analytical results from a *sufficient* number of increments spanning the entire process interval of interest. An example could be a production process over a 24-h period, sampled every 20 min to characterise the variation, including three 8 h shifts. This would total 72 analytical results. More on how to fix an appropriate number of data from which to calculate variograms will be covered in later columns. Here, it is sufficient to state a beginner's rule-of-thumb: no less than 60 data points (analytical results). Often also much shorter time-spans are investigated, for instance, during the filling of a number of bags from a batch (blending) process, **or** something much longer, like daily or seasonal variation, for periods up to an entire year or even more. In general, the variogram is supposed to characterise a salient “process interval of interest”; this is very much an interval that is intimately related to the *specific* process in question, but the common feature is that the process is “covered” with at least 60 increments.

The fundamental operative unit used in the variogram calculation is the lag

parameter, j , describing the distance between two extracted units. Often the lag is expressed as a dimension-less, relative lag by only relating to a series of multipla of the basic minimum lag unit (more specifics later).

Below this column ends with an example of how to *interpret* a variogram; which is only meant to give an impression of the surprising wealth of information that can be gathered from a variographic analysis. Much more to come...

Interpretation of variograms

The practical interpretation of variograms is the most important step in a variographic analysis. The variogram *level* and *form* provide extensive information on the process variation captured (the systematics of the process heterogeneity captured). Normally, three primary types of variograms are encountered (based on TOS' ~60 years of very wide experience):

- The *increasing variogram* (normal variogram shape).
- The *flat variogram* (no autocorrelation along the defining dimension).
- The *periodic variogram* (which is a *superposition* on either of the first two types).

These variograms are outlined in Figure 4. When the variogram type has

been identified, information on further optimisation of routine 1-D sampling can be derived (and there are many other types of information that can be gained from variograms...). The increasing variogram (Figure 4, left top variogram) can be used as an example.

Variograms are not defined for lag $j=0$, as this would correspond to extracting the exact same material increment twice. Even though this is not physically possible, it is still highly valuable to acquire information as to the *expected variation* corresponding to **if it would have been possible** to repeat sampling of the exact same increment. TOS identifies this variation as the so-called “nugget effect” (also termed the “minimum possible error”, MPE). Normally, the first five points of the variogram are extrapolated backwards to *intercept* the ordinate axis to provide an estimate of the magnitude of the nugget effect, but there are also much more tractable model curve-fitting operators available; these are the preferential choice within *geostatistics*. Either way it is the estimate of the Y-axis intercept that carries a wealth of surprising information. There is a reason for the name “MPE” (minimum possible error). The nugget effect/MPE includes all error types that will be influential for sampling systems not

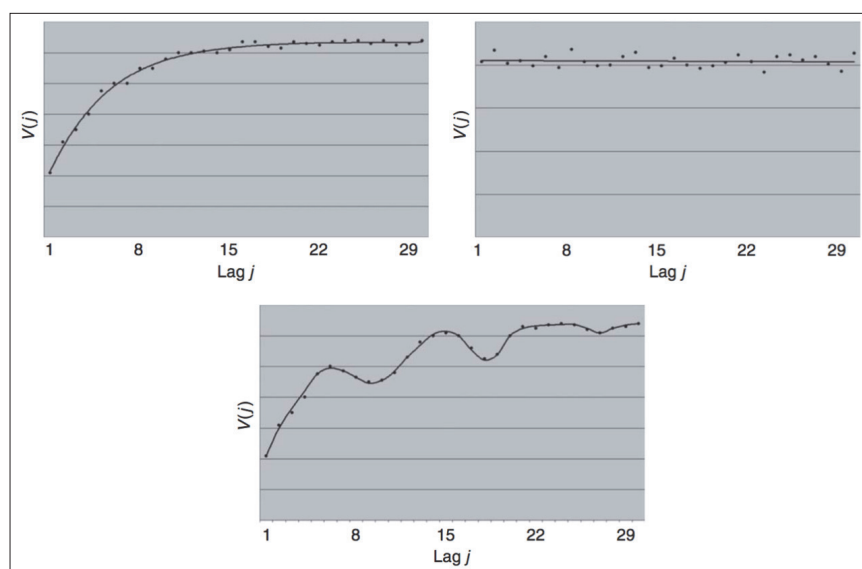


Figure 4. Three basic variogram types. Reproduced with permission from L. Petersen and K.H. Esbensen, “Representative process sampling for reliable data analysis—a tutorial”, *J. Chemometr.* **19**, 625–647 (2005).²

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sufficiently TOS-optimised, e.g. producing significant correct sampling errors (FSE, GSE), incorrect sampling errors as well as the TAE, all contributing to an elevated, *unnecessarily inflated* nugget effect. MPE is therefore an appropriate measure of the absolute minimum error that can be expected in practice using the full complement of sampling error elimination and reduction measures available in TOS. This turns out absolutely not to be the rule within very many process industry sectors—because of a desire to keep the costs of sampling systems as low as possible (which is very often too low for comfort, or rather, to put it precisely, too low to render representativity; much, much more on this aspect in many forthcoming columns).

Figure 5 shows a *generic* increasing variogram, delineating the three basic variogram parameters, *nugget effect*, *range* and *sill*, which is all that is needed to characterise any variogram.

When the increasing variogram becomes more or less flat after a certain multiplicity of unit lags (X-axis), the “sill” of the variogram has been reached. The sill provides information on the expected *maximum* sampling variation if the existing autocorrelation is not taken into account. The “range” of the variogram is found as the lag beyond which there is no autocorrelation. N.B. the “dip” of a smoothed version of the variogram signifies an increase of within-unit autocorrelation as the lag becomes smaller and smaller (classical definition of time-



Figure 6. Manual increment extraction from a conveyor belt defining a dynamic 1-D lot. The scoop used to extract increments is less than half the width of the conveyor belt, imparting significant incorrect sampling error effects to the process sampling. This results in an (unnecessarily) inflated nugget effect, which is one of the means by which variographic process characterisation can also be used for total sampling-plus-analysis system evaluation, see, e.g., References 1 and 3. Photo credit: KHE

series autocorrelation). TOS process sampling is extremely interested in what takes place with the range, i.e. in what characterises pairs of increments with a smaller between-unit distance than the range, to be more fully developed in later columns.

If a significant periodicity is observed (e.g. Figure 4, lower variogram), the sampling frequency must never be similar, since this risks introducing an additional error, an in-phase error). In these cases the specific sampling mode (random sampling, systematic sampling

and stratified random sampling) becomes critically important, which is also explained in a practical application example later.

A complete introduction to variographic characterisation and process sampling is no small matter, and the present initiation will be complemented by a substantial instalment of more columns.

To whet the reader's appetite, Figure 6.

And for the avid and impatient reader, a recent, complete introduction to variographics can be found in Reference 4.

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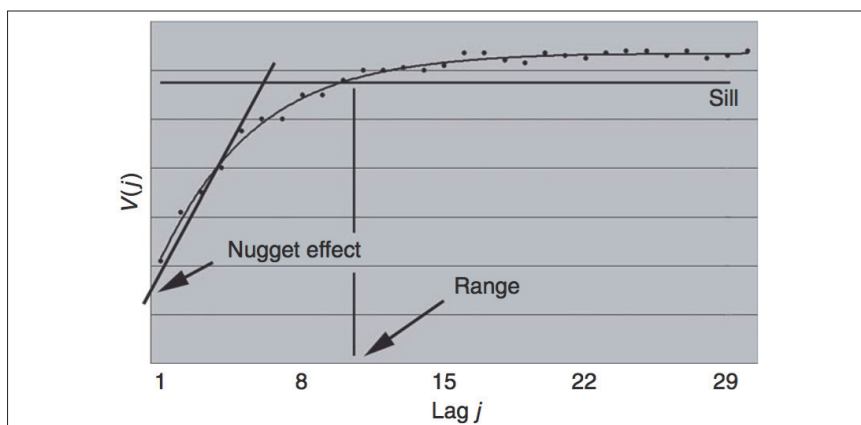


Figure 5. Generic increasing variogram, schematically defining the nugget effect, the sill and the range. Reproduced with permission from L. Petersen and K.H. Esbensen, “Representative process sampling for reliable data analysis—a tutorial”, *J. Chemometr.* **19**, 625–647 (2005).²

PITTCON 2017

Pittcon report
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Ian Michael

I need to make an apology about this year's Pittcon Report. We have had too much to fit into this issue and so cannot include our report on new product introductions at Pittcon 2017. Instead, I urge you to read the report in full online at <http://www.spectroscopyeurope.com/pittcon-2017>. This will also give you the opportunity to explore our new website. I hasten to add that this is not a cunning plan to make you visit the new website!

Online you will find links to pages detailing the new products and with further links to information on the manufacturer's website. As usual, instruments that may have been new at Pittcon but which we have already covered in previous issues are not included. If I have missed anything, you are welcome to let me know and we will add it to the online report.

Pittcon 2018 will be held in Orlando, FL, USA, from 25 February to 1 March. The length of the exhibition has been reduced to three days, 27 February to 1 March, but the conference runs for its usual time.

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Jenway UV/visible spectrophotometer

Jenway has launched the new 7205 UV/Visible spectrophotometer. The 7205 has been designed for fast and easy use in analytical chemistry, routine analysis and



The 7205 UV/vis spectrophotometer from Jenway.

education laboratories. With a broad wavelength range, it is suitable for a variety of applications in quality control, life sciences and food testing etc. The 7205 uses a flash xenon lamp to extend the wavelength range, from a minimum of 335 nm to 198 nm, to include the UV area of the spectrum. Similar to its predecessor, the 7200, the 7205 has scanning

diode array technology, providing excellent wavelength reproducibility. There is a colour touchscreen user interface and the instrument is lightweight with a small footprint.

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X-RAY

New software for S2 Puma in the pharmaceutical industry

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Bruker's S2 Puma ED XRF spectrometer has new 21 CFR 11 compliant software.

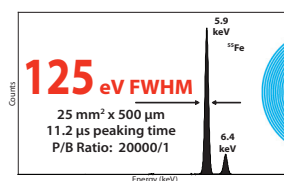
age (IQ/OQ) further supports users in the pharmaceutical industry. With its HighSense™ technology, the S2 PUMA can identify and analyse hazardous toxic trace elements and contaminants from production processes according to Pharmacopeia regulation. Samples can be presented as pressed pellets or in powder form, and the instrument can be configured for measurements in vacuum or under helium to suit any application.

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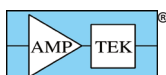
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31 August–2 September, Rhodes, Greece. **15th International Conference on Environmental Science and Technology**. Secretariat, University of Aegean, Voulgaroktonou Str. 30, 11472 Athens, Greece, ✉ cest@gnest.org, ★ <http://cest.gnest.org/cest2017/about>.

4–7 September, Manchester, UK. **The 38th BMSS Annual Meeting**. Royal Northern College of Music, Manchester, ★ <http://www.bmss.org.uk/meetings.shtml>.

8–13 September, Santa Fe, New Mexico, USA. **2017 SciX Conference (formerly FACSS): Annual National Meeting of the Society for Applied Spectroscopy (SAS) / The 44th Annual North American Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies**. ✉ facss@facss.org, ★ <http://www.facss.org>.

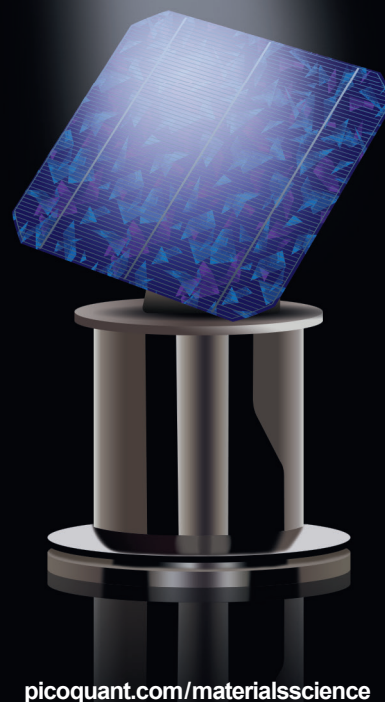
10–14 September, Berg en Dal, Netherlands. **7th International Chemometrics Research Meeting ICRM2017**. ✉ ICRM2017@DutchChemometricsSociety.nl, ★ www.DutchChemometricsSociety.nl/icrm-2017.

17–21 September, Heraklion, Crete, Greece. **10th International Conference on Instrumental Methods of Analysis**. Konstantinos Simeonidis, National Technical University of Athens, Lab. of Inorganic & Analytical Chemistry, Athens, Greece, ✉ ima2017@chemistry.uoc.gr, ★ <http://www.ima2017.gr/index.htm>.

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